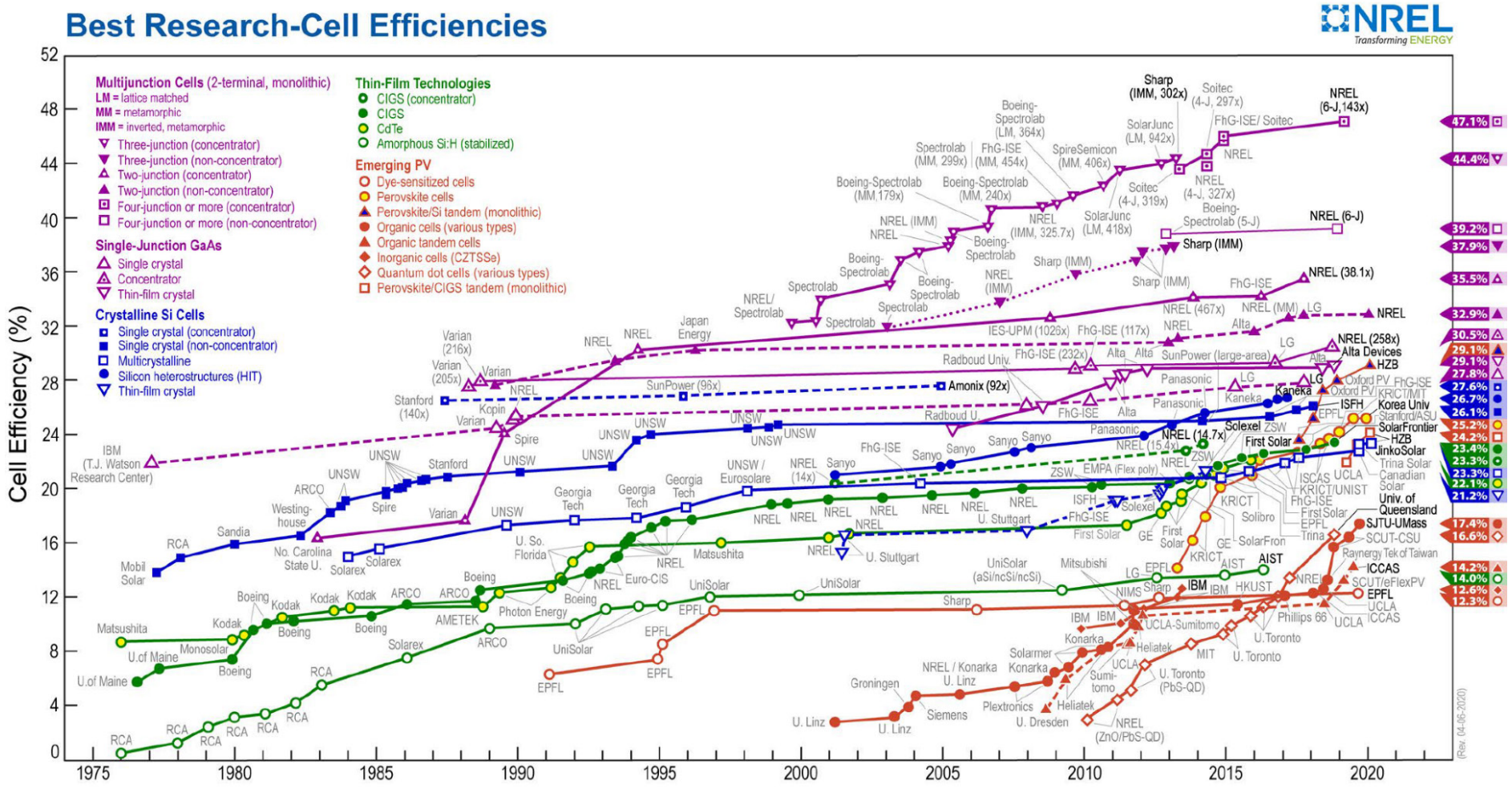
2.2A Organic Photovoltaics (OPV)

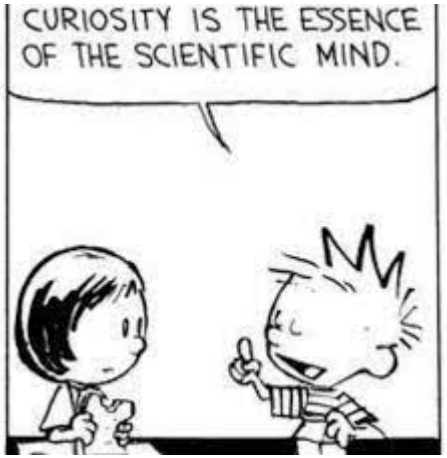


2.2A Organic Photovoltaics (OPV)

Learning goals

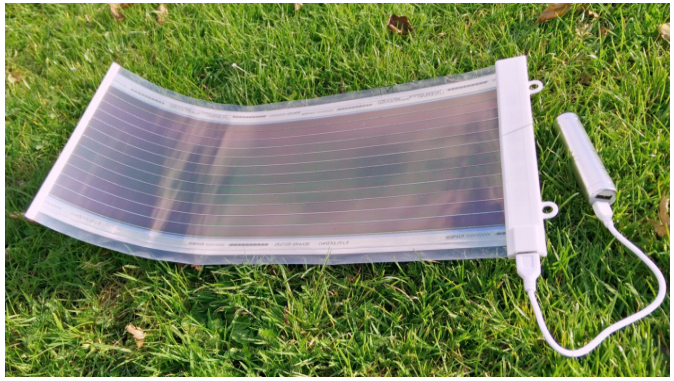
- Summary: motivation
- History
- Materials properties compared to inorganic semiconductors
- Consequences for solar cell design
- What strategies are followed to improve the efficiency
- State-of-the art
- Stability
- Manufacturing
- Current research directions

