

# Low Cost “Plastic” Solar Cells

Solar cells --- Power from the Sun --- must be and will be ---  
a significant contribution to our energy needs.

Two problems that must be solved with solar:

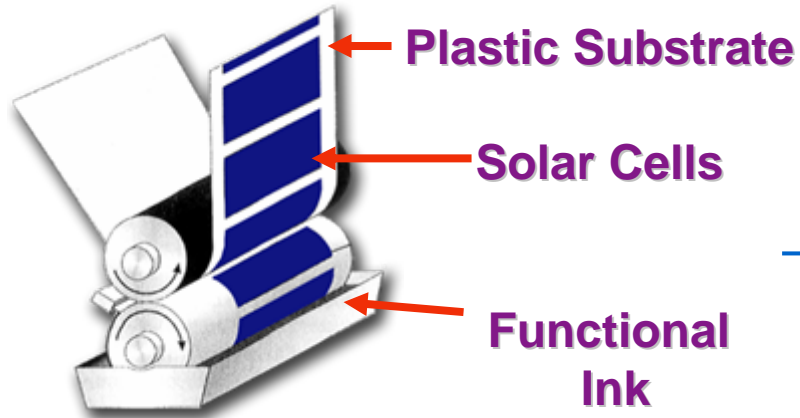
1. Cost
2. Area

# *Semiconducting and Metallic Polymers*



*“inks” ---- with  
electronic functionality!*

The Dream





$TiO_x$

PCPDTE

Fullerene

P3HT/Fullerene

MEH-PPV

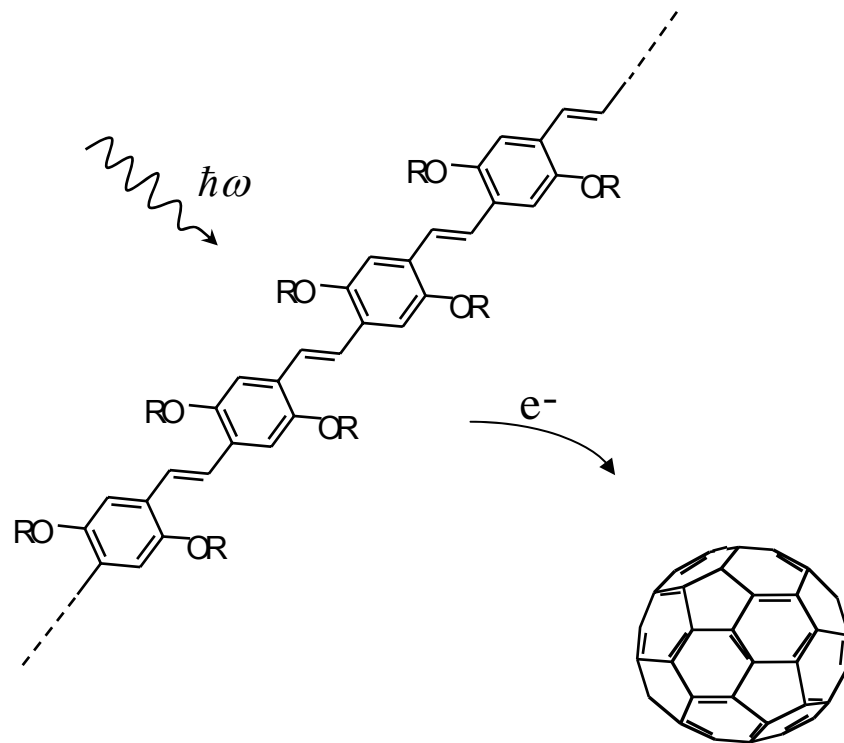
Super

P



# "Plastic" Solar Cells

Ultrafast charge separation with quantum efficiency approaching Unity !



1992

50 femtoseconds!!

# Ultrafast electron transfer is important ---

Charge transfer is 1000 times faster than any competing process,

and

Back charge transfer is inhibited

Therefore,

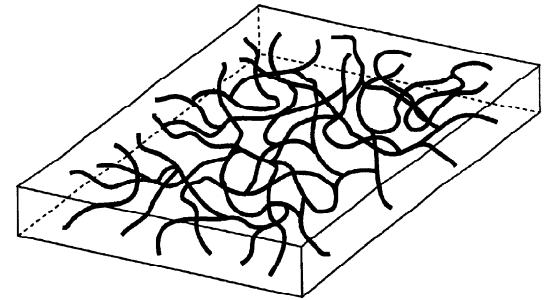
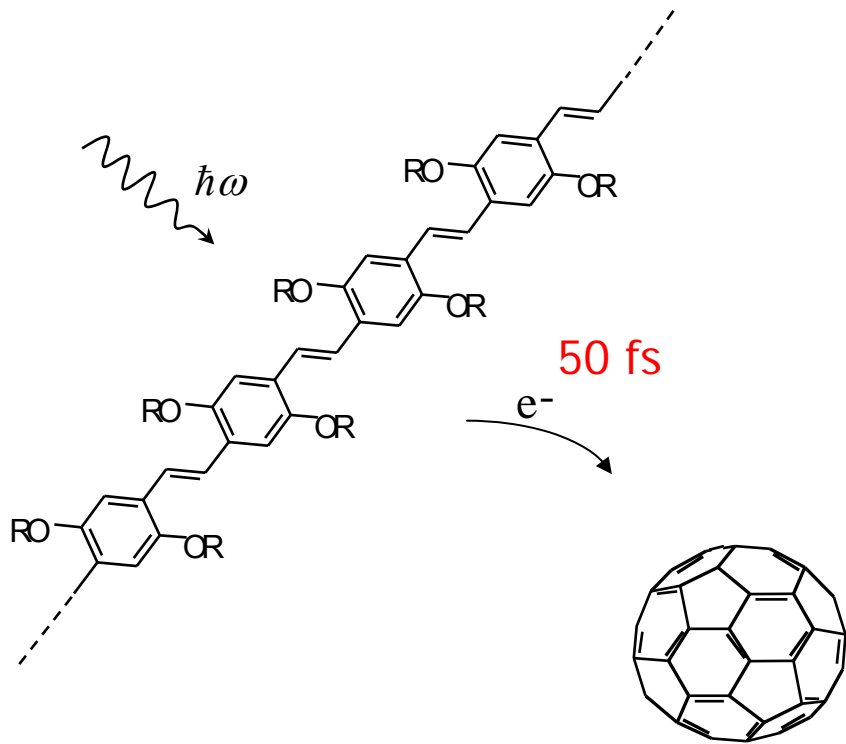
Quantum efficiency for charge separation approaches unity!

Every photon absorbed yields one pair of separated charges!

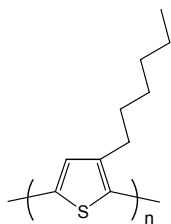
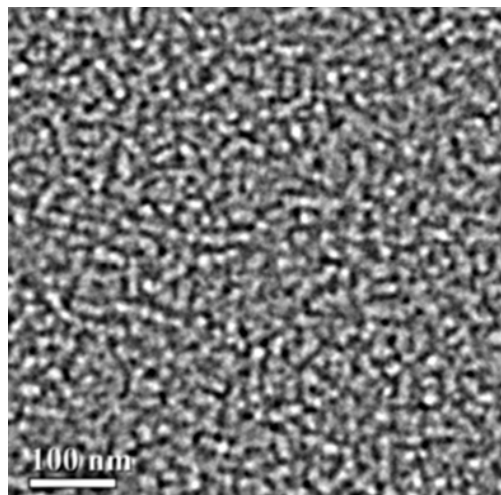
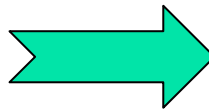
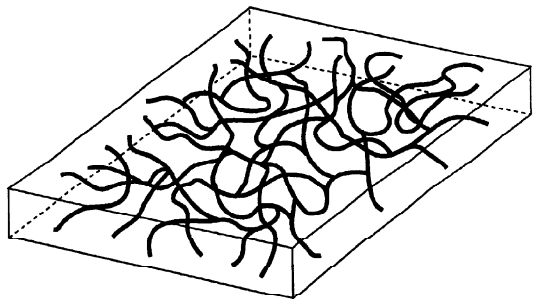
(Route to photovoltaics and photodetectors)

# Ultrafast photo-induced charge separation ----

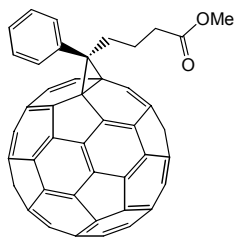
But how do we create a material with charge-separating junctions everywhere??



All must be accomplished at nanometer length scale!



P3HT



PCBM

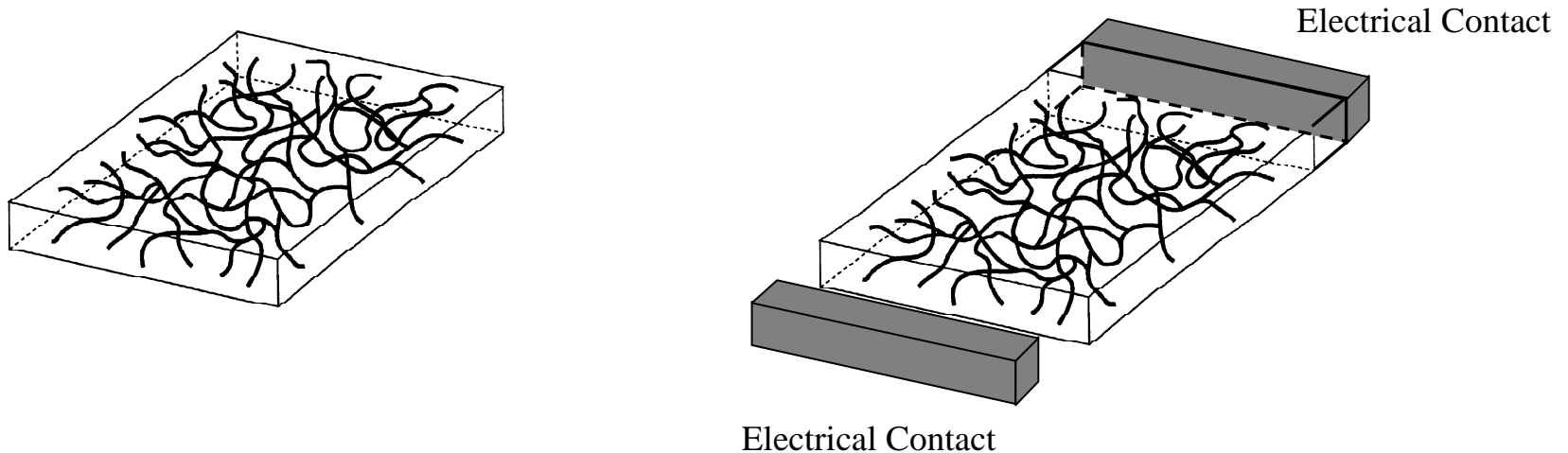
Bulk Heterojunction Material  
Bicontinuous interpenetrating network

