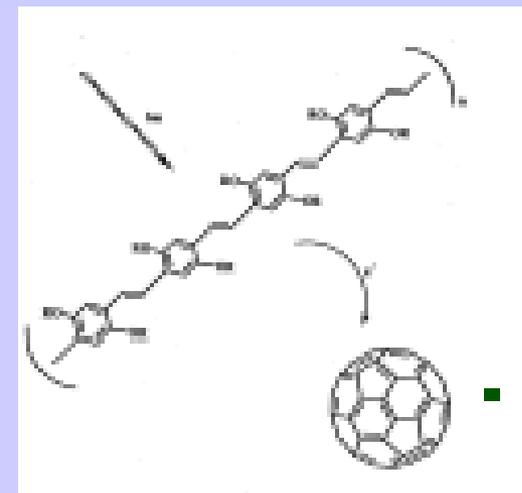
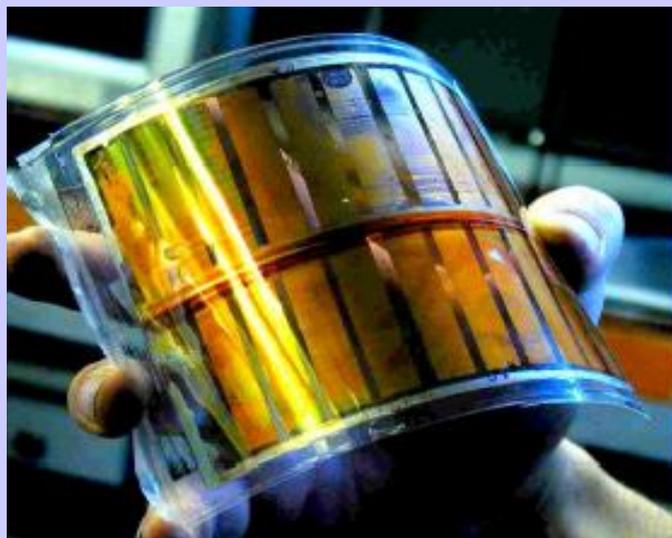




Organic Semiconductor-based Plastic Solar Cells OPVs



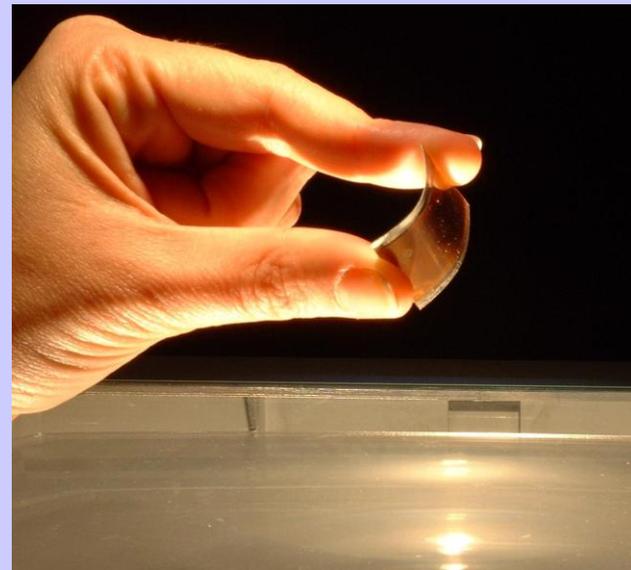
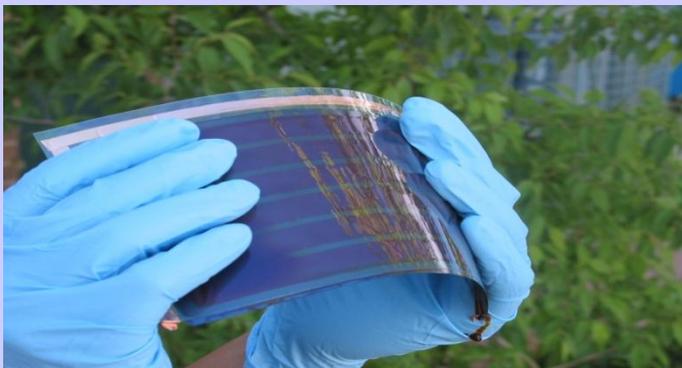
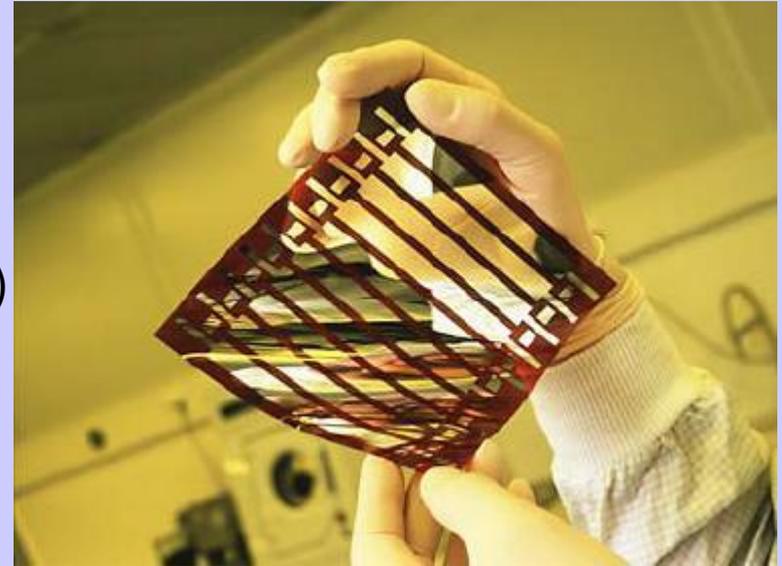
Organic Solar Cell



Why OPVs?

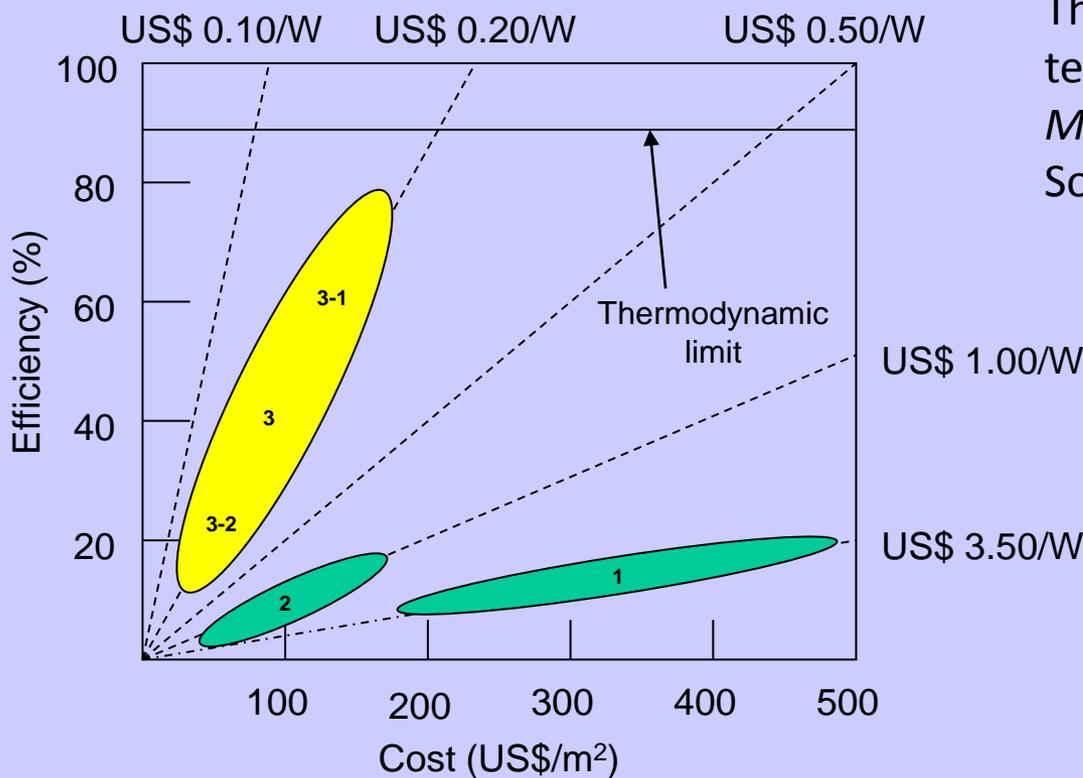
Advantages of Organic PVs (OPVs)

- Processed easily over large area using
 - spin-coating
 - doctor blade techniques (wet-processing)
 - evaporation through a mask (dry processing)
 - printing
- Low cost
- Low weight
- Mechanical flexibility and transparency
- Band gap of organic materials can be easily tuned chemically by incorporation of different functional group





Why OPVs?



