



*Consiglio Nazionale delle Ricerche*

Istituto per la Sintesi Organica e la Fotoreattività (CNR-ISOF)

Bologna (Italy)

# Plastic solar cells

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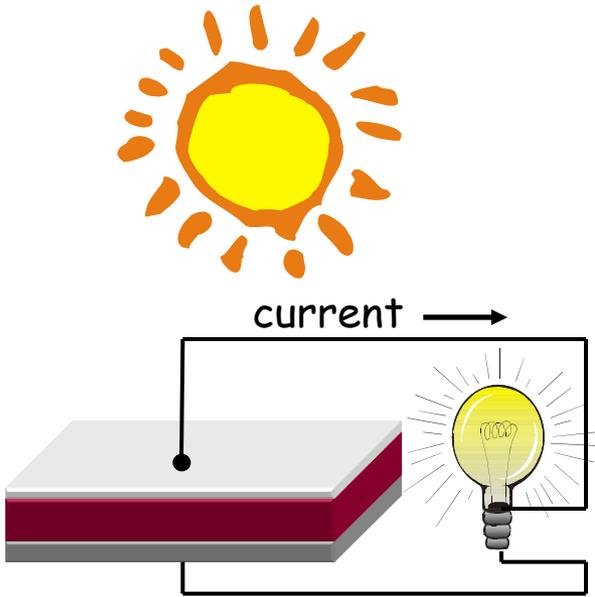
# Outline

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- Organic semiconductors
  - ✓ *Properties*
  - ✓ *Advantages and disadvantages*
- Plastic solar cells: some basics
  - ✓ *Generation of free carriers*
  - ✓ *Materials*
  - ✓ *The role of active layer morphology*
- Current research trends and perspectives
- Concluding remarks

# From solar light to electricity: main steps

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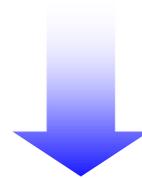
● Absorption of solar light



● Creation of free charge-carriers



● Transport of carriers to the contacts



● Extraction of carriers

## ORGANIC MATERIALS

# Fantastic plastic

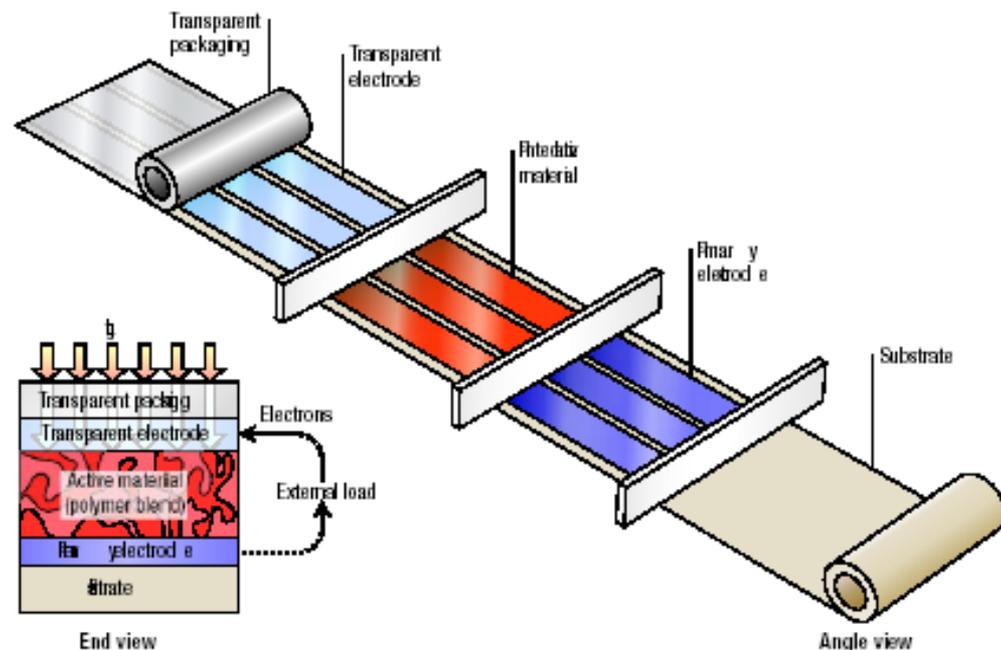
Polymer materials could bring down the cost of electricity production using photovoltaic technology to below \$1 per watt for the first time, and enable mass-market, portable applications for photovoltaic technology.

Russell Gaudiana\* and  
Christoph Brabec†

Konarka Technologies, 100 Foot of John Street,  
Booth Mill South, 3rd Floor Lowell, Massachusetts  
01852, USA

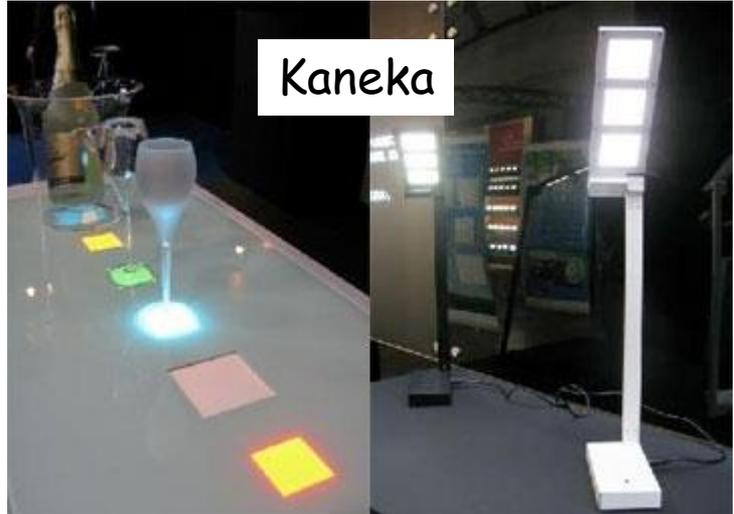
e-mail: \*rgaudiana@konarka.com;  
†cbrabec@konarka.com

**M**uch of the early work on photoactive materials for photovoltaics focused on crystalline silicon, which dominates the commercial solar-energy field today. Several other materials, such as amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), are also now in various stages of commercialization, and are known as thin-film technologies. The lower manufacturing costs and higher production throughput of these materials potentially translate into lower electricity costs. Current thin-film technologies are expected to bring costs reasonably close to \$1 per watt of electricity produced at peak solar power.



**Figure 1** Polymer-based photovoltaic cells can be manufactured using standard printing processes.

# Plastic electronics is a reality



# Advantages of organic semiconductors

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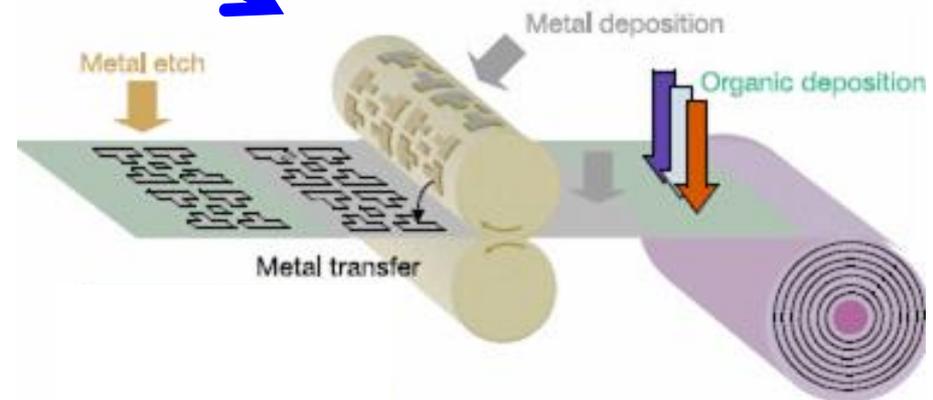
- Facile chemical tailoring of their properties
- High optical absorption coefficients
- Flexible or conformable devices can be fabricated
- Lightness in weight
- Low-cost thin-film technology

*No high temperature processes*

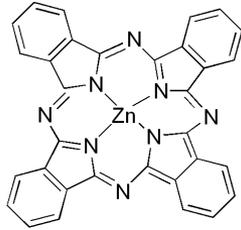
*Solution processable*

*Roll-to-roll coating possible*

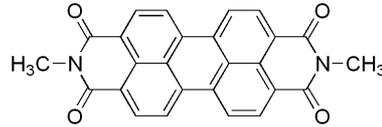
*Large-area device deposition*



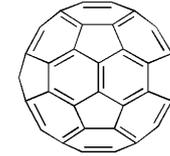
# Polymers and low molecular weight molecules



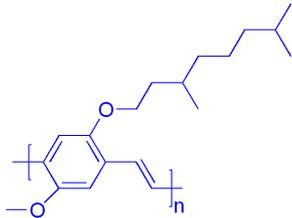
ZnPc



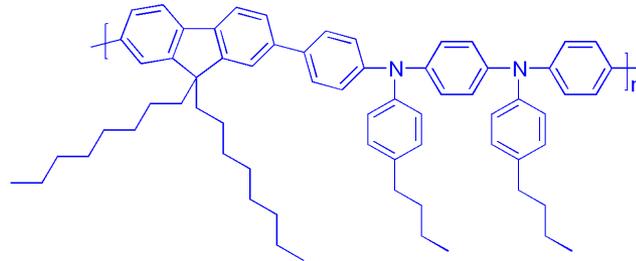
Me-Ptcdi



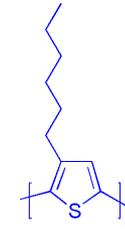
C<sub>60</sub>



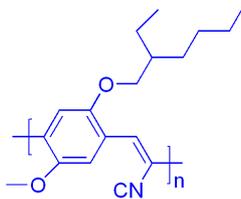
MDMO-PPV



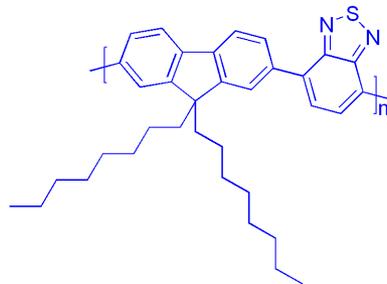
PFB



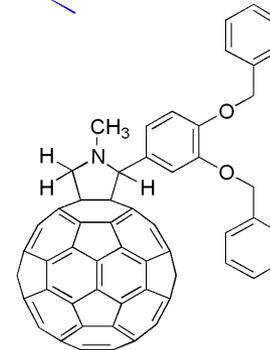
P3HT



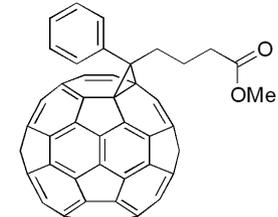
CN-MEH-PPV



F8BT



FPYE

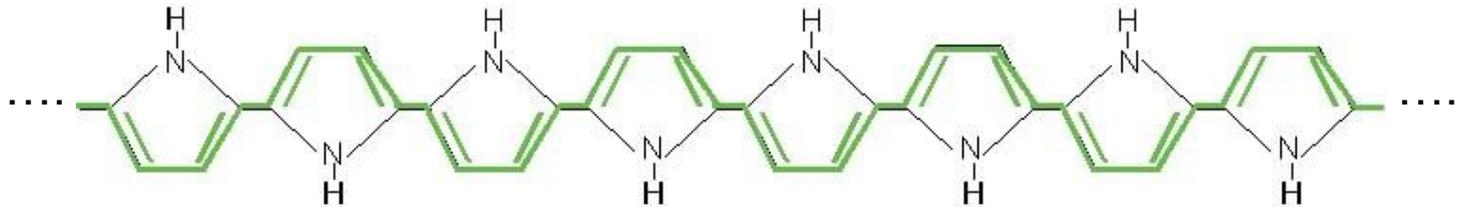


PCBM

# Organic semiconductors: conjugated molecular structures

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- They have a molecular structure with a framework of alternating single and double chemical bonds (conjugation)