*Self-assembled nanoscale material with charge-separating junctions everywhere!*



# "Bulk" D-A Heterojunction Material

**A self-assembled nanomaterial**



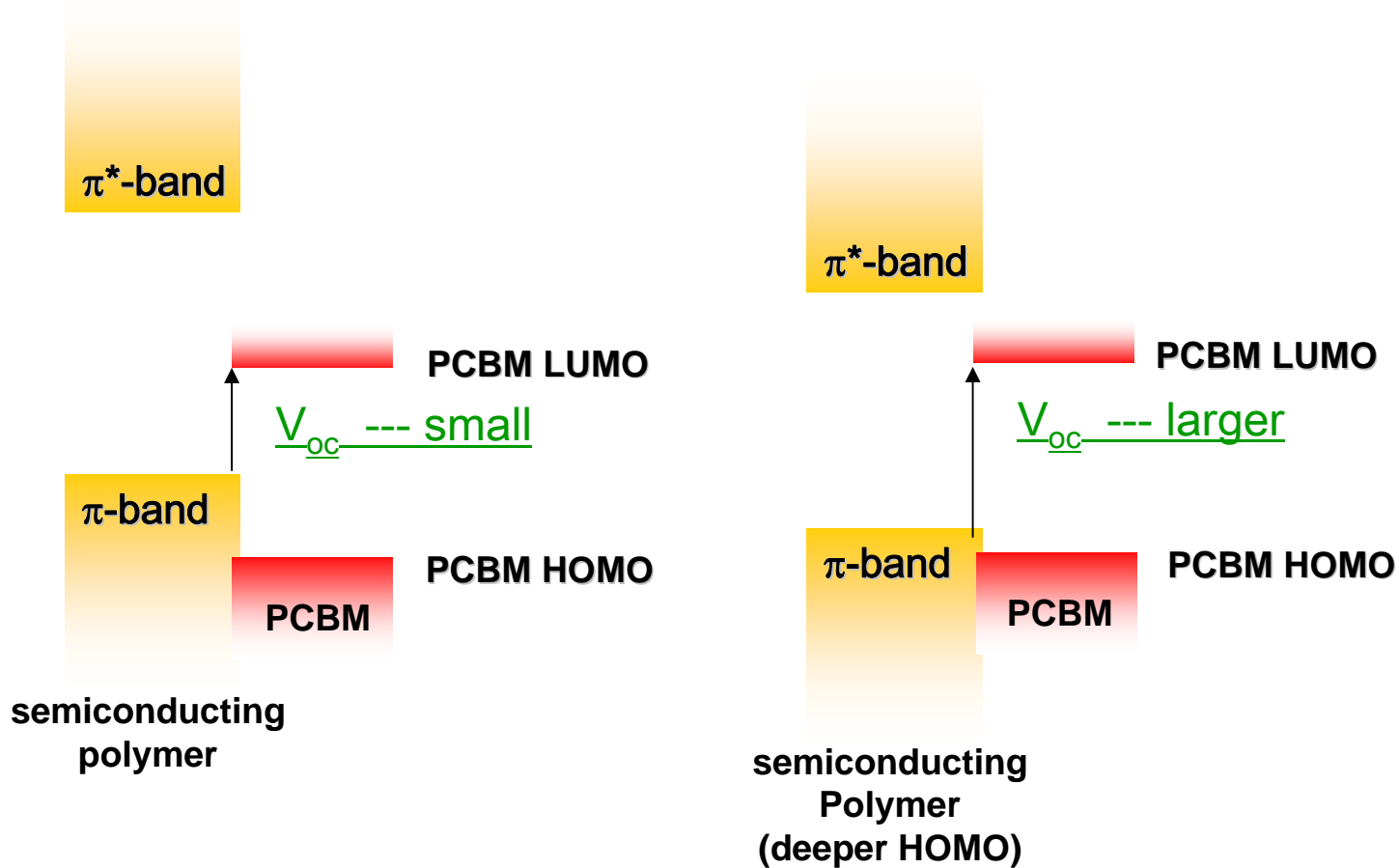
Must break the symmetry --- use two different metals with different work functions.

Electrons will automatically go toward lower work function contact and holes toward higher work function contact

Origin of  $V_{oc}$  --- when irradiated with high light intensity,

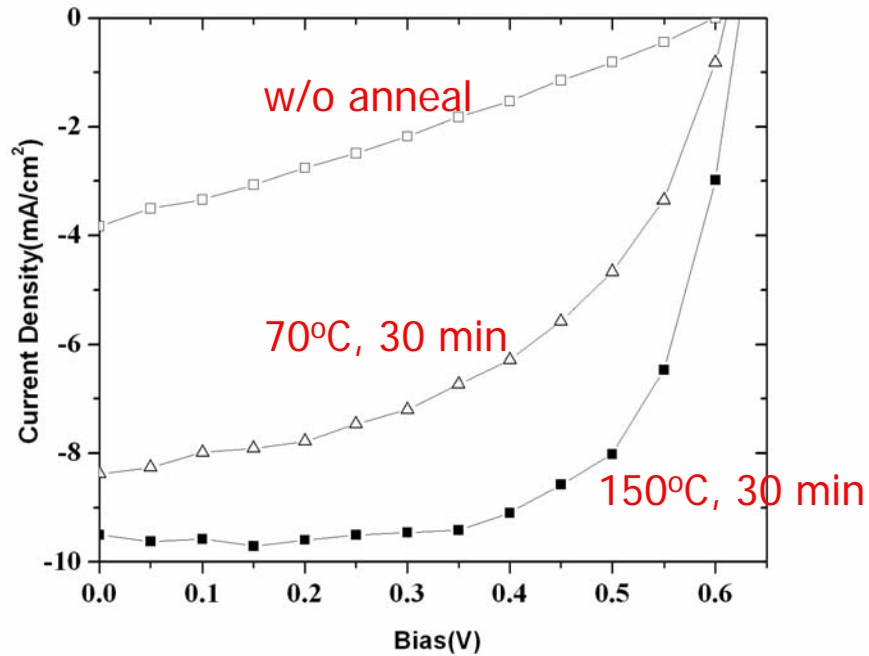
Fermi levels must be equal (holes in the  $\pi$ -band and electrons in PCBM LUMO):

$$V_{oc} \approx E_{PCBM\ LUMO} - E_{polymer\ homo}$$



# Solar Cell Performance

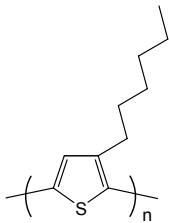
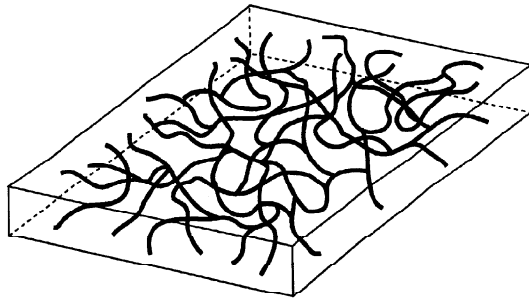
Device structure: ITO/PEDOT/P3HT:PCBM/Al.



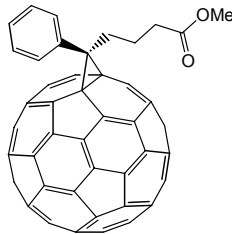
**Eff = 5.0%**  
**V<sub>oc</sub> = 0.625 V**  
**FF = 68%**

Series resistance decreased from 113  $\Omega$  to 7.9  $\Omega$

# "Bulk" Heterojunction Material --- Optimize Nanomorphology



**P3HT**

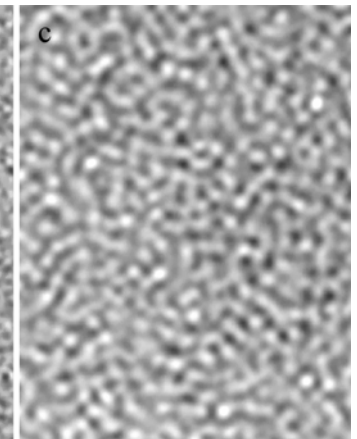
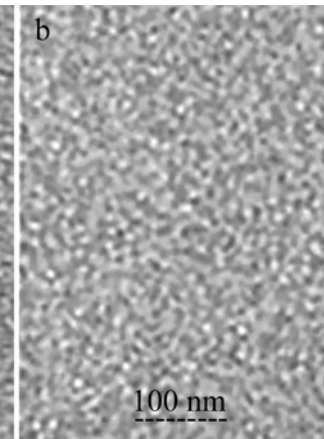
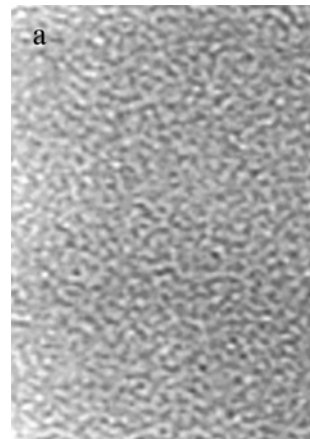