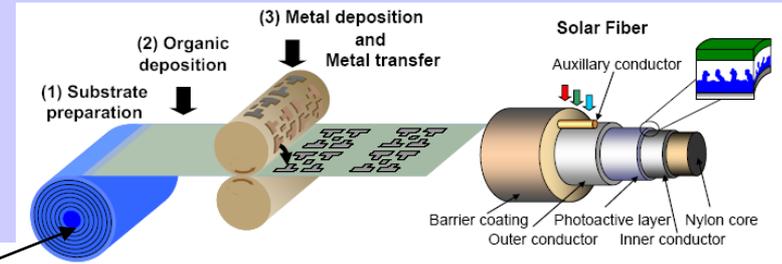
The concept of third-generation PV technologies, originally developed by *Martin Green* of the University of New South Wales

- 1:** PV cell based on silicon wafers
- 2:** thin-film technology
- 3:** high-efficiency thin-film technology using concepts such as hot carriers, multiple electron-hole pair creation, and thermophotonics

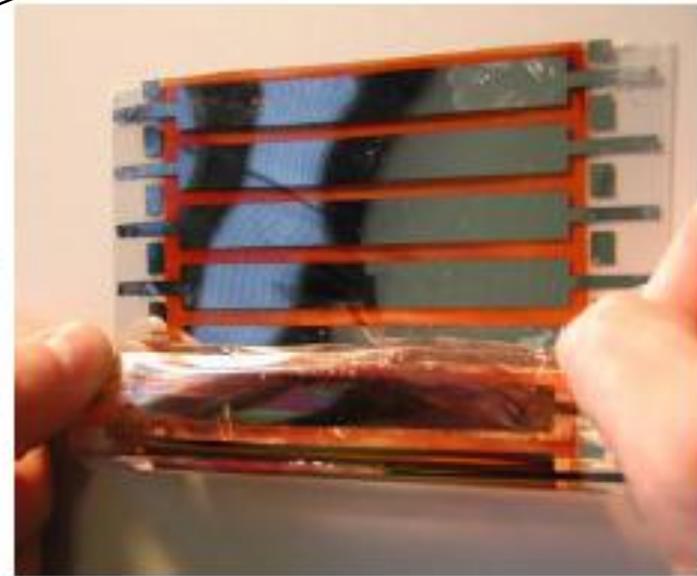
Cost-efficiency analysis for first-, second-, and third-generation PV technologies (labeled 1, 2, and 3, respectively). Region 3-1 depicts very-high-efficiency devices that require novel mechanisms of device operation. Region 3-2 (the region in which organic PV devices lie) depicts devices with moderate efficiencies and very low costs.



Why OPVs?



- OPV shows a promising technological development – efficiencies at 5 % level, no obstacles identified for 10 %
- The usage of reel to reel printing technologies guarantees a favorable cost structure
- The PV market demands low cost flexible solutions
- The energy market demands portable, decentralized renewable energies



OPV is the most promising candidate for a next generation PV



Why OPVs? (Applications)

Polymer Solar Cells Applications

- The low cost of plastic PV may enable solar power in applications where it was previously un-economic
- Disposable solar powered products become a reality
- Flexible and conformable PVs can be integrated more easily into 'soft' or non-planar packaging
- Large-area, flexible solar panels could be used to make solar tents, solar sails, portable solar power modules

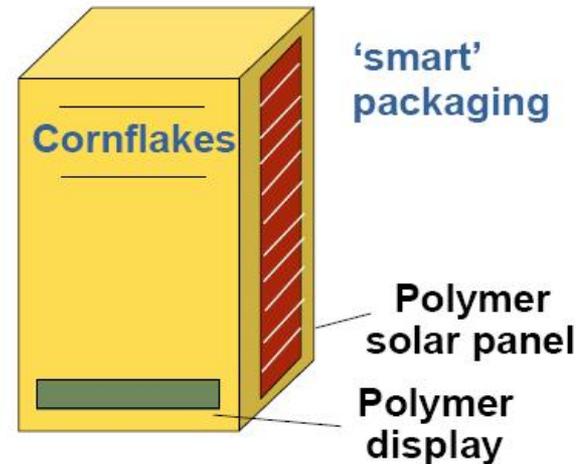


Portable PV

Rechargeable mobile products



PDA wallet





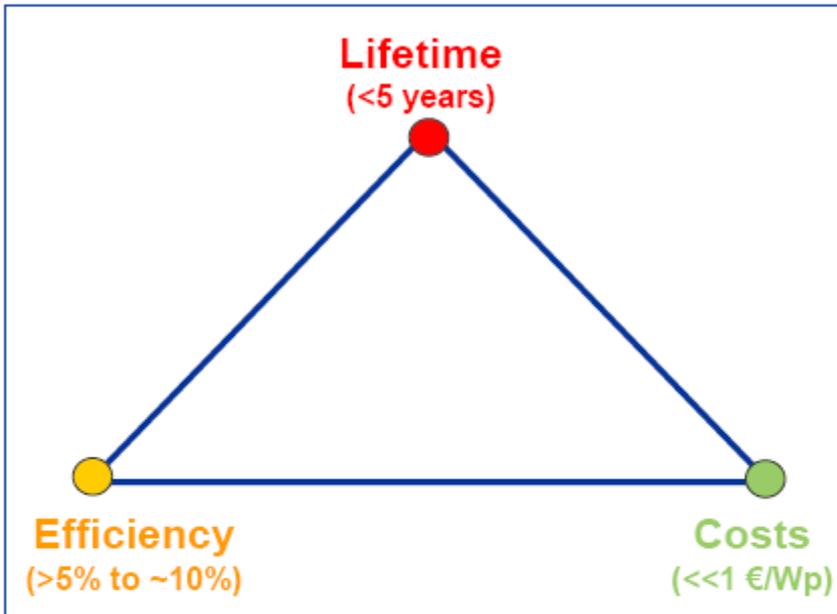
Why OPVs? (Applications)





Requirement of OPVs

Parameters & technological goals



- The most important parameters of every solar technology are efficiency, lifetimes and costs
- The actual application defines which parameter or combination of parameters are more or less important
- Other OPV features like flexibility, weight, transparency are not sufficient to constitute a relevant competitive advantage



- Applications define relevant OPV parameters
- In the medium term there is no direct competition with Silicon

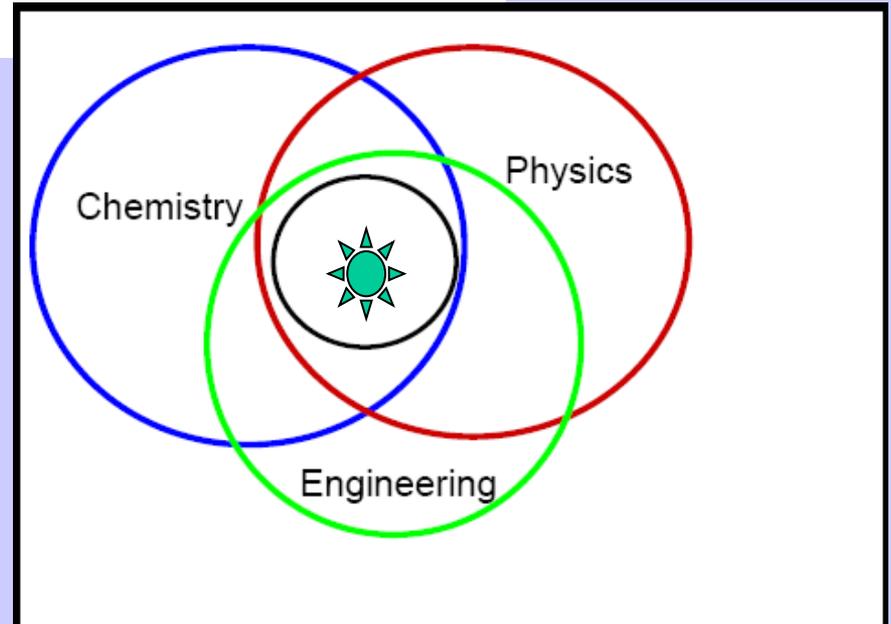


Organic solar cells : three types

- Dye sensitized solar cells: Electrochemical cells
- Small molecule organic solar cells: Made by vacuum deposition
- Polymer solar cells: Made by solution, low temperature processing

Each of these cells face more or less the same challenges:

1. Increase power conversion efficiency
2. Increase stability
3. Develop a technology for large areas





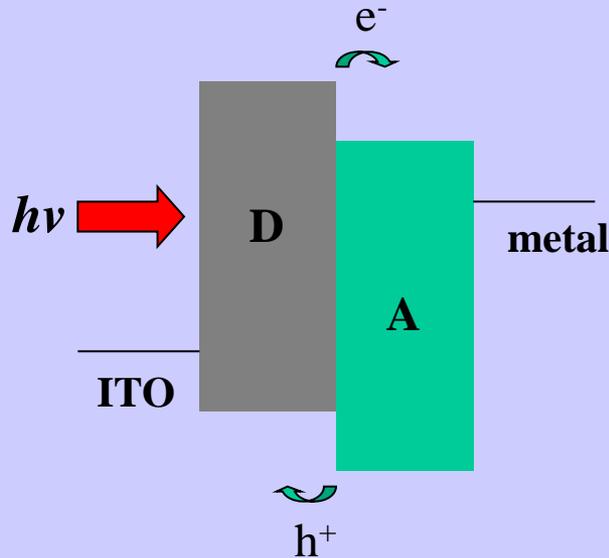
History of OPVs

Some important milestones in the development of organic solar cells

- 2001 - Ramos used *double-cable* polymers in PV cells.
- 2001 - Schmidt-Mende made a self-organised liquid crystalline solar cell of hexabenzocoronene and perylene.
- 2000 - Peters / van Hal used oligomer-C₆₀ dyads/triads as the active material in PV cells.
- 1995 - Yu / Hall made the first bulk polymer/polymer heterojunction PV.
- 1994 - Yu made the first bulk polymer/C₆₀ heterojunction PV.
- 1993 - Sariciftci made the first polymer/C₆₀ heterojunction device.
- 1991 - Hiramoto made the first dye/dye bulk heterojunction PV by co-sublimation.
- 1986 - **Tang published the first heterojunction PV device.**
- 1964 - Delacote observed a rectifying effect when magnesium phthalocyanines (CuPh) was placed between two different metalelectrodes.
- 1958 - Kearns and Calvin worked with magnesium phthalocyanines (MgPh), measuring a photovoltage of 200 mV.
- 1906 - Pochettino studied the photoconductivity of anthracene.
- 1839 - Becquerel observed the photoelectrochemical process.