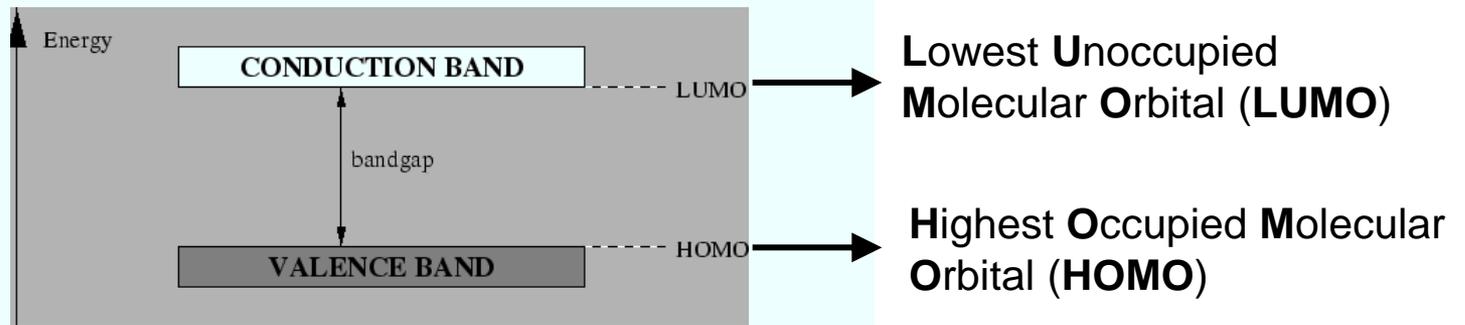
- They have intramolecular covalent bonds, but molecules are held together by weak intermolecular van der Waals interactions



Narrow electronic bandwidth formed in organic semiconductors

# Disadvantages of organic semiconductors

## Narrow electronic bandwidth



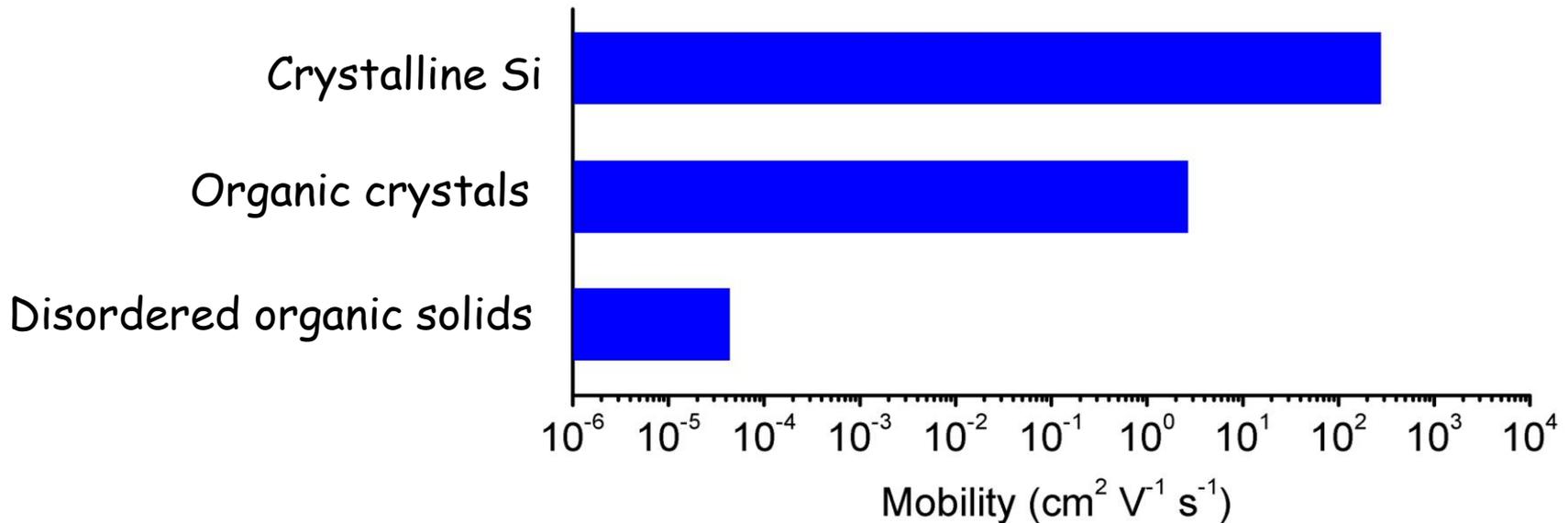
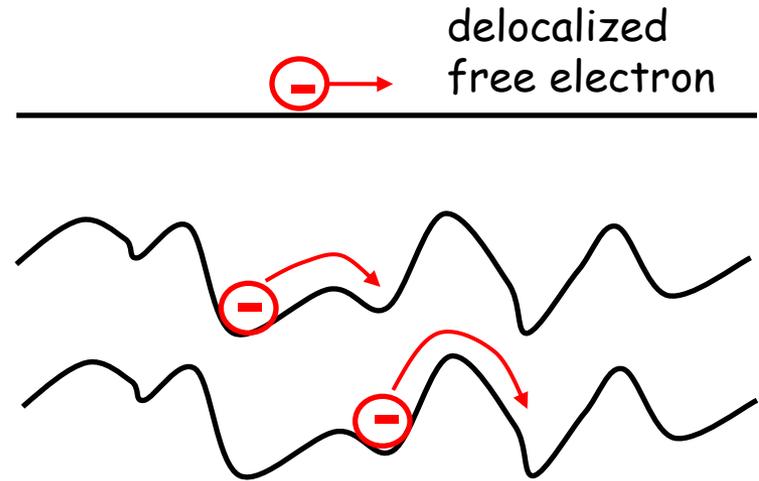
- Absorption spectrum narrower than in conventional inorganic semiconductors
- No band-like charge transport mechanism

# Charge transport in organic semiconductors

No band-like transport mechanism  
but hopping transport between  
localized states



Low charge-carrier mobilities with  
respect to conventional inorganic  
semiconductors



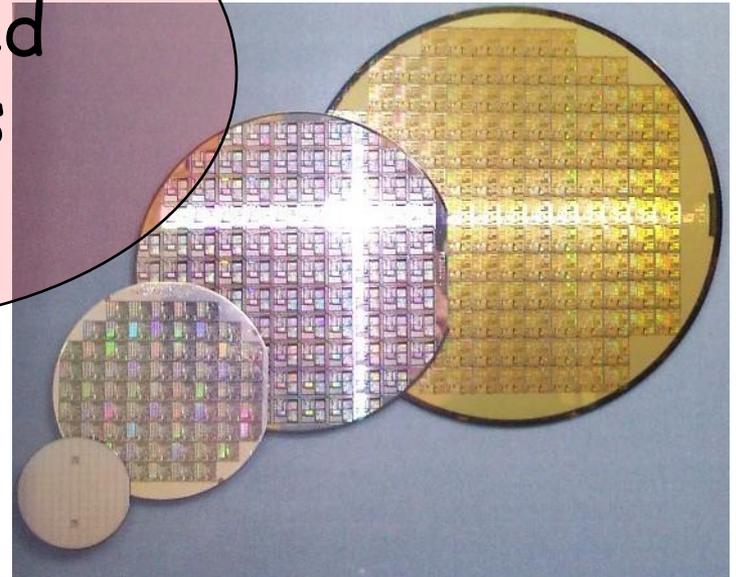
# Conjugated polymers: plastic semiconductors



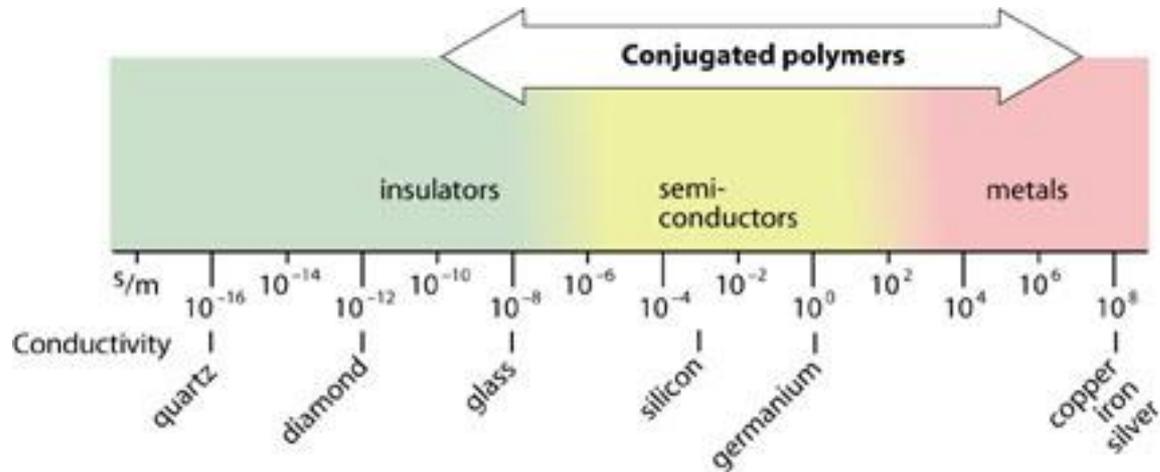
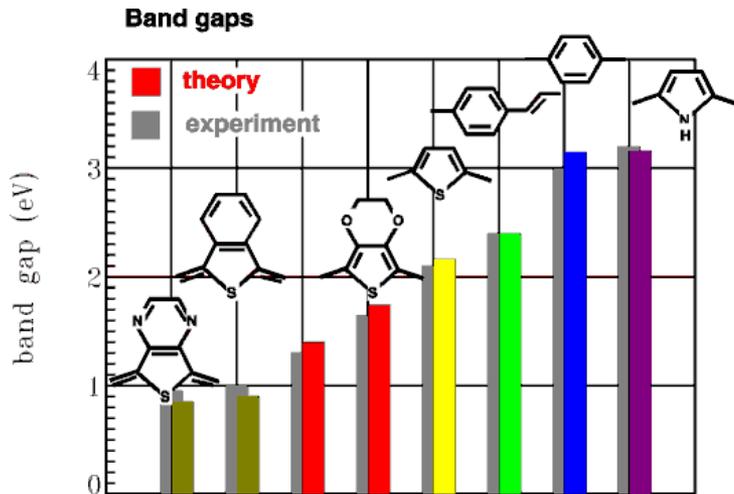
Mechanical properties of common plastics