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



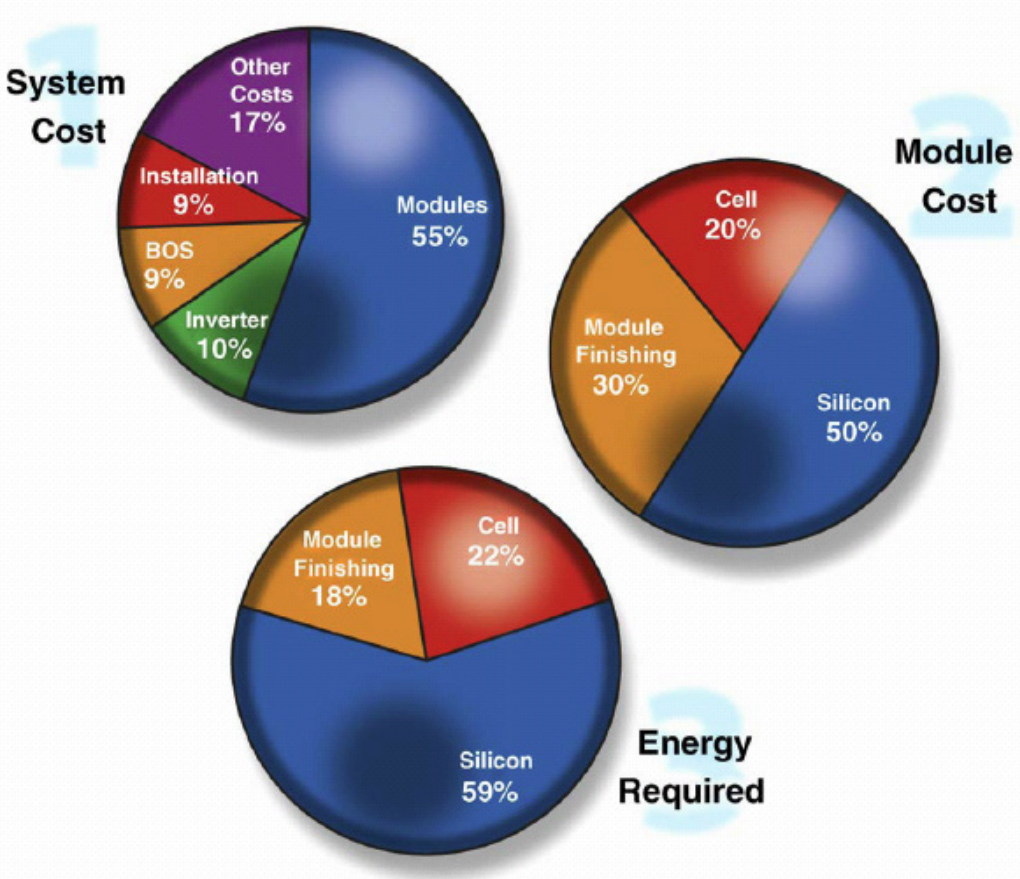
- **Low-cost manufacturing:** Soluble organic molecules enable roll-to-roll processing techniques and allow for low-cost manufacturing.
- **Abundant materials:** The wide abundance of building-block materials may reduce supply and price constraints.
- **Flexible substrates:** The ability to be applied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

Fully printed oPV, CSEM Brazil



Light weight charger, Eight19 Cambridge

Why organic photovoltaics?