PV effect in conjugated polymer



- Light is absorbed in the polymer layer
- Absorption creates a bound electron-hole pair (exciton)
- Exciton is split into separate charges which are collected at contacts

- Exciton must be separated so that a photocurrent can be collected.
- Excitons dissociated by electron transfer to an **acceptor** material, or hole transfer to a **donor**.
- Simplest approach is to make a **donor-acceptor heterojunction**

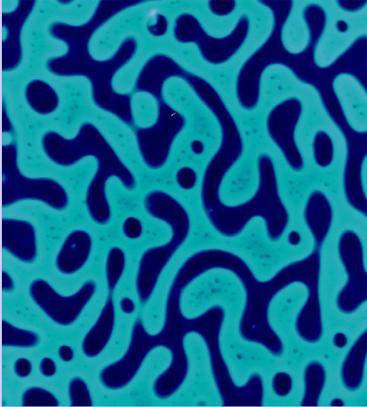


Critical Steps in organic Photovoltaics

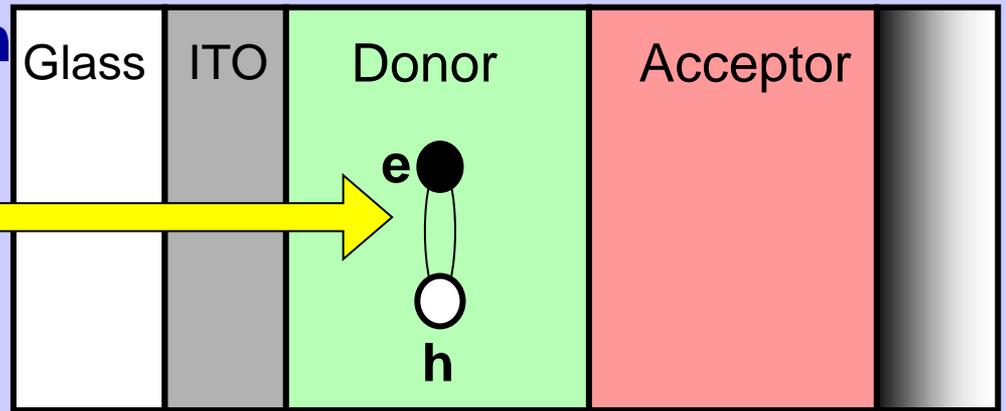
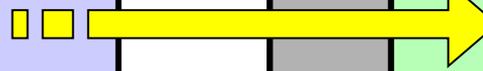
1. Photon Absorption (Band gaps, e.g. 1.3-2.0 eV on earth).
2. Exciton Diffusion (D/A interface within 10-70nm).
3. Charge separation (orbital offsets)
4. Charge transportation (morphology)
5. Charge collection at electrodes.

Key Losses of OPVs

1. Photon loss (light wavelength/spectra vs Band Gap)
2. Exciton Loss (D/A domain size/morphology/Energy Levels)
3. Carrier Loss (Transport Pathway/Morphology/
Molecular Packing/Collection at Electrodes).



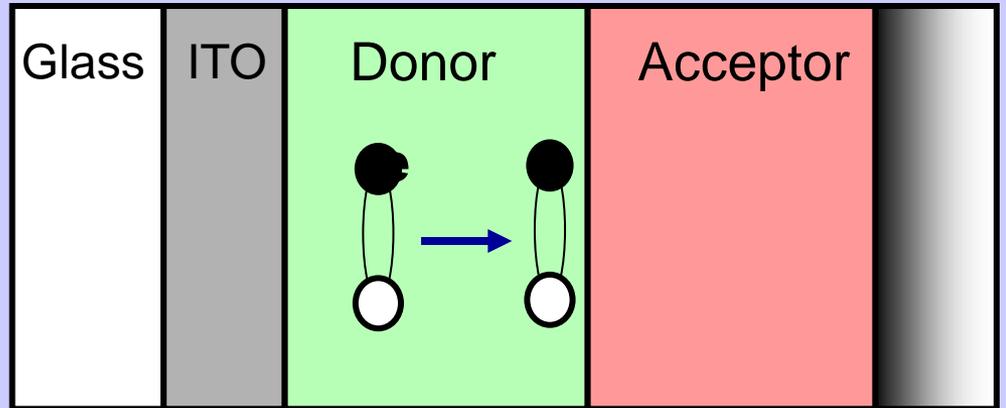
Absorption



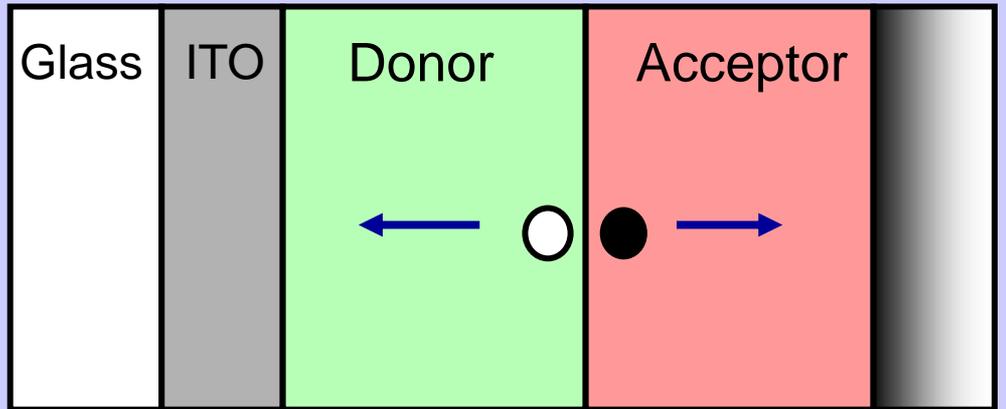
Key role of the morphology !

Energy Migration

Diffusion length ~ 10 nm !!!!

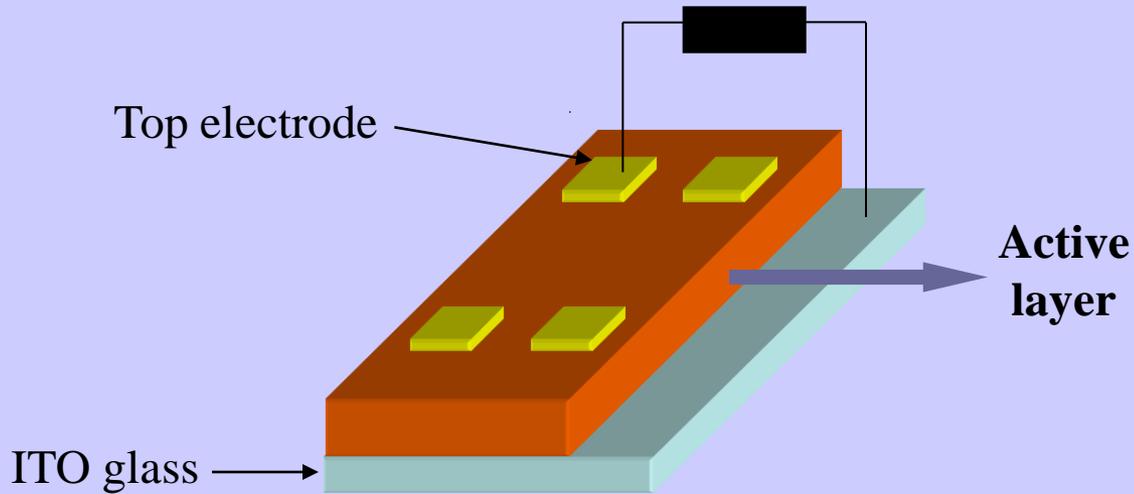


Photoinduced Charge Generation

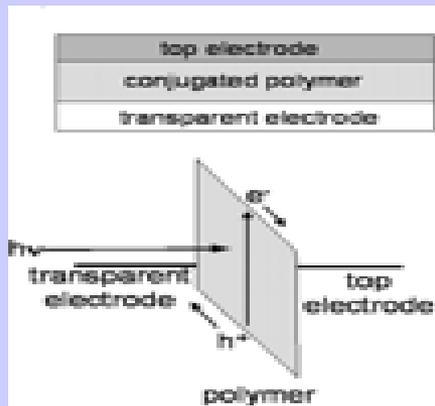




Device architecture



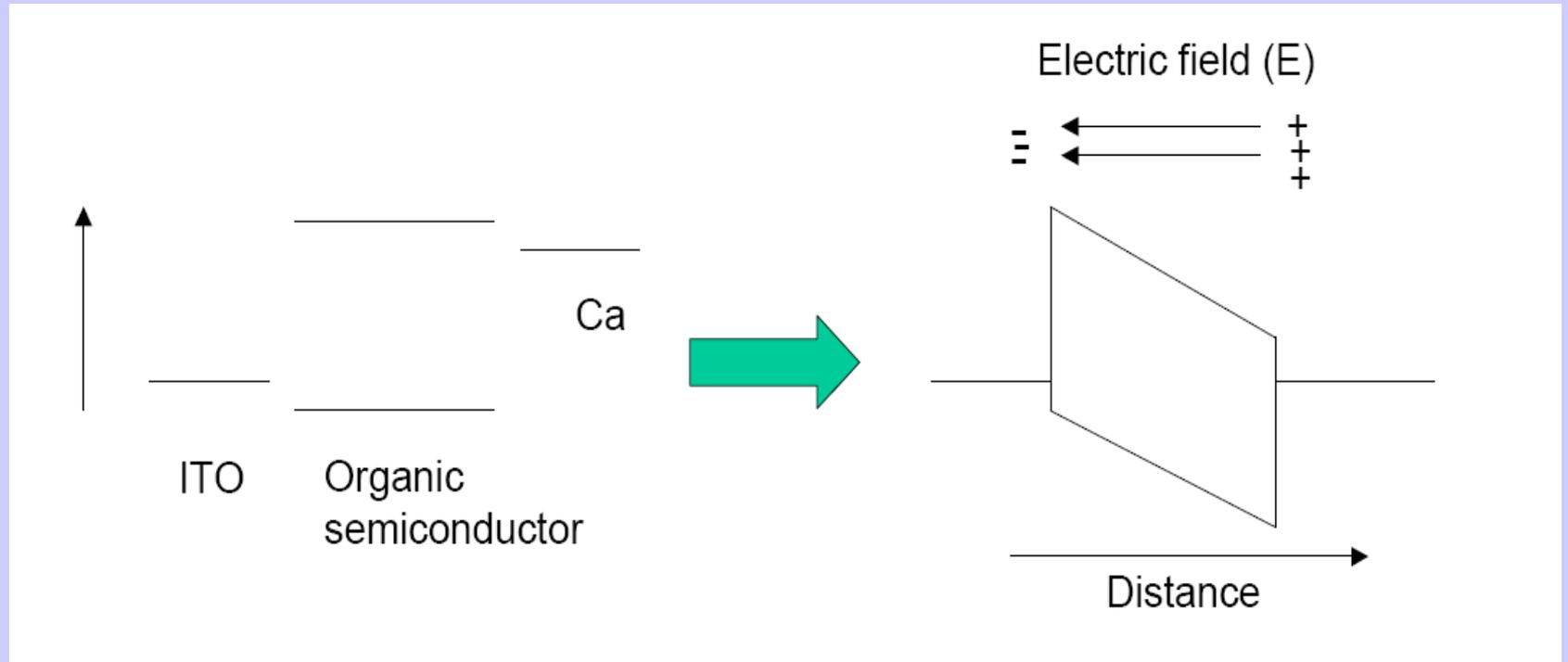
- ✓ Single-layer
- ✓ Bilayer
- ✓ Bulk heterojunction



