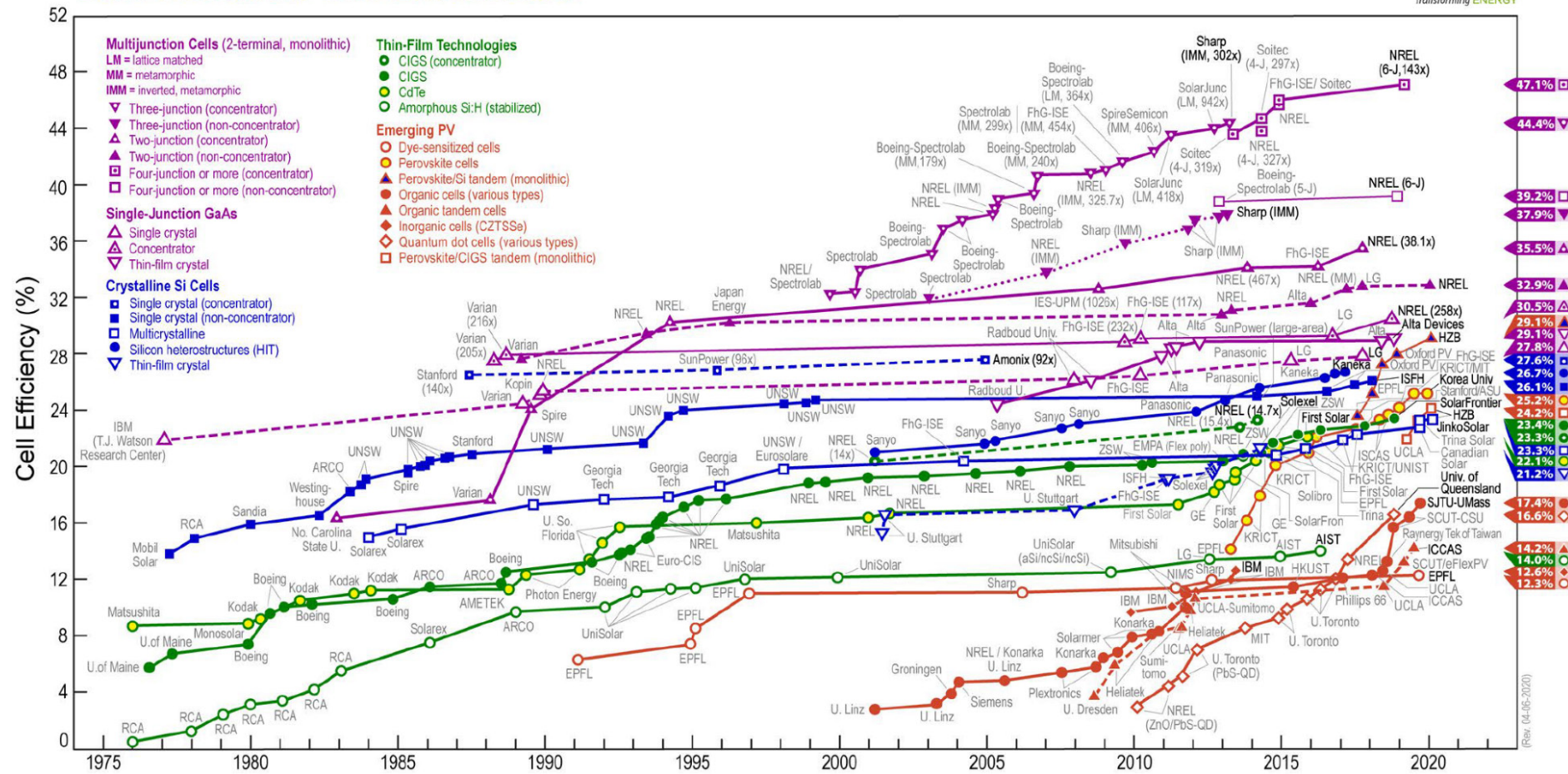


# 2.2A Organic Photovoltaics (OPV)

## Best Research-Cell Efficiencies



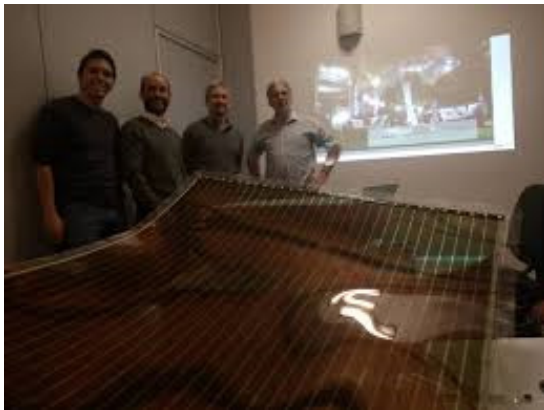
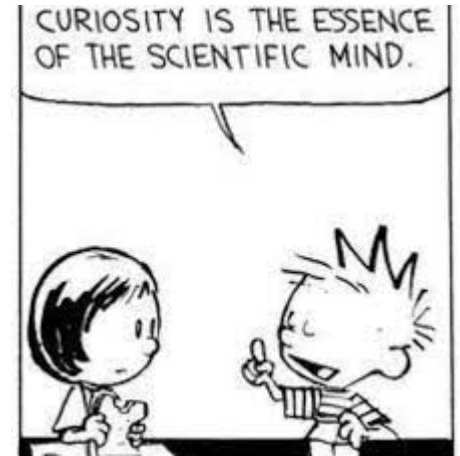
# 2.2A Organic Photovoltaics (OPV)

## *Learning goals*

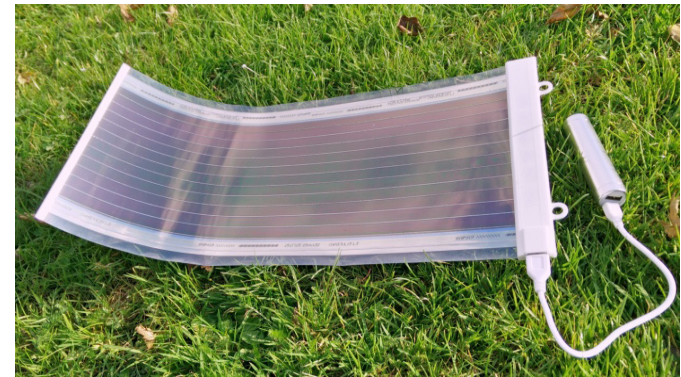
- ❑ Summary: motivation
- ❑ History
- ❑ Materials properties compared to inorganic semiconductors
- ❑ Consequences for solar cell design
- ❑ What strategies are followed to improve the efficiency
- ❑ State-of-the art
- ❑ Stability
- ❑ Manufacturing
- ❑ Current research directions

The **benefits** promised by oPV solar cells include:

- ❑ **Low-cost manufacturing:** Soluble organic molecules enable roll-to-roll processing techniques and allow for low-cost manufacturing.
- ❑ **Abundant materials:** The wide abundance of building-block materials may reduce supply and price constraints.
- ❑ **Flexible substrates:** The ability to be applied to flexible substrates permits a wide variety of uses.



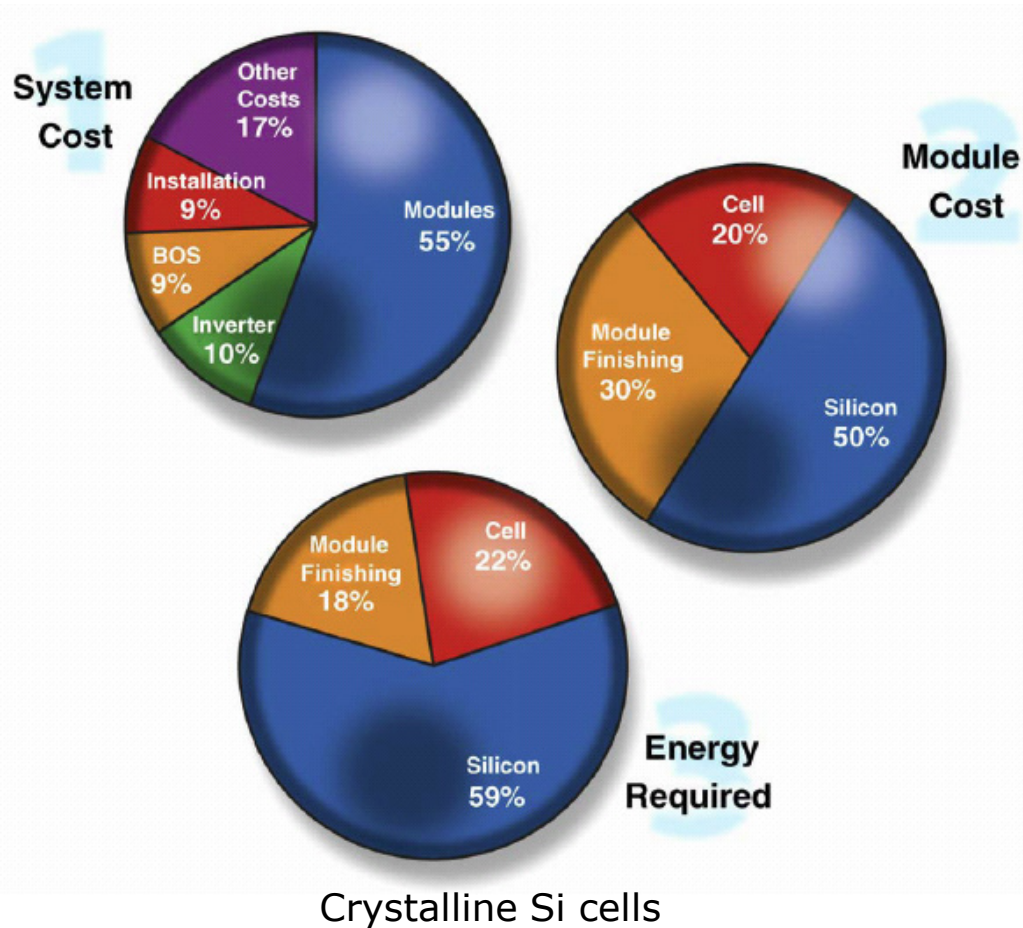
Fully printed oPV, CSEM Brazil



Light weight charger, Eight19 Cambridge



## Why organic photovoltaics?



L.L. Kazmerski, *J. Electron. Spect. Rel. Phen.*, **150**, 105 (2006).

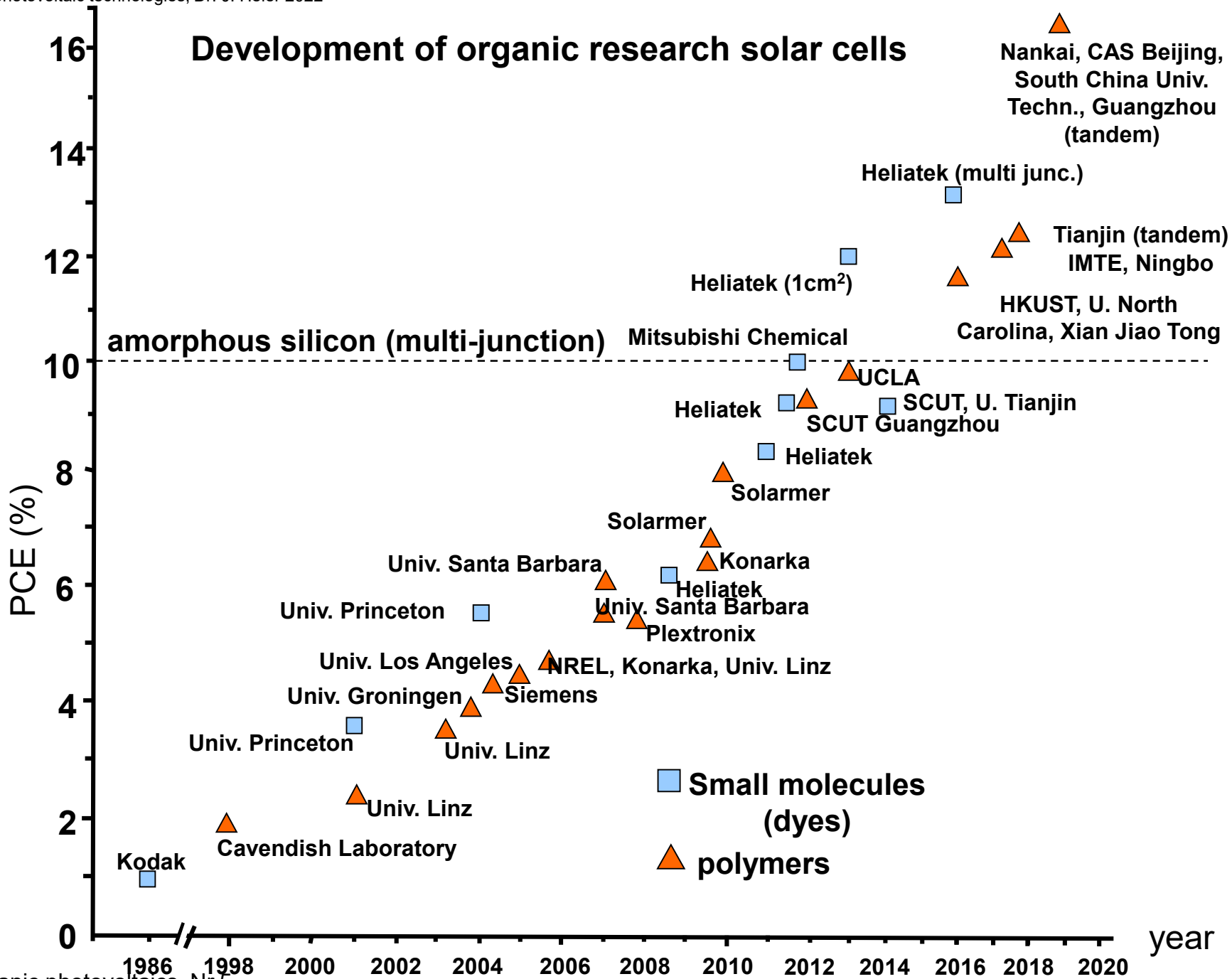
- Renewable energy source
- Cost
  - Hydro/geotherm: 2-10 ¢/kWh
  - Wind: 4-8 ¢/kWh
  - Solar: 25-160 ¢/kWh (2€/W<sub>p</sub>)
  - Coal (comparison): 4 ¢/kWh

Source: World Energy Assessment, 2004 update

- Organics: potential **cost and application advantages!**
  - Cost efficient fabrication (R2R)
  - Lightweight
  - Flexible
  - Mobile
  - Colourful (indoor and façade)
- Improvements in barrier materials needed!



# Development of organic research solar cells



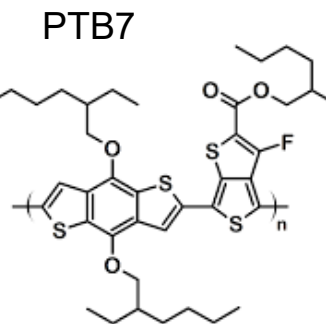
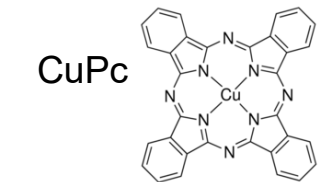
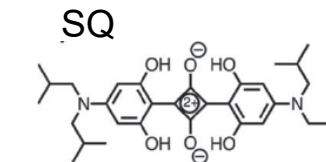
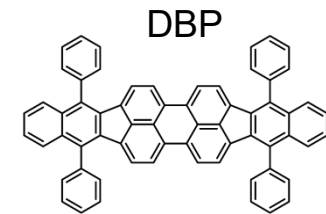
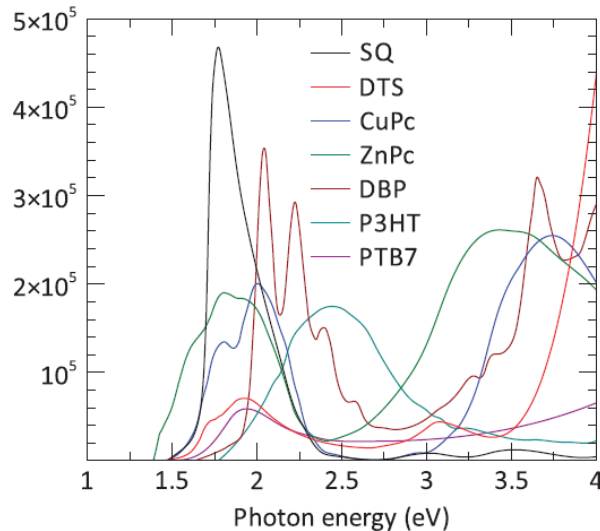
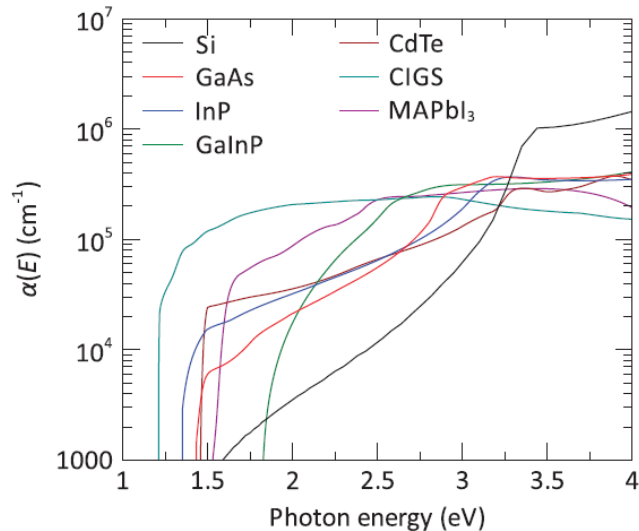
## ***Important milestones in OPV***

- Pochettino (1906): Photoconductivity in anthracene
- Kallmann, Popoe (1959): PV effect in single cryst. anthracene
- H. Meier et al. (1960): PV-cells made of "p-n" heterojunctions
- K. Ghosh et al. (1978): Merocyanine Schottky-barrier cells (0.5%)
- C. W. Tang (1986): CuPc-perylene Heterojunction solar cell (1%)
- N. S. Sariciftci (1993): Polymer / C60 heterojunction devices
- G. Yu et al. (1994): "Bulk-heterojunction concept" between PPV and C60
- C. J. Brabec (2001): Bulk-heterojunction devices with 3%
- W.L. Ma (2005): Fabrication procedure for optimized bulk-heterojunction solar cells (5%)
- H. Y. Chen et al. (2009): PBDTTT polymer bulk-heterojunction (6.8%)
- M. Riede (2011): Vapor deposited organic tandem solar cell using doped layers (6.1%, 2 cm<sup>2</sup>)
- Y. M. Sun (2012): DTS small molecule solution processed (6.1%)
- L. Meng (2018): Solution processed tandem solar cell (17.3%)

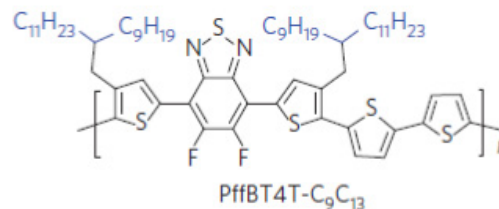
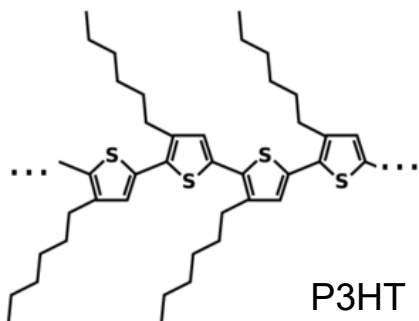
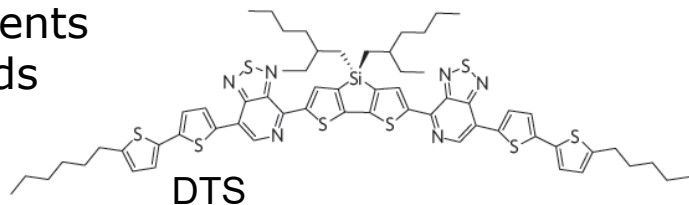
...and many others