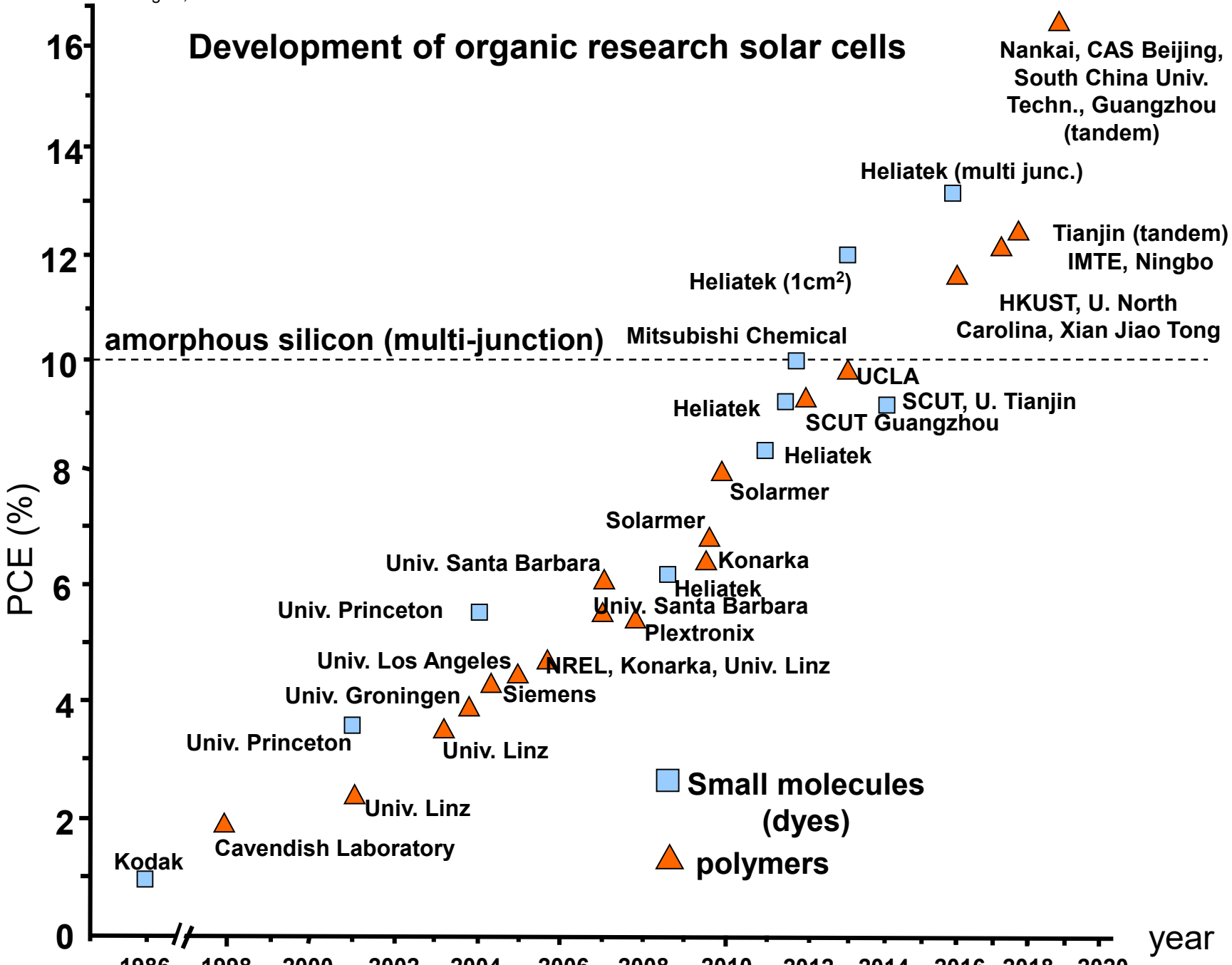
Crystalline Si cells

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_p)
  - 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
PCE (%)
year
amorphous silicon (multi-junction)
Nankai, CAS Beijing, South China Univ. Techn., Guangzhou (tandem)
Heliatek (multi junc.)
Tianjin (tandem)
IMTE, Ningbo
Heliatek (1cm²)
HKUST, U. North Carolina, Xian Jiao Tong
Mitsubishi Chemical
UCLA
Heliatek
SCUT, U. Tianjin
SCUT Guangzhou
Heliatek
Solarmer
Solarmer
Konarka
Univ. Santa Barbara
Heliatek
Univ. Princeton
Univ. Santa Barbara
Plextronix
Univ. Los Angeles
NREL, Konarka, Univ. Linz
Siemens
Univ. Groningen
Univ. Princeton
Univ. Linz
Small molecules (dyes)
Univ. Linz
Cavendish Laboratory
polymers
Kodak
0
2
4
6
8
10
12
14
16
1986
1998
2000
2002
2004
2006
2008
2010
2012
2014
2016
2018
2020