Single-layer PV cell



I. Organic or polymer single-layer PVs



Disadvantage

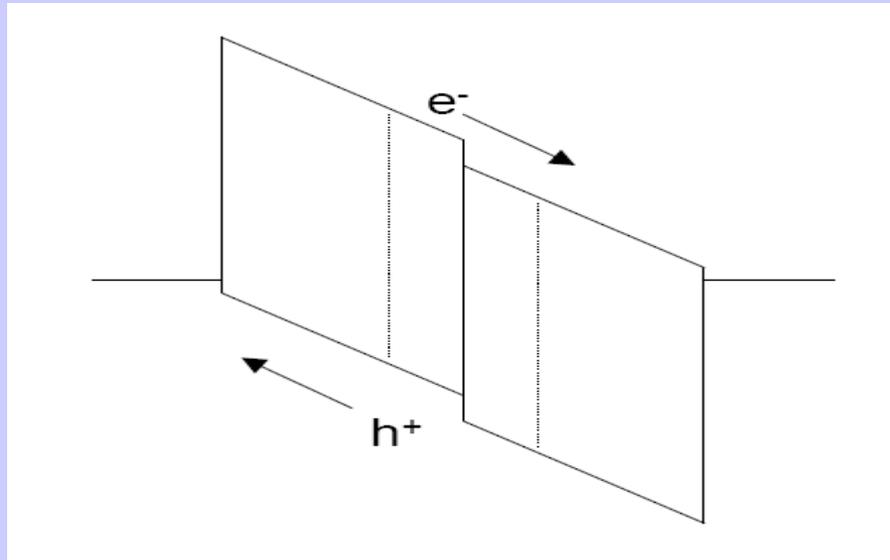
High exciton binding energy
Low mobility



Quantum efficiency < 1 %



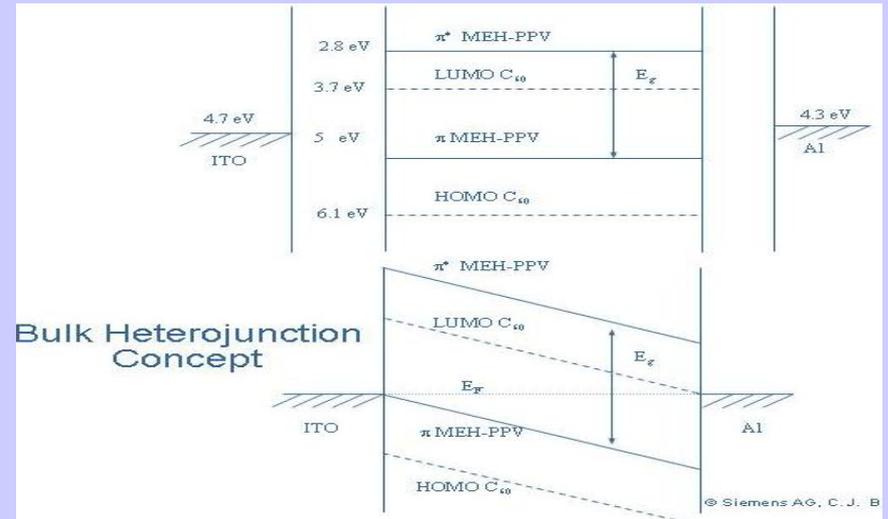
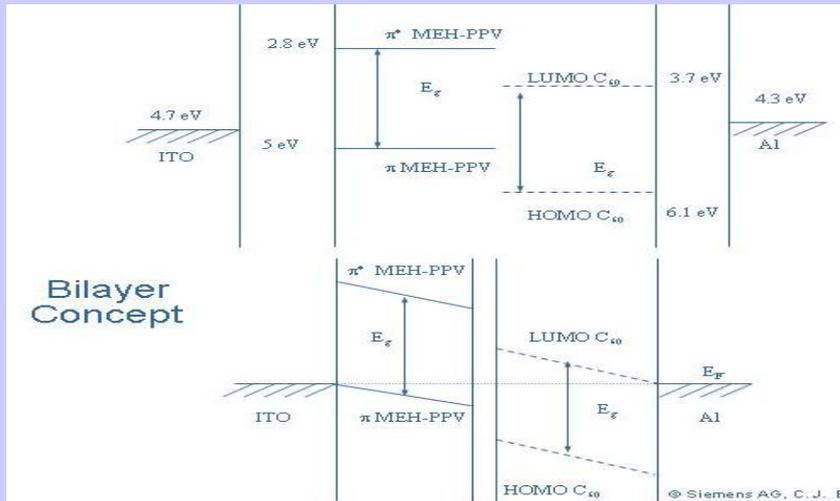
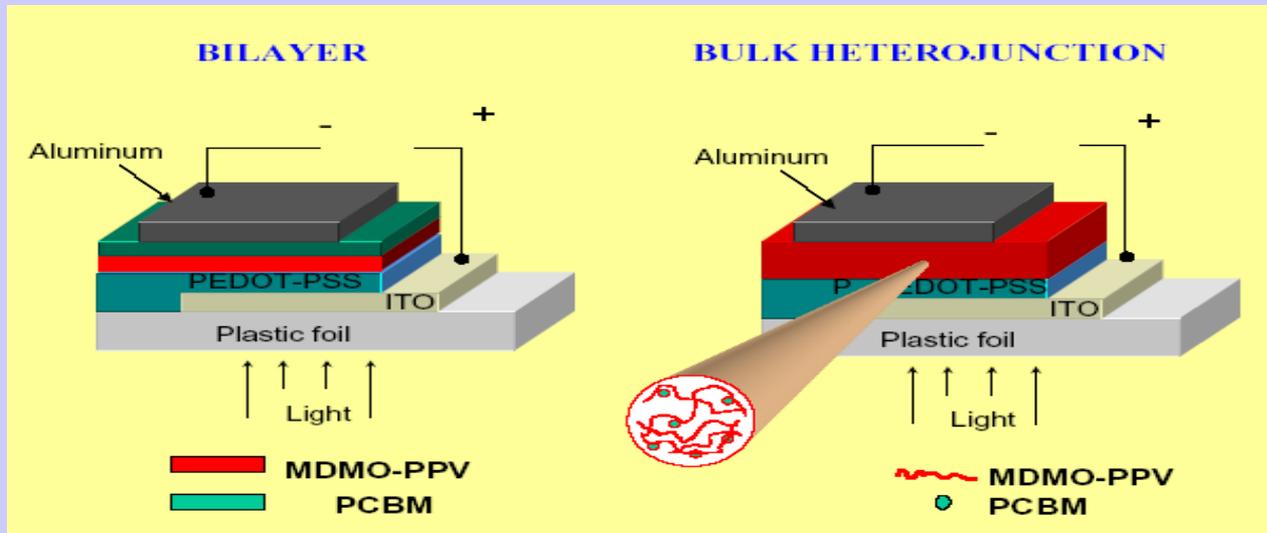
II. Organic or polymer bilayer PVs



- Charge transfer can occur between two semiconductors with offset energy levels.
- **Excitons can diffuse approximately 10 nm to an interface. (less than 20 nm)**
- **A film thickness of approximately 100 nm is needed to absorb most of the light.**
- Polymer bilayer cell showed 1.9 % energy conversion efficiency.
- Small molecule bilayer cell showed 3.6 % power conversion efficiency with 3 layers.