Conjugated polymers

Electronic properties similar to those of conventional semiconductors

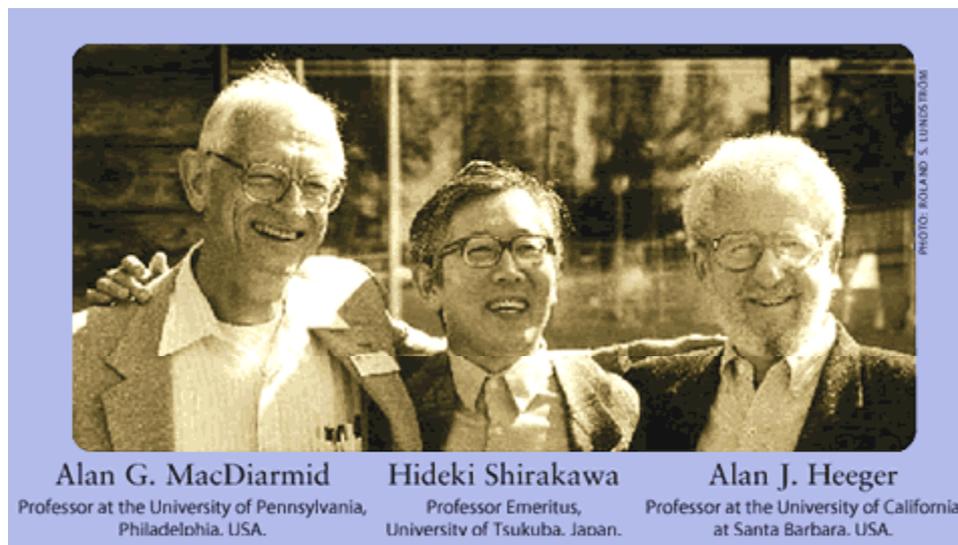


# Conjugated polymers: tunability of their electronic properties



# Nobel Prize for the discovery of conductive polymers

## NOBEL 2000



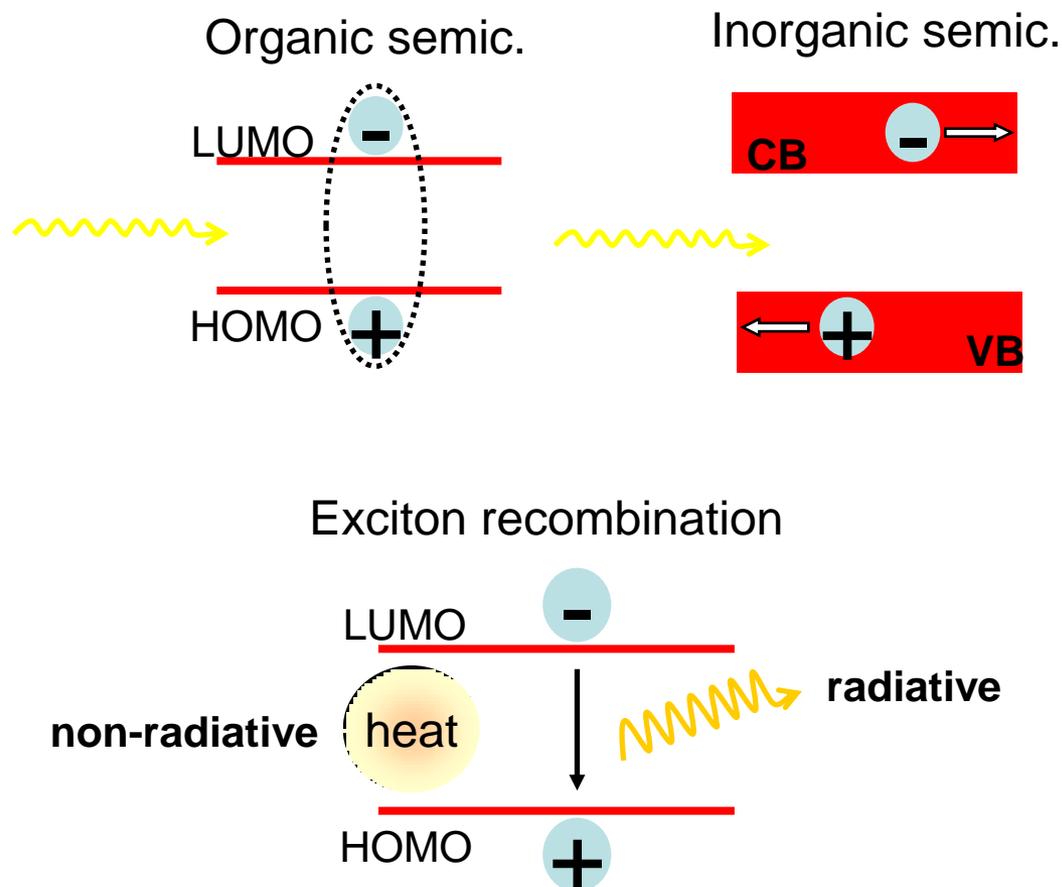
Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have been awarded the Nobel Prize in Chemistry for showing how plastic can be made to conduct electric current. This surprising discovery has radically altered our view of plastic as a material. Conductive polymers today constitute a growing research field of great significance to chemists and physicists alike.

# "Excitonic" character of organic semiconductors

Light absorption results in the formation of strongly bound electron-hole pairs (excitons) in organic materials, rather than free electron-hole pairs directly generated in inorganic semiconductors

To separate the bound electrons and holes, a driving force is required to overcome the exciton-binding energy (around 0.5 eV).

Excitons that are not split recombine, either radiatively or non-radiatively.

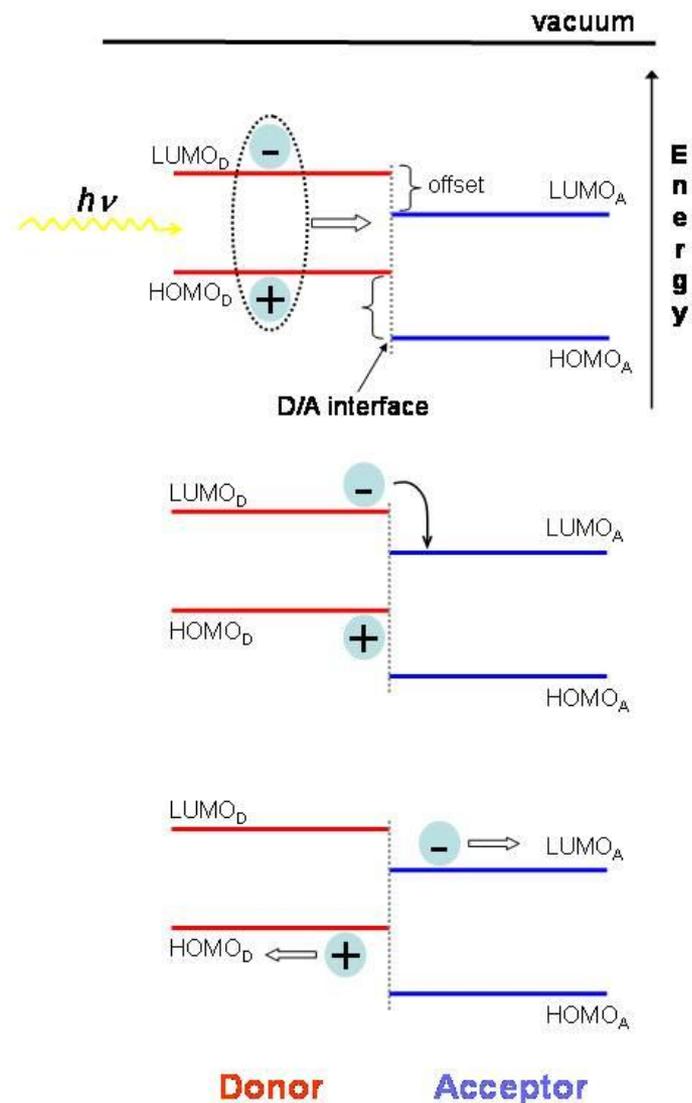


# From excitons to free charge carriers: donor (D) and acceptor (A) materials

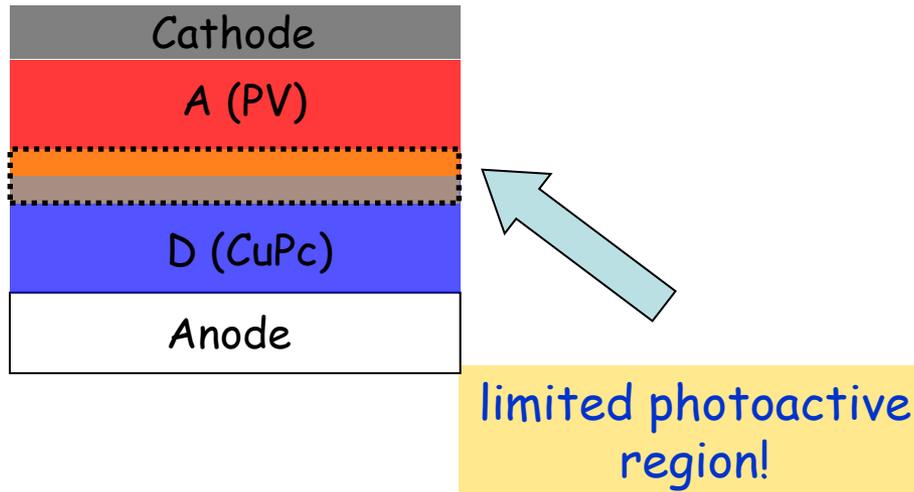
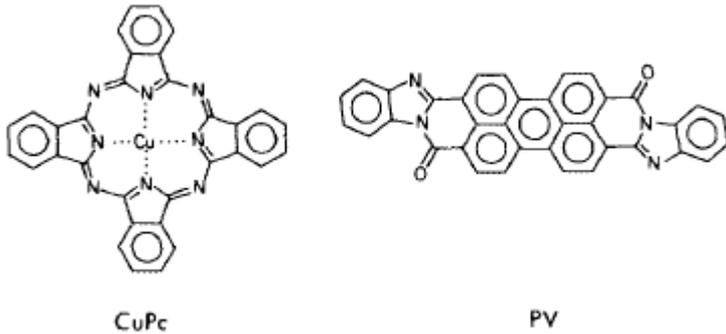
Excitons can be efficiently split at the interface between two materials with dissimilar energy levels: an electron-donor (D) and an electron-acceptor (A)

Excitons dissociate through a photoinduced charge transfer process

Upon charge transfer, electrons are transported in the electron-acceptor material and holes in the electron-donor material



# Tang's cell: the bilayer approach



The photoactive region is limited by the exciton diffusion length (10-20 nm)