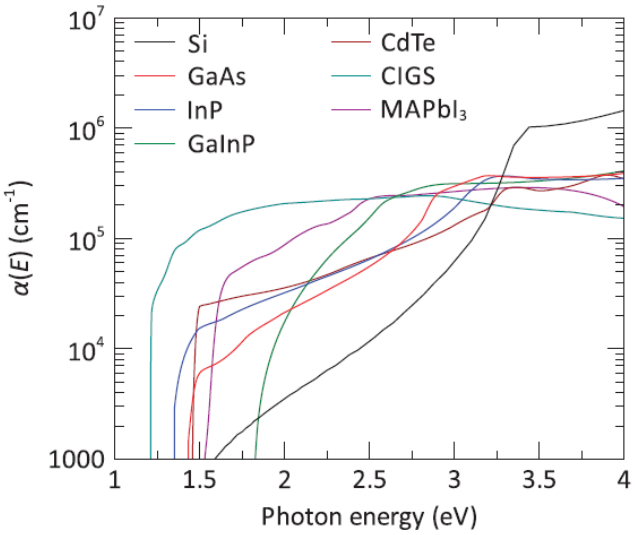
Important milestones in OPV

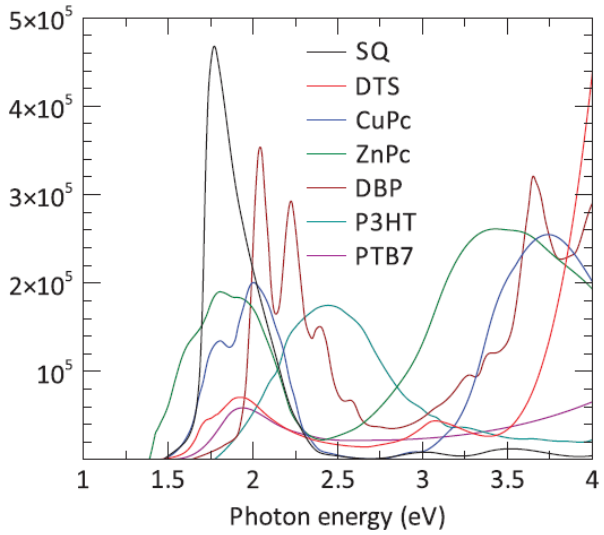
Pochettino (1906):	Photoconductivity in anthracene
Kallmann, Popoe (1959):	PV effect in single cryst. anthracene
H. Meier et al. (1960):	PV-cells made of "p-n" heterojunctions
K. Ghosh et al. (1978):	Merocyanine Schottky-barrier cells (0.5%)
C. W. Tang (1986):	CuPc-perylene Heterojunction solar cell (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^2)
Y. M. Sun (2012):	DTS small molecule solution processed (6.1%)
L. Meng (2018):	Solution processed tandem solar cell (17.3%)

…and many others

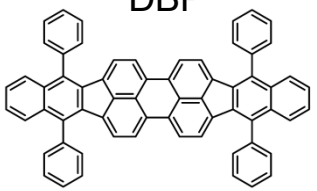
Fundamental differences in materials properties

❑ Optical properties

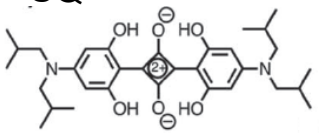




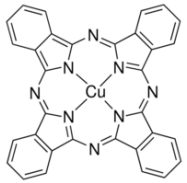
DBP



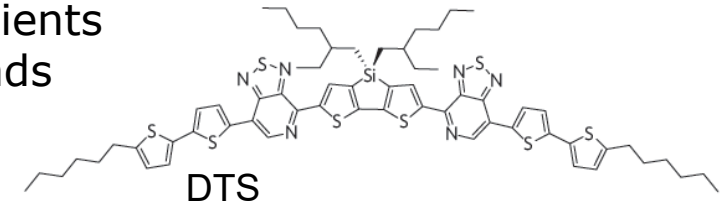
SQ



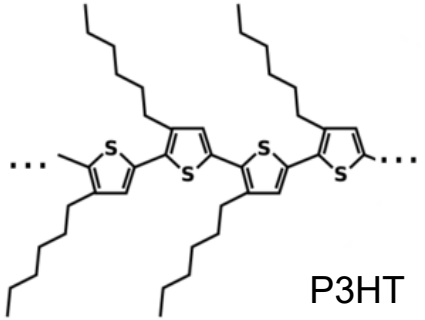
CuPc



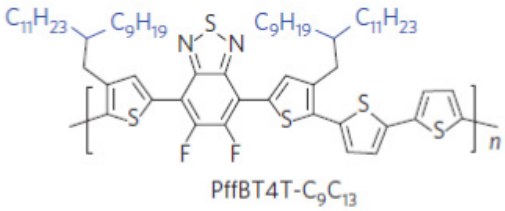
- High absorption coefficients
- Narrow absorption bands
- High bandgap