Device geometries

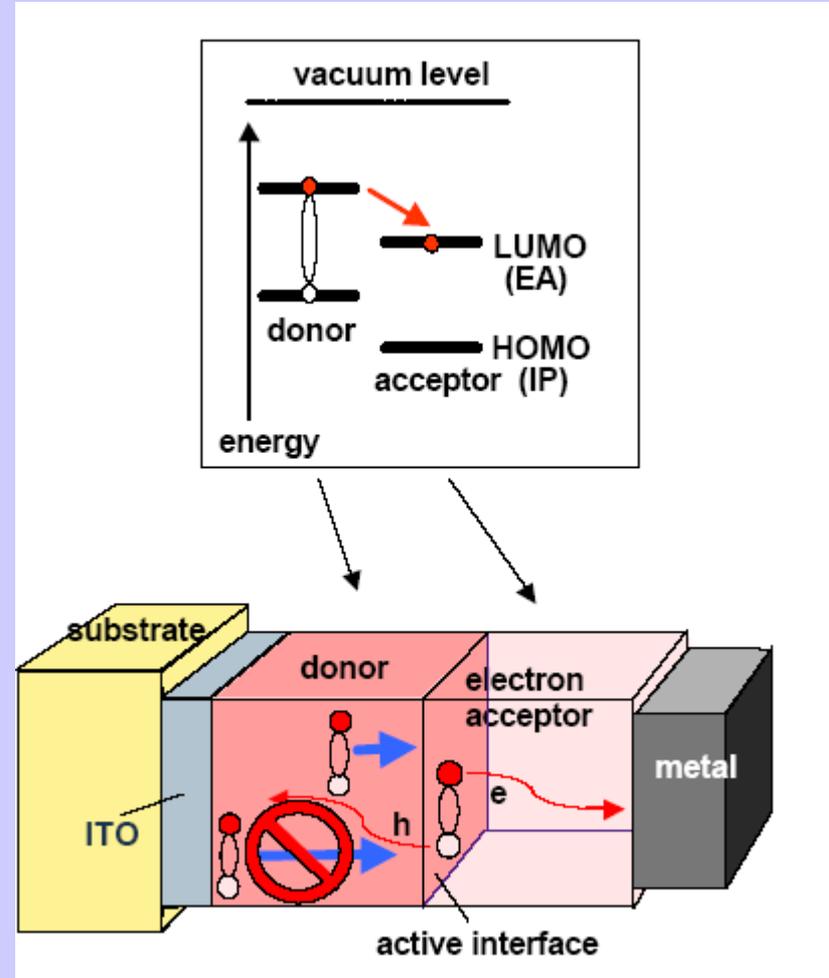




Limitation of organic or polymer bilayer PVs

Separating photoexcited states

- Exciton must be separated so that a photocurrent can be collected
 - Binding energy ~ 0.5 eV
- Excitons dissociated by electron transfer to an acceptor material, or hole transfer to a donor
- Simplest approach is to make a donor-acceptor heterojunction
- First done effectively by C W Tang in 1986
- Limited by imbalance between exciton diffusion range (~ 10 nm) and absorption depth (~ 100 nm)
 - Not all excitons dissociated

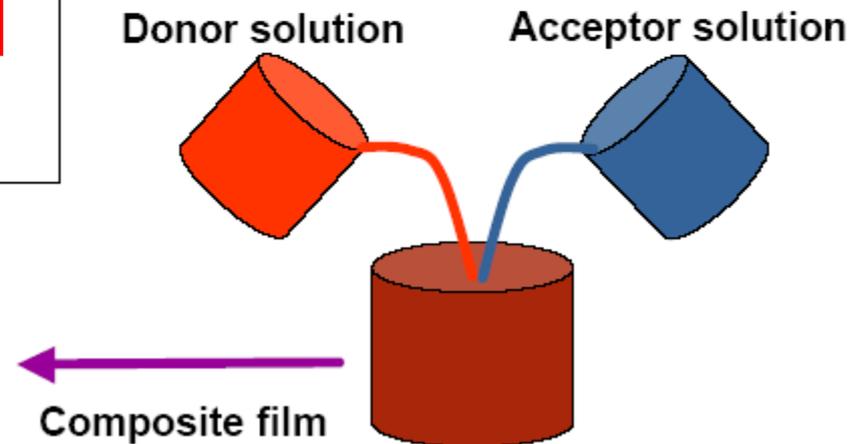
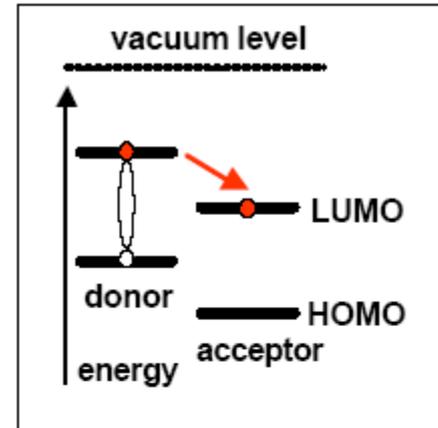
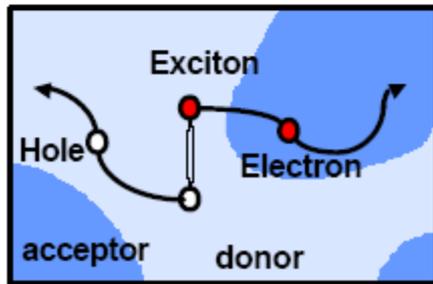




III. Bulk heterojunction (BHJ) PVs

Bulk Heterojunction Devices

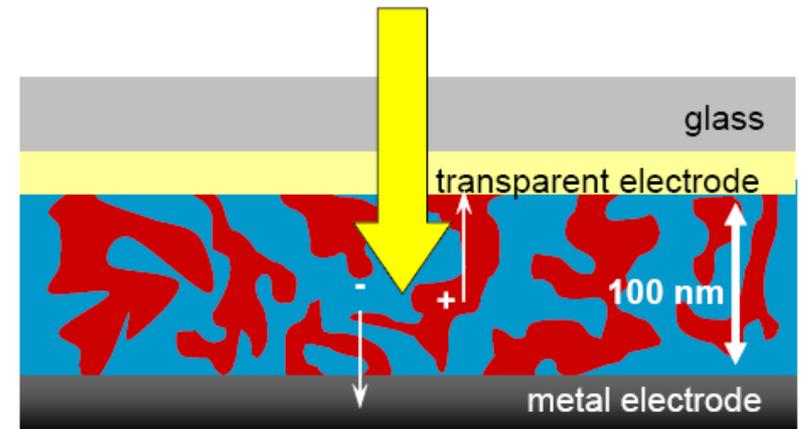
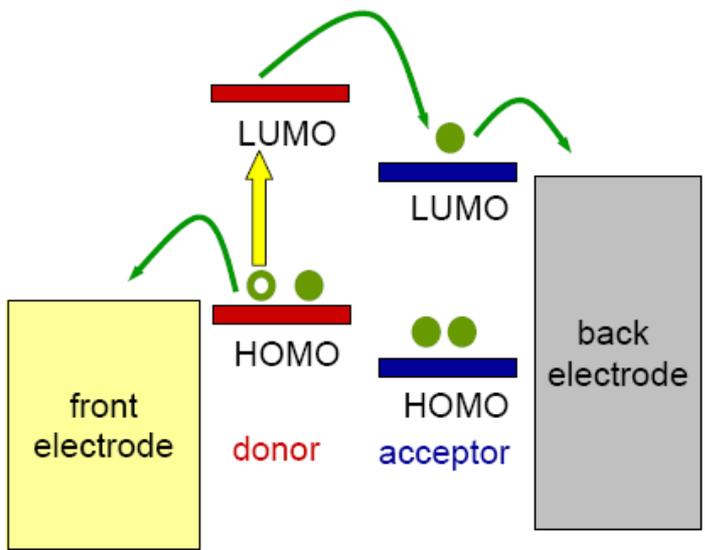
- Solution to the limited exciton diffusion range problem
- Donor and acceptor materials mixed together
- Distribute active interfaces throughout the bulk
- All excitons are within a diffusion range of an interface
- Charges travel to respective electrodes





Bulk heterojunction solar cells

Charge separation in nanostructured composite organic semiconductors



nanoscopic mixing of donor and acceptor to overcome ~ 10 nm exciton diffusion length



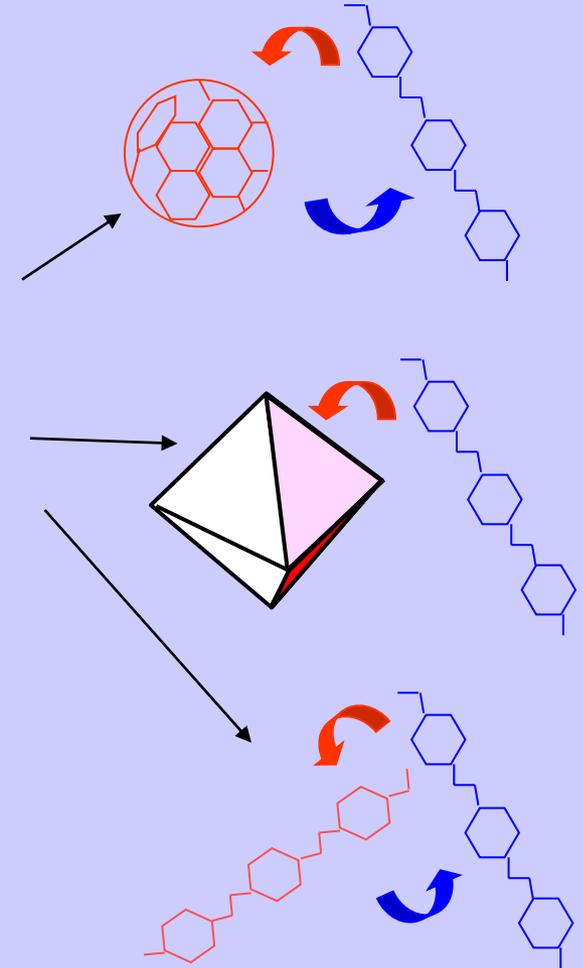
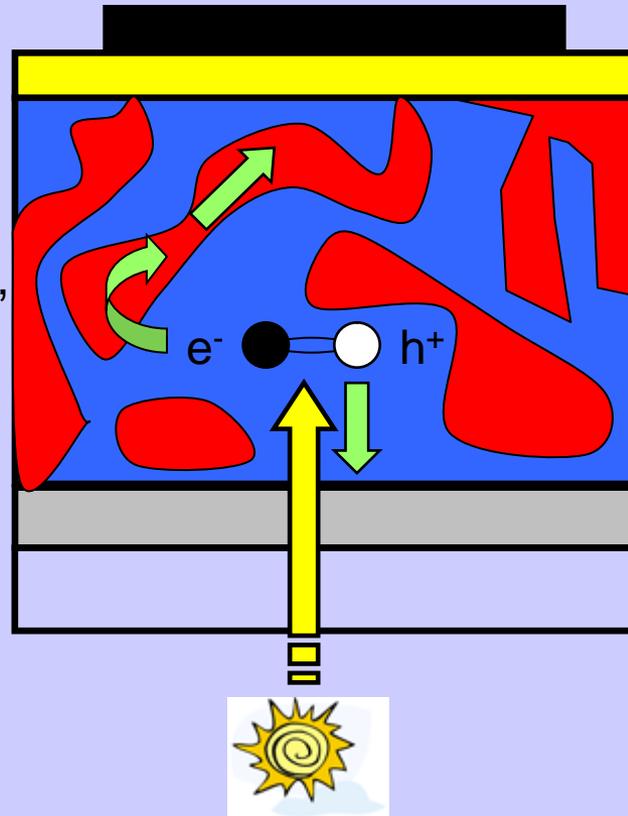
Donor-acceptor bulk heterojunction devices