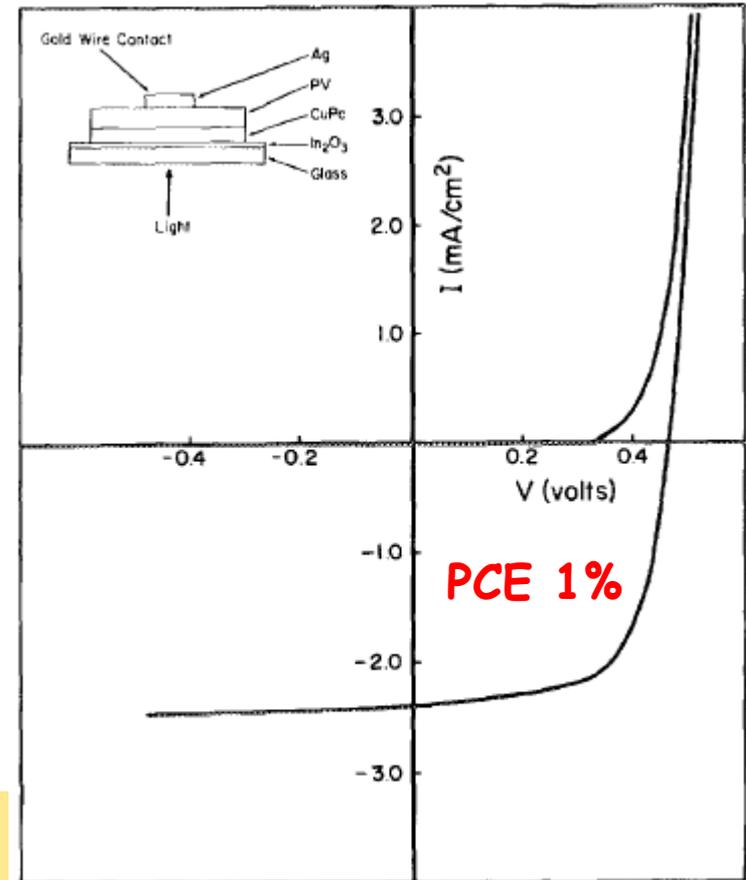
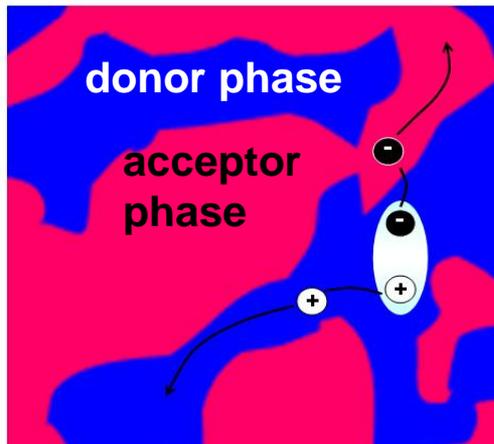
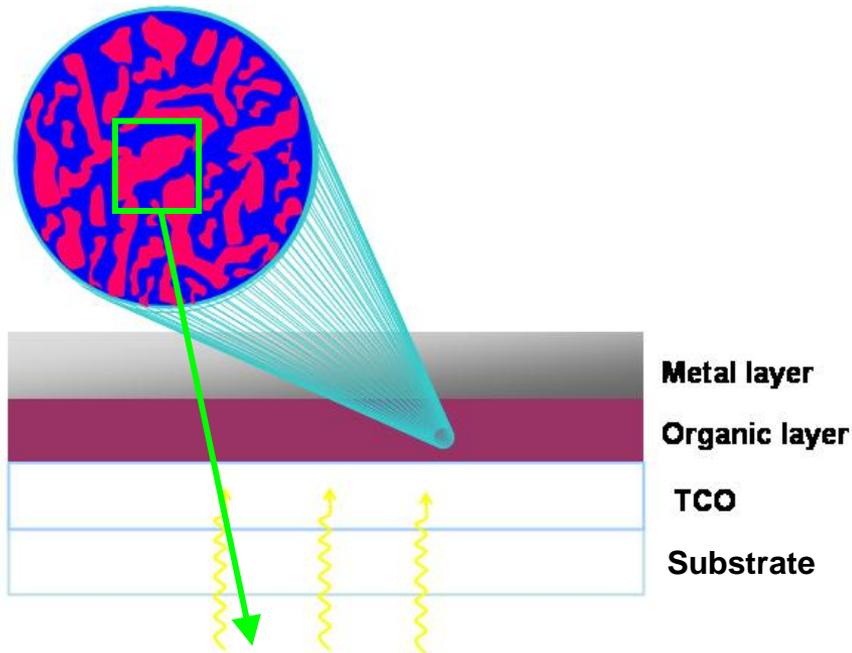


FIG. 1. Configuration and current-voltage characteristics of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell.

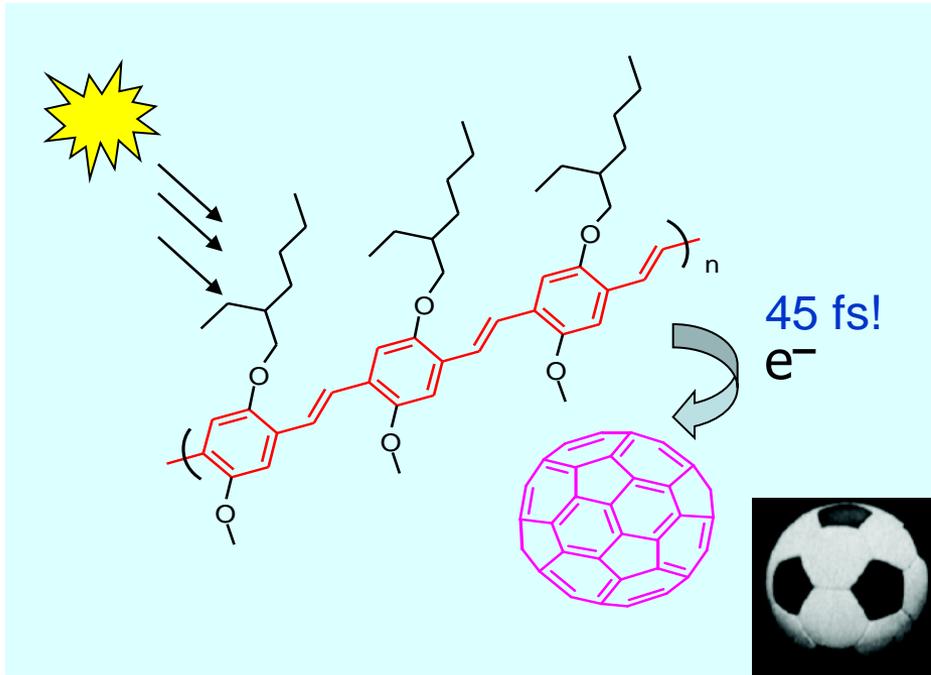
# The bulk-heterojunction (BHJ) approach



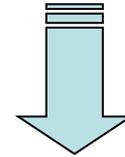
- ❑ Donor and acceptor materials are mixed together on the nanoscale level. Both materials must be very soluble in the same solvent!
- ❑ All photogenerated excitons are within a diffusion length (10-20 nm) of a D/A interface
- ❑ Distributed active interfaces throughout the bulk of the device
- ❑ Percolation limit for both materials has to be reached. The blend morphology has to enable charge-carrier transport in the two different phases in order to minimize recombination

Skill lies in controlling the nanomorphology!

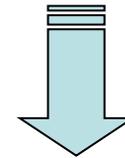
# Conjugated polymers - Fullerene ( $C_{60}$ ): excellent D-A pairs



A number of conjugated polymer-fullerene pairs exhibit ultrafast photoinduced charge transfer (45 fs) with a back transfer of orders of magnitude slower

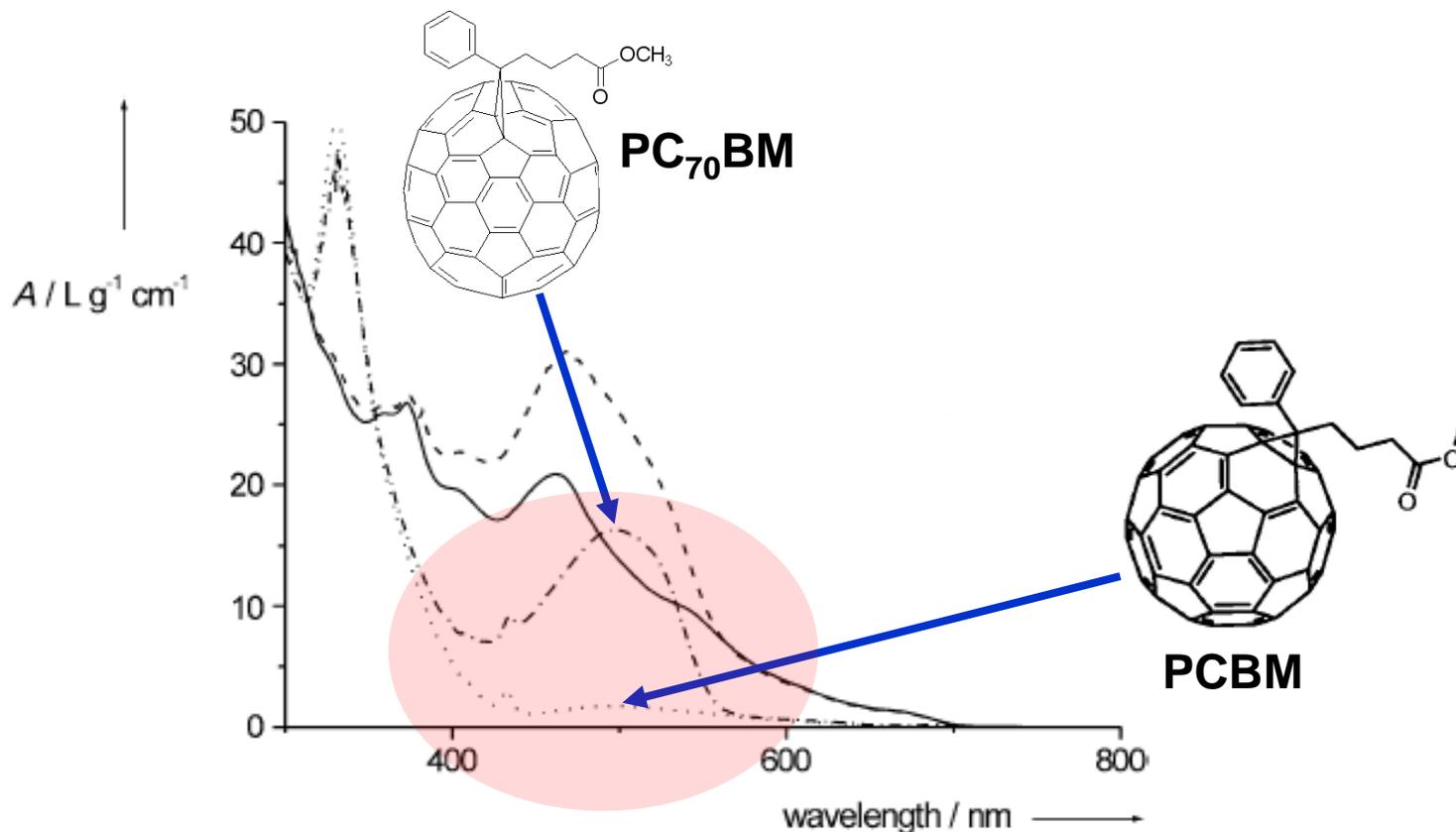


Every photon absorbed yields one pair of separated charges!