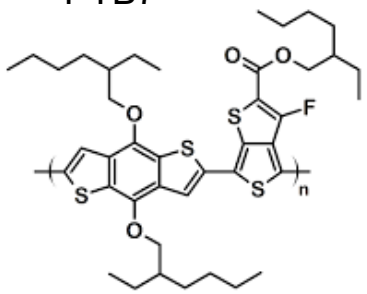
DTS



P3HT



PTB7



F. Alhabri et al., npj Computational Materials (2015) 15003

Fundamental differences in materials properties

❑ Charge carrier mobility

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

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

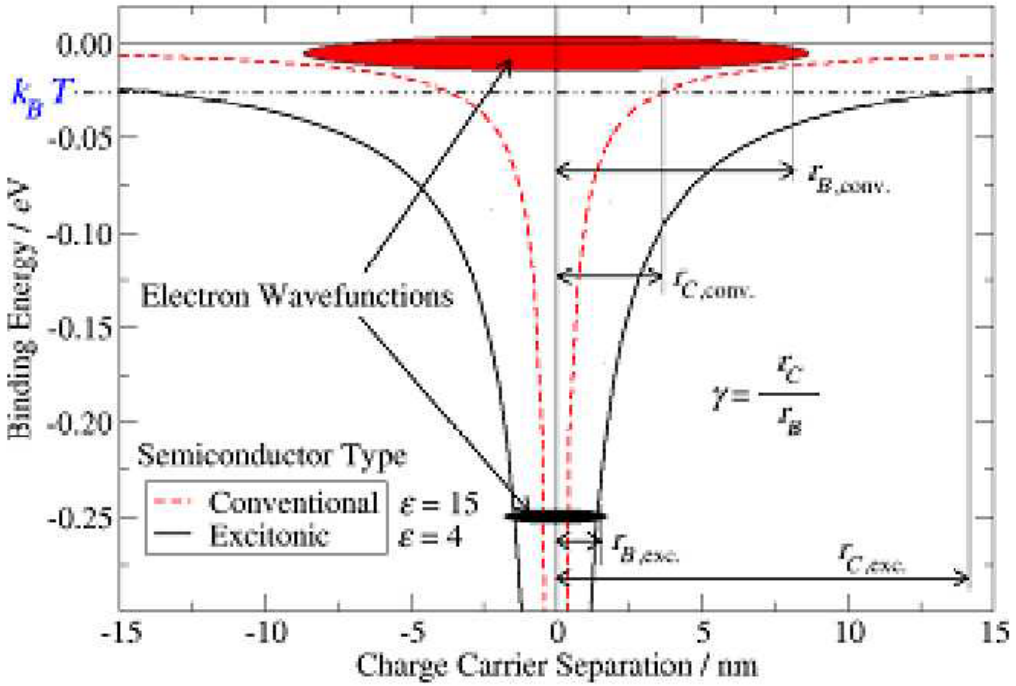
Organic semiconductors			Inorganic semiconductors		
crystalline			*crystalline*		
Anthracene	1.6 (e^-)	1.2 (h^+)	Si	1500 (e^-)	450 (h^+)
Pyrene	0.7 (e^-)	0.7 (h^+)	Ge	3900 (e^-)	1900 (h^+)
b-phthalocyanine	1.1(e^-)	1.4 (h^+)	GaAs	8500 (e^-)	400 (h^+)
Fullerene C_{60}	1.1(e^-)	1.0 (h^+)	InAs	80000 (e^-)	1250 (h^+)
amorphous			*amorphous*		
10^{-5} to 10^{-3} 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 (ε = 3-4) compared to inorganic semiconductors (ε = 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	Si-based inorganic semiconductors
Chemical synthesis	Gained from SiO_2 Purity needed: 99.9999 %
For small molecules, **excellent molecular purities** by gradient sublimation, recrystallization, chromatography, etc.	Crystallization from the melt (crystalline: Czockralski, float-zone, ribbon silicon)
Small molecules are typically applied by evaporation (sometimes also applied from solution)	Wafer cutting (sawing losses) Amorphous silicon: PECVD Doping
Solution processable materials (mainly polymers) can be **applied by printing and coating**	

Fundamental differences in materials properties

❑ Solar cell requirement

Organic semiconductors	Inorganic semiconductors
Charge generation requires **exciton dissociation** interface (only a few nm thick)	Charge generation occurs directly in the bulk semiconductor.
Strong absorption coefficients allow to use thin films of 100 nm. However, the bands are narrow compared to the solar spectrum.	Lower absorption coefficient requires at least 1 micron thick layers (thin film technologies) or 100 microns (c-Si). The absorption band is naturally broad.
Low carrier mobility limits the thickness of the devices to a few 100 nm	High carrier mobility allows to use rather thick films or wafers.
⇨ **Thin films (100 nm) with an exciton splitting interface**	⇨ Thicker films (10-100 microns) with a p-n junction for charge separation. p-i-n architectures are also possible.

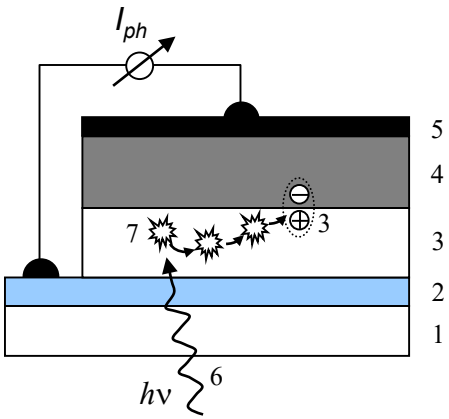
Working principle of organic solar cells

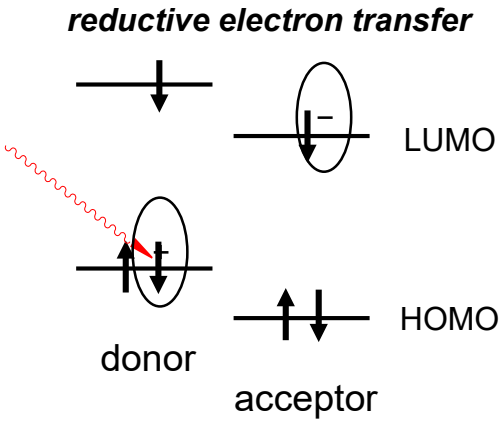
- Response to exciton binding energy

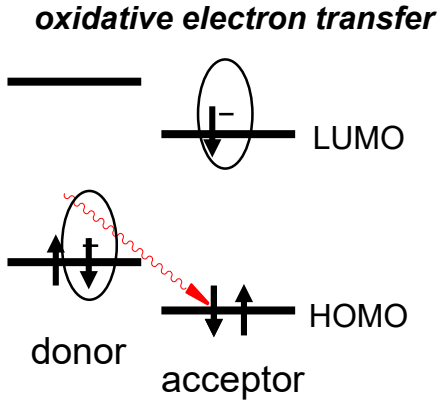
(1) Transparent substrate
(2) Transparent conductive anode
(3) Electron donor
(4) Electron acceptor
(5) Cathode

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)