# Fundamental differences in materials properties

## Optical properties



- High absorption coefficients
- Narrow absorption bands
- High bandgap





# Fundamental differences in materials properties

## Charge carrier mobility

$$J = nev_{drift} = ne\mu E$$

$$\text{mobility } \mu \left[ \frac{\text{cm}^2}{\text{Vs}} \right]$$

Organic semiconductors

Inorganic semiconductors

*crystalline*

*crystalline*

Anthracene	1.6 (e <sup>-</sup> )	1.2 (h <sup>+</sup> )
Pyrene	0.7 (e <sup>-</sup> )	0.7 (h <sup>+</sup> )
b-phthalocyanine	1.1(e <sup>-</sup> )	1.4 (h <sup>+</sup> )
Fullerene C <sub>60</sub>	1.1(e <sup>-</sup> )	1.0 (h <sup>+</sup> )

Si	1500 (e <sup>-</sup> )	450 (h <sup>+</sup> )
Ge	3900 (e <sup>-</sup> )	1900 (h <sup>+</sup> )
GaAs	8500 (e <sup>-</sup> )	400 (h <sup>+</sup> )
InAs	80000 (e <sup>-</sup> )	1250 (h <sup>+</sup> )

*amorphous*

*amorphous*

10<sup>-5</sup> to 10<sup>-3</sup> at high fields (1MV/cm)

Si ≈ 1

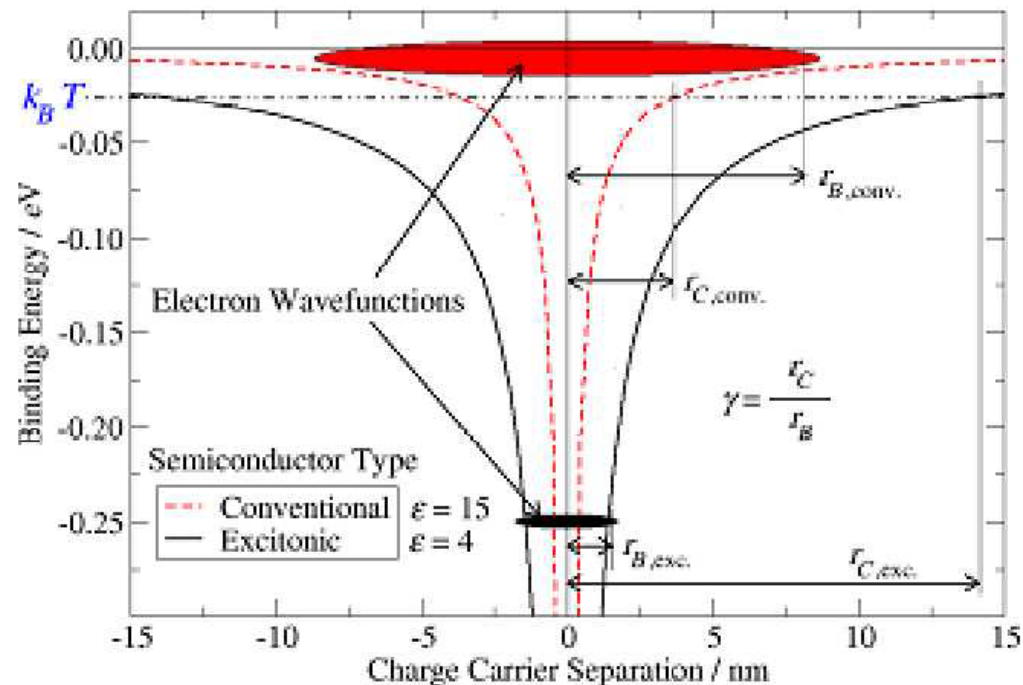
M. Pope, C. E. Swenberg, "Electronic Processes in Organic Crystals and Polymers", Oxford University Press, 1999

S. M. Sze «Physics of semiconductors», Wiley, New York, 1981

## Fundamental differences in materials properties

### □ Exciton dissociation – the exciton binding energy

- **Low dielectric constant** in organic semiconductors ( $\epsilon = 3-4$ ) compared to inorganic semiconductors ( $\epsilon = 10-15$ )
- **Localized** electronic wavefunctions
- **High binding energy** for excitons of about 0.5 eV, excitons can not be thermally separated into free charge carriers at room temperature.
- A large enough **driving force** required for exciton dissociation



# Fundamental differences in materials properties

## ❑ Fabrication possibilities

### Organic semiconductors

Chemical synthesis

For small molecules, **excellent molecular purities** by gradient sublimation, recrystallization, chromatography, etc.

Small molecules are typically **applied by evaporation** (sometimes also applied from solution)

Solution processable materials (mainly polymers) can be **applied by printing and coating**

### Si-based inorganic semiconductors

Gained from  $\text{SiO}_2$   
Purity needed: 99.9999 %

Crystallization from the melt (crystalline: Czochralski, float-zone, ribbon silicon)

Wafer cutting (sawing losses)  
Amorphous silicon: PECVD  
Doping



## ***Fundamental differences in materials properties***

### **❑ Solar cell requirement**

#### **Organic semiconductors**

Charge generation requires **exciton dissociation** interface (only a few nm thick)

Strong absorption coefficients allow to use thin films of 100 nm. However, the bands are narrow compared to the solar spectrum.

Low carrier mobility limits the thickness of the devices to a few 100 nm



**Thin films (100 nm) with an exciton splitting interface**

#### **Inorganic semiconductors**

Charge generation occurs directly in the bulk semiconductor.

Lower absorption coefficient requires at least 1 micron thick layers (thin film technologies) or 100 microns (c-Si). The absorption band is naturally broad.

High carrier mobility allows to use rather thick films or wafers.



Thicker films (10-100 microns) with a p-n junction for charge separation. p-i-n architectures are also possible.

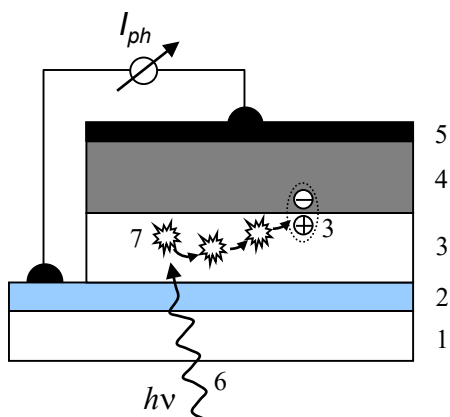
## Working principle of organic solar cells

### □ Response to exciton binding energy

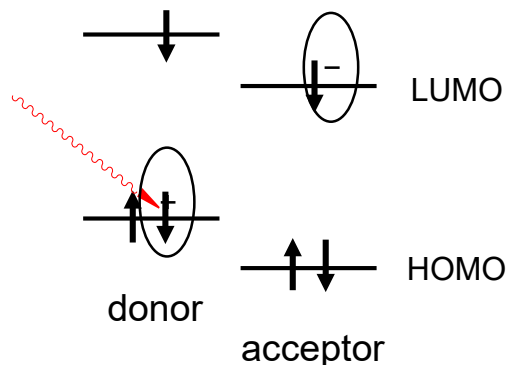
- (1) Transparent substrate
- (2) Transparent conductive anode
- (3) Electron donor
- (4) Electron acceptor
- (5) Cathode

Upon **light absorption** (6), excitons (7) **diffuse** until they recombine or reach the organic heterointerface where **charge generation** into free electron and holes takes place (3)

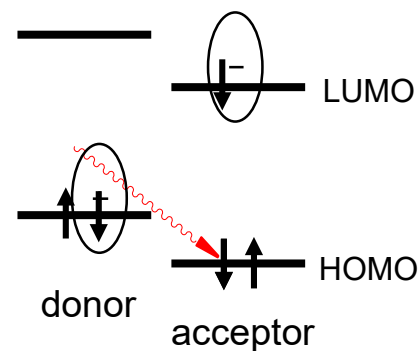
Issue: short exciton diffusion (about 10 nm)



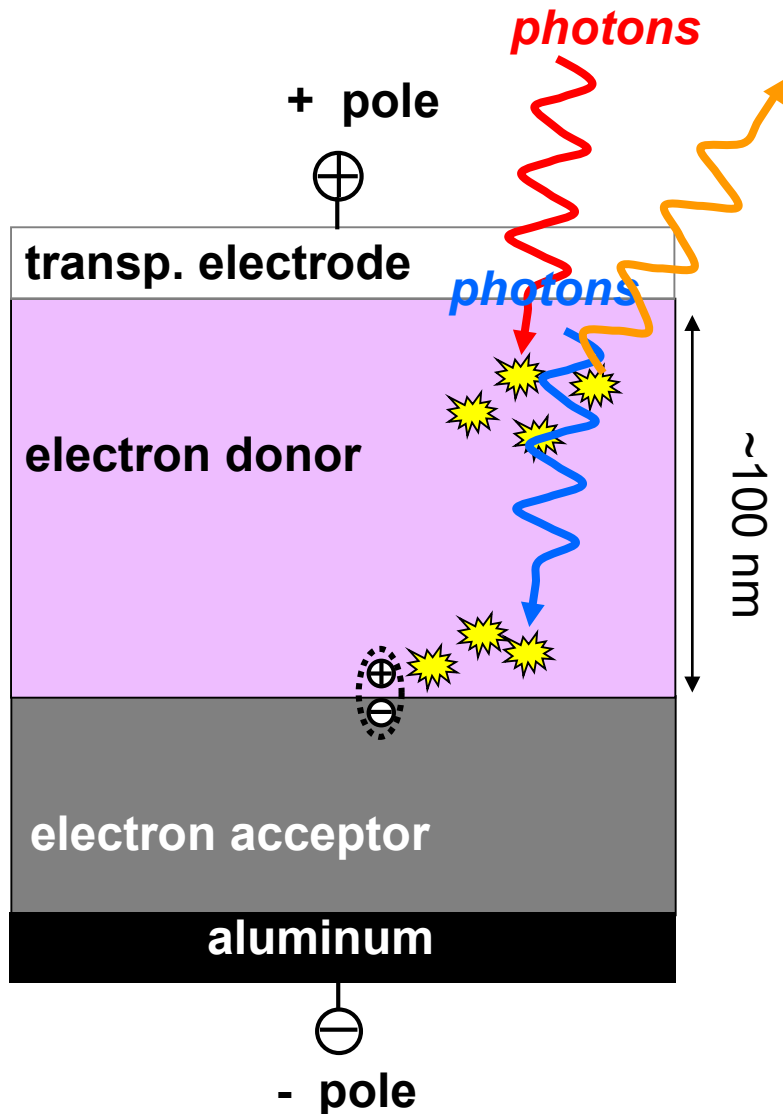
*reductive electron transfer*



*oxidative electron transfer*



## The problem of the exciton diffusion length



$\pi$ - $\pi^*$  transitions in organic semiconductors are very strong and therefore films of 100nm-200nm are thick enough to harvest all the photons within the range of absorption.

Excited states (excitons) have a lifetime of about 1 ns. During this lifetime, their diffusion length is about 5-20 nm.

This condition brings a difficulty, namely that excitons that are excited far from the donor-acceptor interface will not be dissociated at the heterointerface.

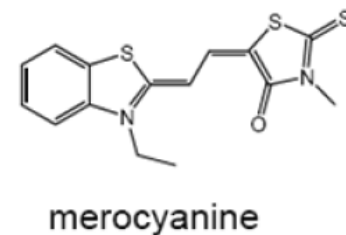
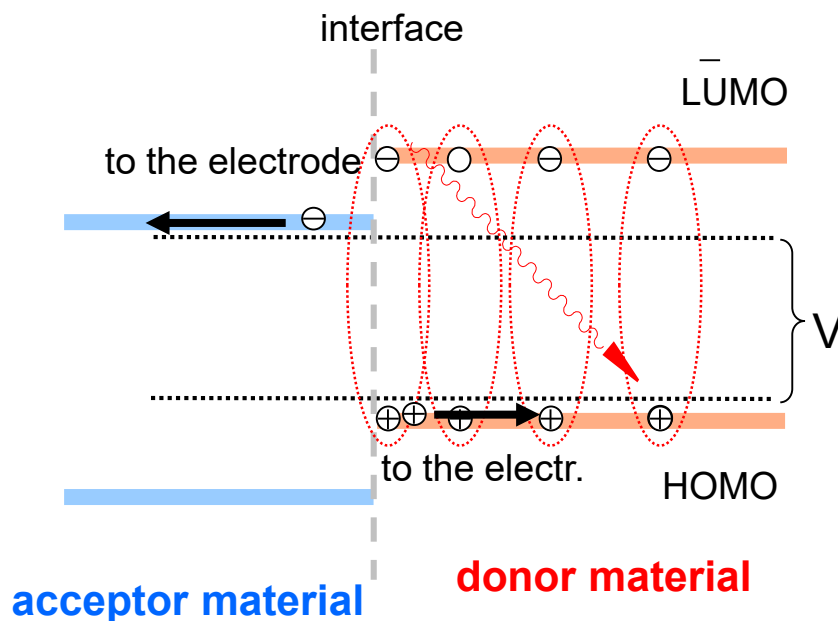
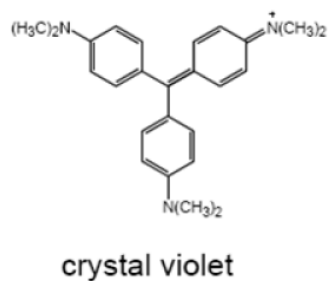
**Compromise** between absorption and exciton dissociation



## First report on organic donor-acceptor solar cells (1960)

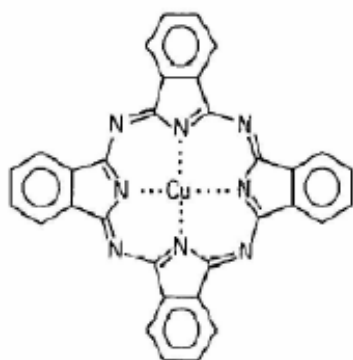
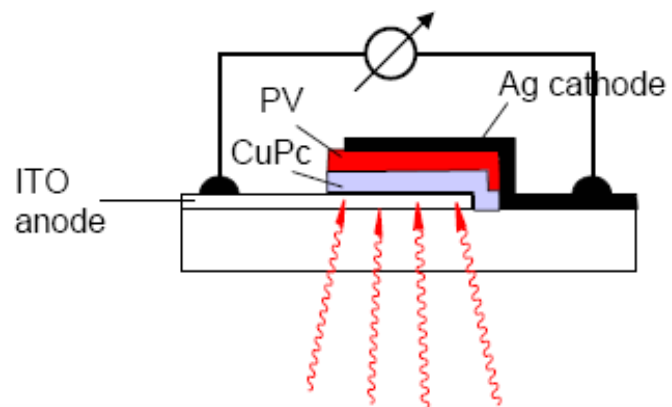
- Analogue to an inorganic p/n junction, a system of p- and n-type organic semiconductors, shows properties of a photodiode with a short circuit current and an open circuit voltage

Hans Meier, Bamberg, 1960



# Organic donor-acceptor solar cells

## Bilayer solar cells reach 1%



CuPc



PV

efficiency: 1%  
fill factor: 0.65



Q. Tang, organic solar cell with power conversion efficiency of 1%

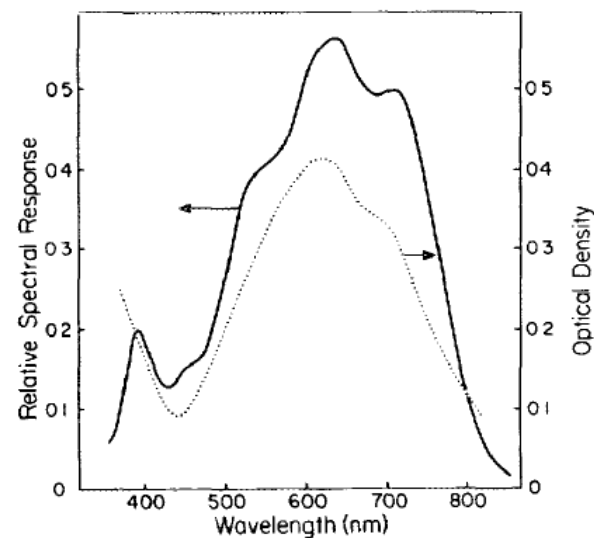
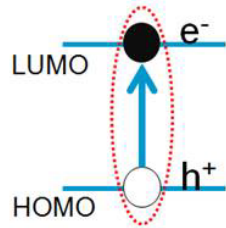


FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

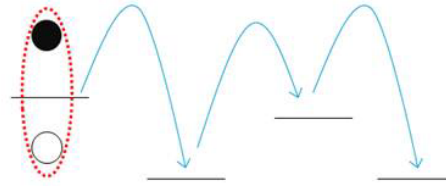
Q. Tang et al., Applied Physics Letters 48 (2), 183-185, 1986

# The physics of organic solar cells



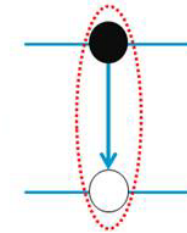
## Exciton creation

An electron is excited due to light absorption  
Electron and hole are Coulombically bound.  
This complex is called an exciton.



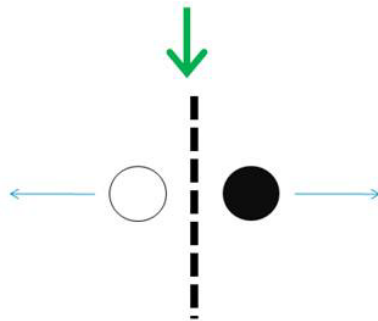
## Exciton transport

Excitons will hop between localized energy states. This is modelled using Forster Resonance Energy Transfer theory.



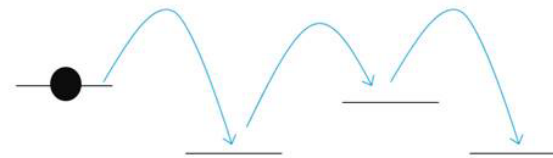
## Loss mechanism: Geminate recombination

If an exciton does not reach an interface, it relaxes back into the ground state.



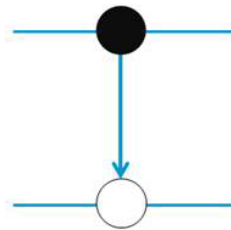
## Exciton dissociation

If an exciton reaches a heterointerface, a free electron and hole are created



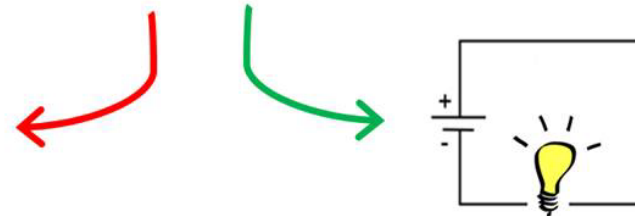
## Charge transport

Charge hopping is modelled using Marcus-Hush theory. It includes Coulomb interaction, electric field, energetic disorder and induced charge effects.