**PCBM**

Before 150°C  
anneal

150°C anneal  
30 min

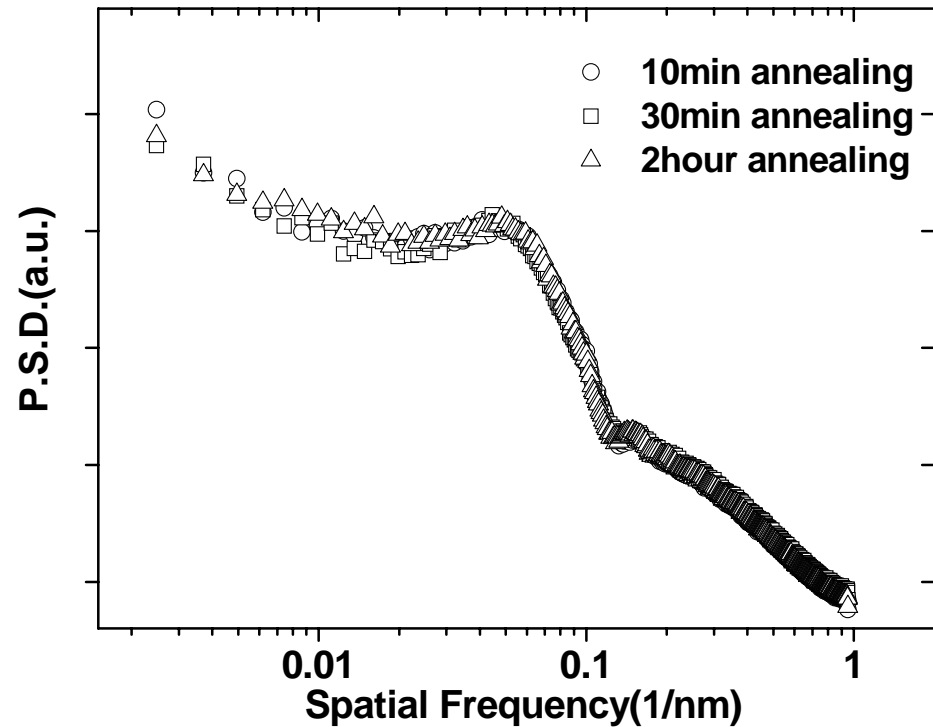
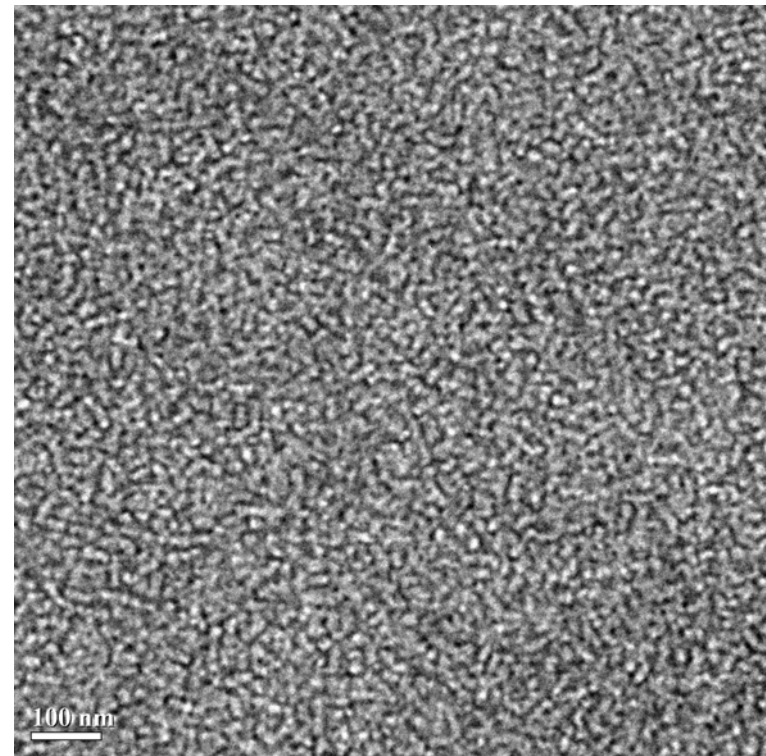
150°C anneal  
2 hours



TEM images of the P3HT/PCBM  
interpenetrating network

After annealing for 10 minutes at 150°C

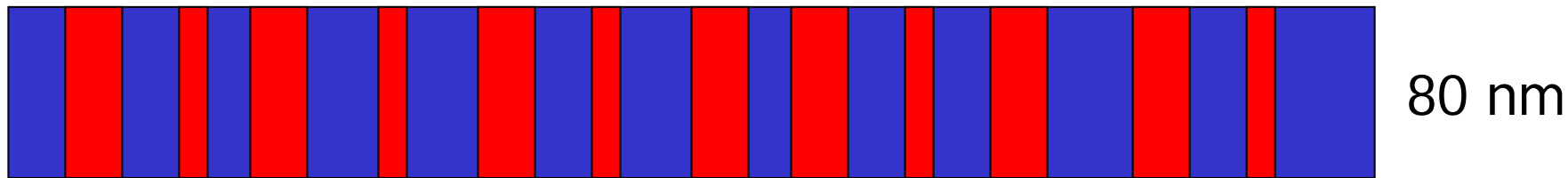
Spatial Fourier Transform



High temperature annealing --- 150° C

1. Stable for long times at High-T
2. 10 minutes sufficient to lock in the nano-scale morphology

Quasi-periodic with "periodicity" of 16-20 nm

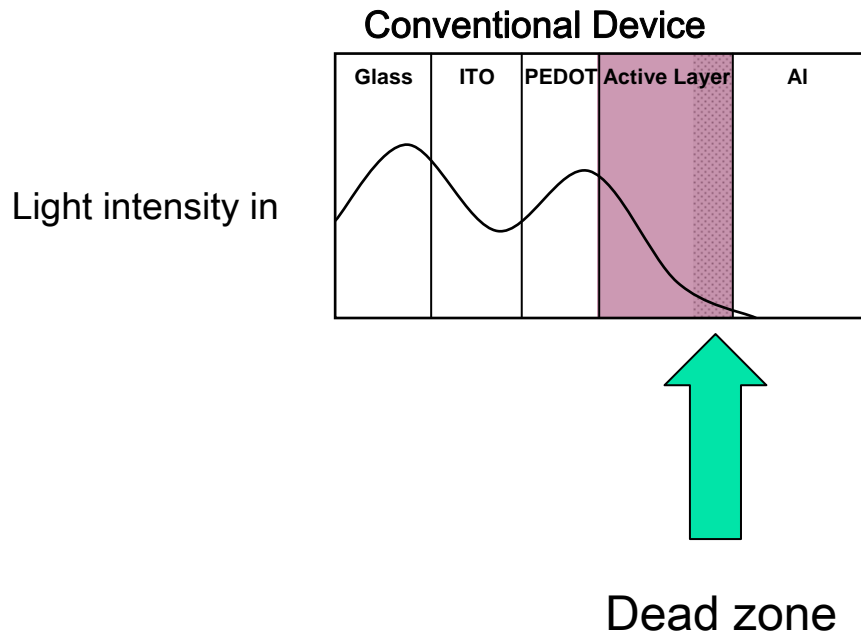


|"Period" 160 -200 Å|

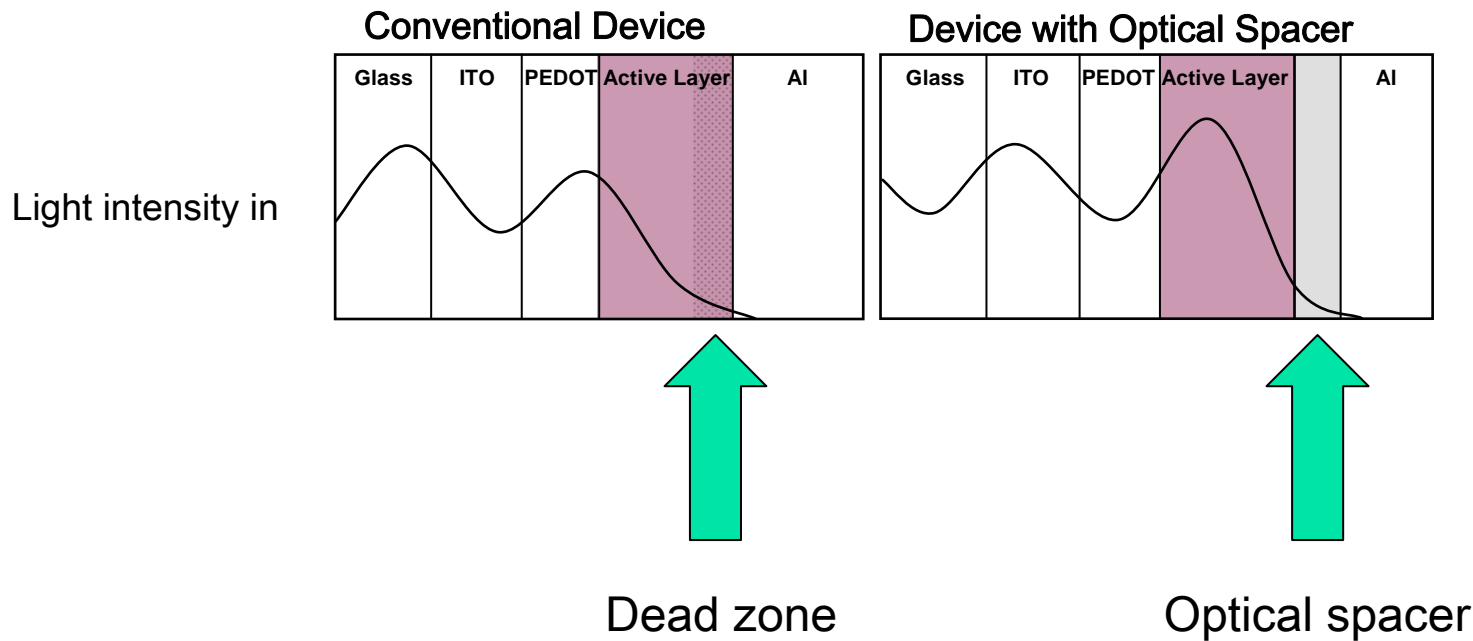
Distance from any point in the material to a  
charge separating interface  $\approx 40\text{-}50 \text{ \AA}$

Less than the mean exciton diffusion length ---  
**High efficiency for charge separation.**