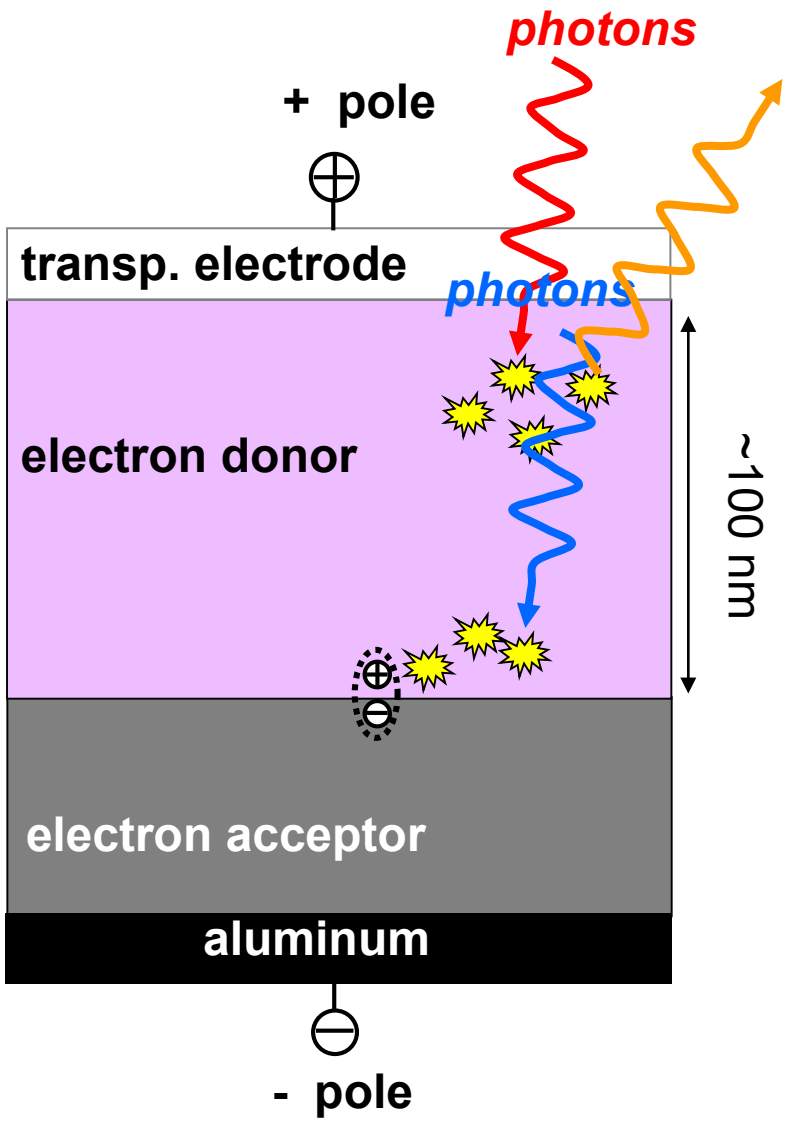
Issue: short exciton diffusion (about 10 nm)







The problem of the exciton diffusion length



π–π^* 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.

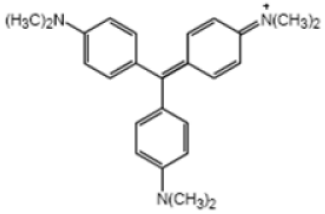
This condition brings a difficulty, namely that excitons that are excited far from the donor-acceptor interface will not be dissociated at the heterointerface.

Compromise between absorption and exciton dissociation

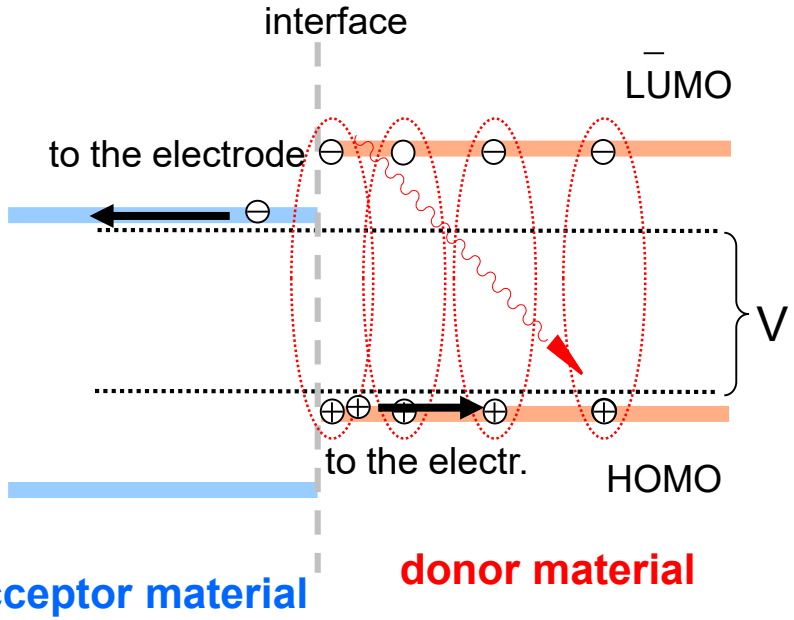
First report on organic donor-acceptor solar cells (1960)

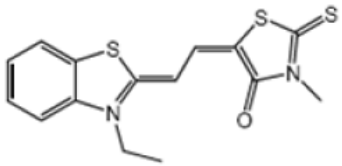
- Analogue to an inorganic p/n junction, a system of p- and n-type organic semiconductors, shows properties of a photodiode with a short circuit current and an open circuit voltage