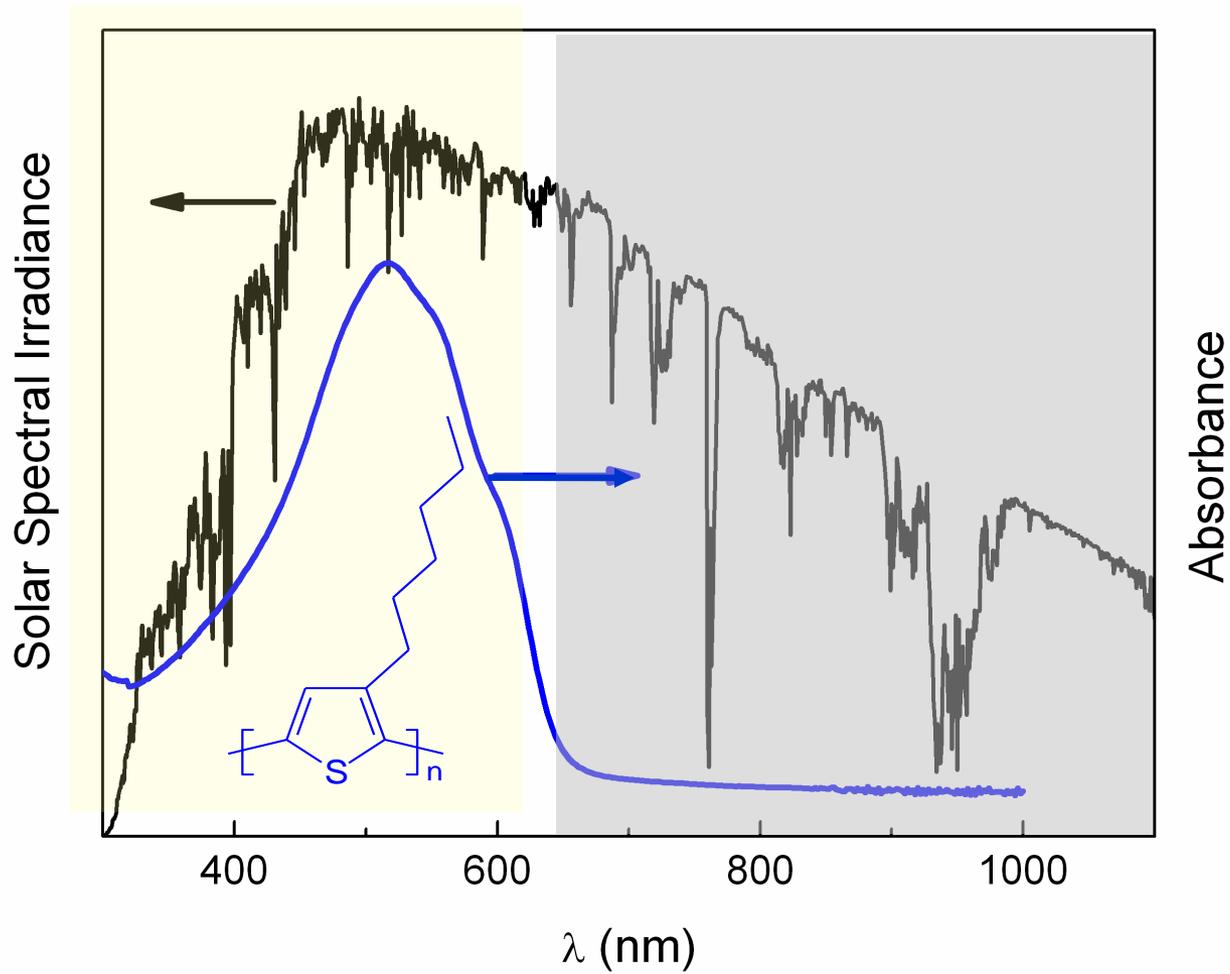
Quantum efficiency for charge separation approaches unity

# Common soluble derivatives of fullerenes

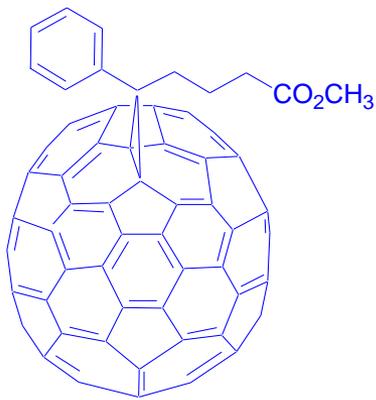
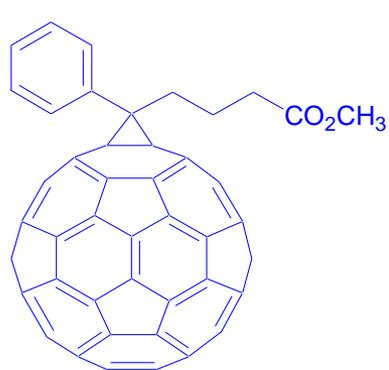
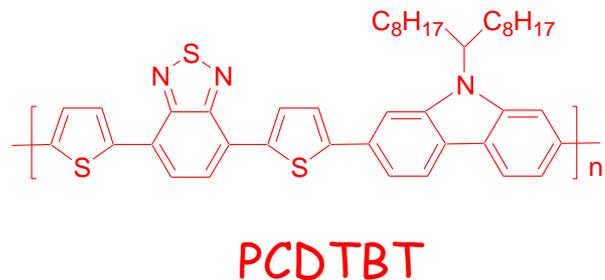
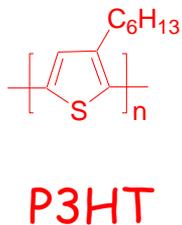
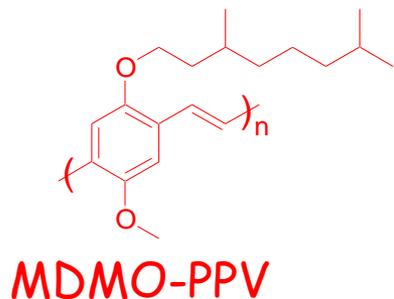


In polymer/fullerene BHJ solar cells, the donor polymer is also the main light absorber component