# New Device Architecture: Optical Spacer

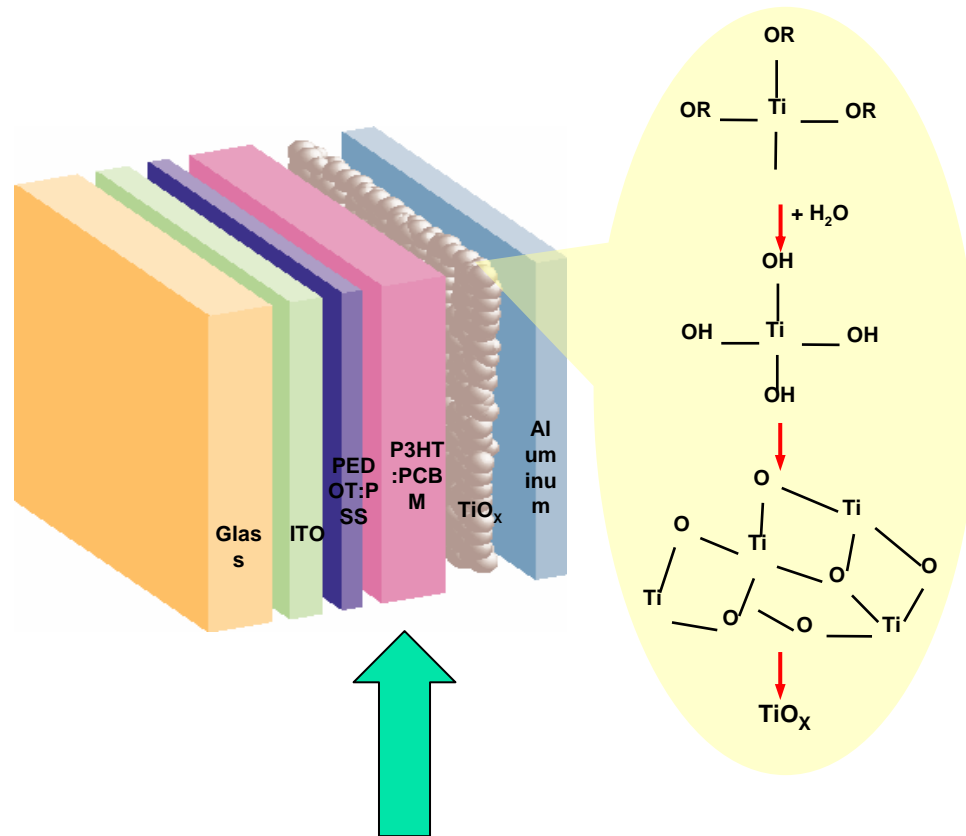


# New Device Architecture: Optical Spacer





# Device architecture: Optical spacer

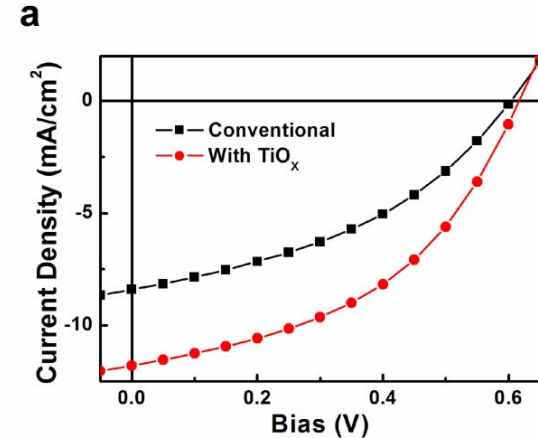


Charge separation layer

# Optical Spacer can improve the Power Conversion Efficiency

Green light (532 nm)  
Efficiency

$$\eta_e = 8.1\% \rightarrow 12.6\%$$



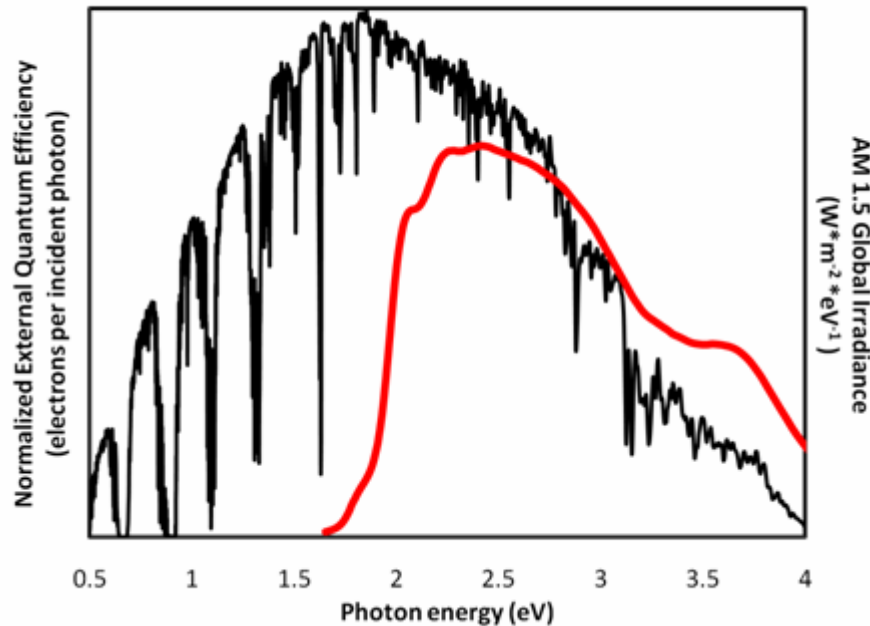
25 % - 50% increase in efficiency

Optical spacer important for low mobility materials where simply making the active layer thicker is not an option

## What can we expect to achieve??

Single layer with efficiency  $> 5\%$  demonstrated with P3HT

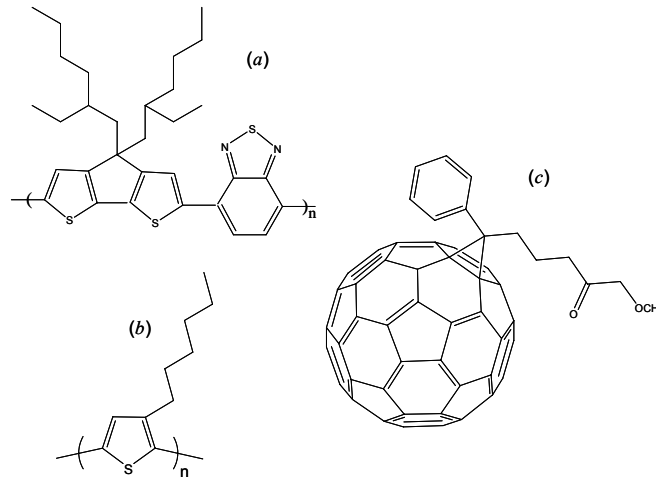
Band gap too large ---Missing more than half the solar spectrum



Opportunity: Potential for factor of 2 improvement using polymer with smaller band gap.

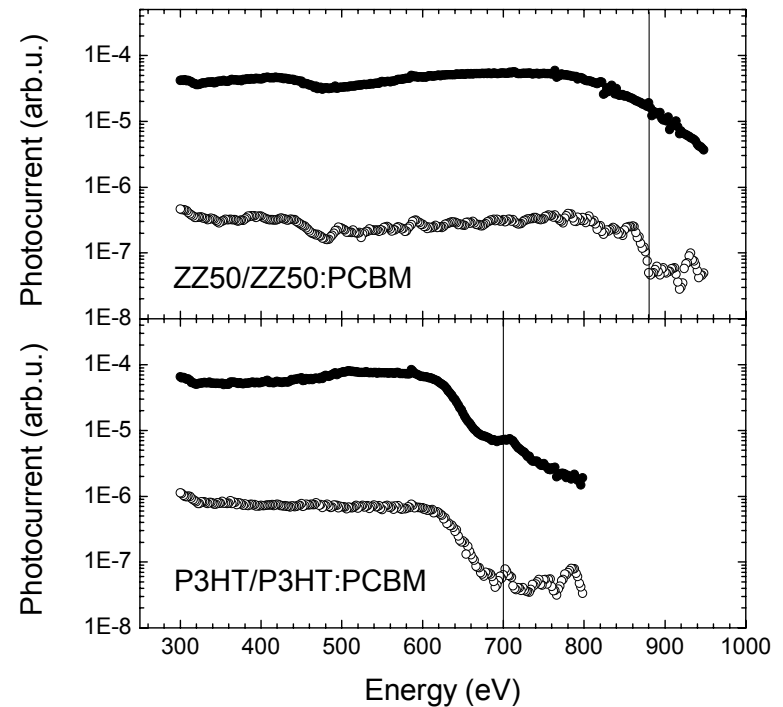
# Semiconducting polymers with smaller band gap?

Zhengguo Zhu  
(ZZ50)

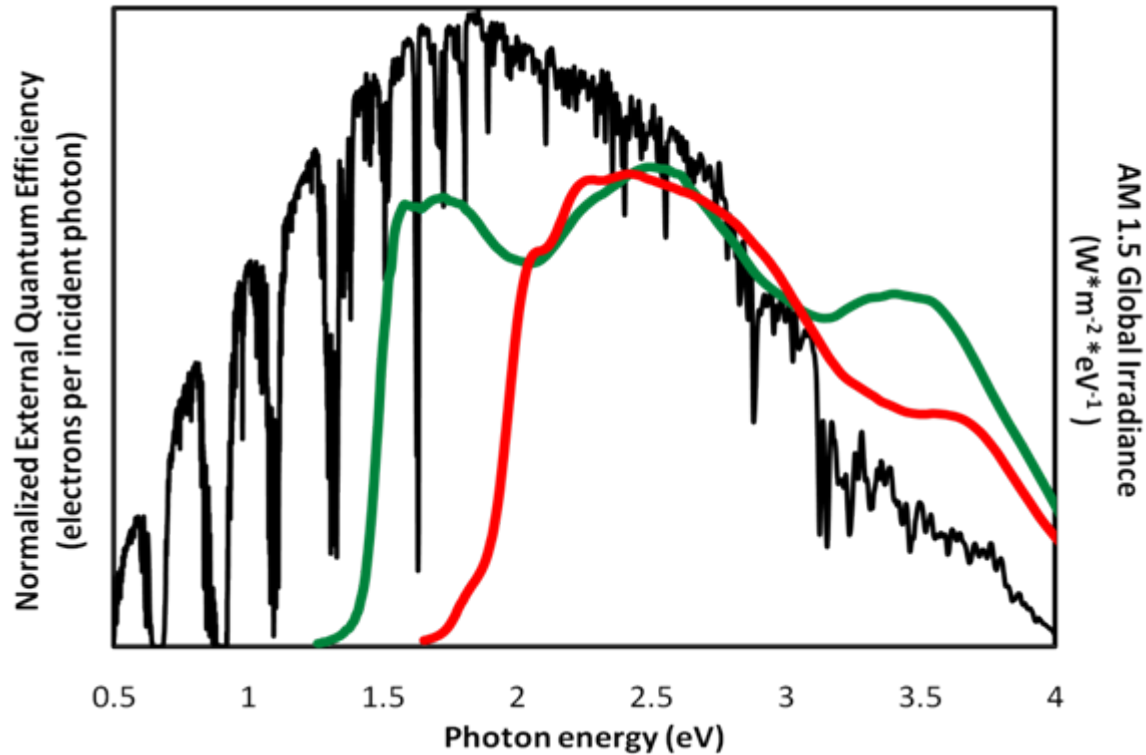


Absorption and photoresponse  
out to 900 nm in the IR.