Al cathode

Donor-Acceptor blend:
e.g. polymer / fullerene,
polymer / nanocrystal,
polymer / polymer

ITO anode

Glass substrate



- Both components deposited from same solution



Optimization for high efficiency

1. Conjugated polymer with low band gap

Maximum photon flux of sun = 700 nm

$$E_g = 1.24 / 0.7 = 1.77 \text{ [eV]}$$

Maximum absorption of photon of sun

2. Bulk heterojunction morphology

exciton diffusion length of conjugated polymer = below 20 nm

3. High carrier mobility

electron and hole mobility of conjugated polymer

I_{sc} : tuning of the **transport property** (mobility); Optimization of cell geometry in dependence of the cell thickness

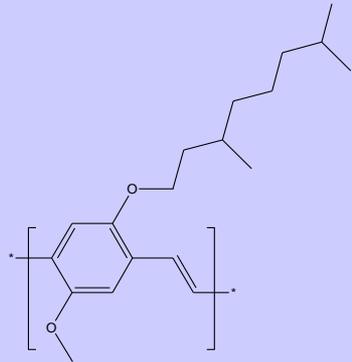
V_{oc} : tuning of the **electronic energy level** of the donor-acceptor system; V_{oc} of ~ 2 V observed in polymeric donor-acceptor system

F.F: tuning of the contacts and **morphology**: lowering of serial resistance

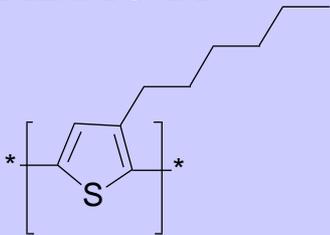
$$\eta = \frac{I_{sc} V_{oc} FF}{P_S} \times 100$$



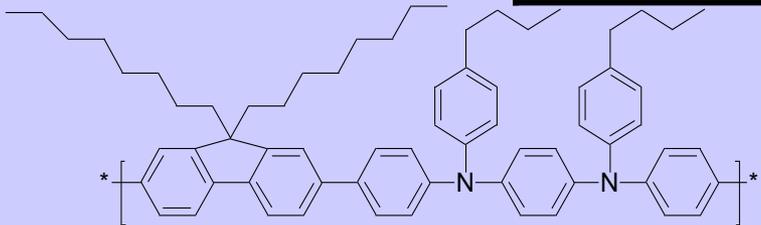
Materials for BHJ organic solar cell



MDMO-PPV

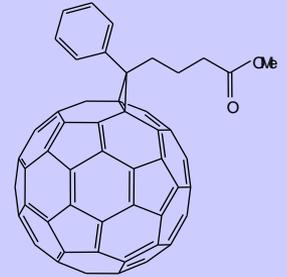


P3HT

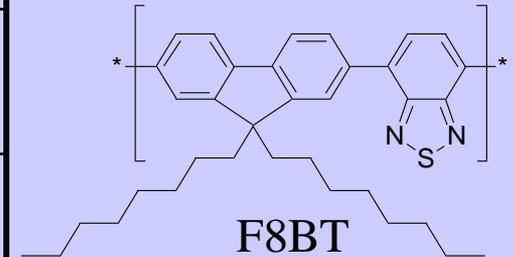


PFB

donor	acceptor
Polymer	C ₆₀ derivative
Polymer	Polymer
Polymer	CdSe nanocrystal
Polymer	Metal oxide nanocrystal
Small molecule	Small molecule



PCBM



F8BT

CuPc
pentacene

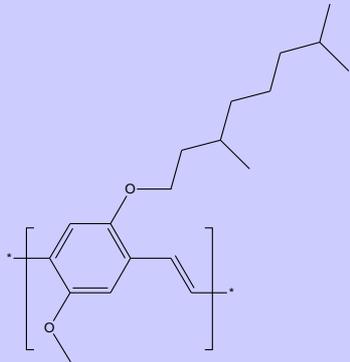


C₆₀

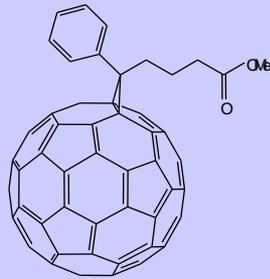
TiO₂ or ZnO
nanoparticles



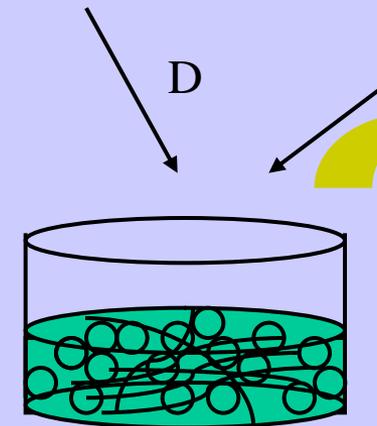
Polymer/PCBM interpenetrating system



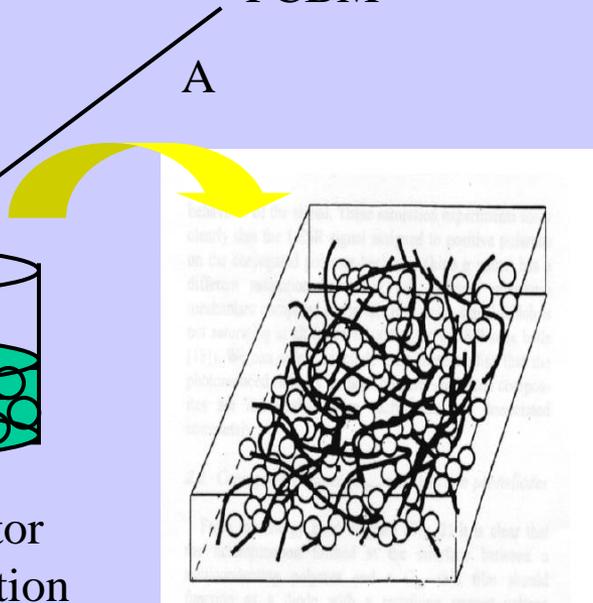
MDMO-PPV



PCBM



Donor/Acceptor
composite solution



$$V_{oc} = 0.82 \text{ V}$$

$$J_{sc} = 5.25 \text{ mA/cm}^2$$

$$FF = 0.61$$

$$\eta_{AM1.5G} = 2.5 \% \text{ (under } 80 \text{ mW/cm}^2\text{)}$$

Metal electrode

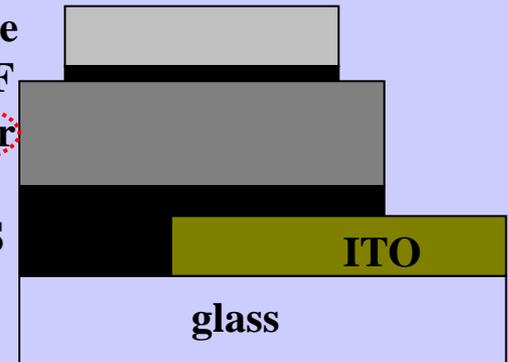
LiF

Active layer

PEDOT:PSS

ITO

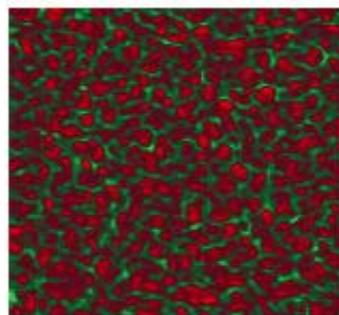
glass



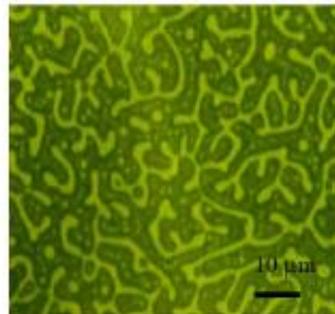


Polymer solution processed cells come in three 'flavors'