# Narrow electronic bandwidth, narrow absorption bands

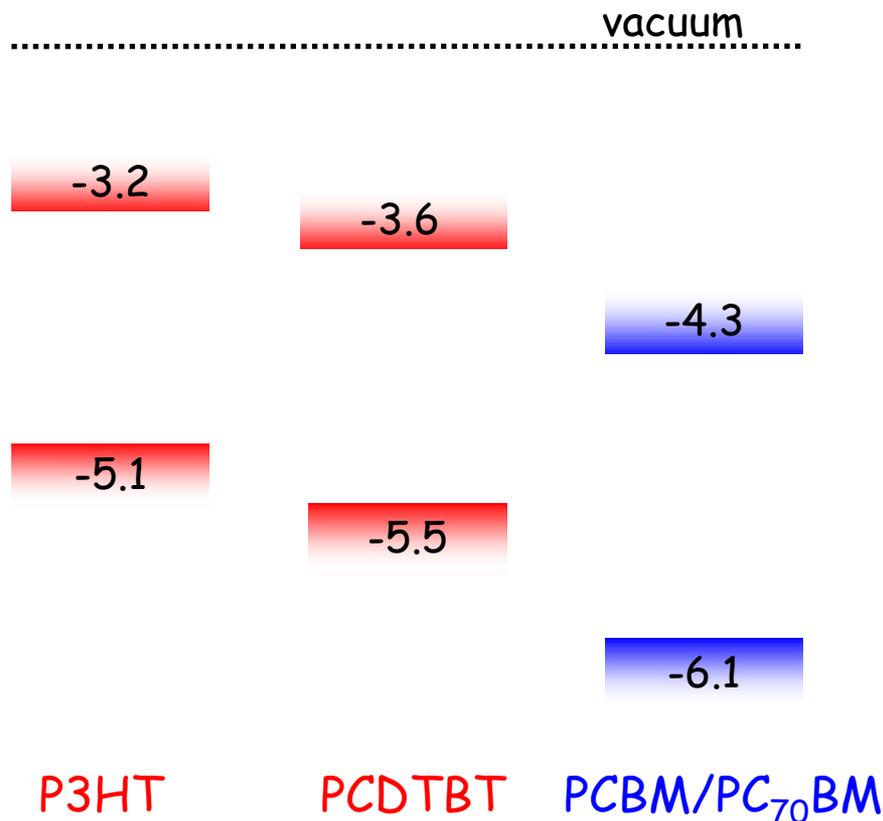


# Common donor and acceptor materials



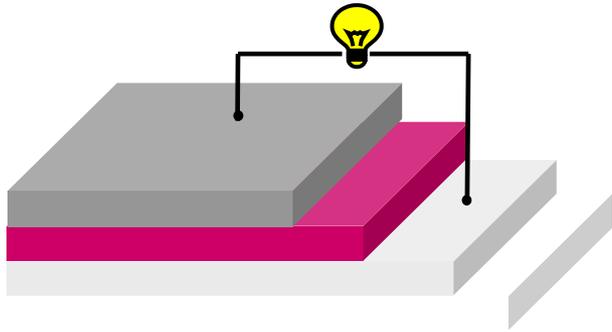
PCBM

PC<sub>70</sub>BM

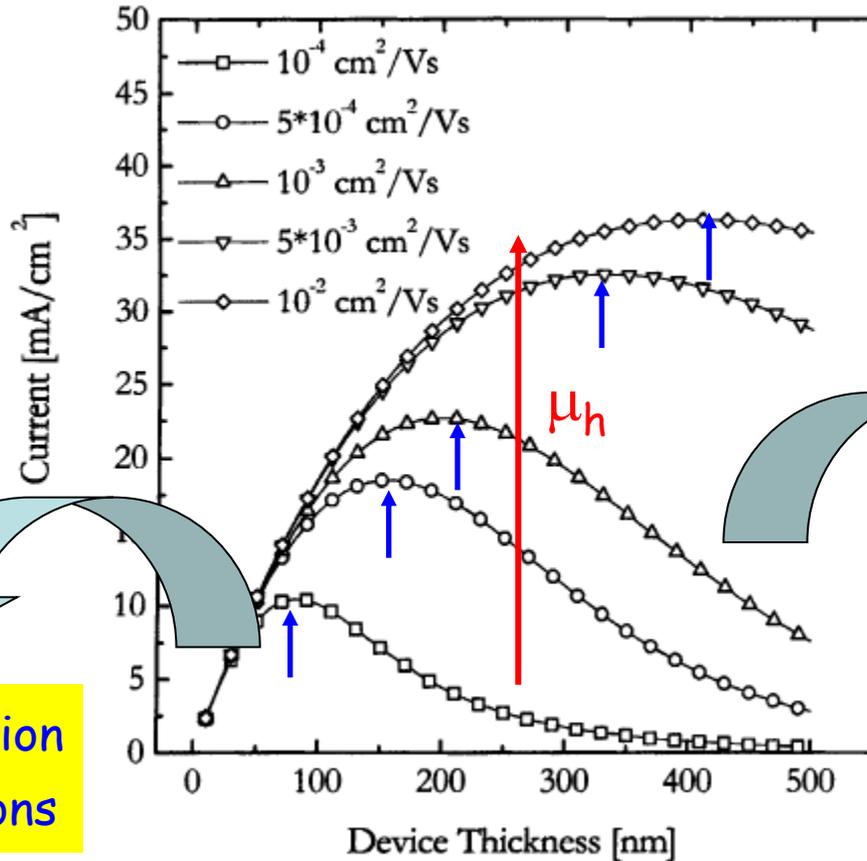


# Ultra-thin film photovoltaic technology

## Polymer:PCBM BHJ solar cells



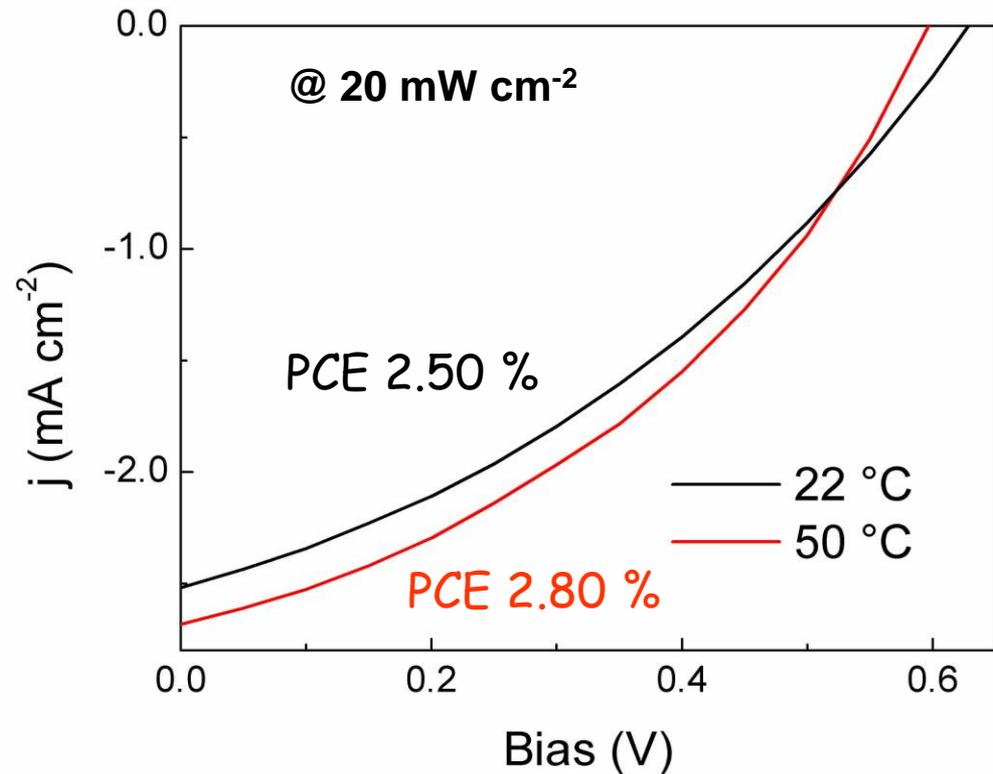
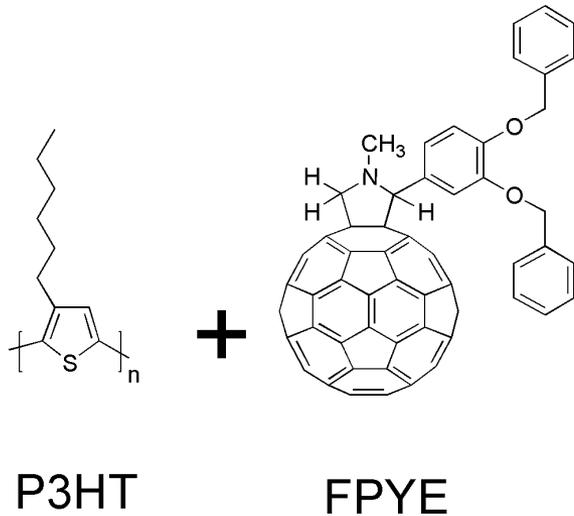
Active layer thickness:  
100-300 nm



Absorption  
limitations

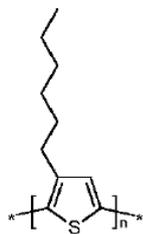
Transport  
limitations

# Positive temperature dependence of efficiency

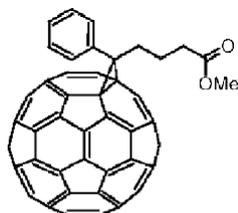


A consequence of the (poor) charge transport mechanism!

# The crucial role of blend morphology

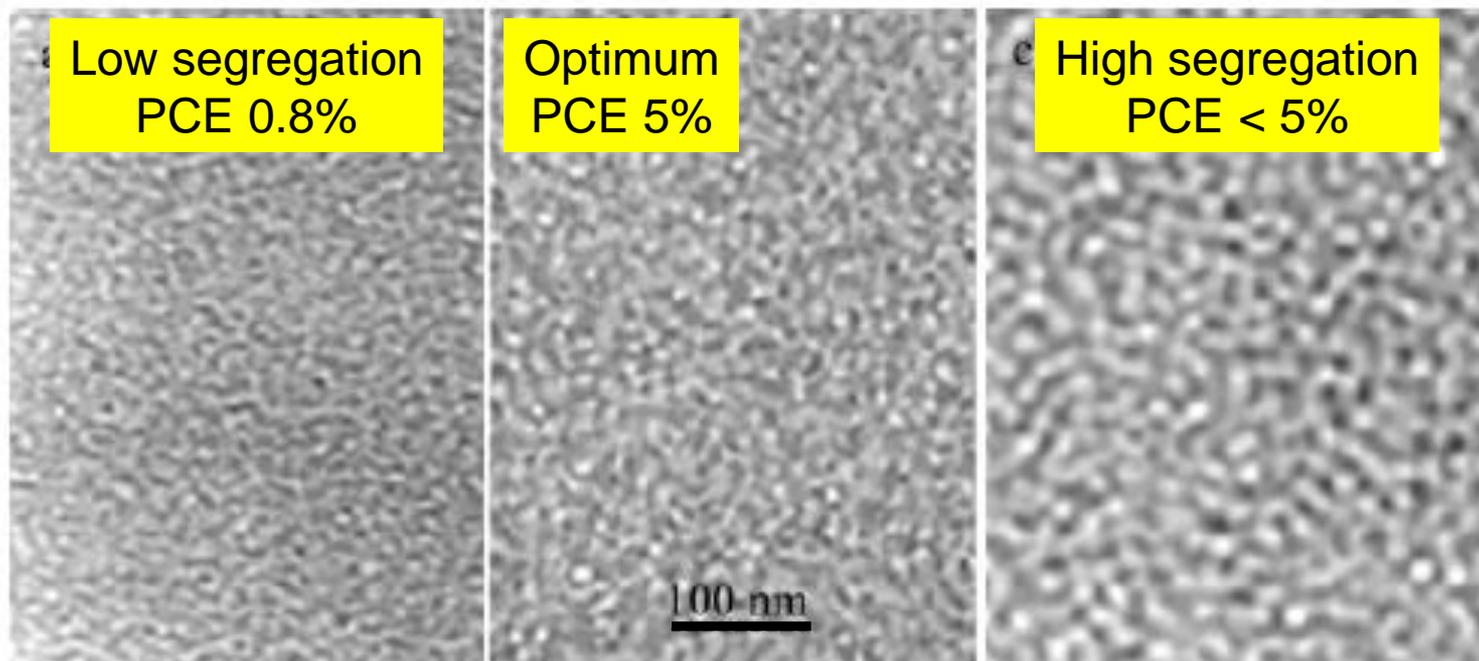


P3HT

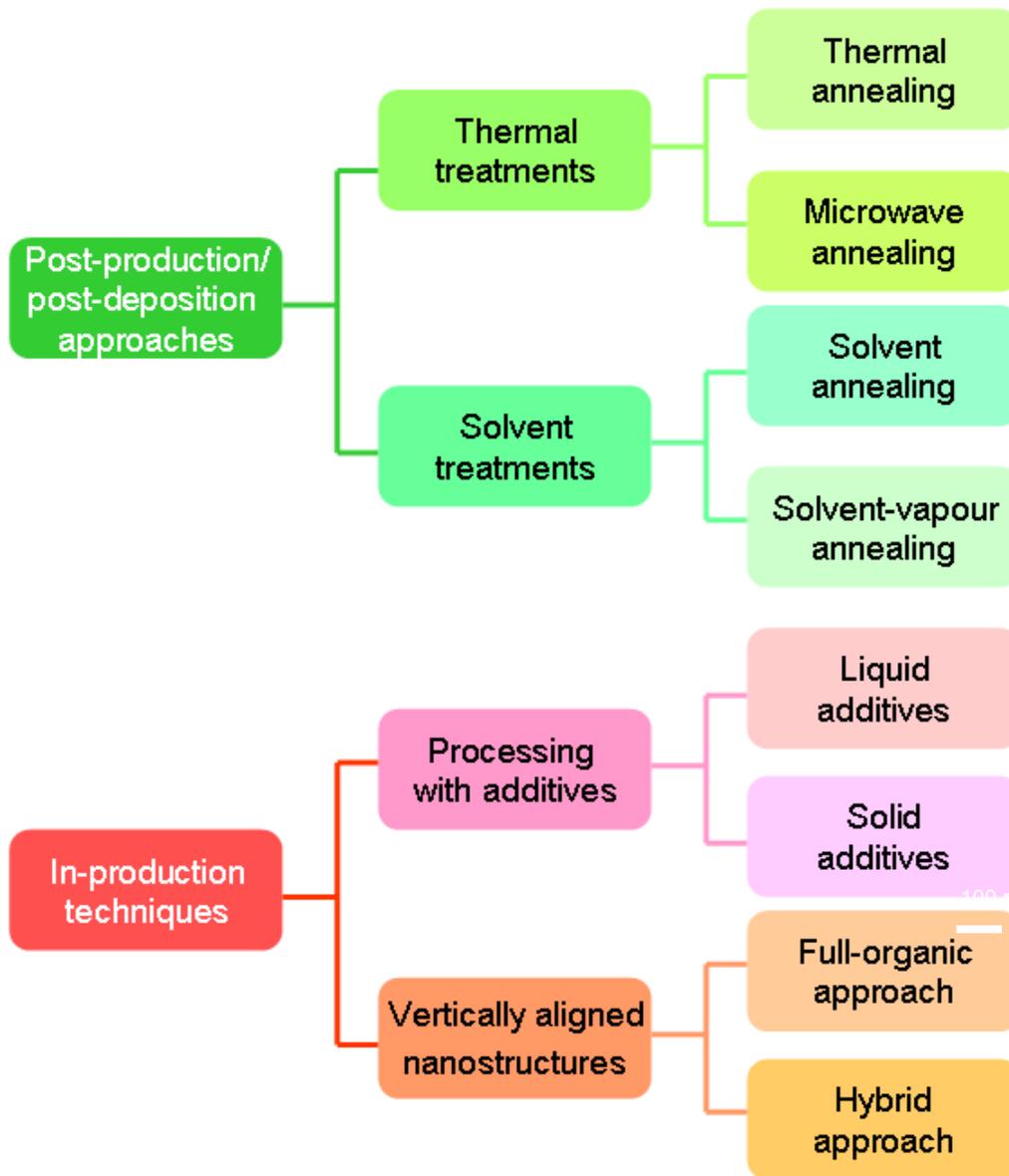


PCBM

P3HT:PCBM (1.0:0.8 by wt)