Should be capable of 7% in single cell  
and >10% in a Tandem Cell with P3HT



With ZZ50 ---



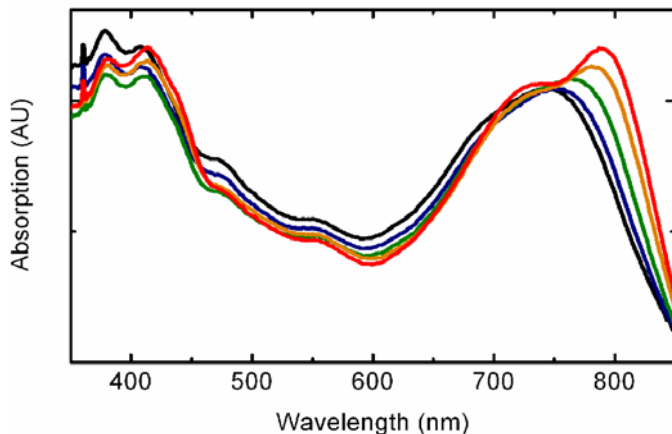
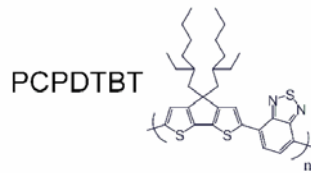
Progress --- but still missing all incident power in the IR beyond 900 nm.  
Need smaller gap materials

# Morphology Control with Alkane-dithiols as Processing Additives

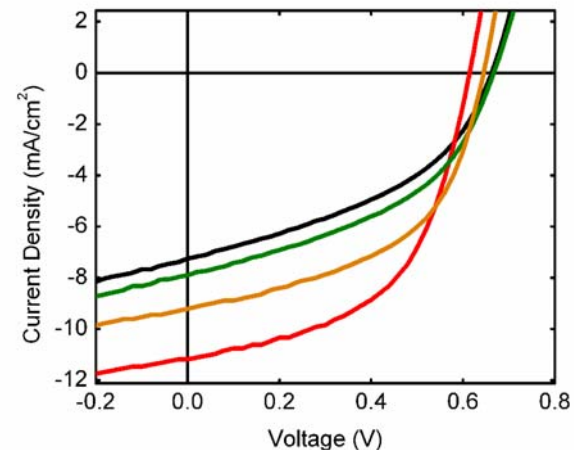
(Nature Materials, Published online May 27, 2007)

Add 2.5% alkanedithiol into solvent (chlorobenzene)

1,3-propanedithiol (blue), 1,4-butanedithiol (green),  
1,6-hexanedithiol (orange) and 1,8-octanedithiol (red)

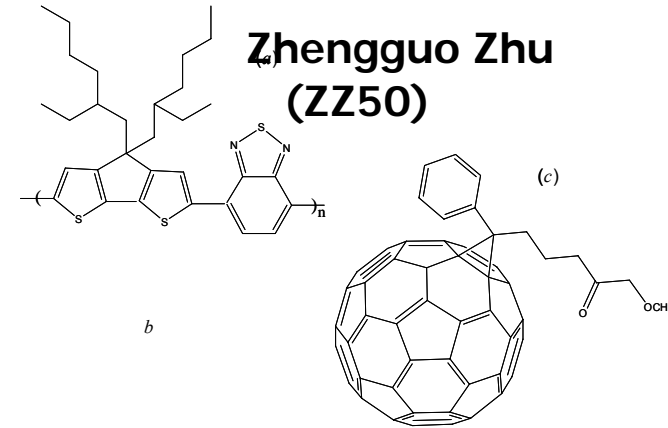
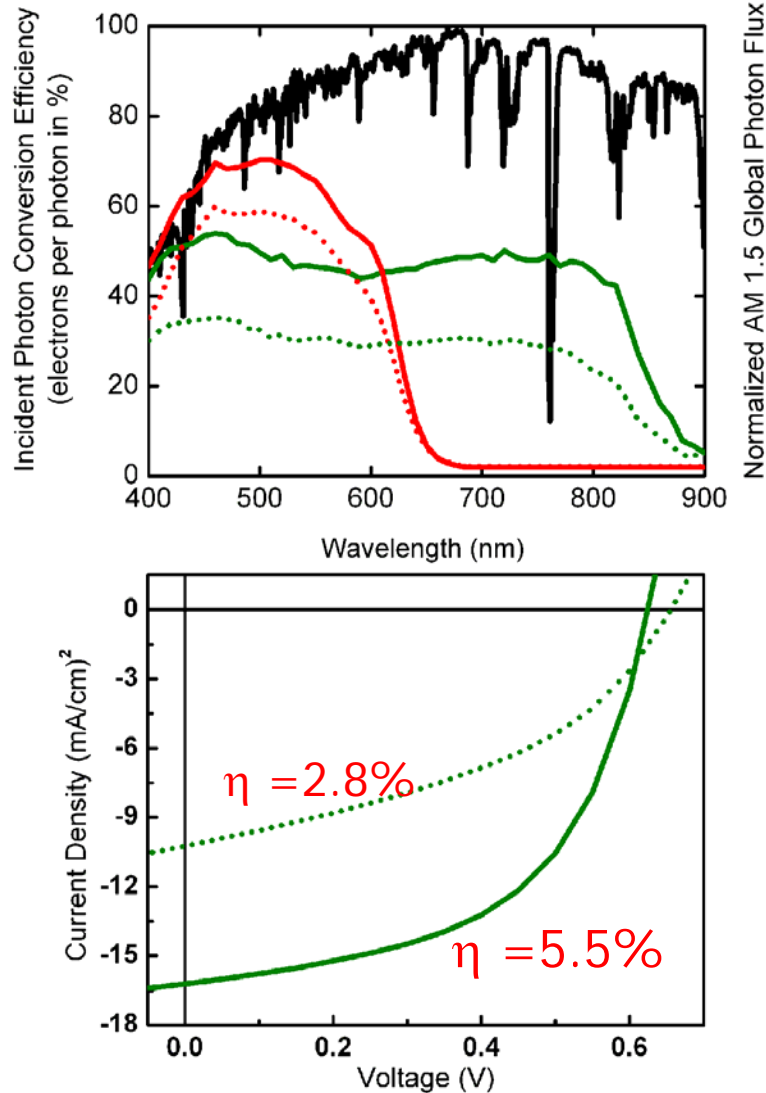


Spectra sharpen and red-shift



Higher  $j_{SC}$  --- higher efficiency

# Processing Additives for Morphology control



Factor of 2 Improvement  
by using octane-dithiol  
as processing additive

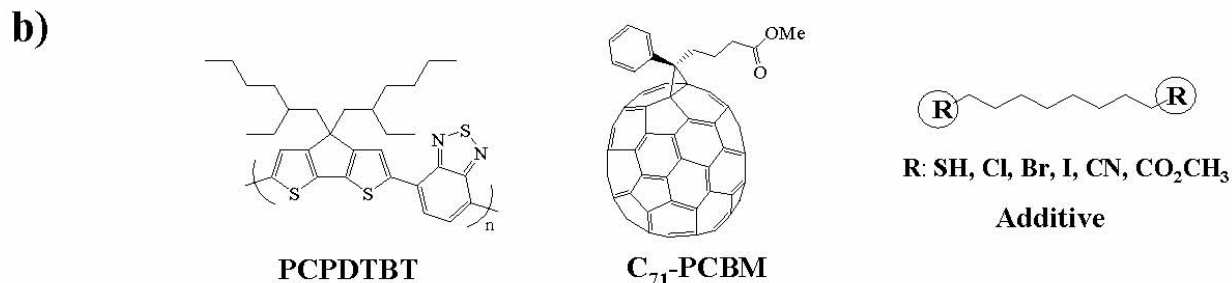
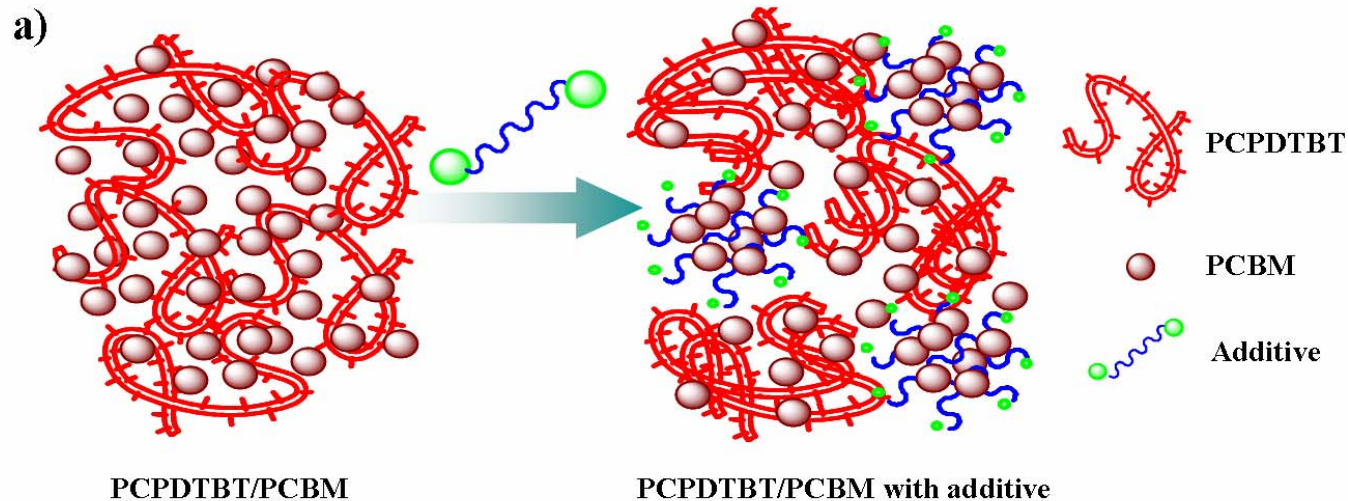
Nature Materials  
Published online May 27, 2007

Best performance for a single cell architecture

# Processing Additives for Morphology Control of Bulk Heterojunction Materials

## Mechanism:

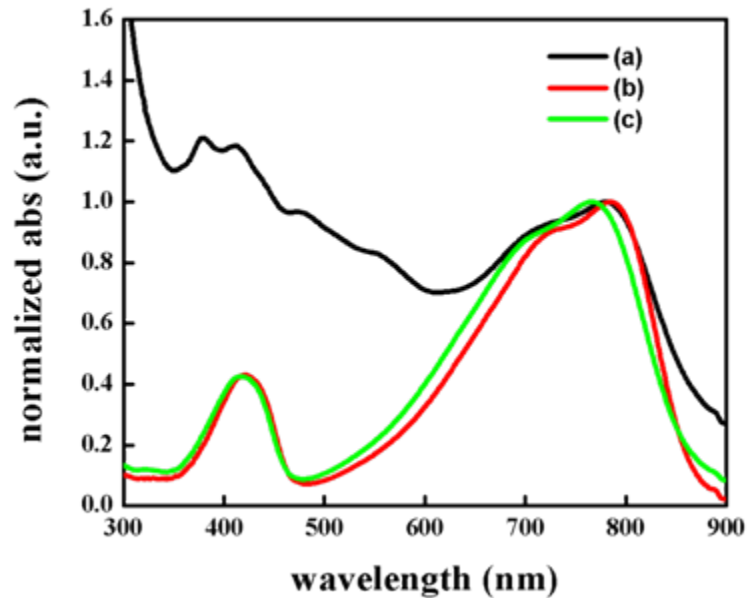
- (i) Selective (differential) solubility of the fullerene component
- (ii) Higher boiling point than the host solvent.