## Loss mechanism: bimolecular recombination

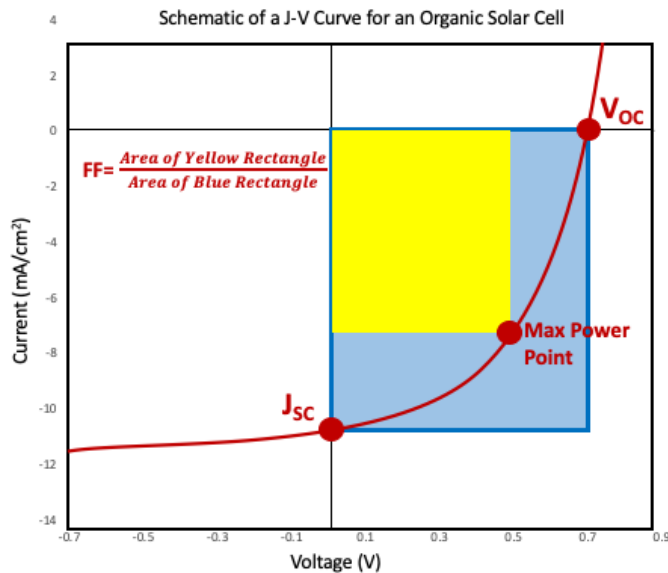
Free electrons and holes can still recombine depending on their proximity to each other



## Charge extraction

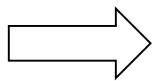
Charge carriers that reach their respective electrodes are considered extracted. An injection barrier can be included in the model

## How to design efficient organic solar cells?



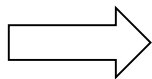
$$\eta = \frac{P_{\max}}{I_{\text{in}}} = \frac{J_{\text{mpp}} V_{\text{mpp}}}{I_{\text{in}}} = \frac{J_{\text{sc}} V_{\text{oc}} FF}{I_{\text{in}}}$$

❑ Increase  $V_{oc}$  and FF



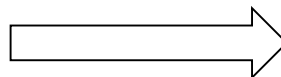
reduce recombination, optimize LUMO and HOMO levels

❑ Increase  $J_{sc}$



increase absorption; match with solar spectrum

❑ Short exciton diffusion length

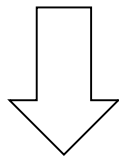
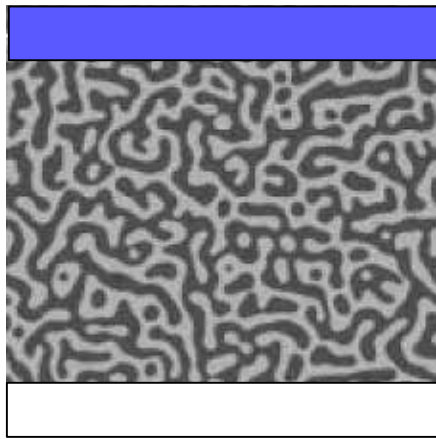


morphology

## How to design efficient organic solar cells?

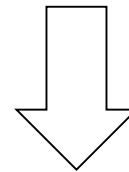
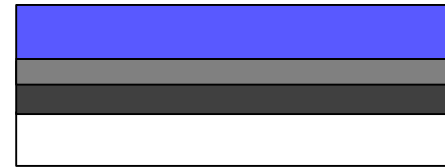
- Geometrical considerations: 2 options

Interconnected donor-acceptor phase



Phase separated bulk heterojunction  
Solution processing from polymer  
blends

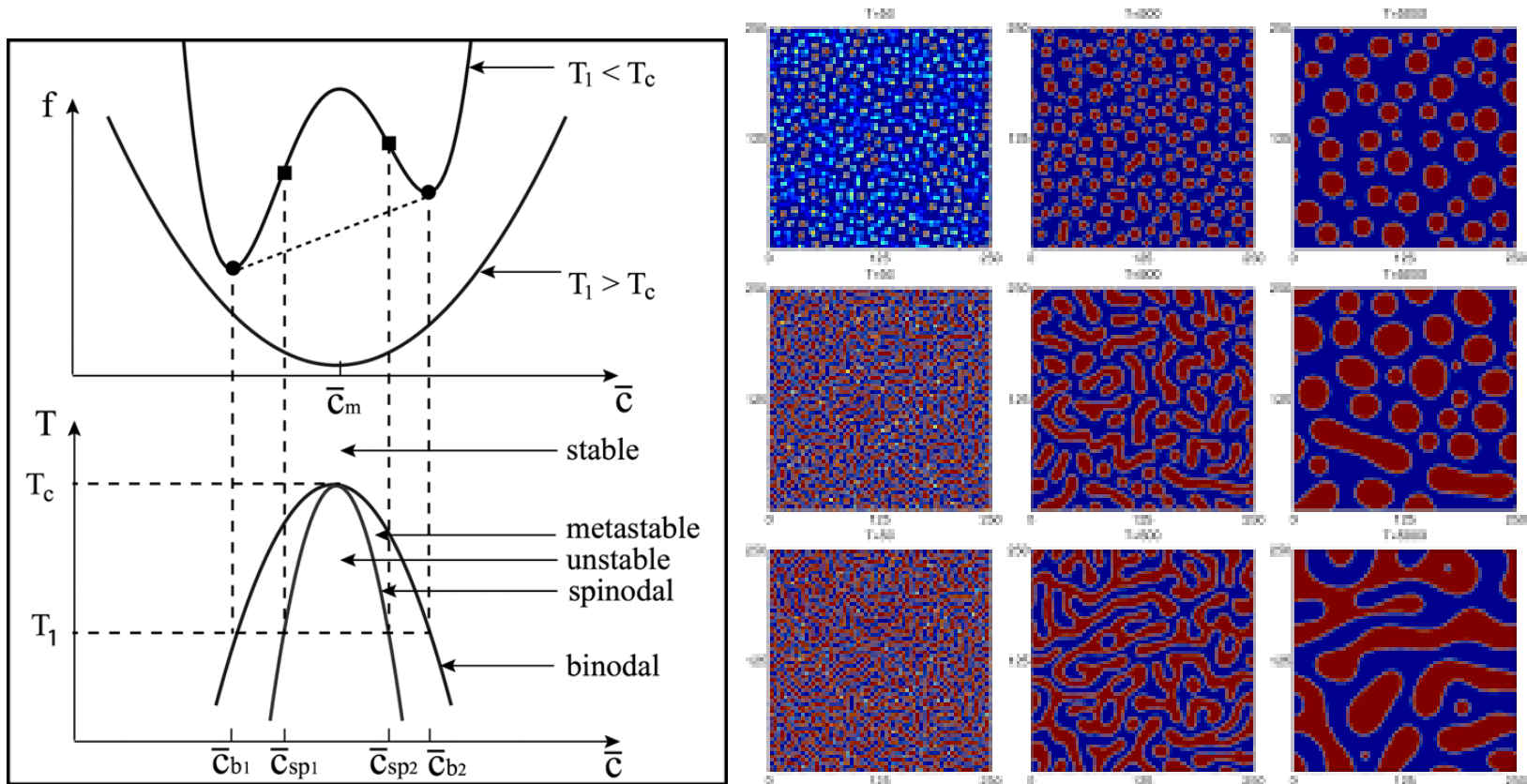
Thin films with very high  
absorption coefficients



Evaporation of small molecules

# How to design efficient organic solar cells?

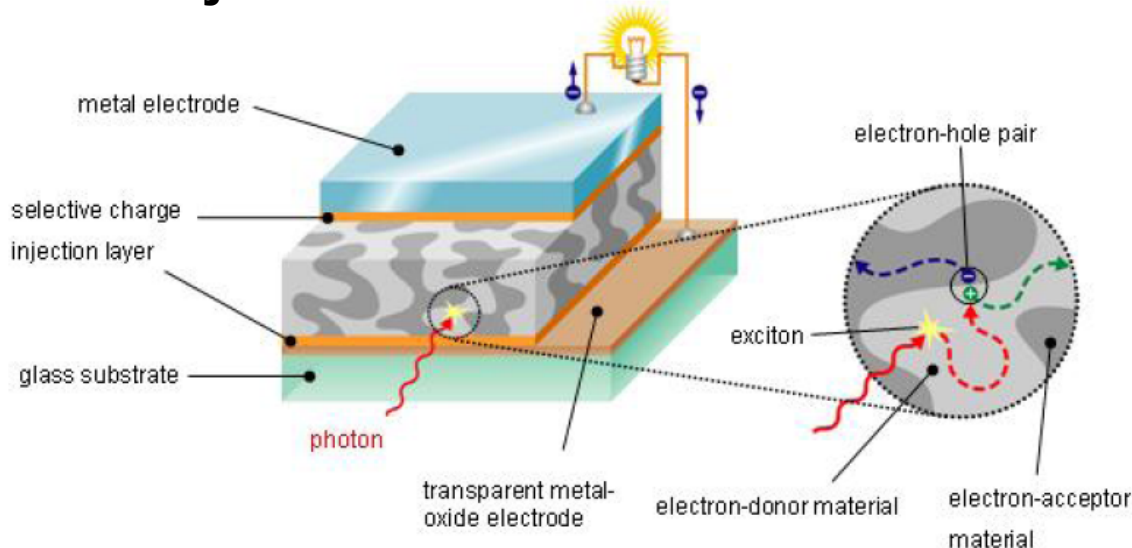
## ❑ Bulk heterojunction solar cells: spinodal decomposition





# How to design efficient organic solar cells?

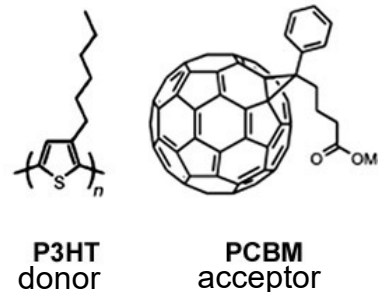
## ❑ Bulk heterojunction solar cells



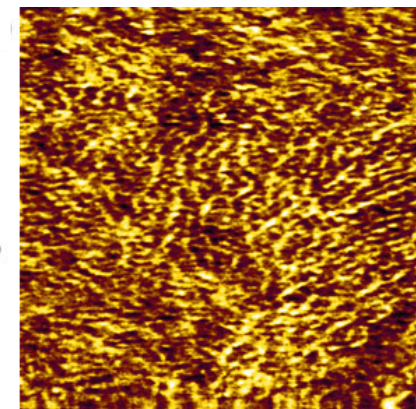
empirical estimation:

$$\eta = \frac{P_{\max}(\text{electric})}{P_{\text{in}}(\text{light})} = FF \cdot \overline{IPCE} \cdot Abs \cdot \frac{eV_{oc}}{h\nu} = \frac{1}{2} \cdot \frac{3}{4} \cdot \frac{3}{4} \cdot \frac{1}{2} = 14\%$$

**P3HT** and **PCBM** are reference materials for organic solar cells. Power conversion efficiency of 4% in this system is limited by the limited width of the absorption spectrum of P3HT (onset at about 630 nm).



Allan Heeger, UCSB bulk-heterojunction using conjug. polym.

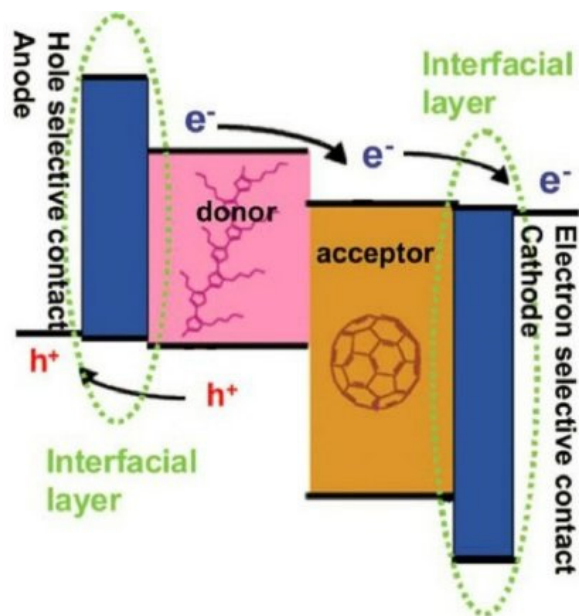


## How to design efficient organic solar cells?

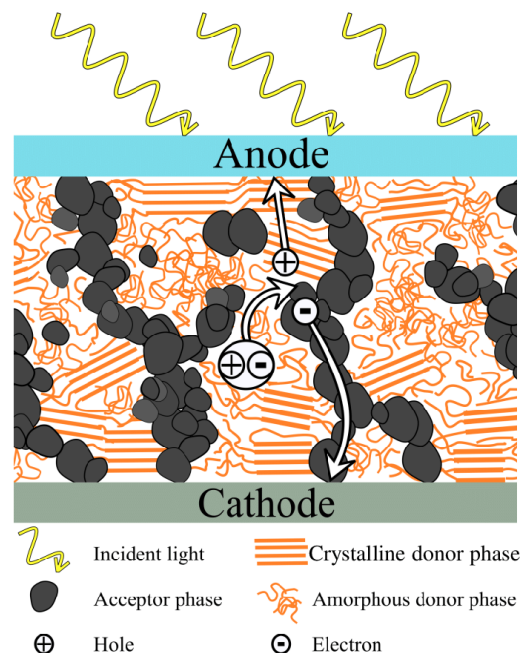
### □ Energy levels of the electrodes?

Selectivity of electrode contacts is most important in bulk heterojunction.

Frequently blocking layers are introduced.



Interfacial Layer Engineering for Performance Enhancement in Polymer Solar Cells, *Polymers* 2015, 7(2), 333-372.

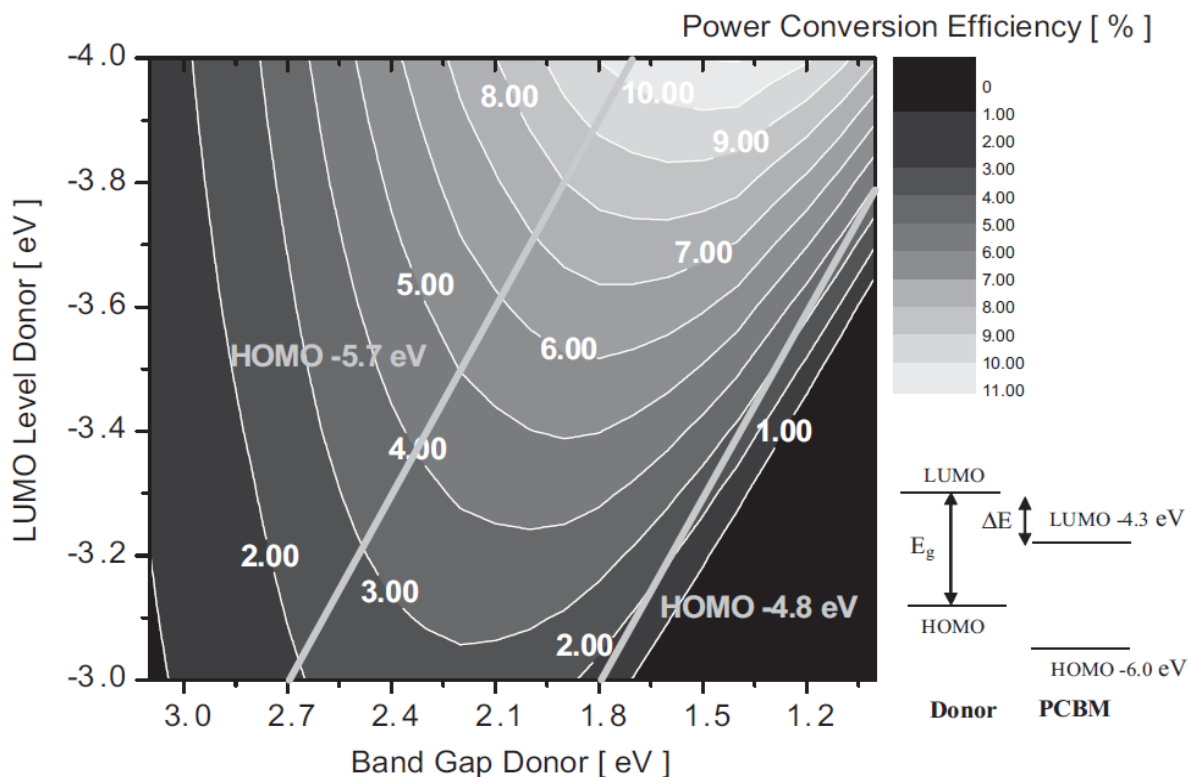


Impact of Solubility of Organic Semiconductors for Solution-Processable Electronics on the Structure Formation: a Real-Time Study of Morphology and Electrical Properties, *Soft Matter*, 2018, 14 (13).

# How to design efficient organic solar cells?

## □ HOMO – LUMO levels, band gap

Calculated efficiencies for LUMO Level and Band Gap of donor for PCBM acceptor

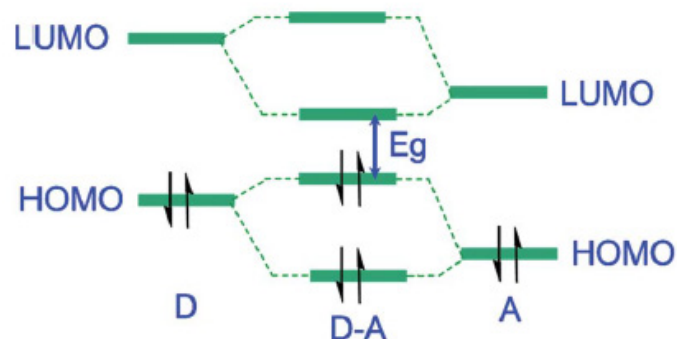


Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10 % Energy-Conversion Efficiency, Adv. Mater. 2006, 18, 789–794

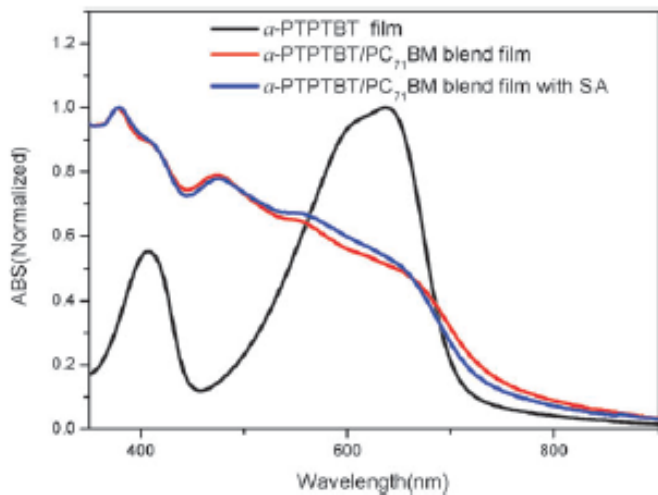
# How to design efficient organic solar cells?

## Donor-acceptor conjugated copolymers

- Donor-acceptor co-polymers are the best performing organic semiconductors for OPV today
- Most of the films are blends with PC<sub>71</sub>BM (see next slide)
- Not only the bandgap E<sub>g</sub> is important, but also the microstructure of the blend films



## P5g and blend absorption



C. C. Yi et al, *Chem. Commun.*, 2010, **46**, 6503–6505

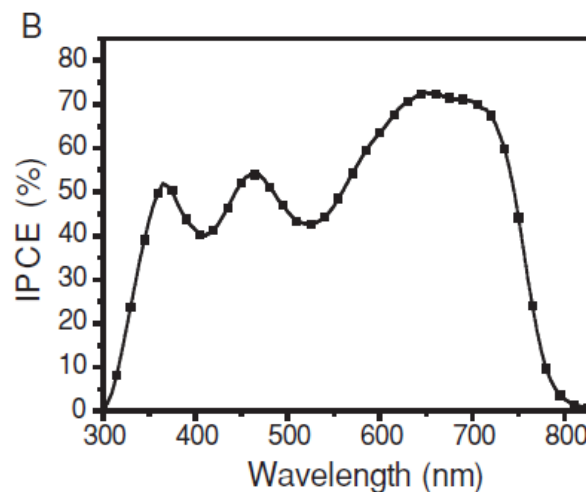
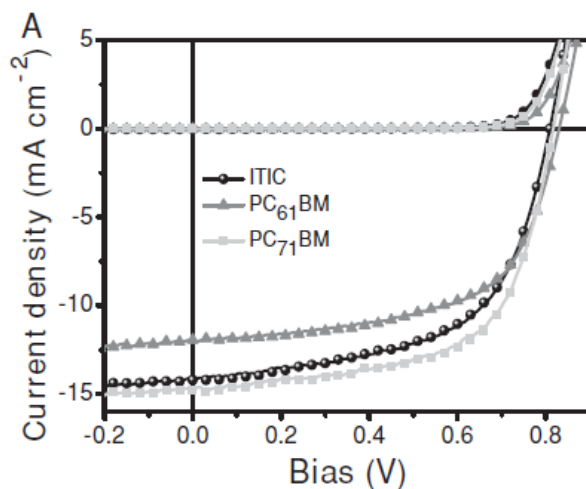
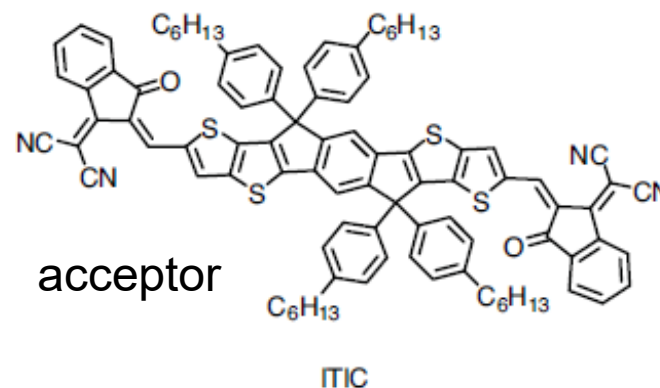
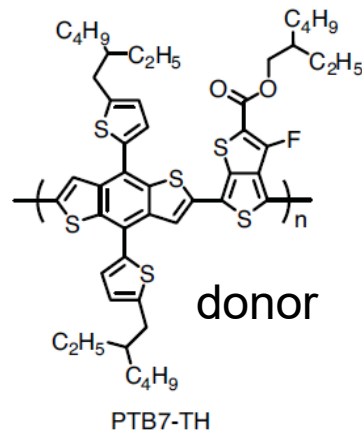
Z. Guo et al., *J. Mater. Chem.*, 2012, 22, 4178