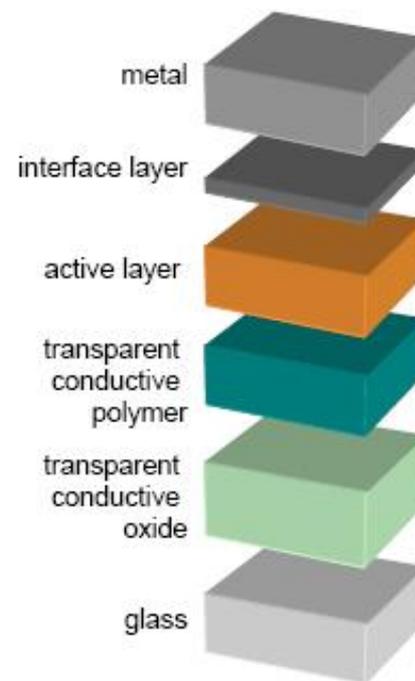
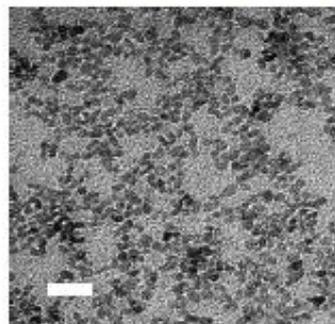
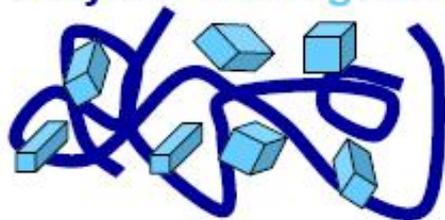
Polymer – fullerene



Polymer – polymer

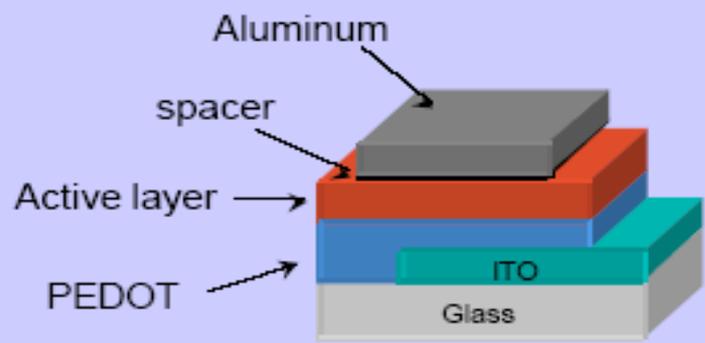


Polymer – inorganic





Production



ITO coated glass or plastic serves as substrate.

Preparation of ITO-cleaning

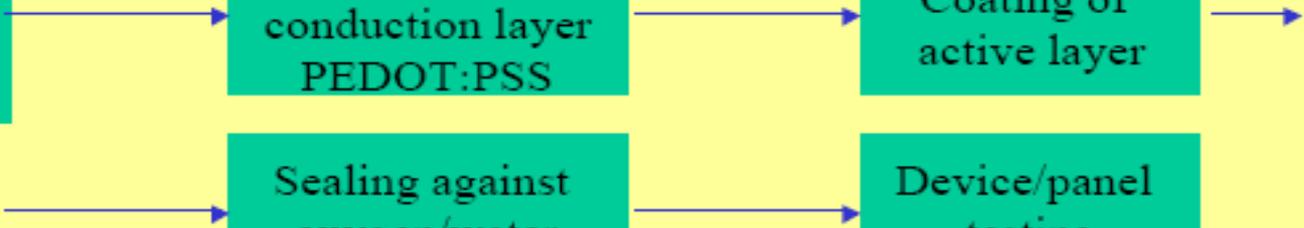
Coating of hole conduction layer PEDOT:PSS

Coating of active layer

Evaporation of top contact

Sealing against oxygen/water

Device/panel testing





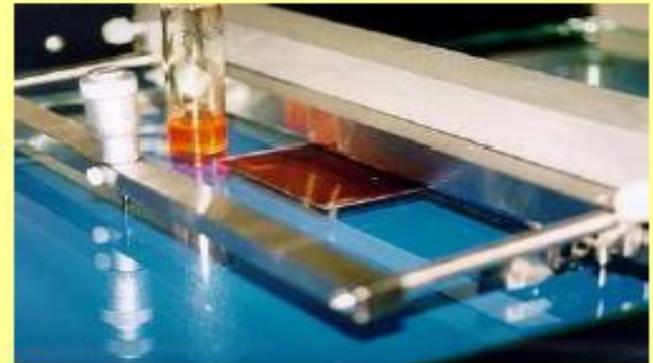
Film preparation

Spin Casting is a easy coating technique for small areas. Material loss is very high.



Doctor Blade Technique was developed for large area coating

Doctor Blade Technique has no material loss

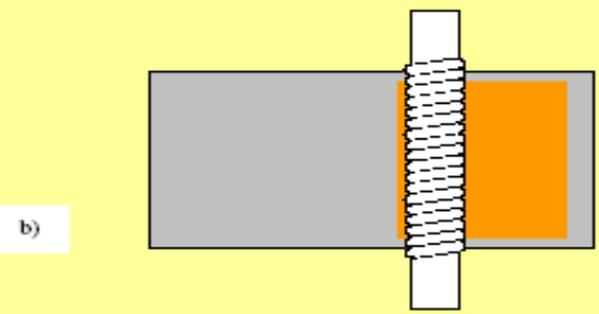
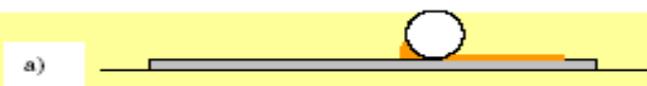
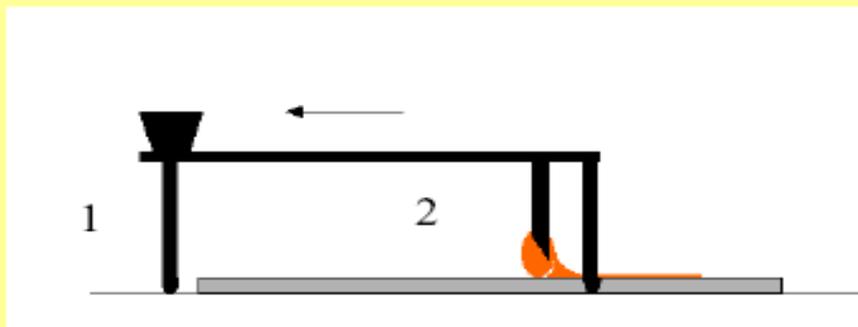


FILM THICKNESS IS ~ 100 nm



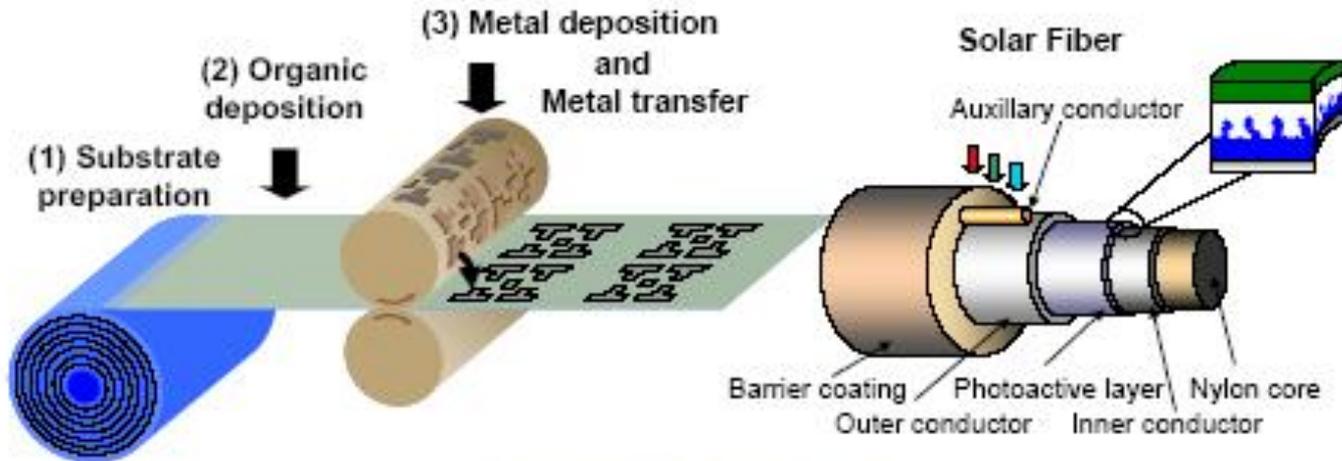
Film preparation

Large Area Thin Film Production using Doctor/Wire Blading

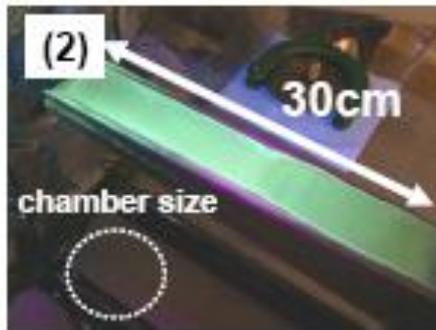




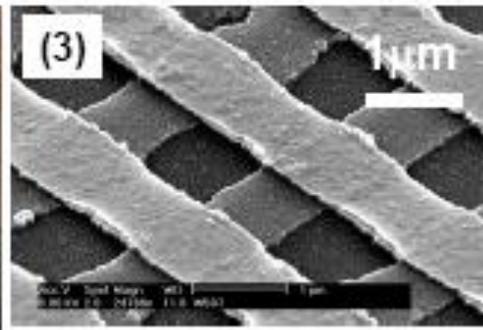
Cheap: Roll-to-Roll Processing



(1)
Roll-to-roll coater
(Applied Films)