# Absorption Spectra

PCPDTBT film (green)

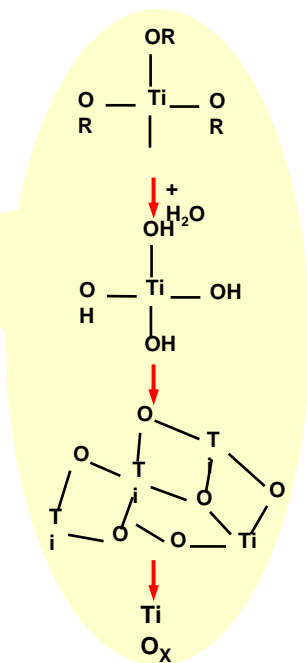
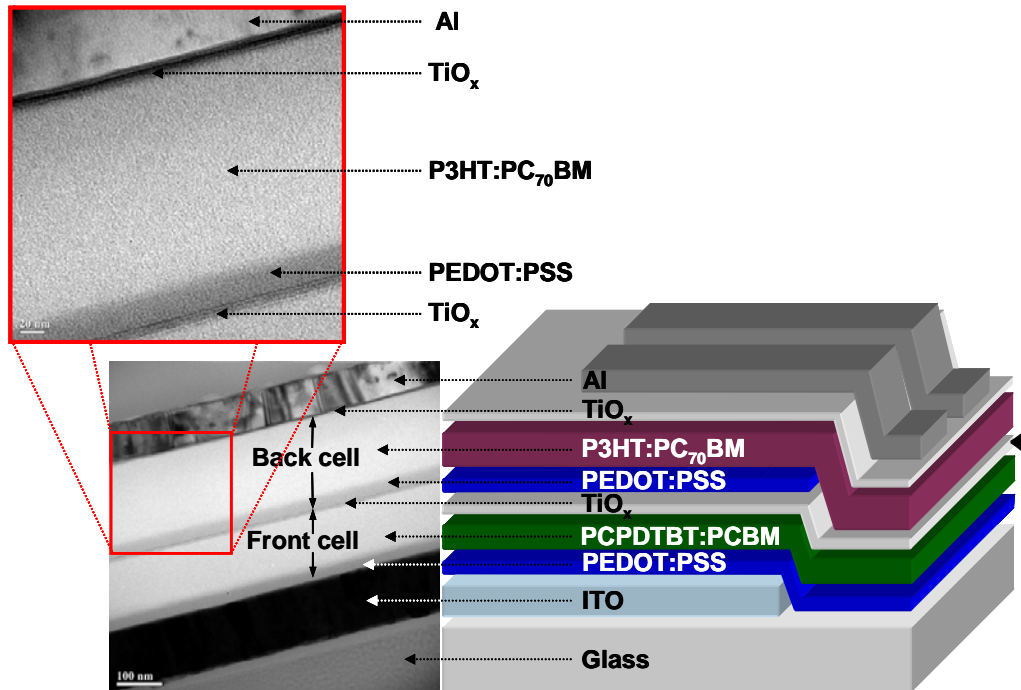


PCPDTBT:C71-PCBM films processed with 1,8-octanedithiol ---  
Before removal of C71-PCBM with alkanedithiol (black),  
After removal of C71-PCBM with alkanedithiol (red)

The PCBM is completely removed by the alkane-dithiol!

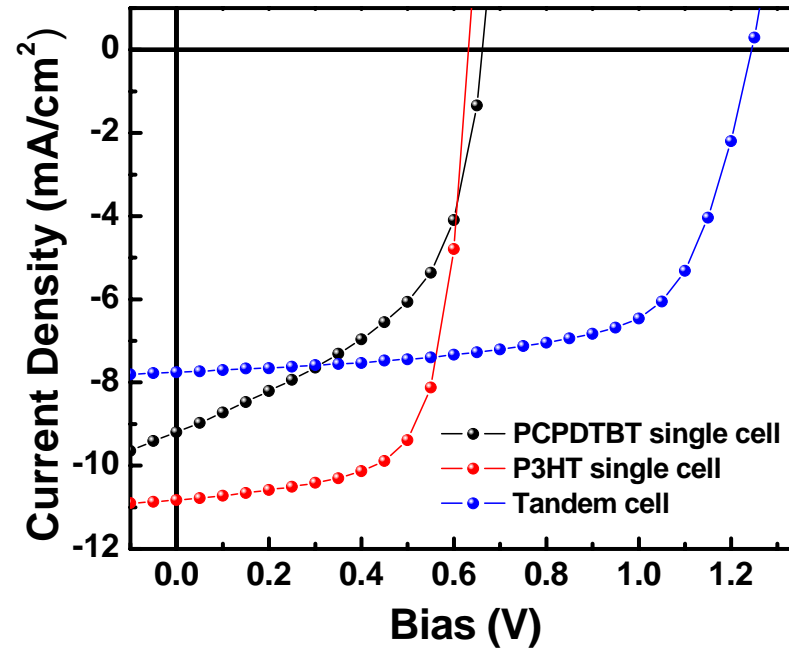
# Multi-layer Tandem Cell

(equivalent to two solar cells in series)



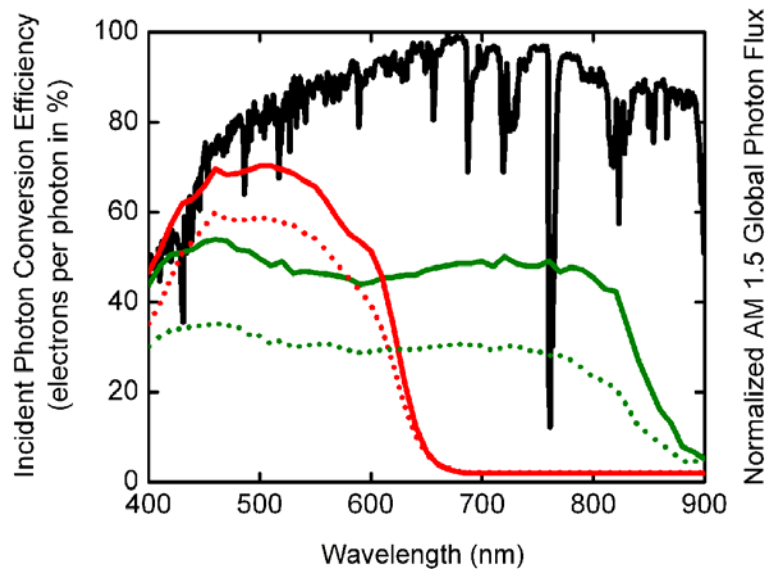
# Tandem Cell

(Multilayer architecture equivalent to two solar cells in series)



Open circuit voltage doubled --- Efficiency 6.5%

We can do even better ----



Increased performance of  
each of the two subcells ---

Already demonstrated  
(using the Processing Additive).

Goal for coming months: 8-10 %

## In the Tandem Cell, the TiOx layers serve six separate functions:

1. Optical spacer that redistributes the light intensity to optimize the efficiency of the back cell.
2. With TiOx layer between the charge separating layer and the aluminum cathode --- much improved air stability
3. The TiOx functions as a low resistance electron transport layer
4. TiOx layer breaks the symmetry and thereby creates the open circuit voltage.
5. TiOx functions as a hole blocking layer  
(top of the valence band at - 8.1 eV)
6. TiOx layer enables the fabrication of tandem cells. The transparent TiOx layer is used to separate and connect the front cell and the back cell.

Polymer Solar cells: Present status --- 5 - 6 % with P3HT  
(and with several other materials with similar spectra)

What can we expect (hope) to achieve??

New Architecture --- optical spacer --- 25-50% improvement

New Polymers with energy gap well matched to the  
solar spectrum

Opportunity for x2 improvement

Better charge collection efficiency (optimize morphology)

Opportunity for 25% improvement

Increased open circuit voltage (deeper HOMO for semiconducting polymer)

Opportunity: Potential for > 50% improvement

Tandem Cell ---

Opportunity: Potential for > 50% improvement

Reality of each of these has been demonstrated.

Goal: Achieve all these advances in the same system

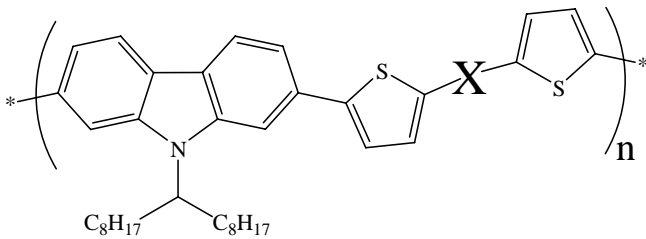
$$(1.25 \times 2 \times 1.25 \times 1.5 \times 1.5 = 7)$$

Clear vision of technology pathway to BHJ  
solar cells with efficiencies exceeding 20%

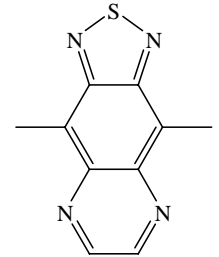
# New materials are the key to progress

## Examples:

LeClerc and colleagues (JACS published on the web 12/21/07)

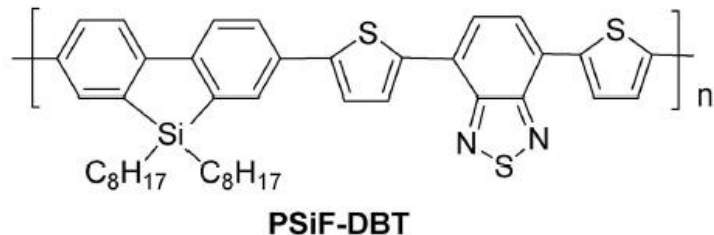


With X = acceptor such as



3.6% with PCBM

Yong Cao and colleagues (in press)