Donor \ Acceptor Combination	Acceptor	Donor	Efficiency (%)	Wavelength (nm)
			4.5%	653nm
	or		5.4%	689nm
			6.3%	653 nm
			4.5%	653nm
			5.4%	689nm
			6.3%	653 nm
			5.5%	886 nm
			5.1%	855nm
			2.8%	855nm
			6.4%	709nm
			3.5%	689nm
			0.8%	886nm

## How to design efficient organic solar cells?

- ☐ Acceptor absorption complementary to donor absorption

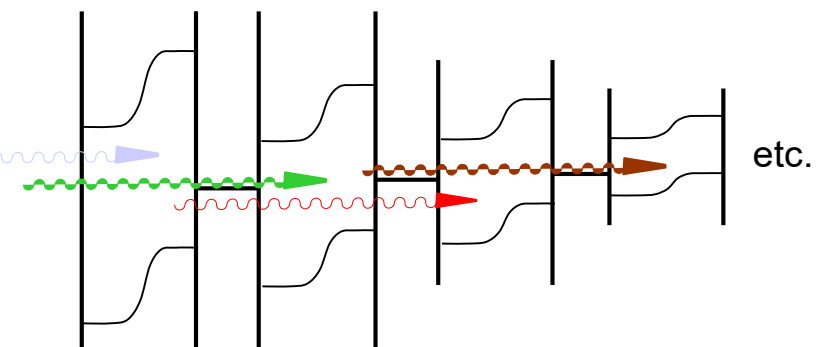
6.8% organic solar cell using non-fullerene acceptors



# How to design efficient organic solar cells?

## Multi-junctions

- Allows for increased photon harvesting, enhanced efficiency
- Need for NIR absorbing donors



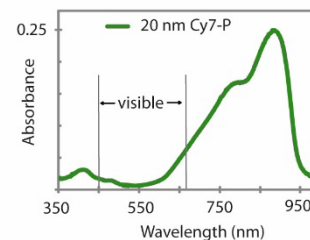
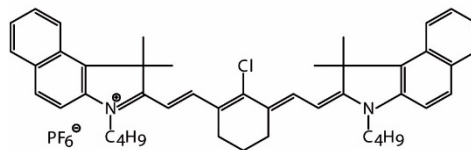
Ideal bandgaps:

1 junction (1.35 eV): 31%

2 junctions (1.56eV, 0.94 eV): 50%

3 junctions (1.91eV, 1.37eV, 0.94eV): 56%

36 junctions: 72%



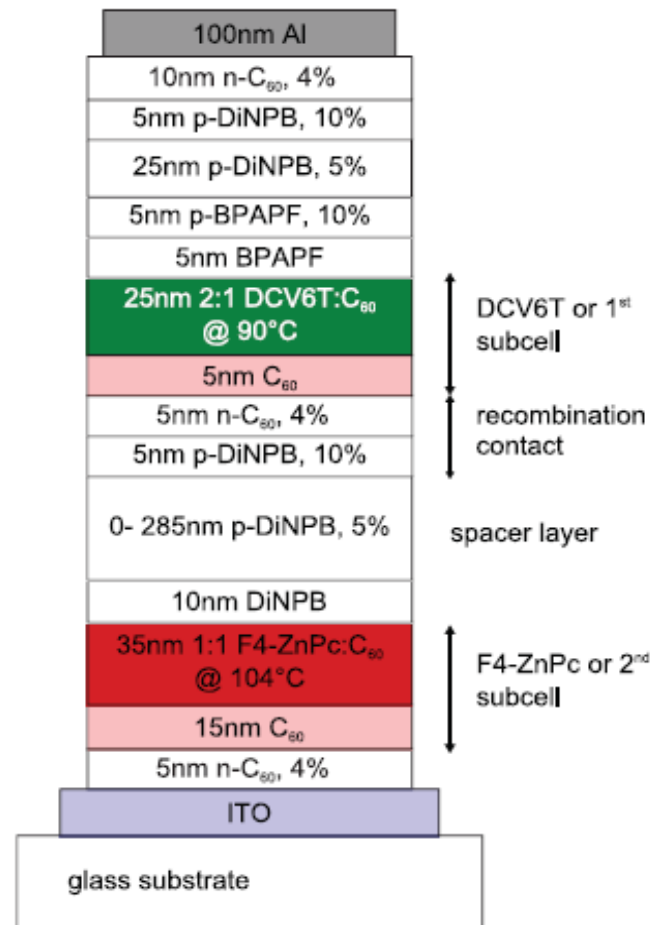
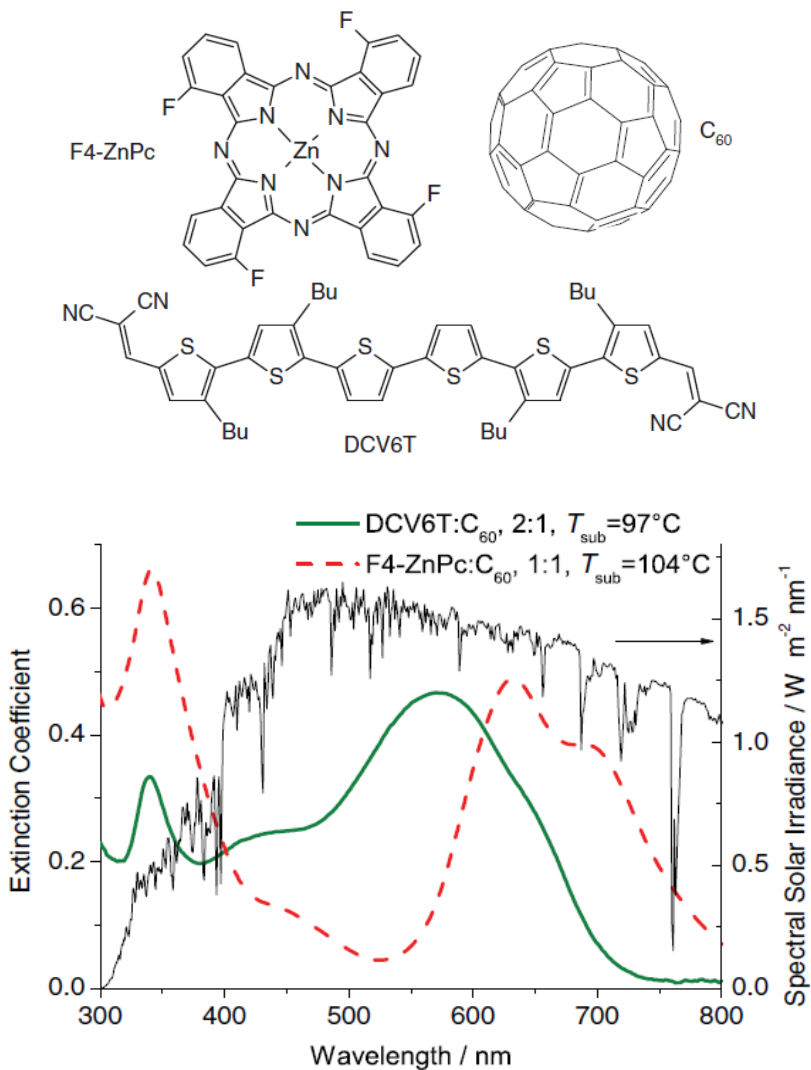
The solar cell absorbs solely in the NIR domain



# How to design efficient organic solar cells?

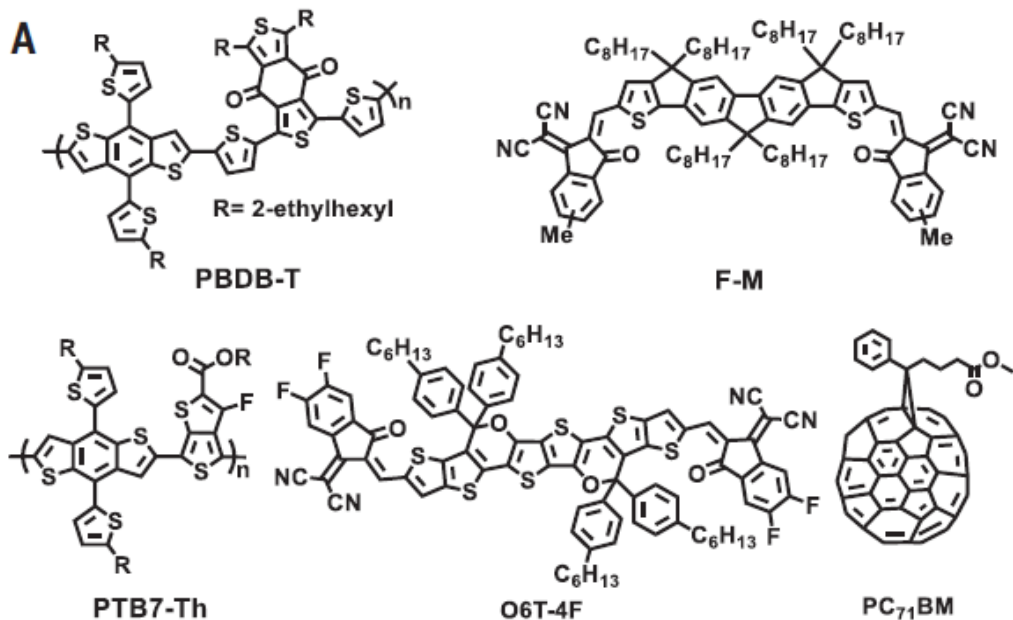
Match solar spectrum – 6.1 % in small molecule multijunction cell

Adv. Funct. Mater. 2011, 21, 3019–3028



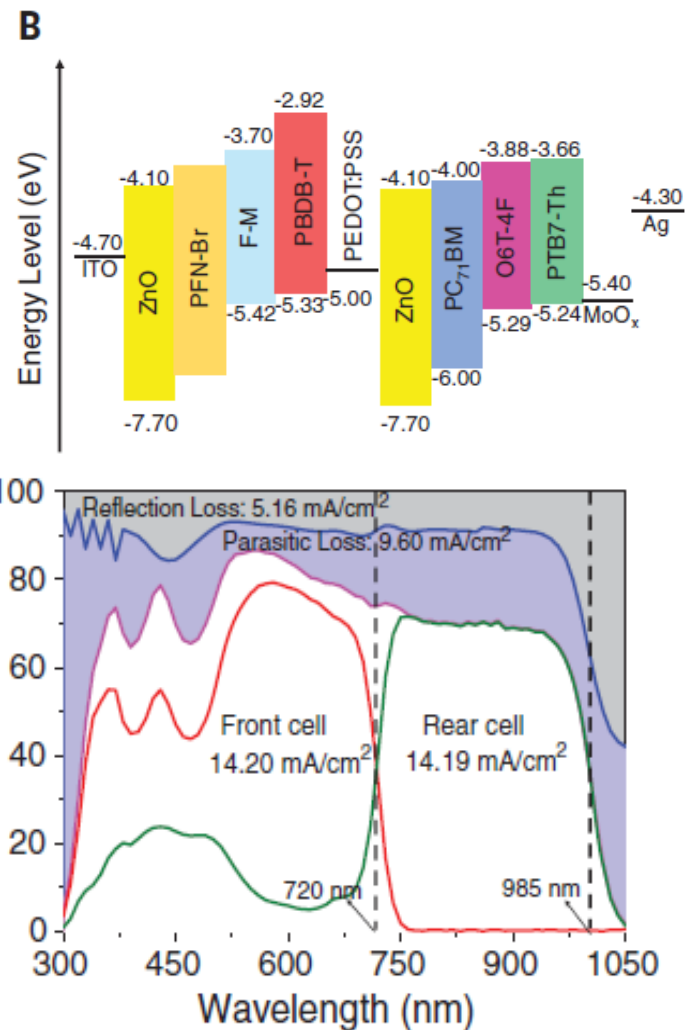
# How to design efficient organic solar cells?

## Organic and solution-processed tandem solar cells with 17.3% record efficiency



- Broad band absorption
- Perfect current matching
- Optical optimization

L. Meng et al., Science 361, 1094–1098 (2018)



# How to design efficient organic solar cells?

## Record cells

Received: 29 October 2020

Accepted: 5 November 2020

DOI: 10.1002/pip.3371

**ACCELERATED PUBLICATION**



## Solar cell efficiency tables (version 57)

**TABLE 2** ‘Notable exceptions’ for single-junction cells and submodules: ‘top dozen’ confirmed results, not class records, measured under the global AM1.5 spectrum ( $1000 \text{ Wm}^{-2}$ ) at  $25^\circ\text{C}$  (IEC 60904-3: 2008 or ASTM G-173-03 global)

Classification	Efficiency (%)	Area ( $\text{cm}^2$ )	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ ( $\text{mA}/\text{cm}^2$ )	Fill factor (%)	Test centre (date)	Description
Organic (thin film)	$18.2 \pm 0.2^{\text{l}}$	0.0322 (da)	0.8965	$25.72^{\text{e}}$	78.9	NREL (10/20)	SJTU Shanghai/Beihang U.

# How to design efficient organic solar cells?

## Record cells

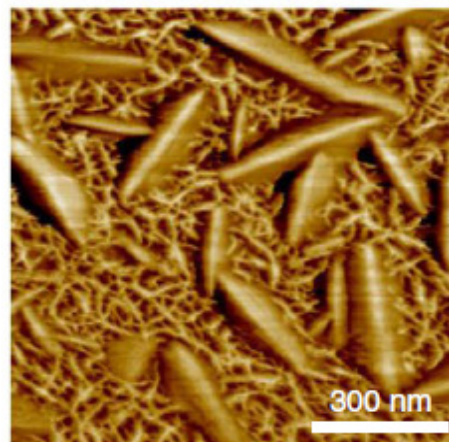
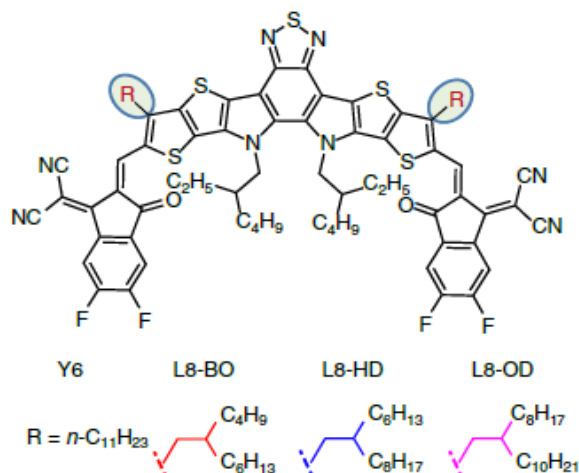
nature energy

ARTICLES

<https://doi.org/10.1038/s41560-021-00820-x>

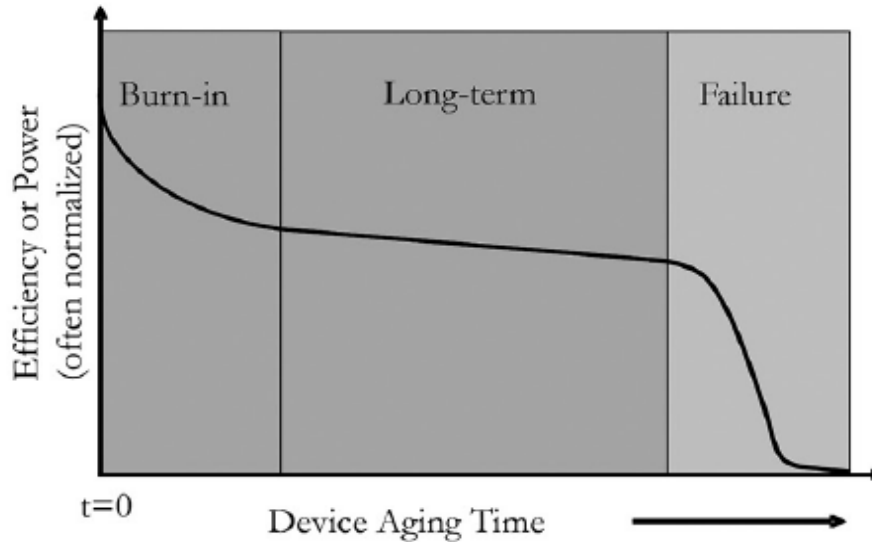


## Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells



# Stability / degradation

## □ Three different regimes



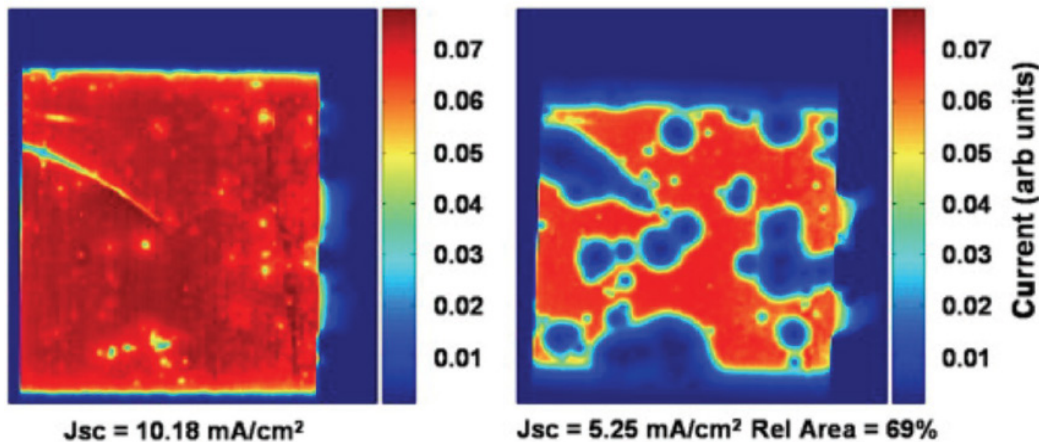
- Photo-induced burn-in: Initial exponential degradation
- Long-term regime: Continuing degradation
- Failure: Rapide and complete device degradation

## □ Different stress factors

- Water and oxygen from atmosphere (extrinsic)
- Intrinsic in the dark («movement of material»)
- Intrinsic under light (electrochemical reactions)

## Stability / degradation

- ❑ Extrinsic degradation
  - ❑ Low work function metals oxidize when exposed to atmosphere (even in the dark)
    - ❑ => encapsulation, inverted geometry
  - ❑ Photooxidation causes organic films to loose optical density, via a free-radical reaction
    - ❑ => encapsulation
  - ❑ Mechanical failure (delamination under elevated temperature)

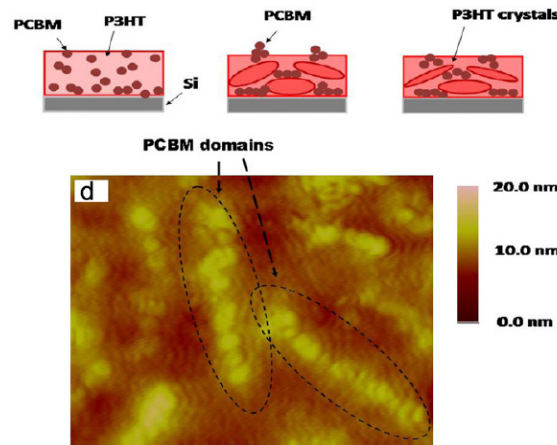


Laser beam induced current (LBIC) map of a solar cell before (left) and after (right) prolonged illumination in ambient conditions. In the degraded solar cell, dead zones clearly form around pinhole defects and there is significant ingress around the edges of the device.