# Protocols for the optimization of active layer properties



N. Camaioni, et al., *J. Mater. Chem.*, 12, (2002) 2065

N. Camaioni, et al., *Adv. Mater.*, 14, (2002) 1735

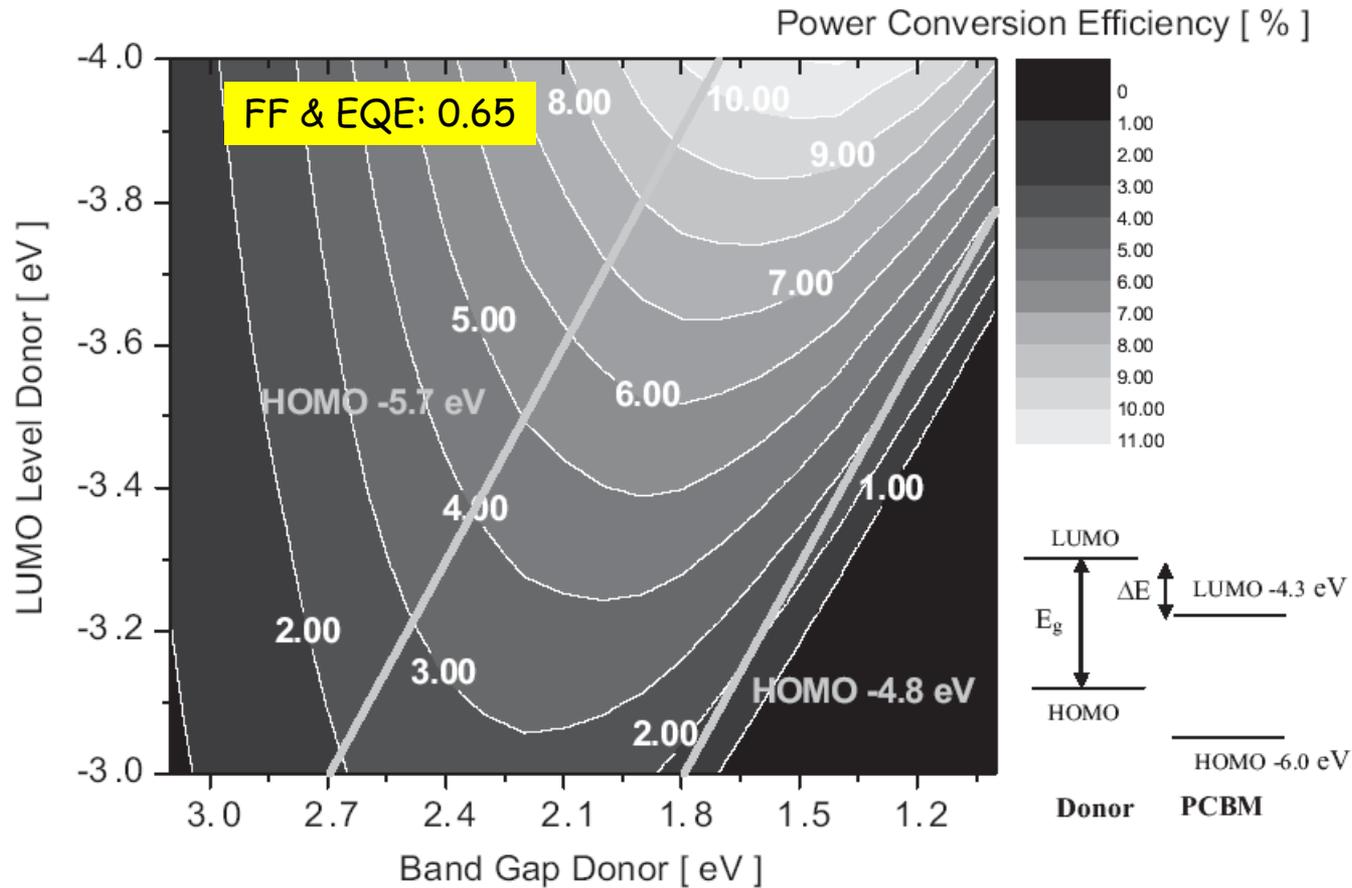
W. Ma et al., *Adv. Funct. Mater.* 15 (2005) 1617

G. Li et al., *Nature Mater.* 4, (2005) 864

J. Peet et al., *Nature Mater.* 6, (2007) 497

These protocols often induce also an improvement of the optical and transport properties of the active layer