5.4% with PCBM

Note: Both have high  $V_{oc}$  --- 0.9 V Deeper HOMO



# Air-stable polymer electronic devices

Thin layer of amorphous  $\text{TiO}_x$  ( $x < 2$ ) improves performance

and

Enhances Lifetime

Polymer Based Solar Cells

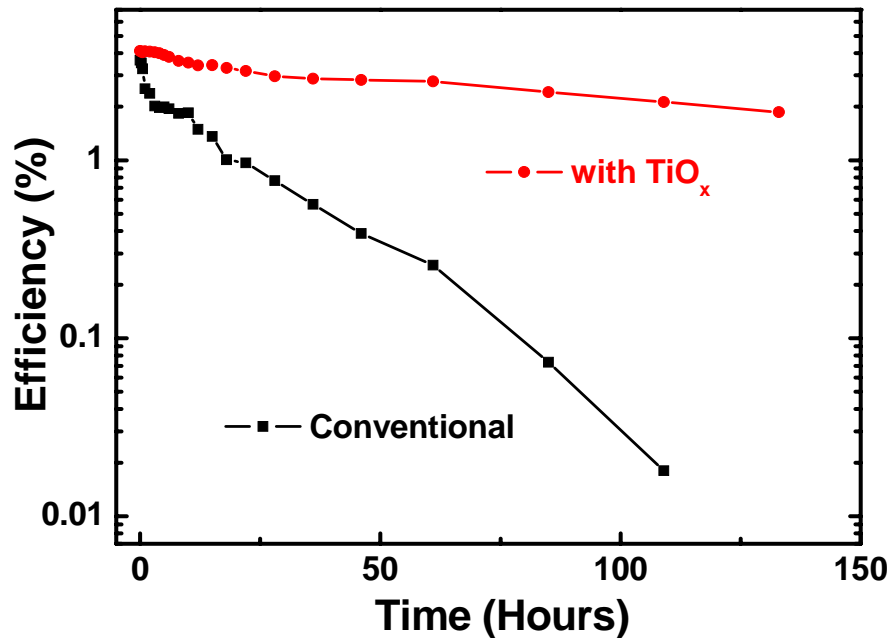
Polymer LEDs

Polymer FETs

Adv Mater. 2007

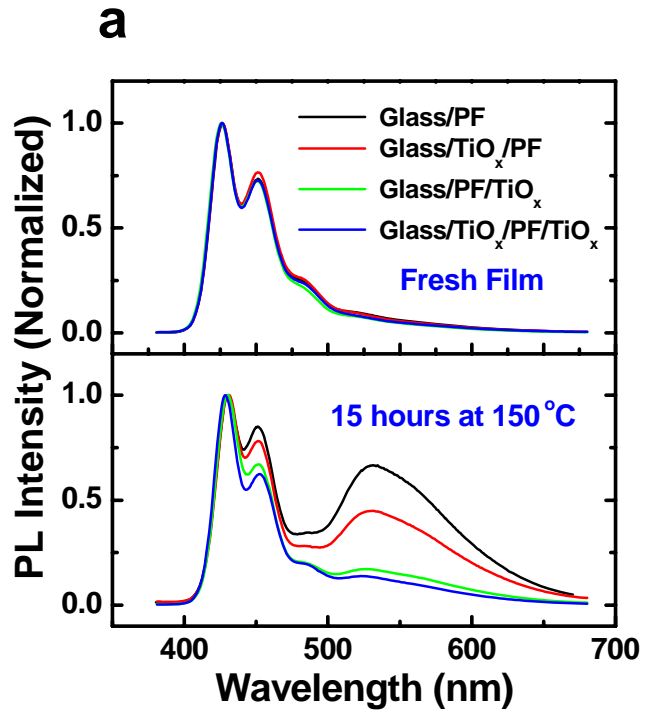
# Bulk Heterojunction Solar Cells

Single  $\text{TiO}_x$  passivation layer significantly enhances the lifetime  
**Factor of 100 !**

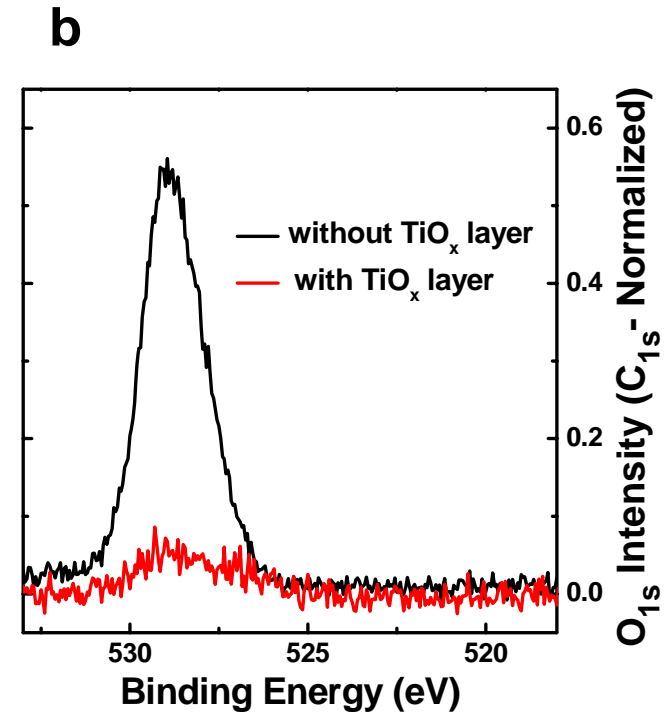


**Goal: Simple inexpensive barrier materials will be sufficient for achieving long lifetime.**

# Background scientific information



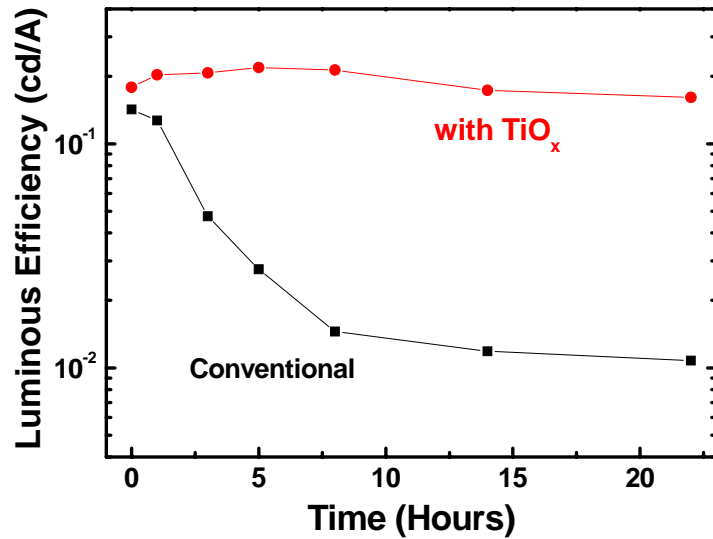
TiO<sub>x</sub> prevents oxidation  
of polyfluorene (PF)



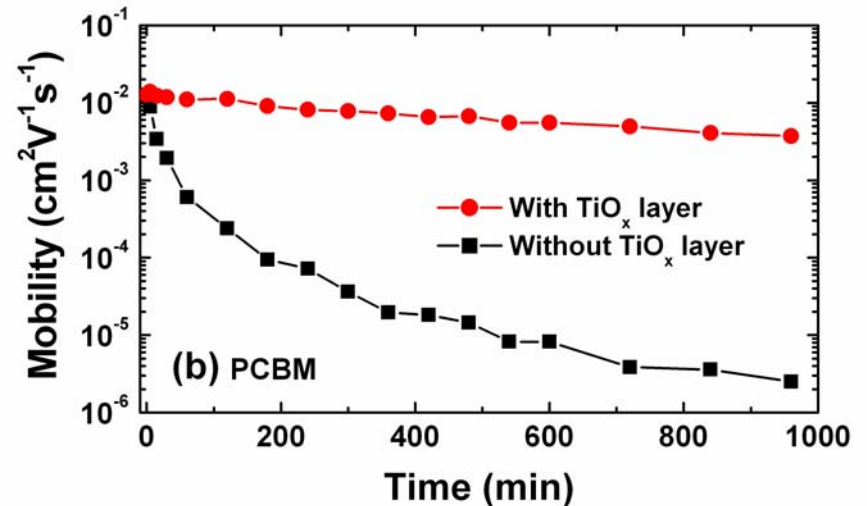
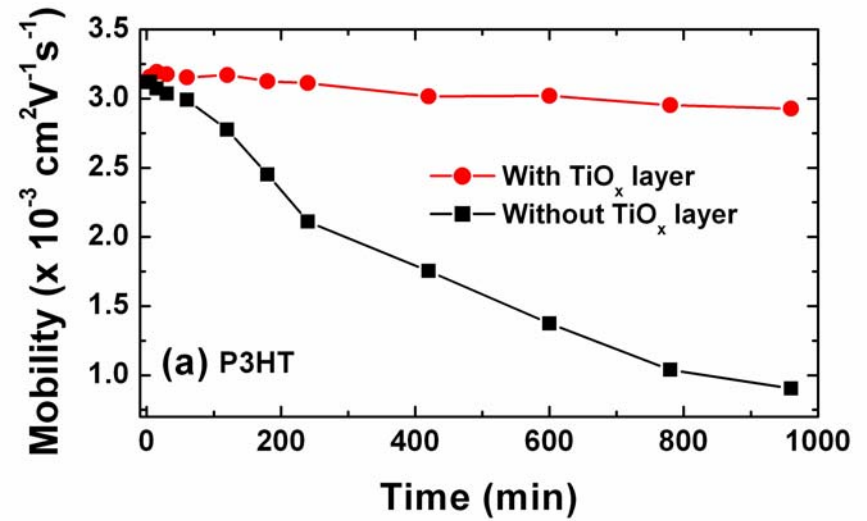
XPS of the O1s/C1s ratio  
in the PF after  
48 hrs at 150°C in air