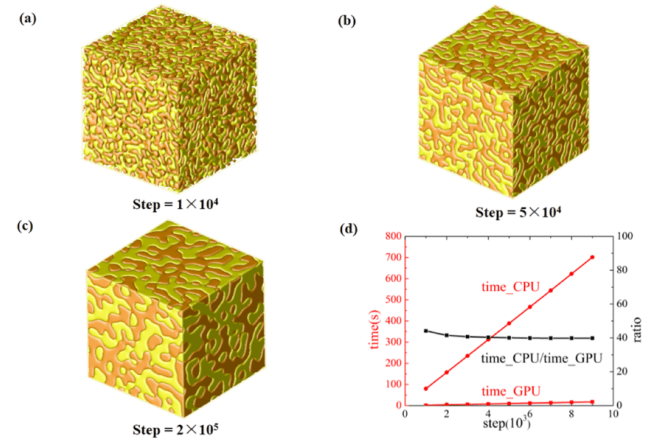


# Stability / degradation

- ❑ Intrinsic degradation (also observed in well encapsulated cells)
  - ❑ Dark, frequently observed around  $T_g$ 
    - ❑ Crystallization, macroscopic phase separation, hole blocking segregation layer



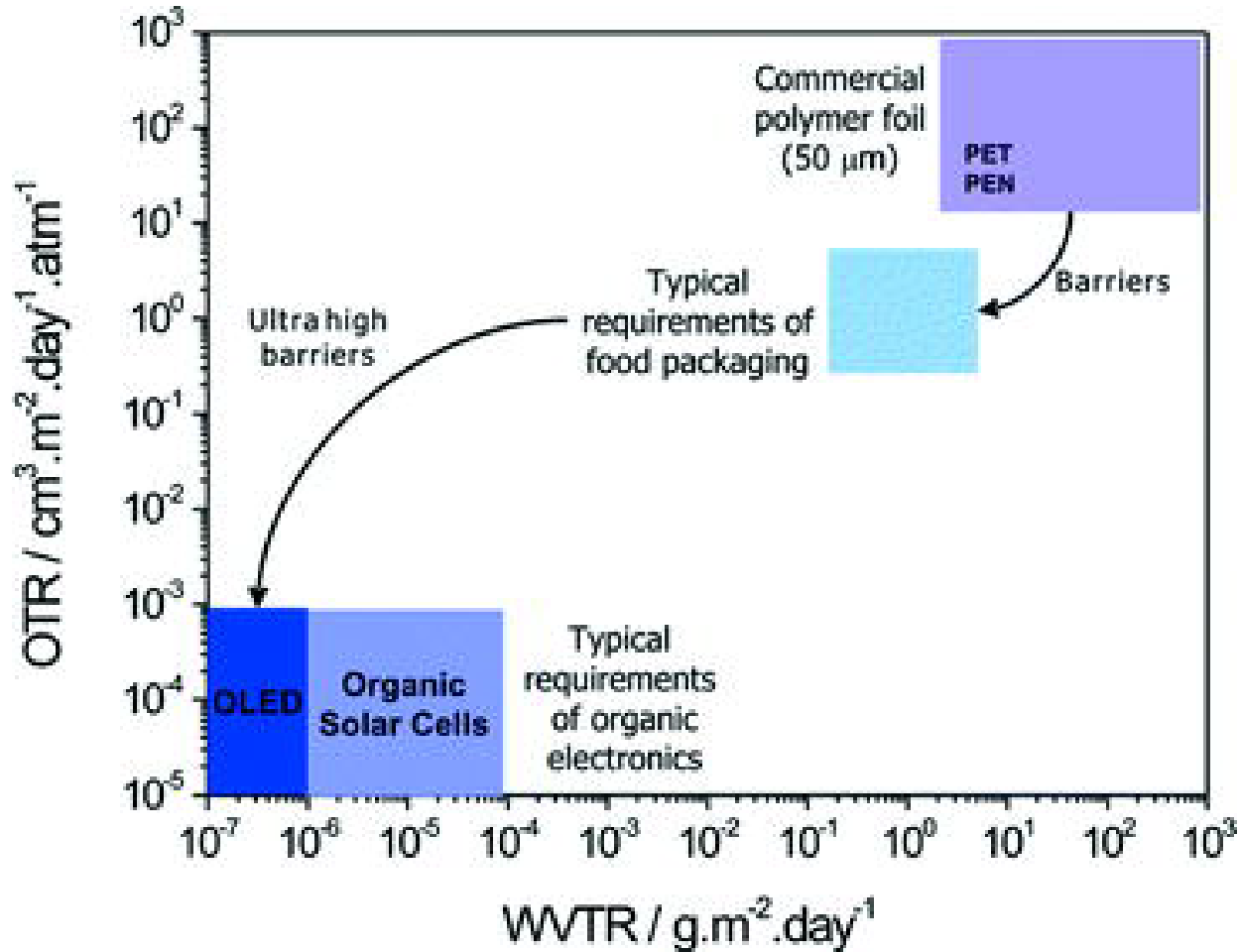
Solar Energy Materials & Solar Cells 107 (2012) 112–124



AIP Advances 7 (2017) 105216

- ❑ Light
  - ❑ Photoinduced burn-in
    - ❑ Different causes: e.g. dimerization of PCBM, photoinduced traps increase recombination

# Encapsulation

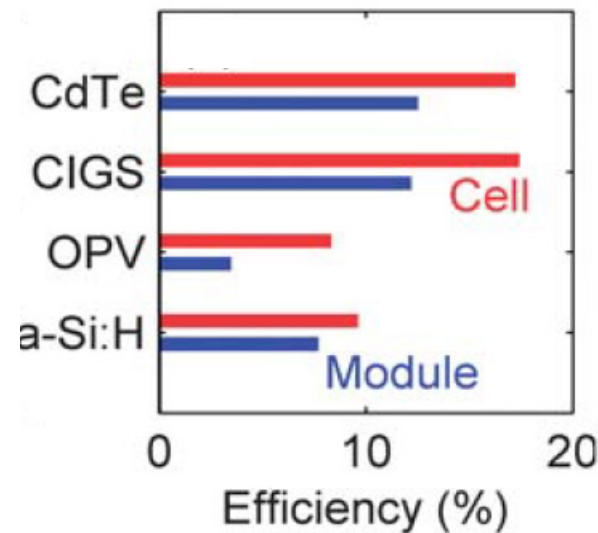
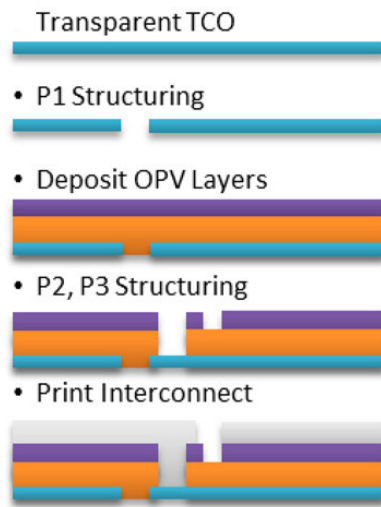
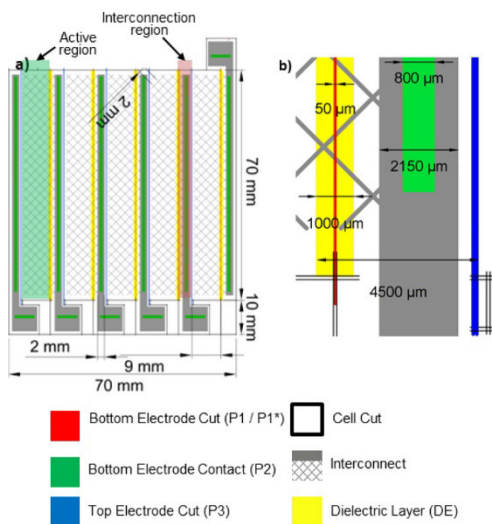


Waldauf C., et al. (2009) Bulk Heterojunction Solar Cells for Large-Area PV Fabrication on Flexible Substrates. In: Wong W.S., Salleo A. (eds) Flexible Electronics. Electronic Materials: Science & Technology, vol 11.

# Efficiency loss when moving from laboratory cell to module

**TABLE 1** Confirmed single-junction terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m<sup>2</sup>) at 25°C (IEC 60904-3: 2008 or ASTM G-173-03 global)

Classification	Efficiency (%)	Area (cm <sup>2</sup> )	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill factor (%)	Test centre (date)	Description
Organic (minimodule)	12.6 ± 0.2r	26.129(da)	0.8315 <sup>c</sup>	21.32 <sup>c,j</sup>	71.1	FhG-ISE (9/19)	ZAE Bayern (12 cells) <sup>20</sup>
Organic (submodule)	11.7 ± 0.2r	203.98 (da)	0.8177 <sup>c</sup>	20.68 <sup>c,j</sup>	69.3	FhG-ISE (10/19)	ZAE Bayern (33 cells) <sup>20</sup>

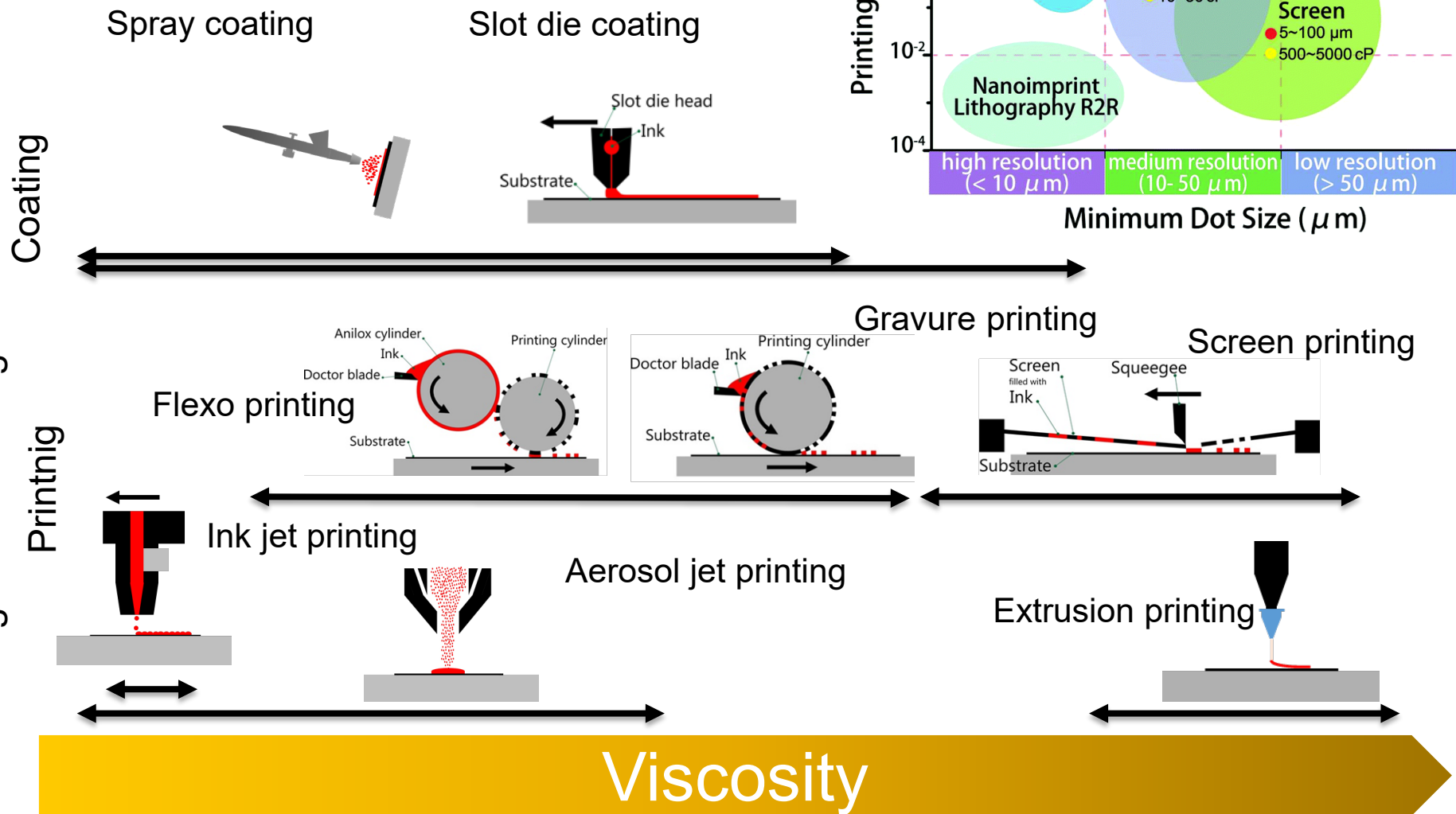


ACS Appl. Electron. Mater. 2020, 2, 756–762

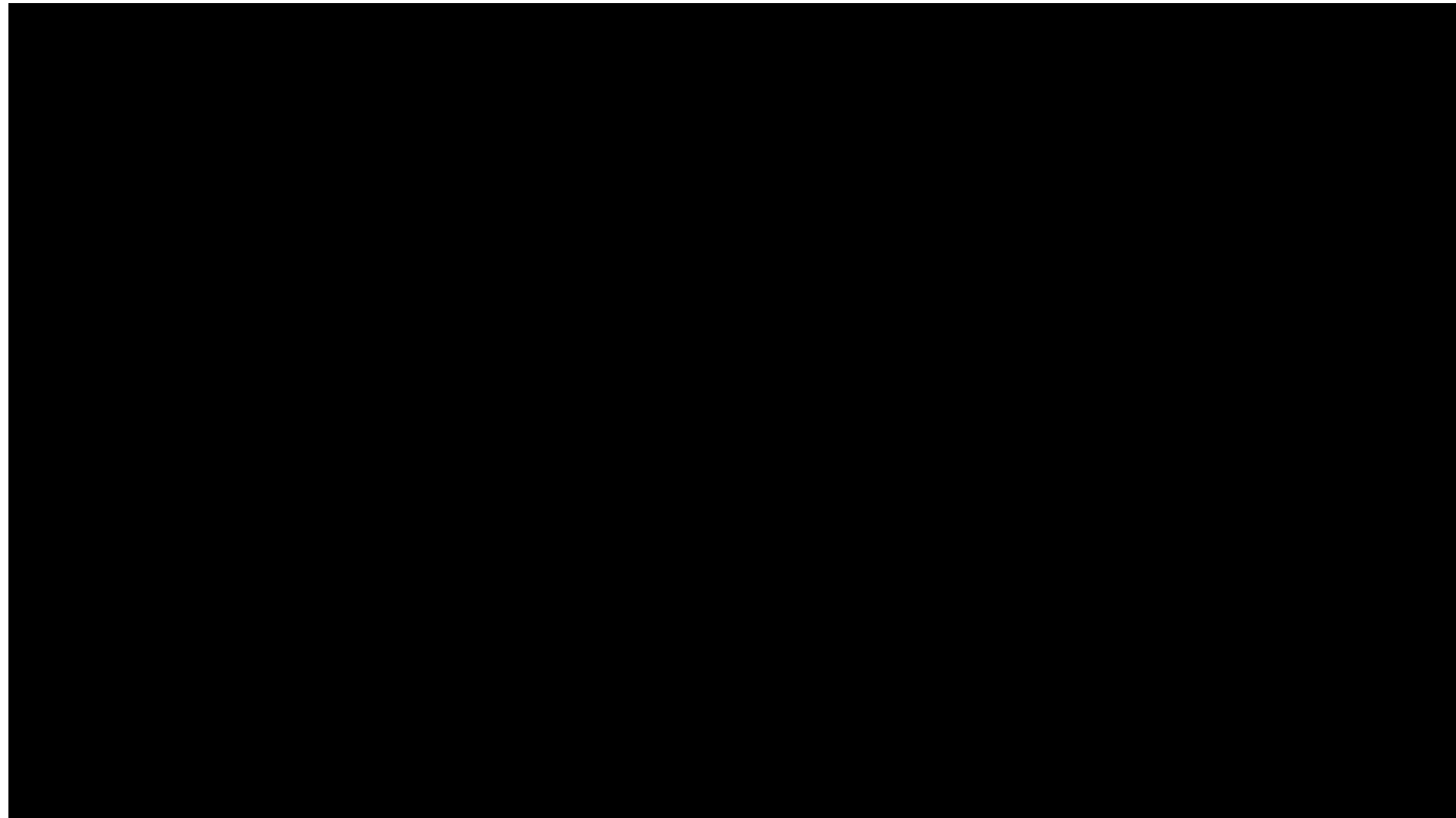
Energy Environ. Sci., 2013, 6, 782

# Printing and coating techniques

Wu, *Nanoscale*, 2017, 9, 7342-7372

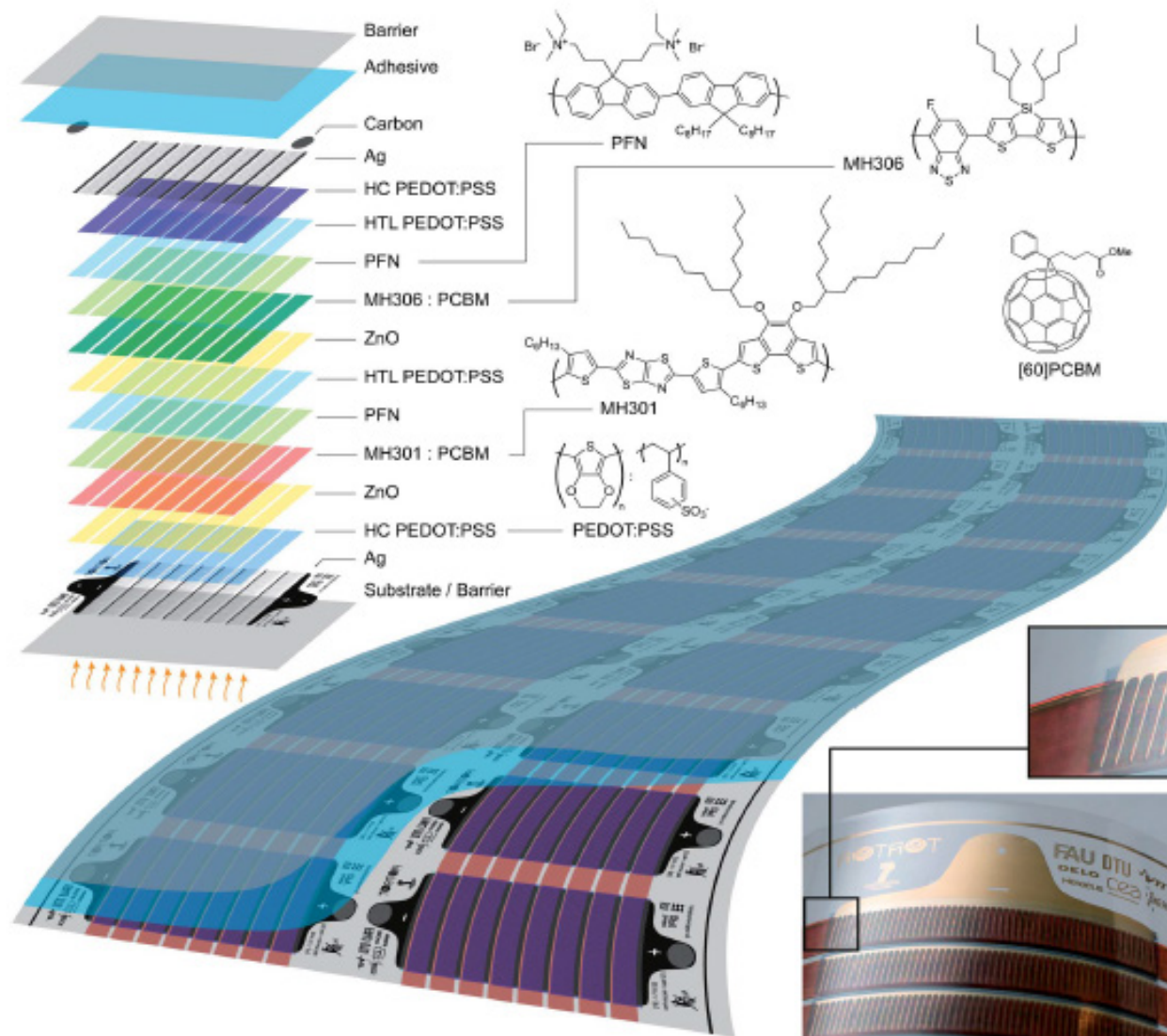


## *Printing at Empa*



# Scalable, ambient atmosphere roll-to-roll manufacture of encapsulated large area, flexible organic tandem solar cell modules

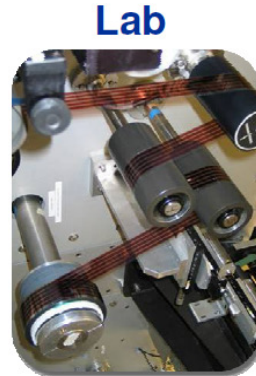
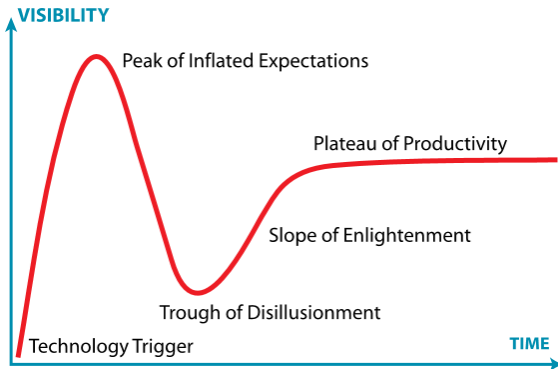
Energy Environ. Sci., 2014, 7, 2925





# Printed organic solar cells: Trough of Disillusionment

Founded in 2001 as a spin-off  
from University of  
Massachusetts Lowell



2006  
5 cm  
1kWatt



2007  
25 cm  
1MWatt



2008  
150 cm  
1GWatt

## 2021: Konarka files for bankruptcy

Organic solar film  
manufacturer, Konarka  
Technologies, Inc. is the  
latest solar company to file  
for bankruptcy protection  
under chapter 7 of the U.S.  
Federal bankruptcy laws.