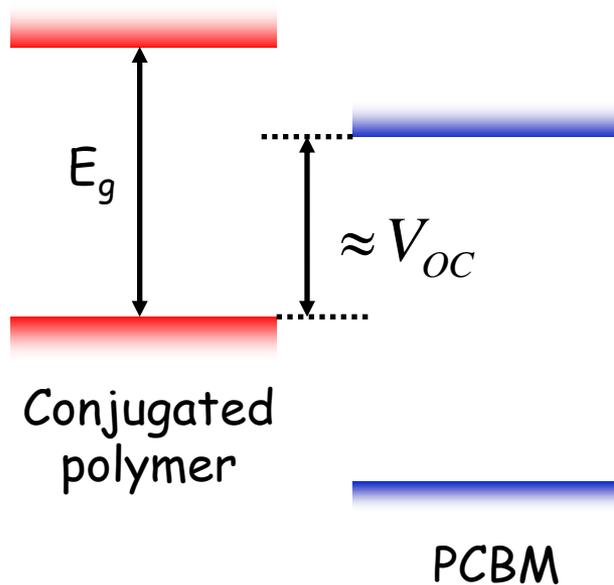
# Perspectives



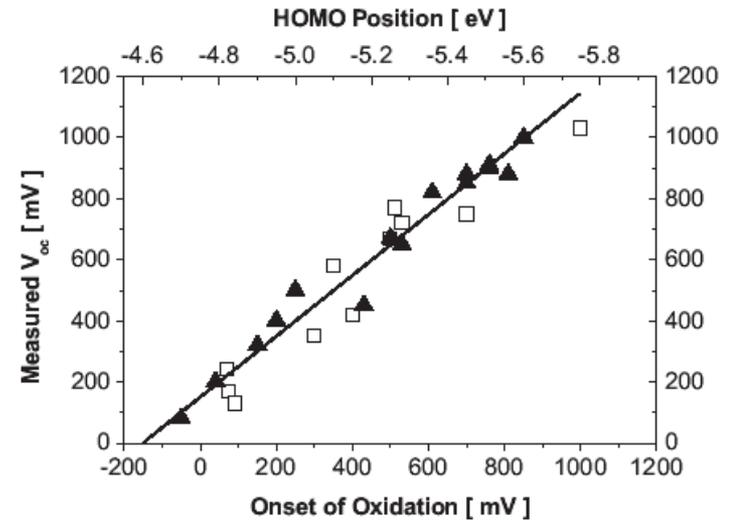
*Adv. Mater.* 18 (2006) 789

Conjugated polymers with optimised energy levels are required

# Current direction: development of polymers with optimised energy levels



$$V_{OC} \approx \frac{1}{e} (HOMO_{Polymer} - LUMO_{PCBM})$$

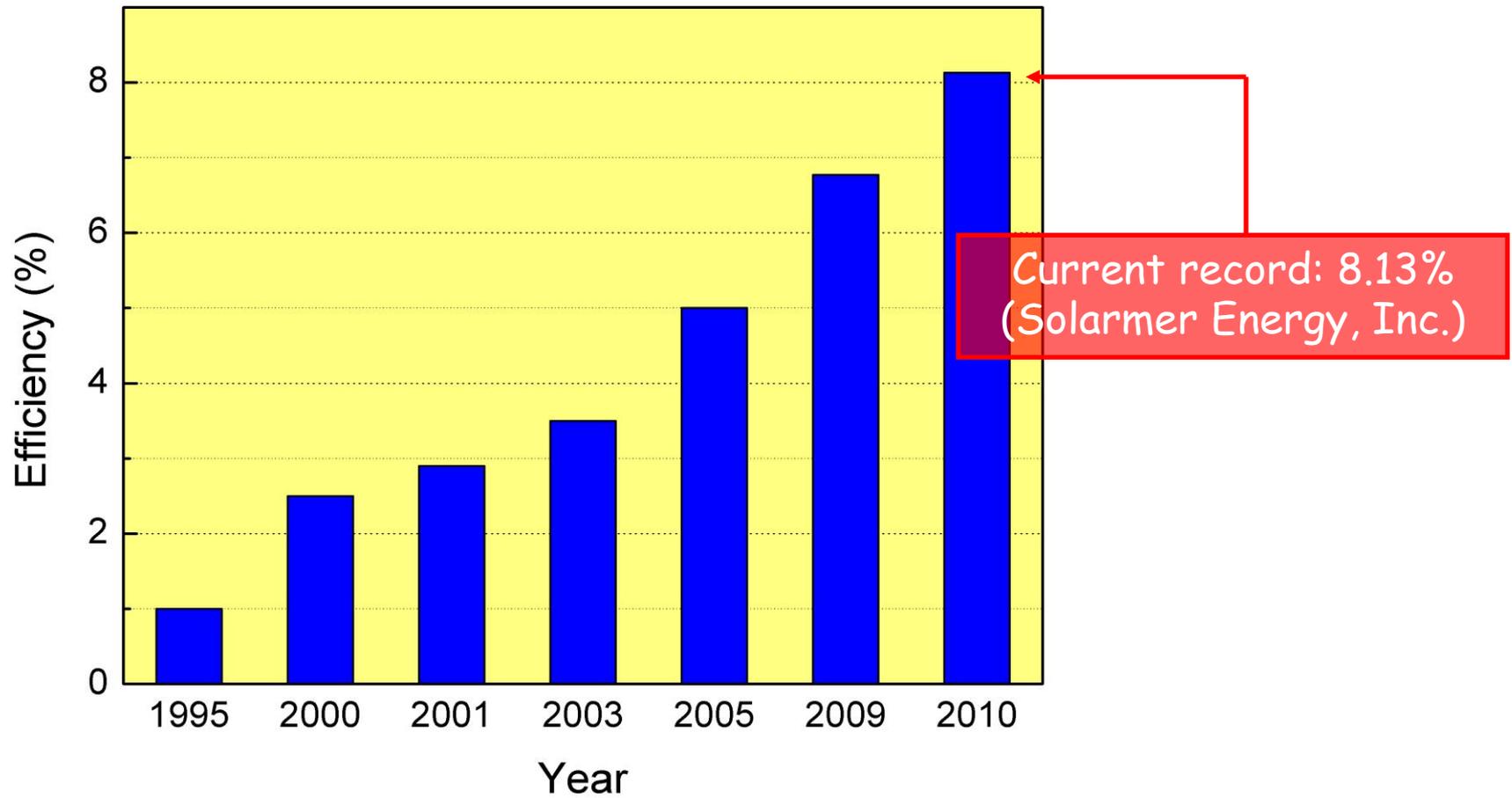


M.C. Scharber et al., *Adv. Mater.* 18 (2006) 789

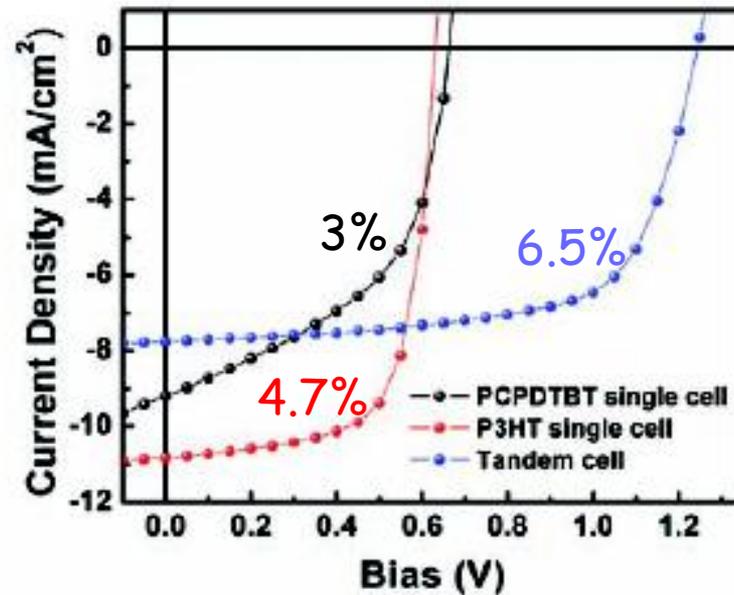
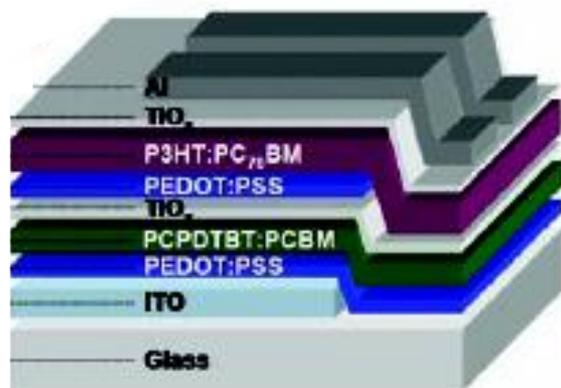
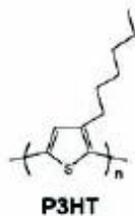
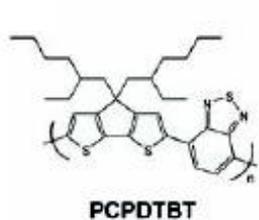
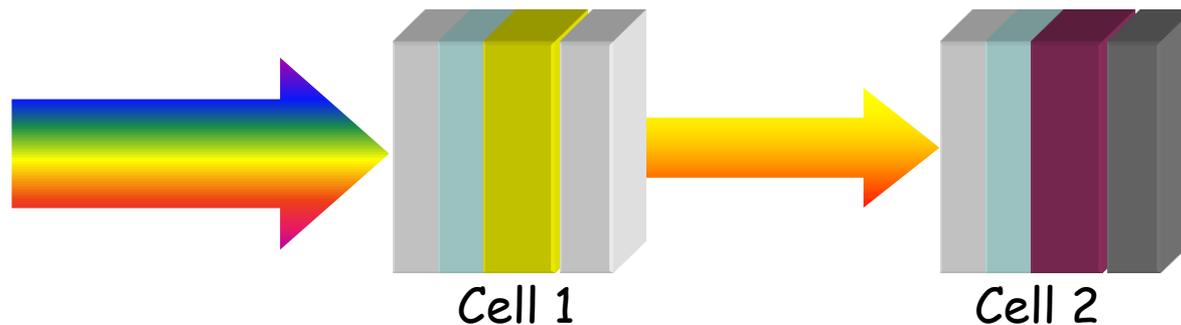
- Polymers with a low energy gap ( $E_g < 2$  eV) for higher short circuit current
- Polymers with a deep HOMO level for higher open circuit voltage
- High hole mobility

# Efficiency evolution and state of the art

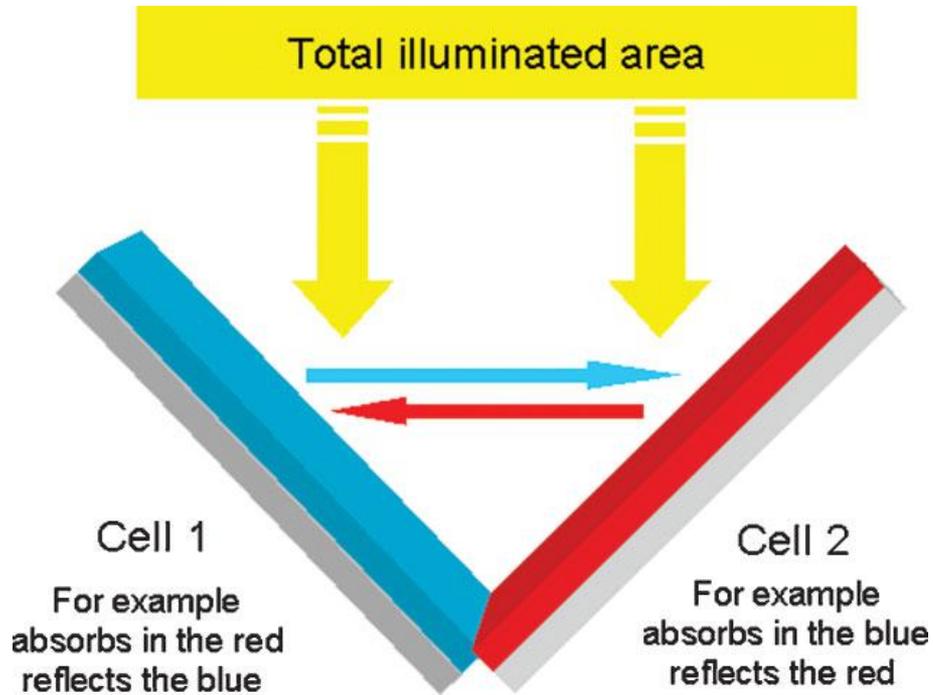
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# Plastic tandem solar cells



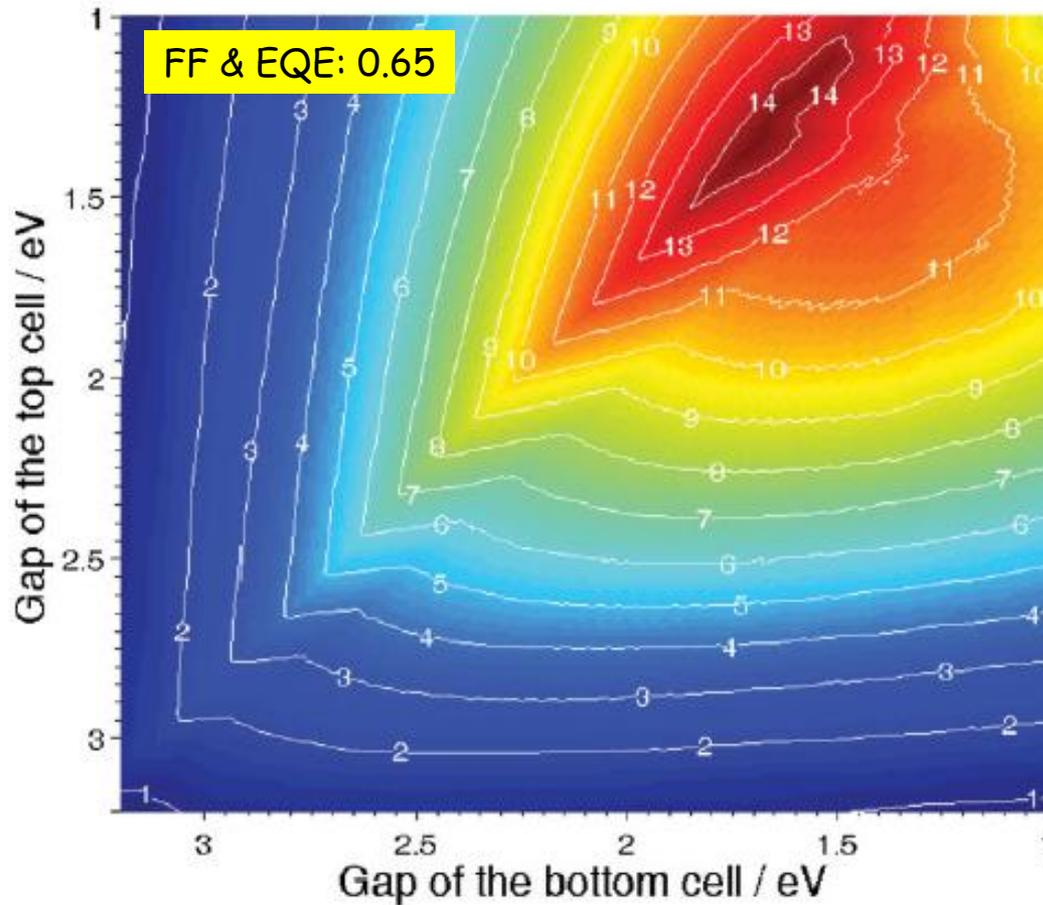
# Folded solar cells



[www.ifm.liu.se/biorgel/Research\\_OptoElectronics.html](http://www.ifm.liu.se/biorgel/Research_OptoElectronics.html)

K. Tvingstedt et al., *Appl. Phys. Lett.* 2007, 91, 123514

# Perspectives for tandem plastic solar cells



PCE up to 15%

# Roll-to-roll production of plastic PV modules



KONARKA



# Plastic photovoltaic modules

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# Applications



# Applications

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# Applications

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**San Francisco MTA**

# Applications

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# Concluding remarks

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- Semitransparent, lightweight, flexible printable photovoltaic modules can be produced (are produced)
- The colour of the modules can be tuned
- The performance of plastic solar cells are steeply increasing
- Efficiency up to 15% have been predicted for tandem structures
- Chemistry will have a great role in the development of innovative smart materials

Thank you for your attention!