Hans Meier, Bamberg, 1960



crystal violet

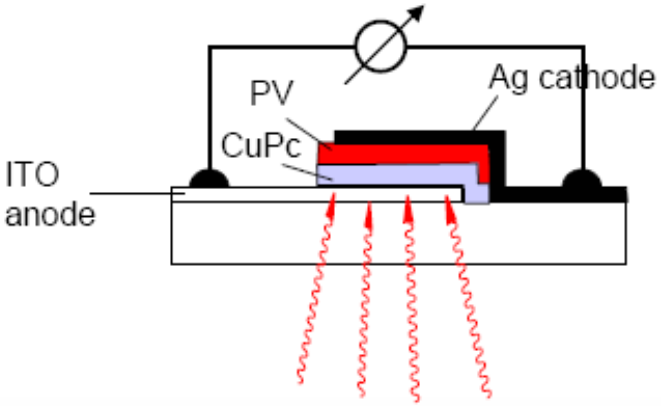


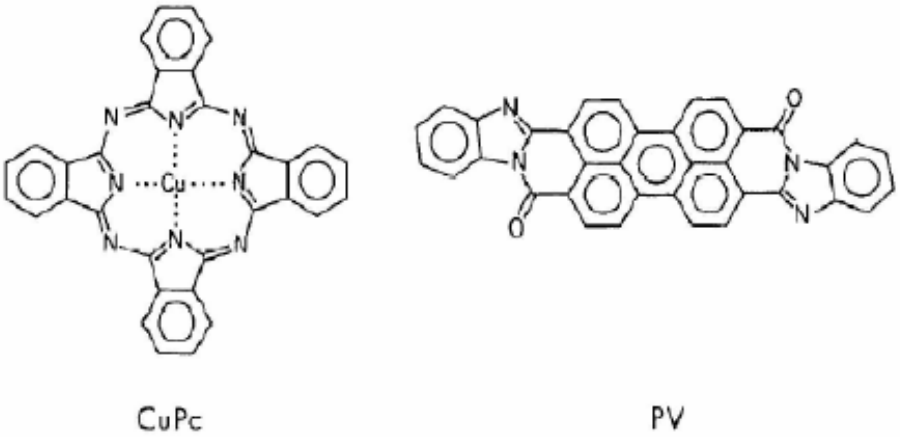


merocyanine

Organic donor-acceptor solar cells

Bilayer solar cells reach 1%





efficiency: 1%
fill factor: 0.65

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

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

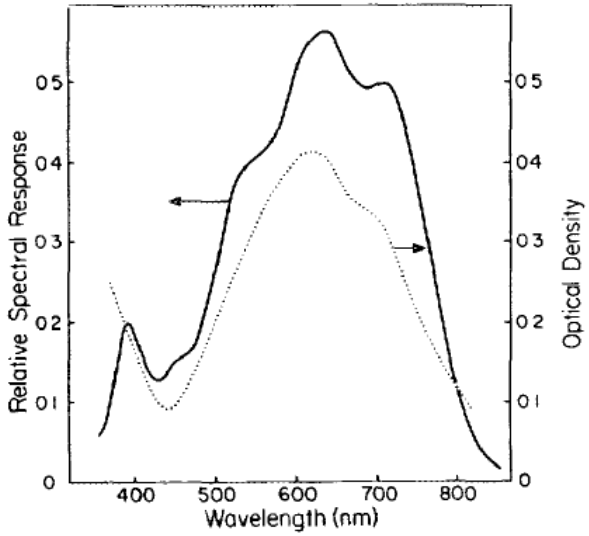
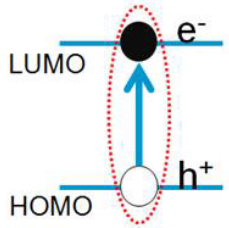
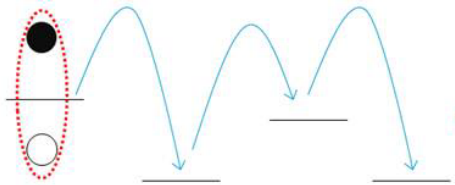


FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

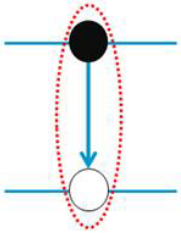
The physics of organic solar cells



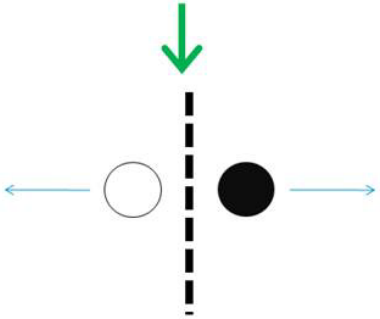
Exciton creation
An electron is excited due to light absorption
Electron and hole are Coulombically bound.
This complex is called an exciton.



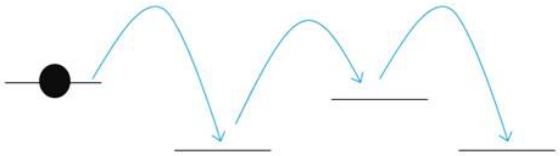
Exciton transport
Excitons will hop between localized
energy states. This is modelled using
Forster Resonance Energy Transfer theory.