Color Bag - Standard GW



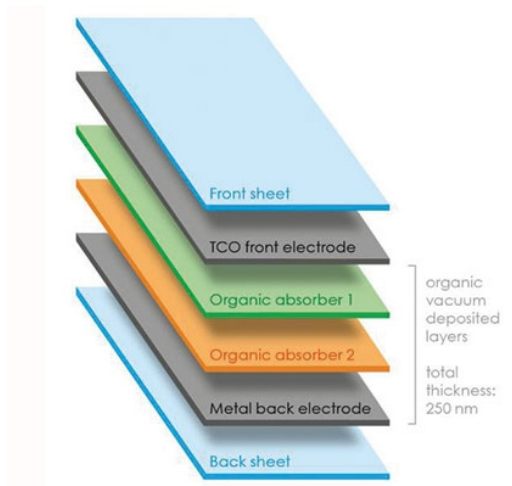
Rollable power supply



Shading elements

## Evaporated roll-to-roll modules at Heliathek

Industrial grade solar films are delivered to its first strategic customers in a variety of geographies, “We have now installed the core production machines and are currently working on the ramping them up towards high-volume roll-to-roll mass-production”



## ***Issues***

- ❑ Short operational lifetime of OPV modules

## ***Current research***

- ❑ Improving the absorber material
- ❑ Multijunction architectures
- ❑ Improved encapsulation
- ❑ Alternative contact materials
- ❑ Up-scaling
- ❑ Losses in module fabrication

# 2.2A Organic Photovoltaics (OPV)

## *Learning outcome*

### ❑ Motivation

- *Chemical synthesis of materials, cheap manufacturing, design freedom*

### ❑ History

- *Long development phase*

### ❑ Materials properties compared to inorganic semiconductors

- *Formation of excitons with short diffusion length, narrow absorption band*

### ❑ Consequences for solar cell design

- *Bulk heterojunction or thin film tandem devices*

### ❑ What strategies are followed to improve the efficiency

- Donor-acceptor polymers, complementary absorption donor-acceptor, expand to NIR

### ❑ State-of-the art

- 18.2% efficiency, pilot plants for printing

### ❑ Current research directions

- Stability and upscaling

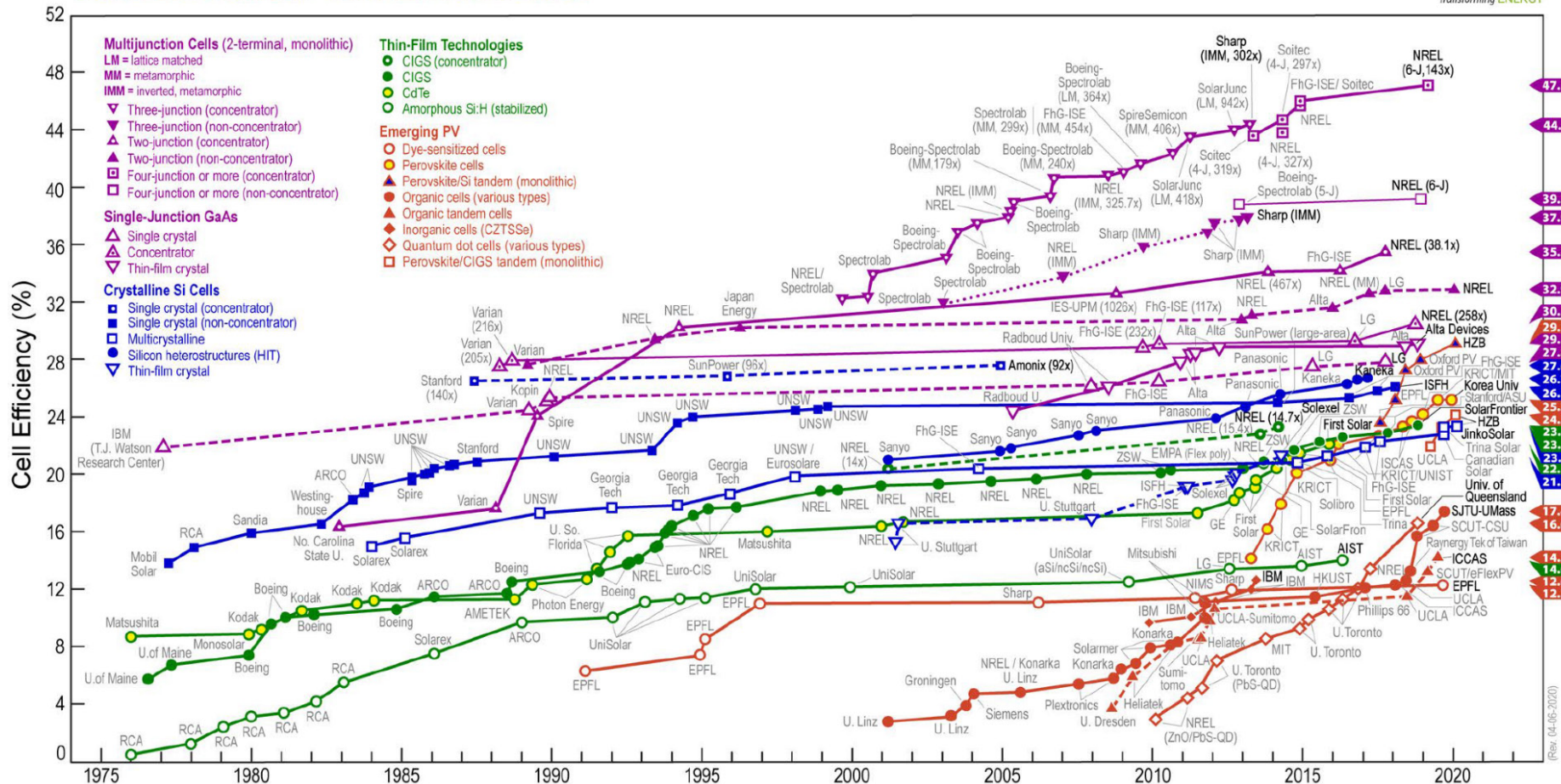
# 2.2B Dye sensitized solar cells (DSSC)

## *Learning goals*

- ❑ How does a Dye Sensitized Solar Cell (DSSC) work
- ❑ History
- ❑ Materials
- ❑ Kinetics of charge generation process
- ❑ Strategies for improvement
- ❑ Current status

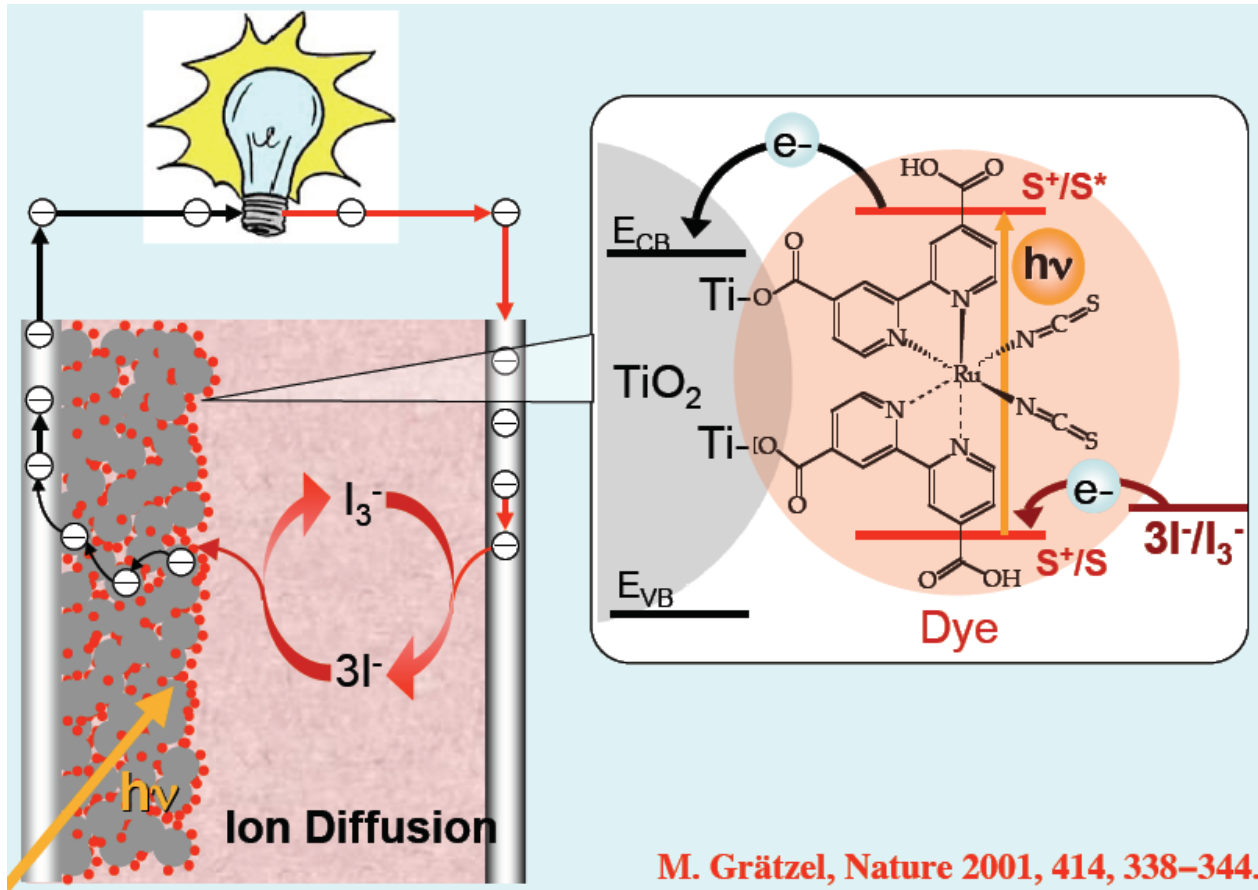


# Best Research-Cell Efficiencies



(Rev. 04-05-2020)

## Working principle of DSSC



*M. Grätzel, EPFL  
Dye sensitized  
Solar cells*



## ***Working principle of DSSC compared to «normal» solid state solar cell***

- ❑ Solid state solar cell: illumination causes a difference in electrochemical potential (separation of Fermi levels)  
Charge carriers don't recombine but are separated in an internal electric field  
Note: both, negative and positive charge carriers participate (ambipolar device).
- ❑ In a photoelectrochemical cell, at two interfaces charge transport switches from electronic to ionic and vice versa
- ❑ In a DSSC, one of these interfaces is a semiconductor
- ❑ A DSSC is a unipolar device (electrons only), because the semiconductor is not directly excited (wideband semiconductor)  
=> reduced recombination

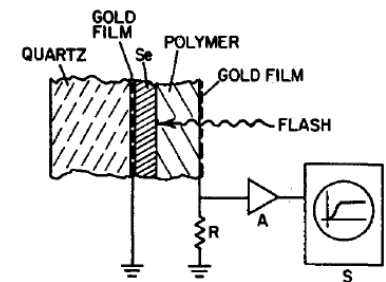
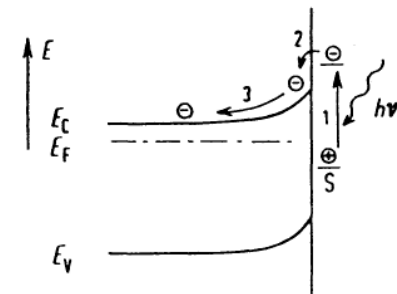
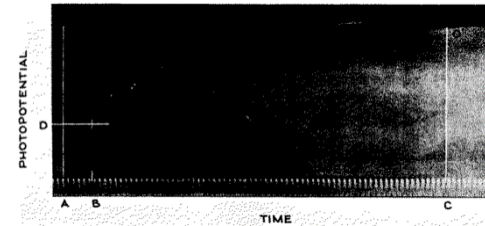
## Important milestones in dye sensitization and DSSCs

1839 Bequerel discovers the photovoltaic effect

1887 Moser (Vienna University) reported the first dye sensitized photoelectric effect on chlorinated silver plates.

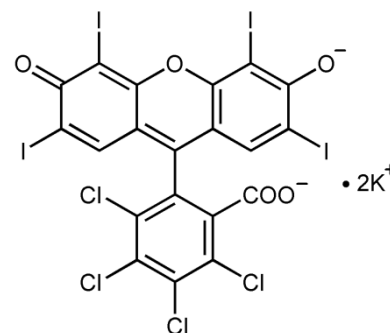
1940 S. E. Sheppard, W. Vanselow, G. P. Happ  
Photovoltaic cells with AgBr Electrodes, J. Phys. Chem., 44, 4, 411-421

1968 H. Gerischer and H. Tributsch, Mechanism of dye-sensitization. Rose bengal on ZnO, Ber. Bunsenges. Phys. Chem. 72 (1968) 437.



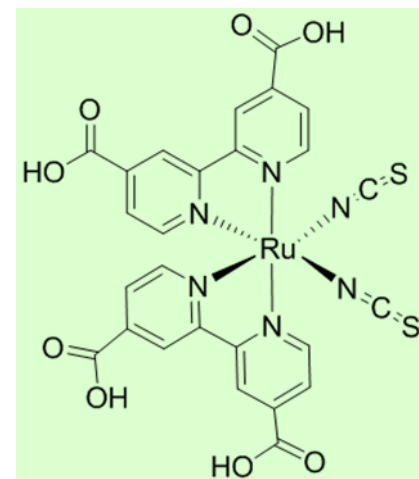
## Important milestones in dye sensitization and DSSCs

1976 Tsubomura and co-workers: powdered high porosity multi-crystalline ZnO, sensitized with rose bengal. Light absorption was significantly increased. The cell had an energy conversion of 1.5%. *Nature* Volume: 261 Issue: 5559 Pages: 402-403



1970's Memming, *Z. Phys.Chem.* **1975**, 98, 303–316,  
 Constable, *Nature* 1979, 280, 571–573,  
 Gerischer *Photochem. Photobiol.* 1972, 16, 243–260,  
 Wide band gap photoelectrochemical cells (mostly in water). Flat TiO<sub>2</sub> surfaces.

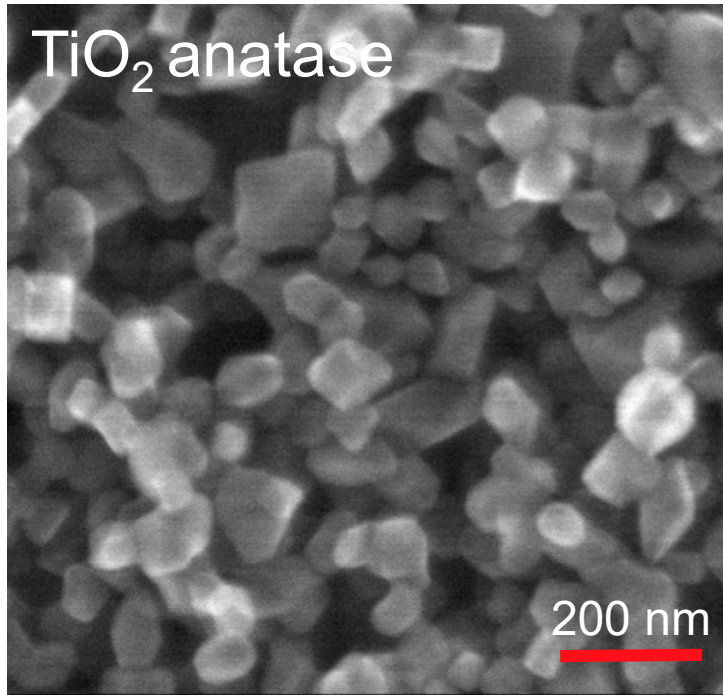
1985 Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. Highly Efficient Sensitization of Titanium Dioxide. Colloidal Nanoparticles, *J. Am. Chem. Soc.* 1985, 107, 2988–2990



## ***The real break-through came with the development of **nanoporous photoanodes*****

- 1990 B. O'Regan, B. Moser, J. Anderson, M. Grätzel, M. Vercellotti. Vectorial electron injection into transparent semiconductor membranes and electric field effects on the dynamics of light-induced charge separation. *J. Phys. Chem.* **1990**, *94*, 8720–8726. colloidal solutions, mesoporous film, **sintering to promote coupling between the nanoparticles**
- 1991 B. O'Regan, M. Grätzel et al. at EPFL, Switzerland, presented a **prototype** of the **current dye-sensitized solar cell**, which had an improved conversion efficiency of 7.12% with a **Ru-based dye**; B. O'Regan, M. Grätzel, *Nature*, 353 (1991), p. 737

## *The virtues of the nanostructured oxide film*



1. The high internal surface area (1000x projected surface) enables efficient light harvesting by the adsorbed sensitizer

2. The photo-injected electrons are screened by positive ions present at the oxide surface oxide

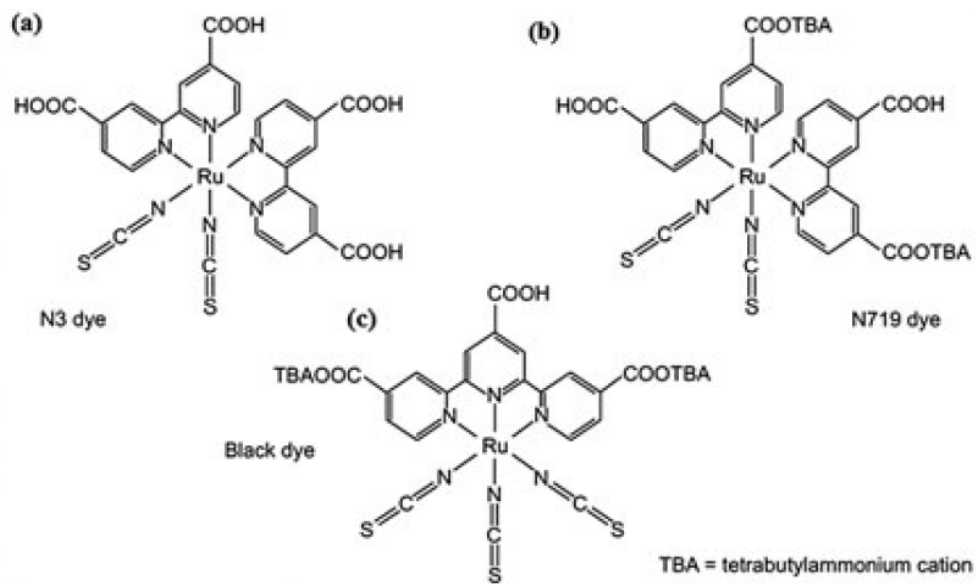
3. The insulating nature of the oxide nanocrystals prevents energy transfer quenching of the excited sensitizer by conduction band electrons

Semiconductor of choice is Titanium dioxide

- cheap
- abundant
- non-toxic
- Progress in colloidal and sol-gel chemistry, nanoparticle synthesis

## Dye:

- ❑ Absorb all light below 800 nm ( $E_g = 1.5$  eV)
- ❑ Attachment groups to draft to  $TiO_2$  surface
- ❑ Energy level of the excited state well matched to the lower bound of the conduction band
- ❑ Redox-potential sufficiently high such that it can be regenerated
- ❑ High stability



1993:  $\eta = 10.3$  % with dye N3 (Cis- bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II))  
 2005:  $\eta = 11.2$  % with dye N719