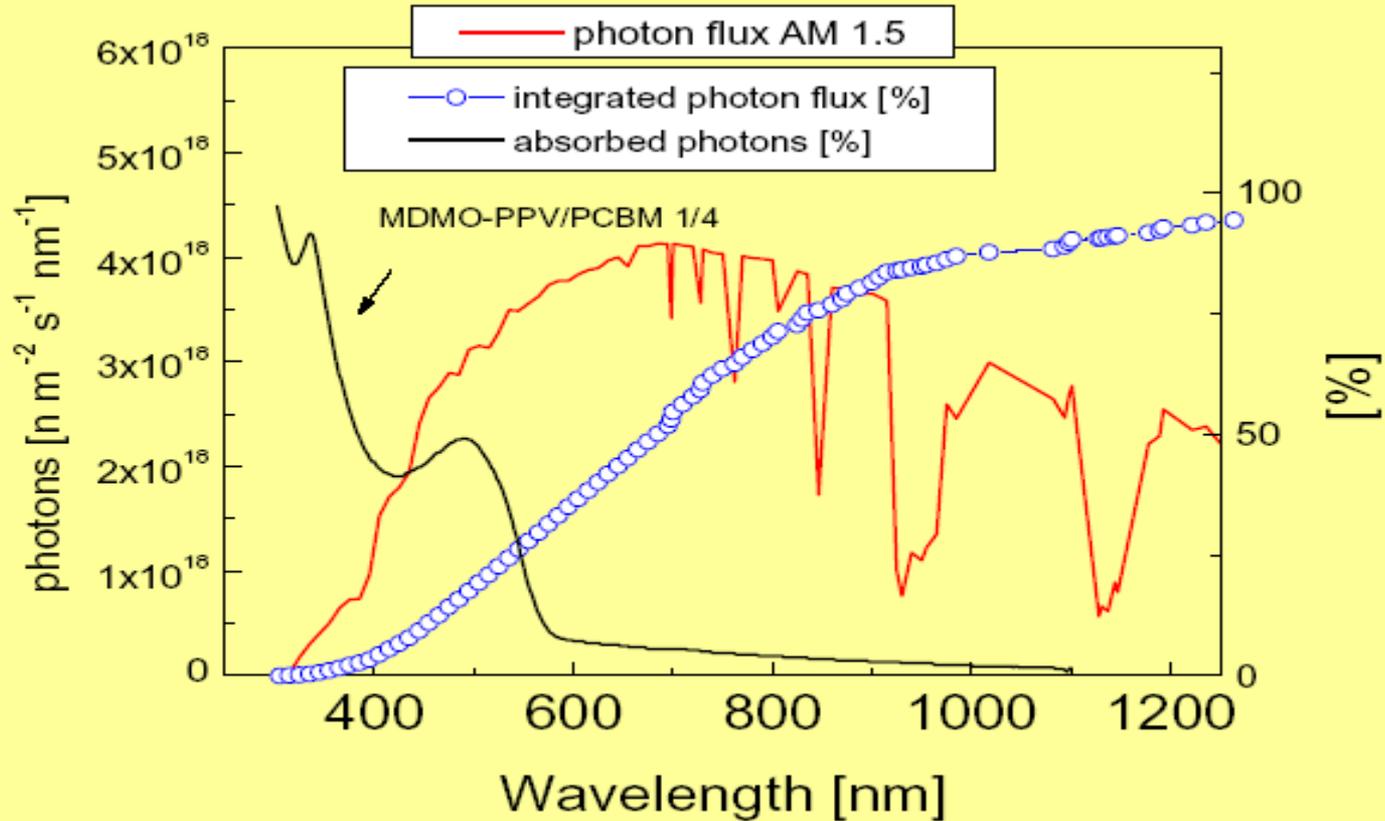
(2)
M. Shtein, unpublished



(3)
P. Peumans, unpublished



Materials issue - matching the solar emission

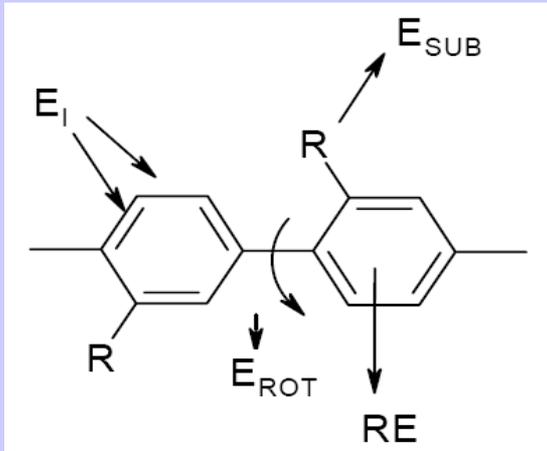


The flexibility in chemical tailoring is necessary for matching the absorption of the PV material to the solar emission spectrum.



Bandgap engineering

< The parameters determining the bandgap of conjugated polymers >



E_{ROT} : the energy contribution from bond length alternation

RE : the resonance energy

E_I : the energy caused by the inter ring torsion angle

E_{SUB} : the influence of the substituents.

$$E_G = E_I + RE + E_{ROT} + E_{SUB}$$

1. Aromatic form shows higher stabilization energy and therefore the higher bandgap.
2. **Resonance energy** leads to an energy stabilization and so to an increased splitting of the HOMO-LUMO energy.
3. **Torsion between the ring** plain interrupts the conjugation and therefore increases the bandgap.
4. **Electron donating groups** raise the HOMO level and **electron withdrawing groups** lower the LUMO.
5. In the solid phase, additional **intermolecular effects** between the chains have to be taken into account, which generally leads to broader bands and a lower bandgap.



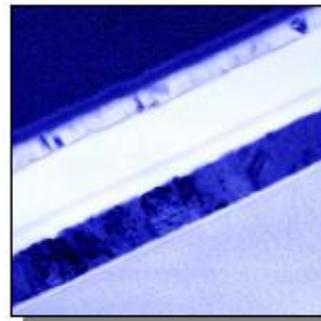
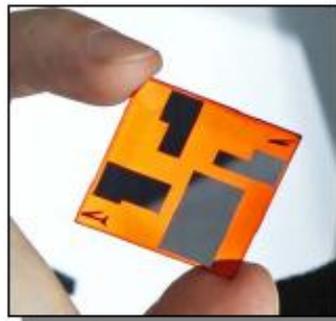
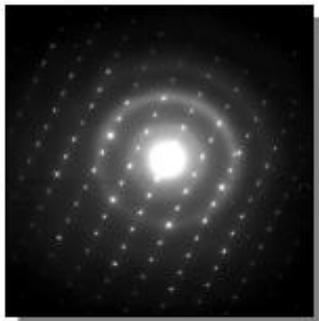
What has been achieved and what remains to be done

Efficiencies of 4-5% have been reached

The performance is an intricate combination of:
photophysics
charge transport
nanoscale morphology
electrodes and device architecture

What remains to be done:

new materials to increase voltage and spectral overlap
increase transport and collection
establish long lifetimes
develop a real technology





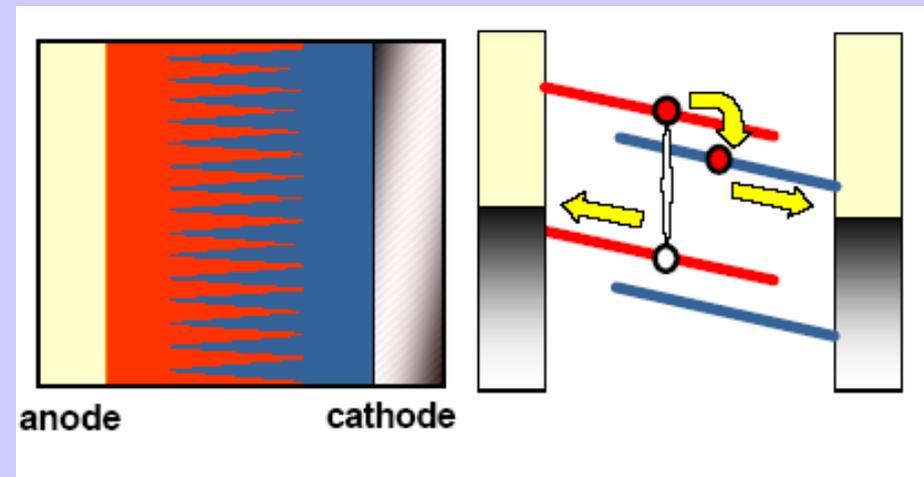
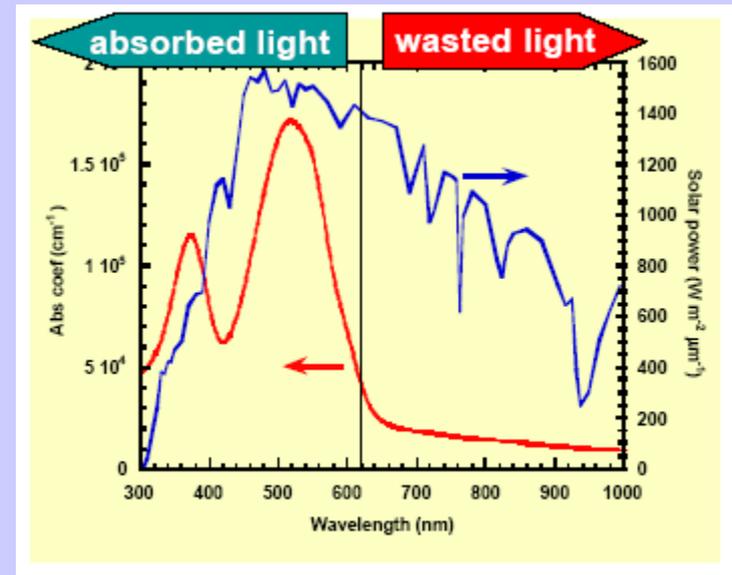
Summary: optimization

Materials

- Up to now, polymers for PVs have largely been taken into account for optimum results and maximum efficiency
- Too much work has been done to develop new polymers optimized to absorb solar radiation
- Materials optimized for electron or hole transport

Device Architecture

- Morphology of polymer blend crucial to determining device performance
- Morphology can be controlled through careful processing, surface treatment and materials design





Thank you for your attention

Think green with cheap materials