# Similar enhancement in lifetime for LEDs and FETs

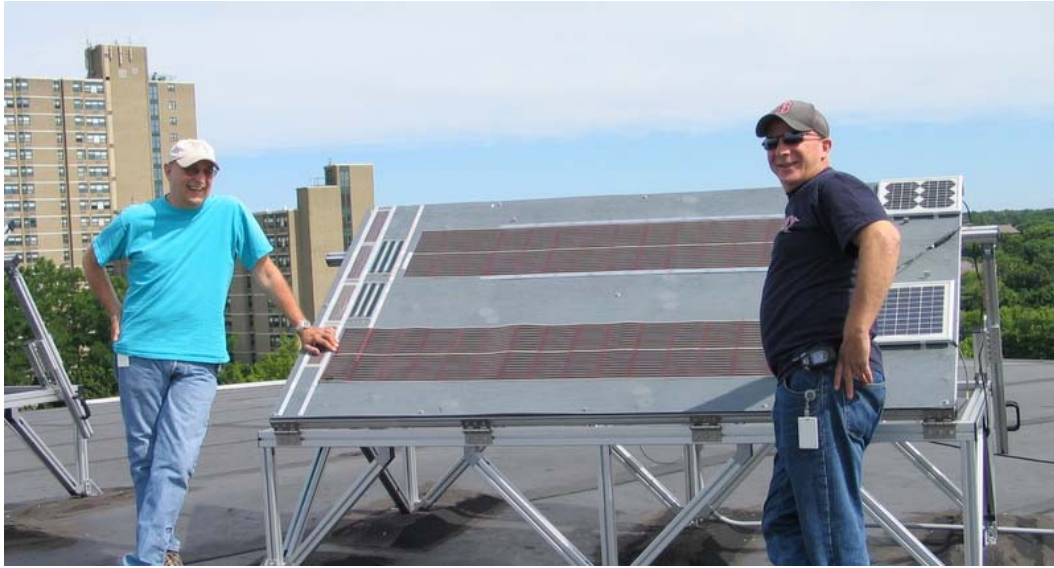
## LEDs



## FETs

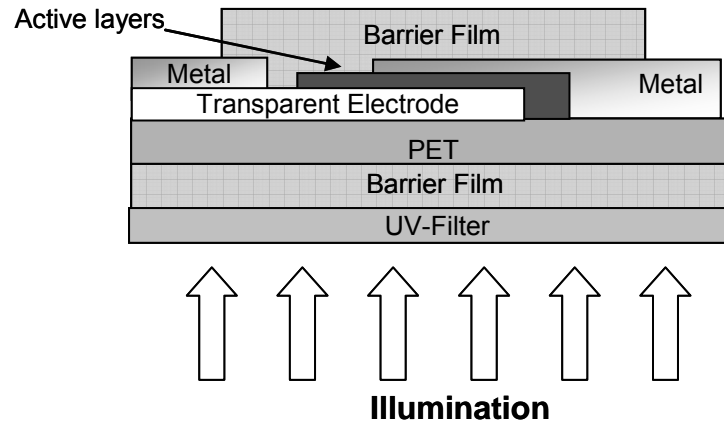


# Rooftop testing of BHJ solar cells at KONARKA



# Lifetime: Rooftop and Accelerated Degradation

## Flexible devices packaged with commercial, low cost barrier films (Konarka)



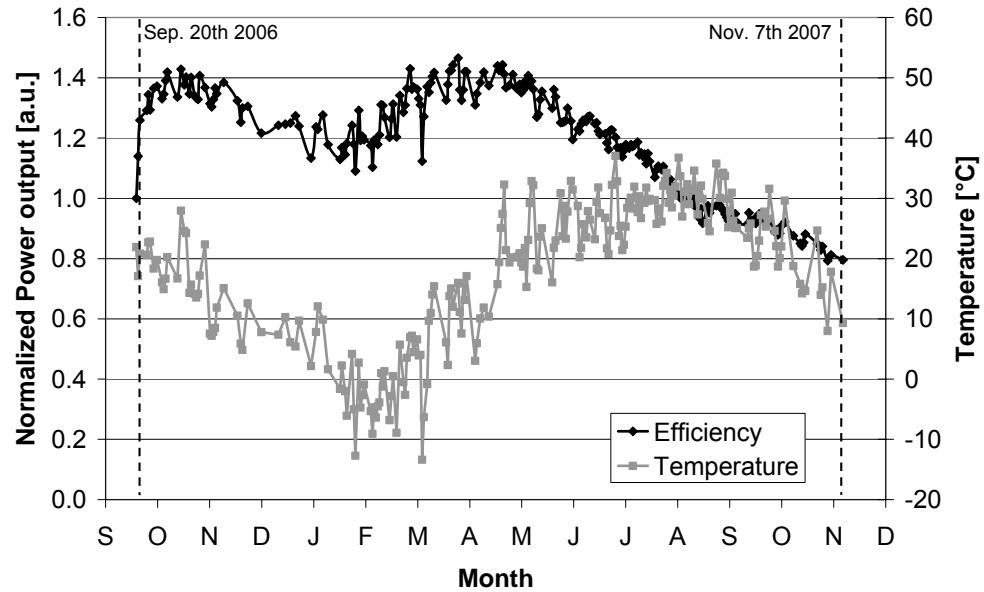
### Flexible Organic P3HT:PCBM Bulk-Heterojunction Modules with more than 1 Year Outdoor Lifetime

Jens A. Hauch, Pavel Schilinsky, Stelios A. Choulis, Richard Childers, Markus Biele and Christoph J. Brabec

### Long-Lived Flexible Organic Solar Cells

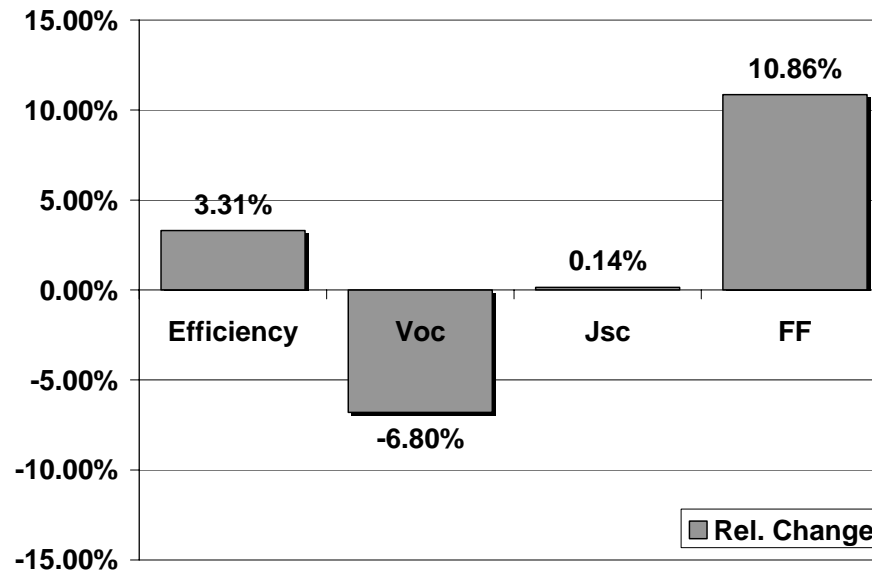
Jens A. Hauch, Pavel Schilinsky, Stelios C. Choulis, Sambatra Rajoelson and Christoph J. Brabec

# Outdoor rooftop lifetime (Konarka)



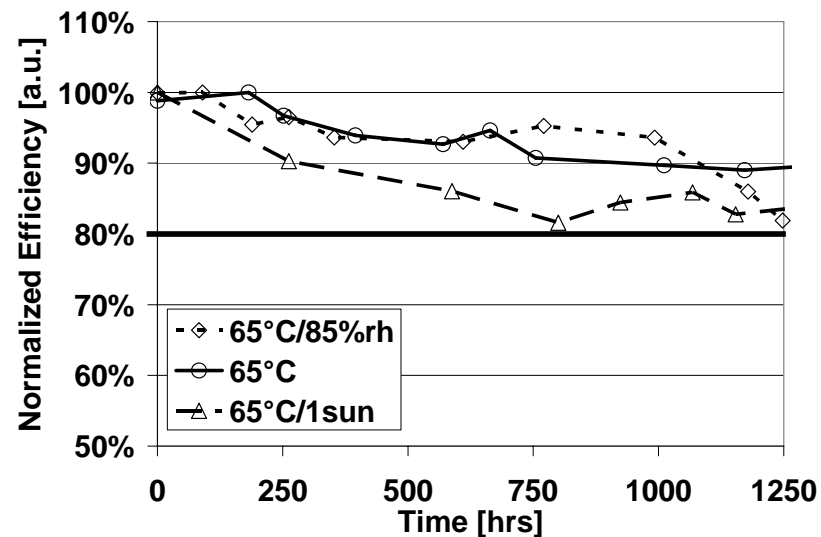
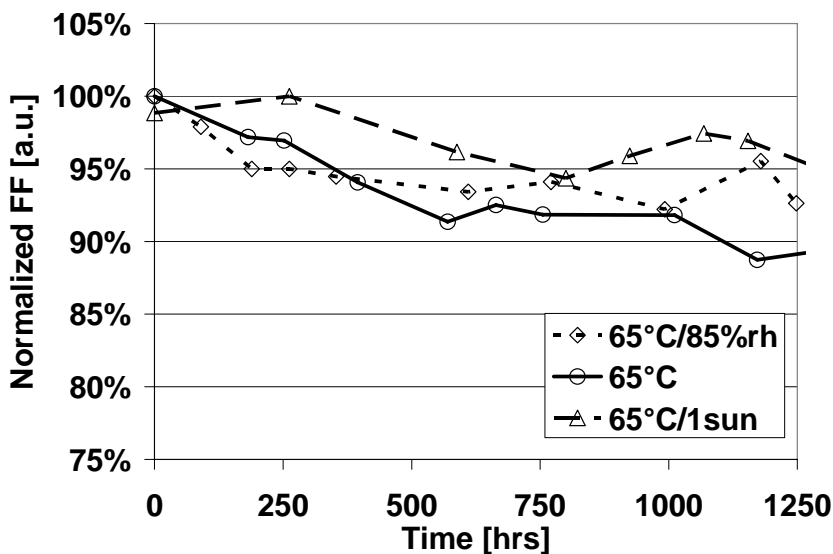
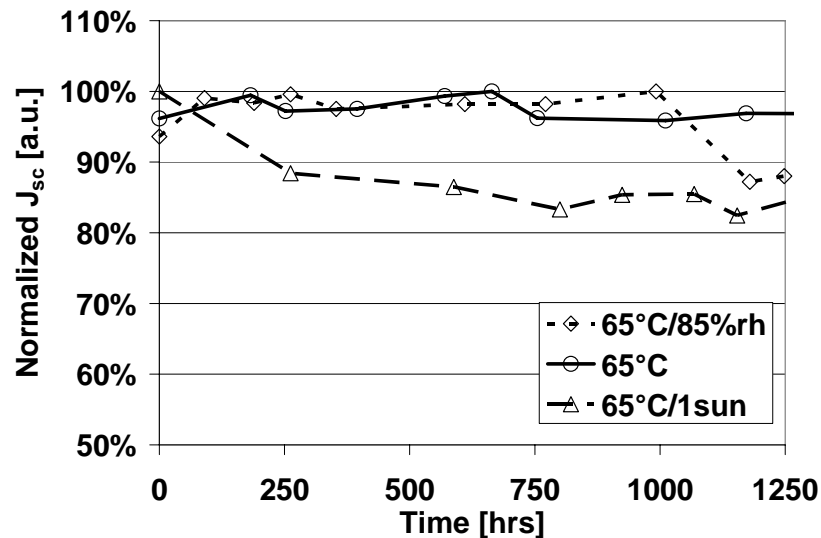
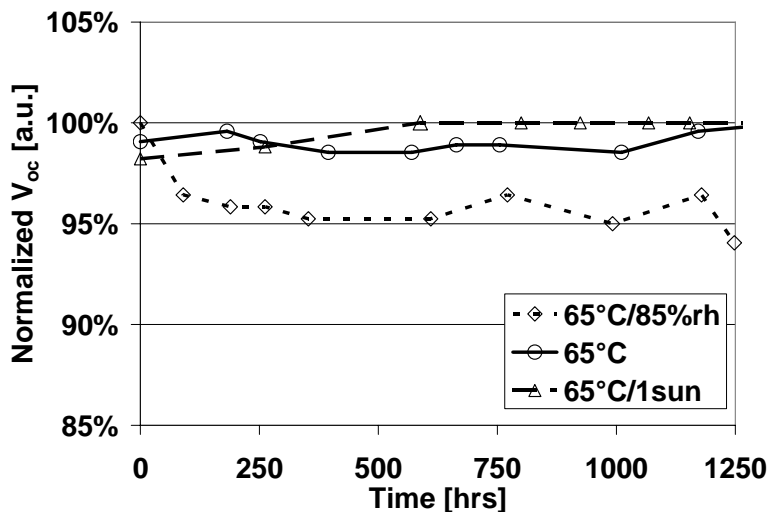
Efficiency actually increased ---

Drop in power output after 1 year due to small shift in the maximum power point (from 0.87V to 0.8V).



# Accelerated Degradation ---

## Flexible devices packaged with commercial, low cost barrier films (Konarka)





**Goal: Efficiency > 10 - 15% with polymer  
"bulk heterojunction" nano-materials**



Low Cost Roll-to-Roll manufacturing by  
printing and coating technologies

# Acknowledgement



Professor Kwanghee Lee ---UCSB and GIST (Korea)

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Prof G. Bazan, D. Moses, J. Peet

Christoph Brabec and colleagues at Konarka