- ❑ Ruthenium is very expensive; search for alternatives

## *It is easy to fabricate a DSSC*

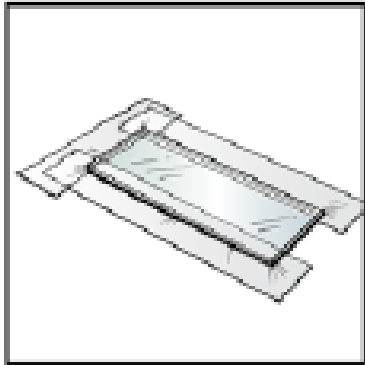


Abb. 1

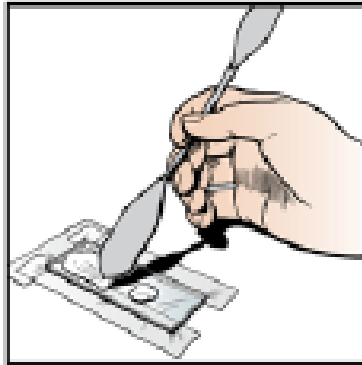


Abb. 2

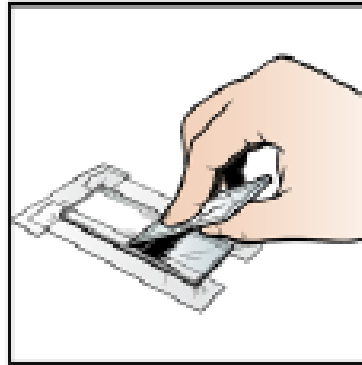


Abb. 3



Abb. 4

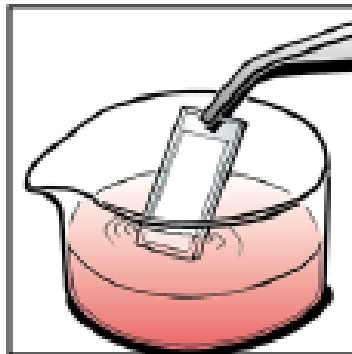


Abb. 5



Abb. 6

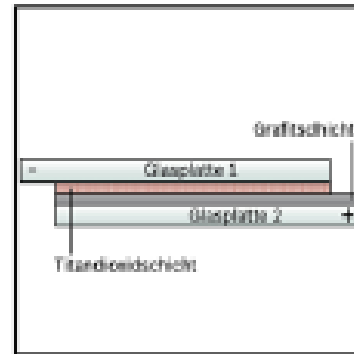


Abb. 7

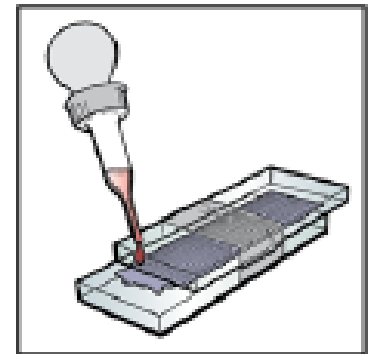


Abb. 8

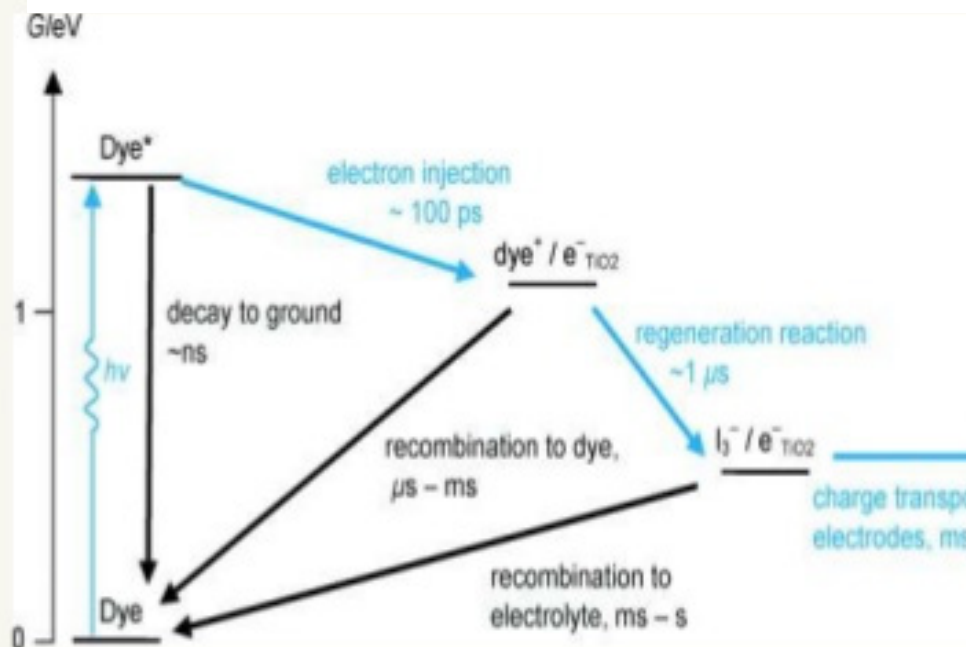
2010 Robert Bosch Stiftung GmbH. Gesamtherstellung: Zeitbild Verlag Berlin.



# DSSC kinetics

□ Kinetic competition drives charge separation

1. **Absorption**  
 $\text{Dye} + h\nu \rightarrow \text{Dye}^*$
2. **Electron Injection**  
**v. Decay to Ground**  
 $\text{Dye}^* \rightarrow e^-_{\text{TiO}_2} + \text{Dye}^*$  (100 ps)  
 $\text{Dye}^* \rightarrow \text{Dye} + h\nu$  (~ns)
3. **Regeneration Reaction**  
**v. Recombination to Dye**  
 $\text{Dye}^* + \text{I}^- \rightarrow \text{Dye} + \text{I}_3^-$  (~1  $\mu\text{s}$ )  
 $\text{Dye}^* + e^-_{\text{TiO}_2} \rightarrow \text{Dye}$  ( $\mu\text{s} - \text{ms}$ )
4. **Charge Transport**  
**v. Recombination to Electrolyte**  
 $\text{I}_3^- + e^-_{\text{Pt}} \rightarrow \text{I}^-$  (ms - s)  
 $\text{I}_3^- + e^-_{\text{TiO}_2} \rightarrow \text{I}^-$  (ms - s)

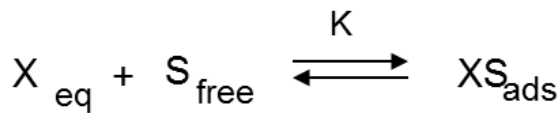
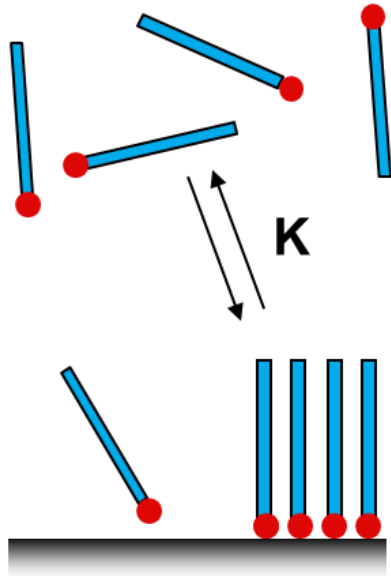


$$\eta_{\text{collection}} = 1 / (1 + \tau_{\text{trans}} / \tau_{\text{rec}}) \cong 1$$

$\tau_{\text{trans}}$ : transport through  $\text{TiO}_2$   
 $\tau_{\text{rec}}$ : recombination

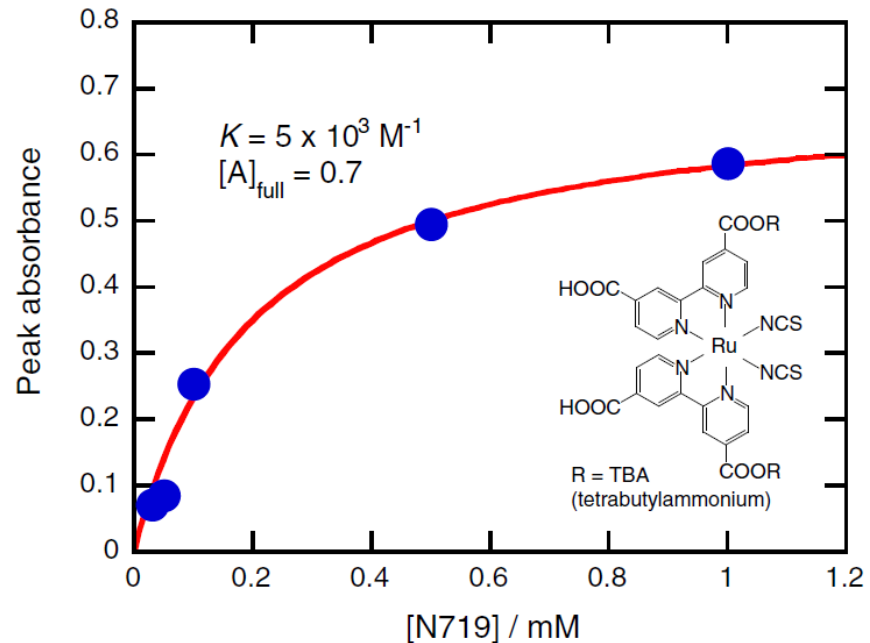
## Adsorption of dye onto surface:

- Dye work most efficiently when chemisorbed onto the surface



$$K = \frac{c_{ads}}{c_{eq}(S_{max} - c_{ads})}$$

## Adsorption thermodynamics of N719 on TiO<sub>2</sub>



- surface area / molecule: 1nm<sup>2</sup>
- Temperature dependence yields adsorption enthalpy

R. Katoh, K. Yaguchi, A. Furube, Chemical Physics Letters 511 (2011) 336–339

R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, Inorg. Chem. 33 (1994) 5741.

## ***Lifetime assessment:***

**For a lifetime of 20 years a dye molecule needs to stand 100 mio. turnovers**

For 1cm<sup>2</sup> of porous TiO<sub>2</sub>, the effective surface area is 1000 cm<sup>2</sup>

Maximum number of adsorbed N719 molecules:  $\frac{1000 \text{ cm}^2}{10^{-14} \text{ cm}^2} = 10^{17}$

Full sunlight intensity 100 mW/cm<sup>2</sup>

yields (half of the photons are absorbed, average wavelength =700 nm) number of photons/s.  $\frac{50 \text{ mW cm}^{-2}}{2.8 \times 10^{-19} \text{ J}} = 1.7 \times 10^{17} \text{ s}^{-1}$

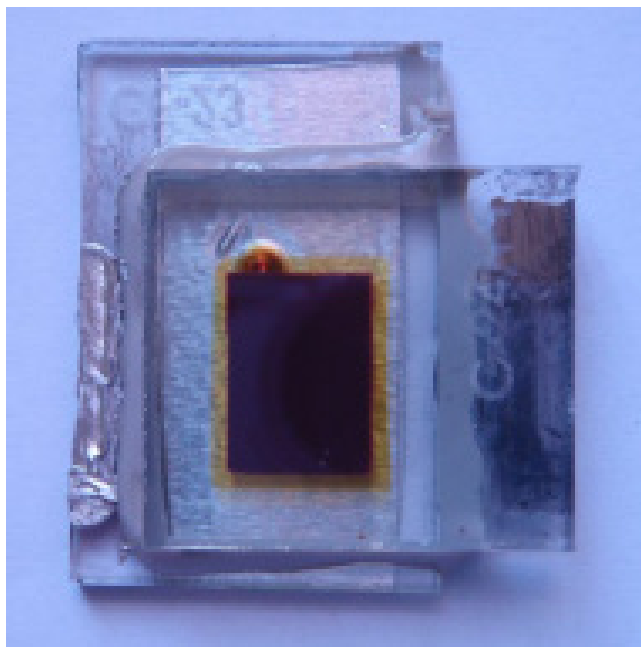
20 years are about 3 years of steady, full sunlight irradiation:

$$3 \times 365 \times 24 \times 3600 = 9.46 \times 10^7 \text{ s}$$

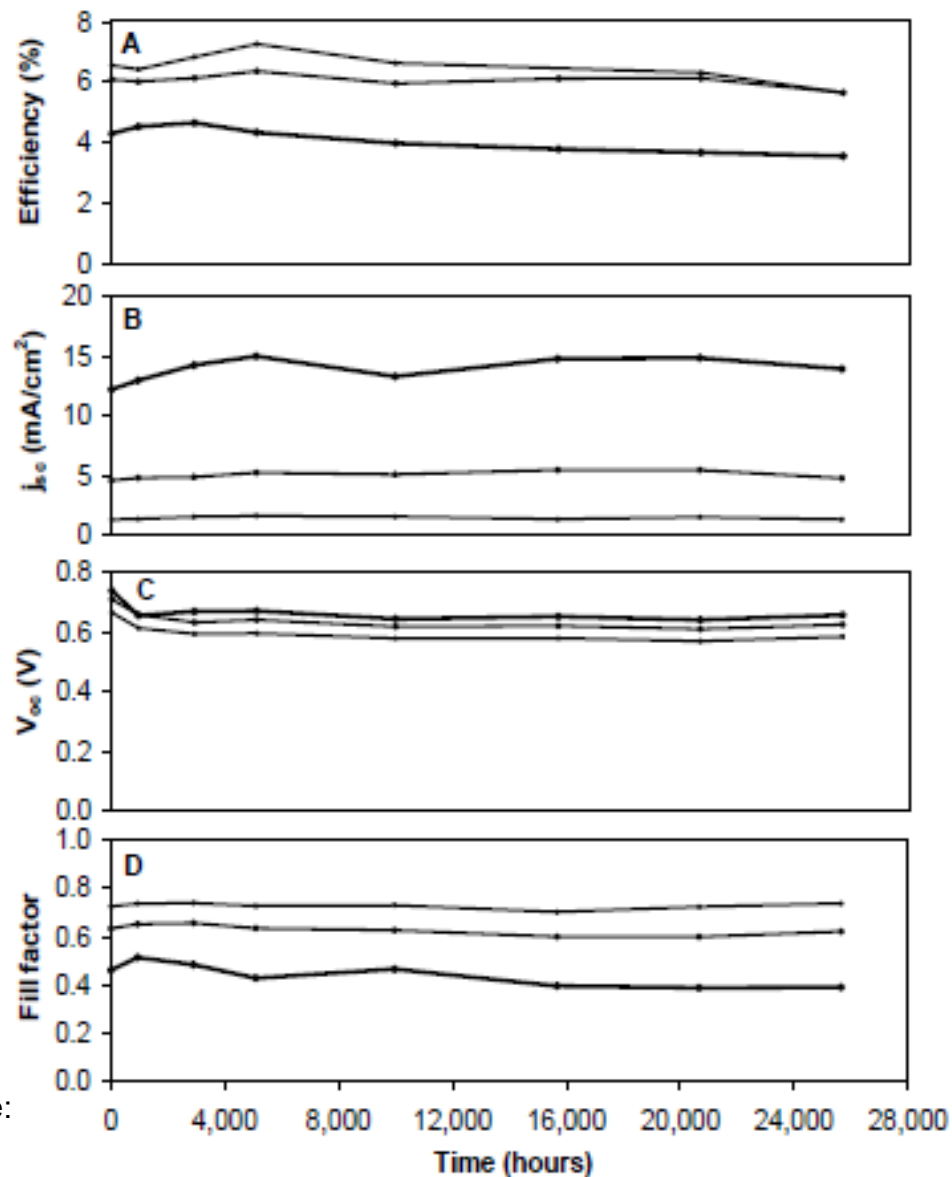
Number of cycles / molecule:  $\frac{9.46 \times 10^7 \times 1.7 \times 10^{17} \text{ s}^{-1}}{10^{17}} = 1.6 \times 10^8$

## Long term stability of DSSCs

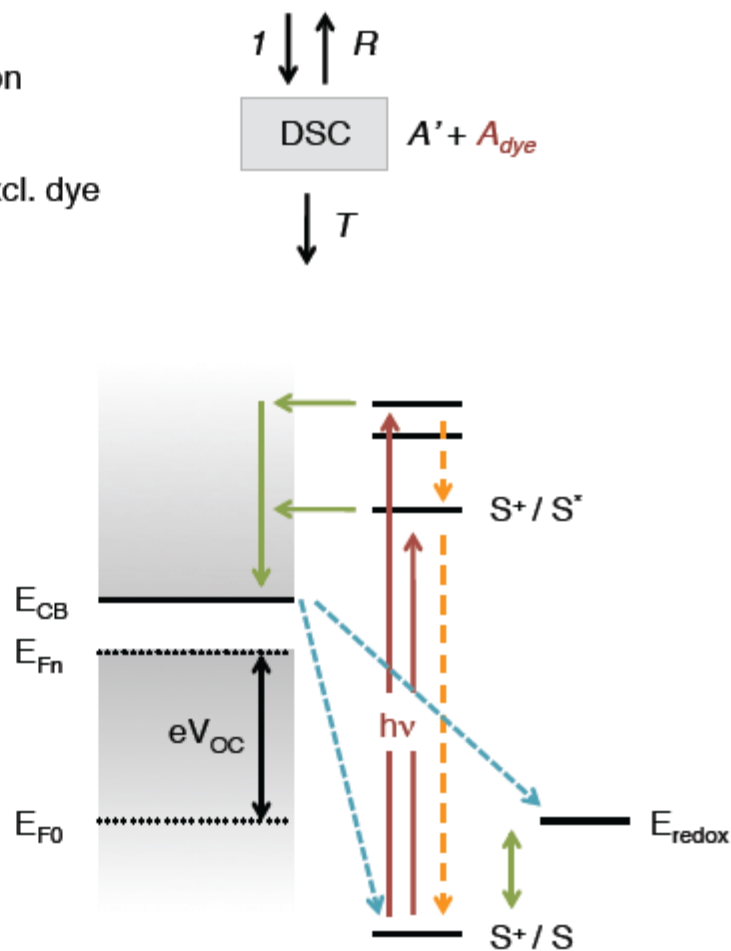
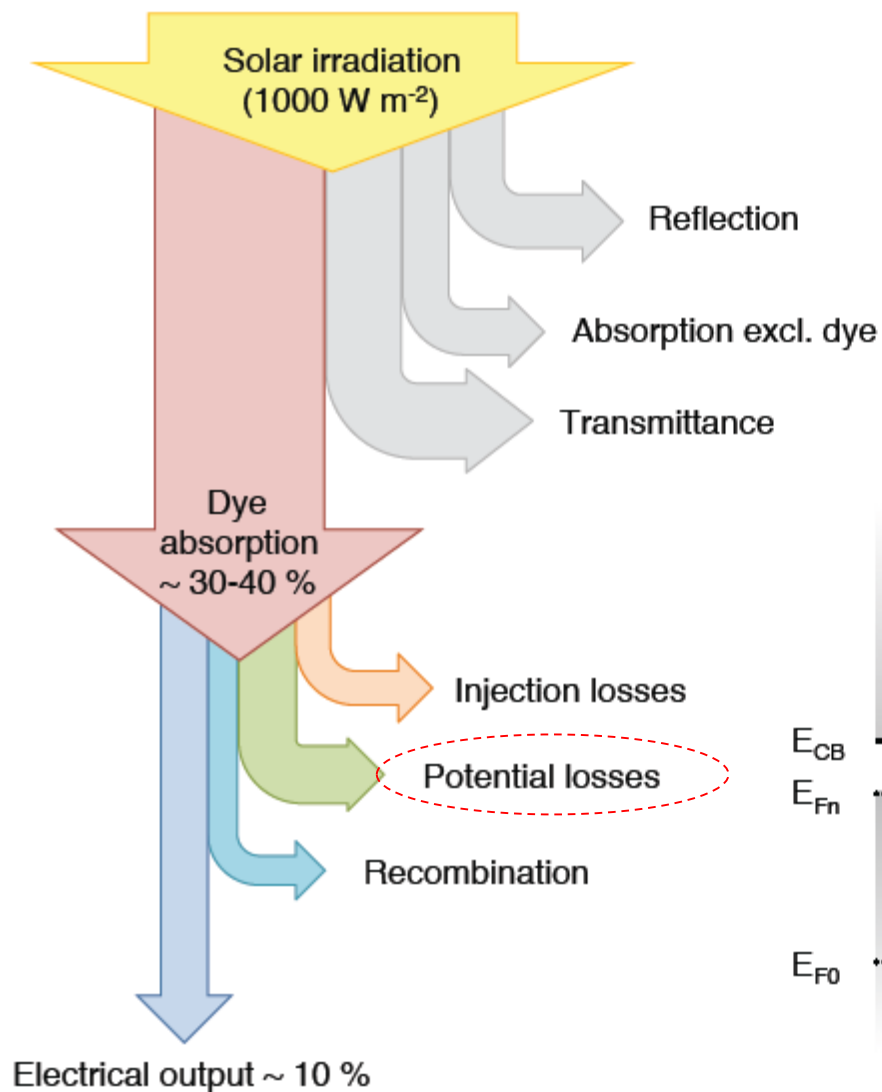
Dye Z907



Efficiencies (A), short circuit currents (B), open circuit voltages (C) and fill factors (D) of solvent based cell, periodically assessed at 1 sun (bold lines), 0.33 sun (intermediate line width) and 0.1 sun (thin lines), as a function of light soaking time at 0.8 sun, with cell temperature maintained at 55-60°C and close to maximum power point

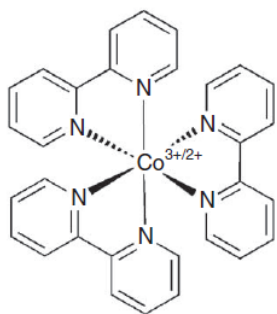
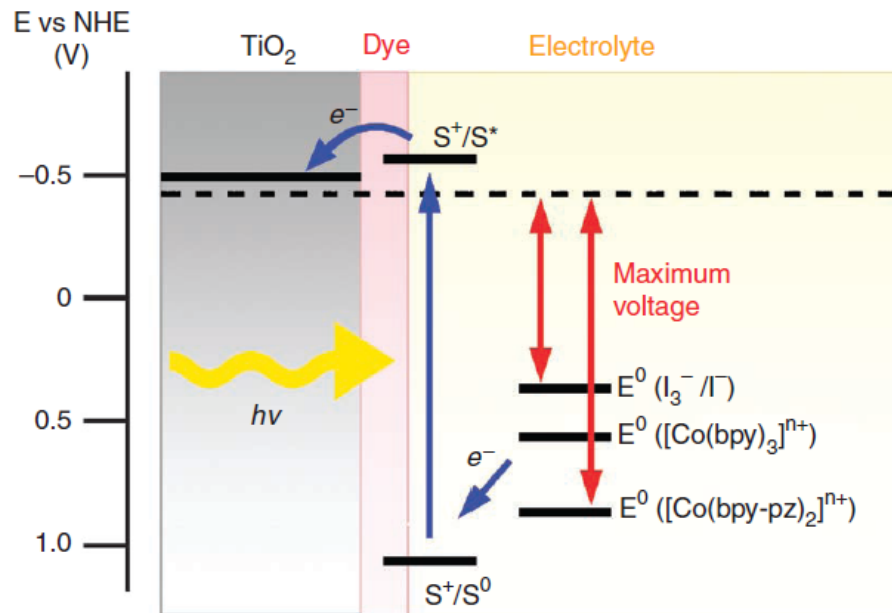


# Challenges in DSSCs

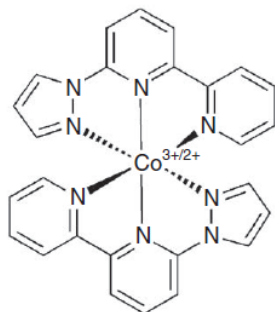


S. Wenger, thèse No. 4805 (2010), Epfl, Lausanne

# New redox mediators

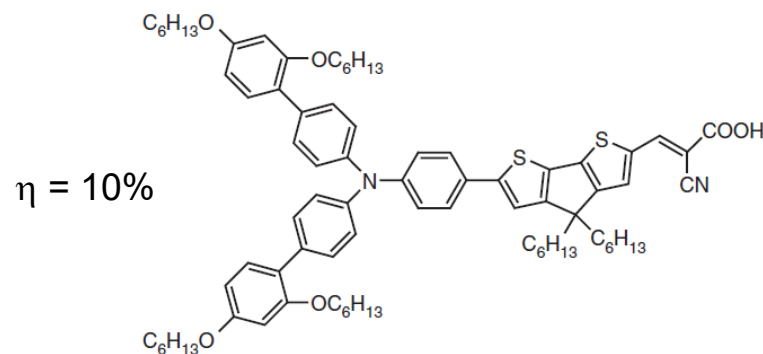
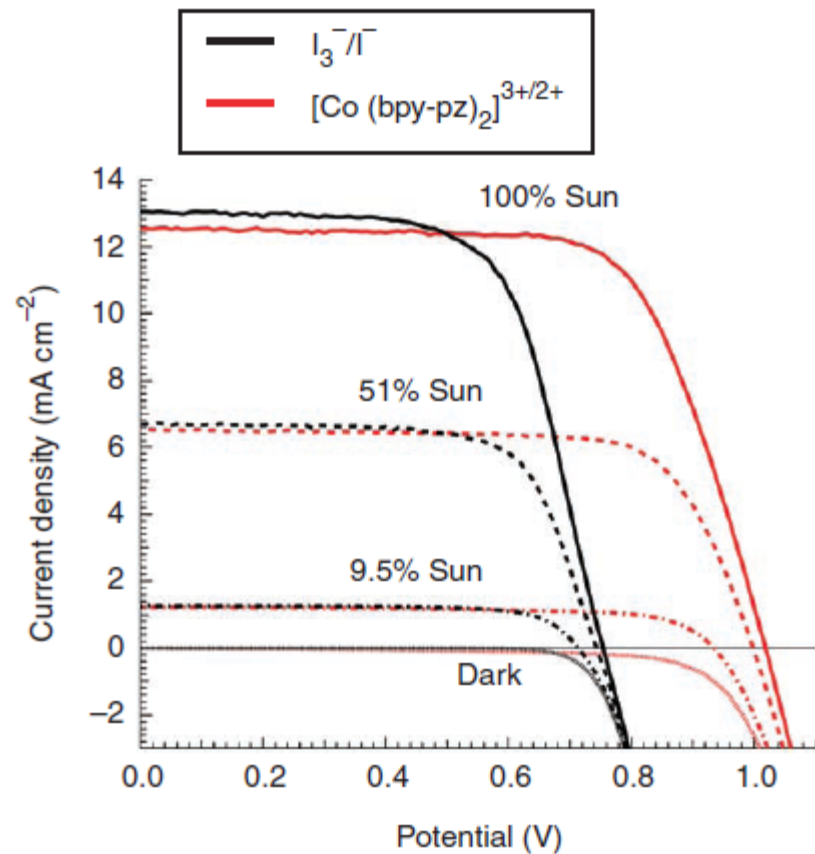


Co(bpy)<sub>3</sub>

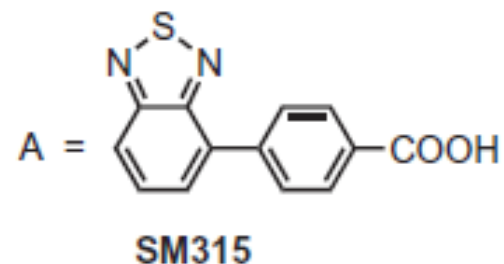
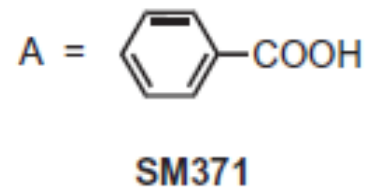
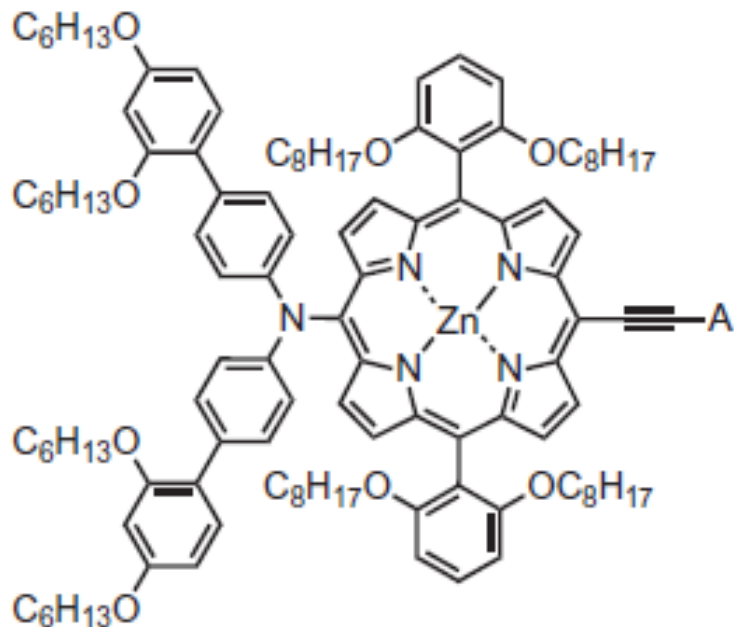


Co(bpy-pz)<sub>2</sub>

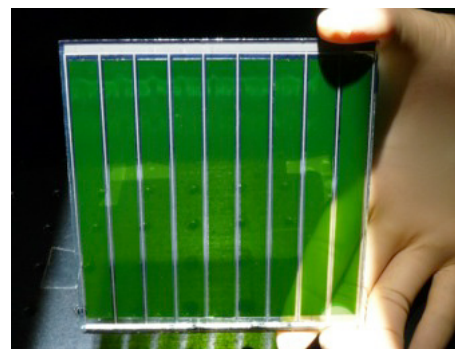
Jun-Ho Yum et al., Nature communications, 3:631, 2011



## Porphyrin-Sensitized Solar Cells with Cobalt (II/III) – based Redox Electrolyte



PCE = 13%



Simon Mathew, Aswani Yella et al., Nature Chemistry, 2014, DOI: 10.1038/NCHEM.1861



## *The present technical status of dye sensitized solar cells*

- ❑ **Power conversion efficiency** (PCE) measured under AM 1.5 standard sunlight (STC): laboratory cells: 13 %, tandem cells: 15-16%, modules: 9.9 %.
- ❑ **Outdoor performance advantages over competition:** a 10 % PCE rated DSSC module produces over one year the same amount of electricity as 15 % rated Si module (Sony)
- ❑ **Electricity from ambient and indoor light:** DSSC outperforms all competitors, recent breakthrough in sensitizer/redox shuttle design further increased the lead (PCE 26 % for OSRAM 300 fluorescent tube).
- ❑ **Stability** > 20 years outdoors (Dyesol).
- ❑ **Energy pay back time:** < 1 year (3GSolar ECN, life cycle analysis)
- ❑ **Industrial development:** has been launched by many industrial companies mass production of light weight flexible modules started in 2009 by G24Innovation ( [www.g24i.com](http://www.g24i.com), bankrupt in 2012, re-emerged as G24i Power with new investors), Solaronix, H.Glass

Received: 29 October 2020 | Accepted: 5 November 2020

DOI: 10.1002/pip.3371

**ACCELERATED PUBLICATION**

## Solar cell efficiency tables (version 57)

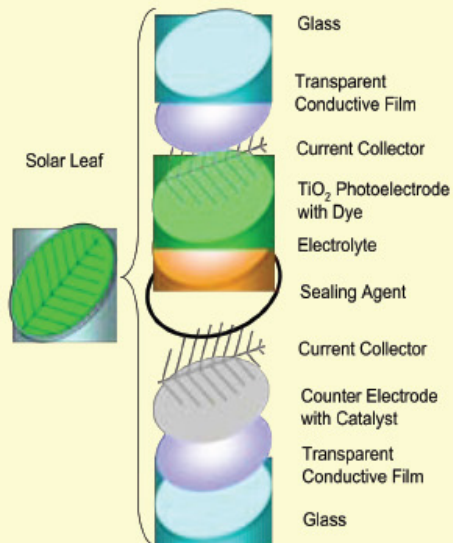
Classification	Efficiency (%)	Area (cm <sup>2</sup> )	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill factor (%)	Test centre (date)	Description
<i>Dye sensitized</i>							
Dye (cell)	11.9 ± 0.4n	1.005 (da)	0.744	22.47 <sup>o</sup>	71.2	AIST (9/12)	Sharp <sup>17</sup>
Dye (minimodule)	10.7 ± 0.4n	26.55 (da)	0.754 <sup>c</sup>	20.19c <sub>p</sub>	69.9	AIST (2/15)	Sharp, seven serial cells <sup>18</sup>
Dye (submodule)	8.8 ± 0.3n	398.8 (da)	0.697 <sup>c</sup>	18.42c <sub>q</sub>	68.7	AIST (9/12)	Sharp, 26 serial cells <sup>19</sup>
Dye sensitized	12.25 ± 0.4 <sup>j,m</sup>	0.0963 (ap)	1.0203	15.17 <sup>b</sup>	79.1	Newport (8/19)	EPFL <sup>37</sup>

## Beautiful demonstrators

### Artificial Plant with Leaves exhibited at EXPO 2005

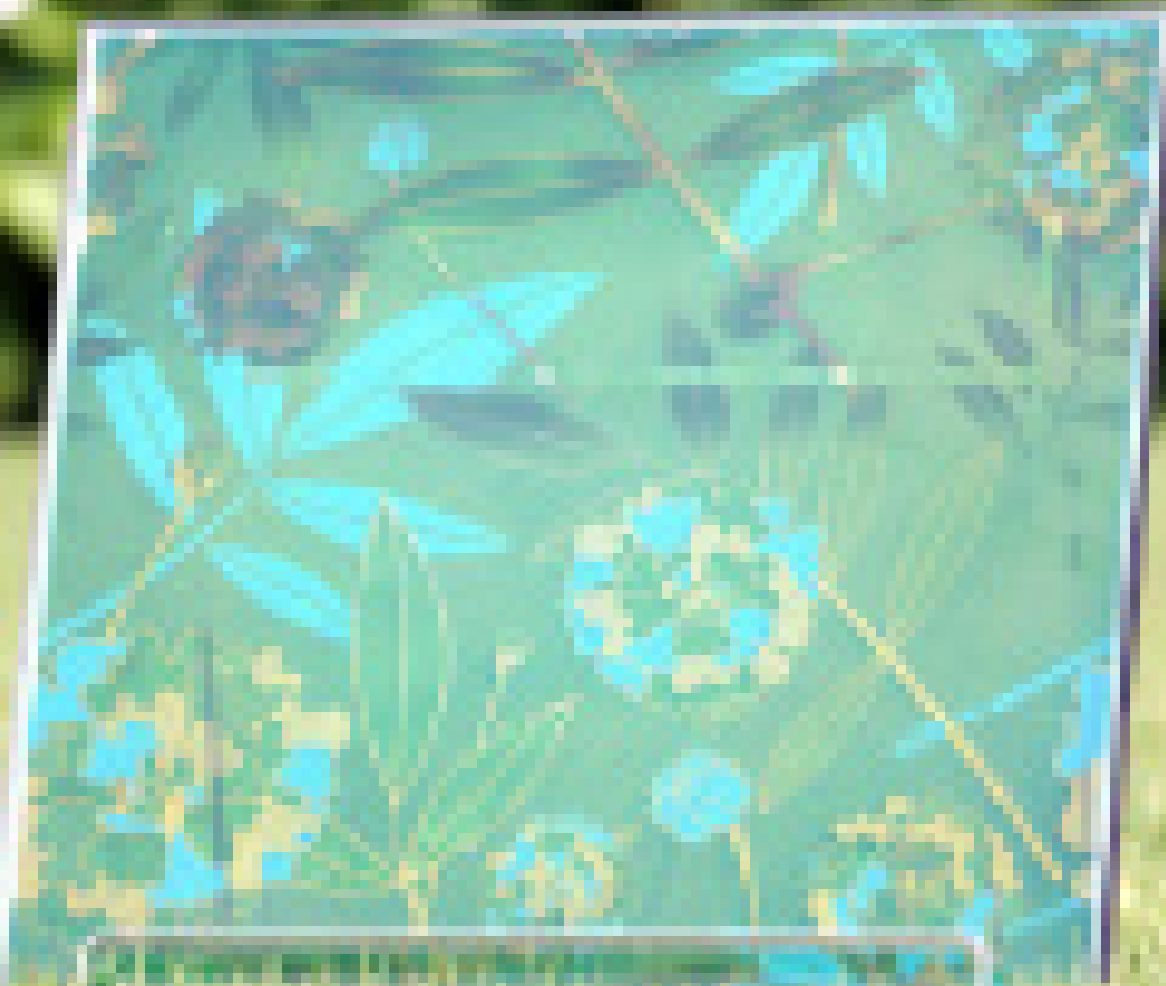


Butterflies flutter and stop using the electricity generated by this plant under the intermittent lightings.



Leaf-shaped transparent DSC with four colors





Courtesy Sony Inc



# Large dye sensitized solar cell module produced by the Fraunhofer Institute for Solar Energy in Freiburg Germany, Courtesy Dr, Andreas Hinsch

 **Fraunhofer**  
ISE



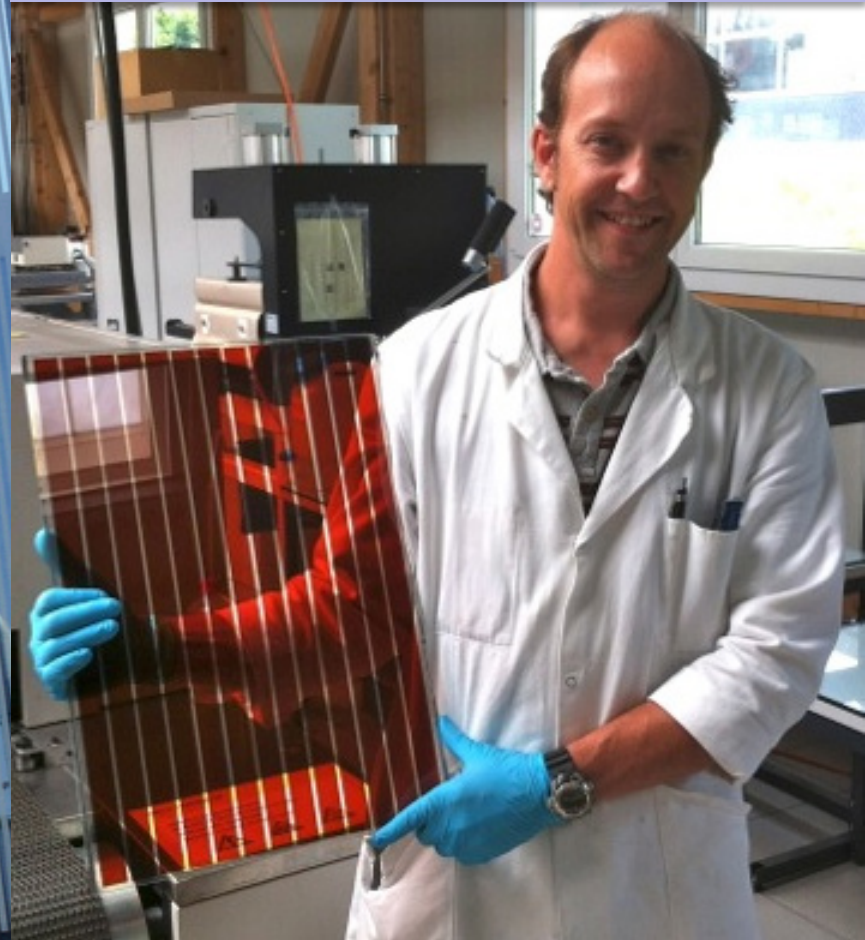
<http://www.ise.fraunhofer.de/presse-und-medien/presseinformationen/presseinformationen-2011/auf-dem-weg-in-die-fassade-fraunhofer-ise-praesentiert-weltweit-groesstes-farbstoffsolarmodul-in-siebdruck>



2.2B Dye sensitized solar cells Nr.23



Dr Michael Scott from Solaronix holding a freshly fabricated glass panel transforming light into electricity.



**SOLARONIX**

« efficiently innovative »





New Congress center at EPFL to be opened in May 2014 uses glass panels featuring dye sensitized solar cells for electricity production

## *R2R fabrication at G24i*





## ***G24i R2R factory in Cardiff (since 2009, now G24i Power)***



## 2.2B Dye sensitized solar cells (DSSC)

### *Learning outcome*

- ❑ How does a Dye Sensitized Solar Cell (DSSC) work
  - *Excited dye injects electron to semiconductor*
  - *photoexcited dye oxidizes the reduce form of a redox species*
- ❑ History
  - *Long history*
- ❑ Materials
  - *Mesoporous  $TiO_2$ , Ruthenium dye, Iodide-Triiodide Redox System*
- ❑ Kinetics of charge generation process
  - *Always favorable*
- ❑ Strategies for improvement
  - *Few: solid state electrolyte, new redox mediators*