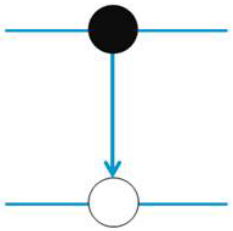
Loss mechanism: Geminate recombination
If an exciton does not reach an interface,
it relaxes back into the ground state.



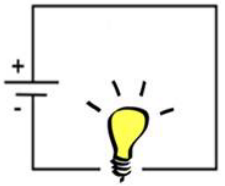
Exciton dissociation
If an exciton reaches a heterointerface,
a free electron and hole are created



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

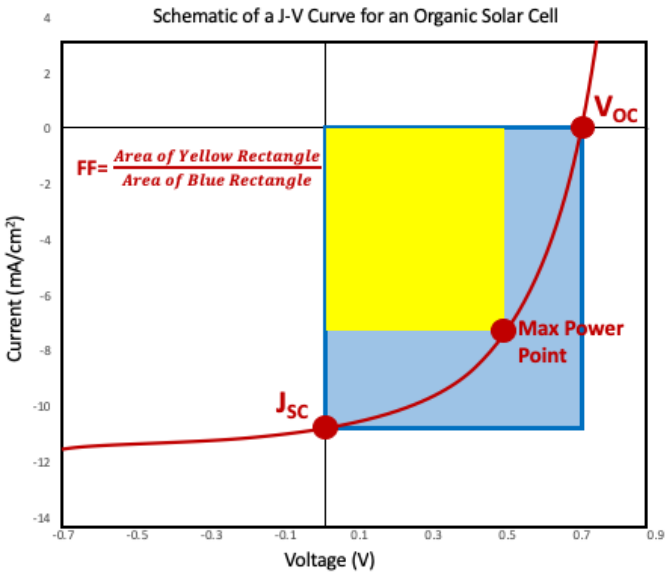


Loss mechanism: bimolecular recombination
Free electrons and holes can still
recombine depending on their proximity
to each other



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?



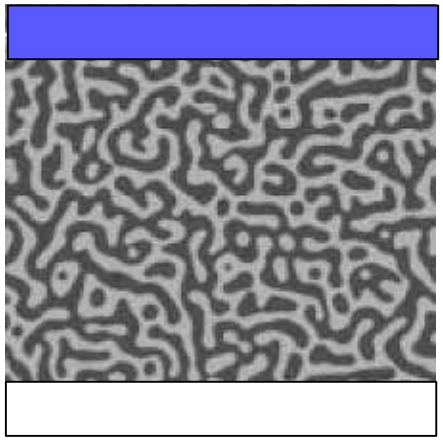
$$\eta = \frac{P_{max}}{I_{in}} = \frac{J_{mpp}\,V_{mpp}}{I_{in}} = \frac{J_{sc}\,V_{oc}\,FF}{I_{in}}$$

- 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?

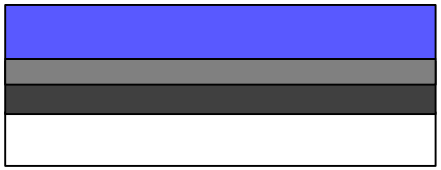
- Geometrical considerations: 2 options

Interconnected donor-acceptor phase



Phase separated bulk heterojunction
Solution processing from polymer blends

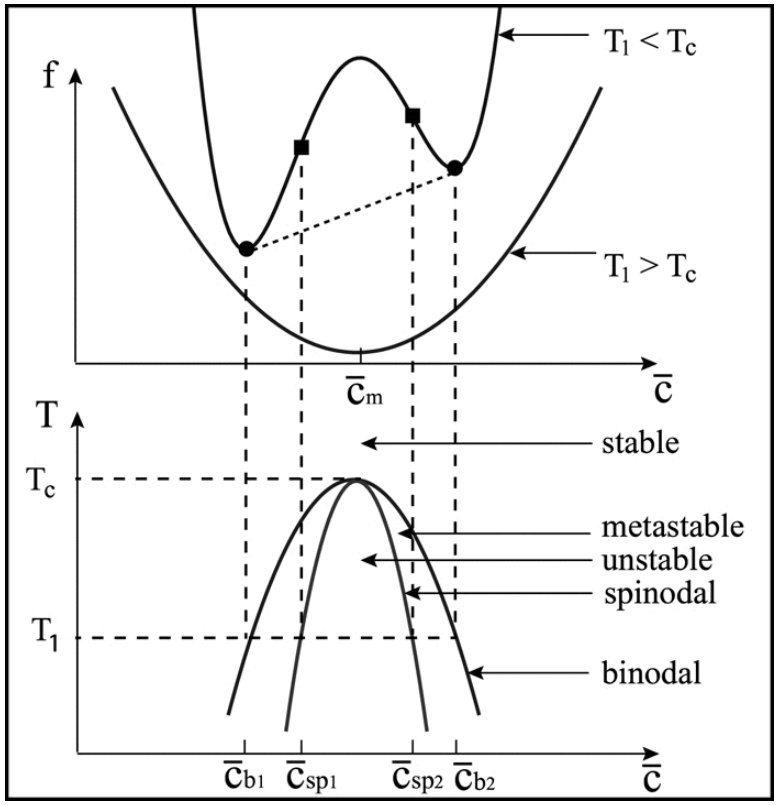
Thin films with very high absorption coefficients

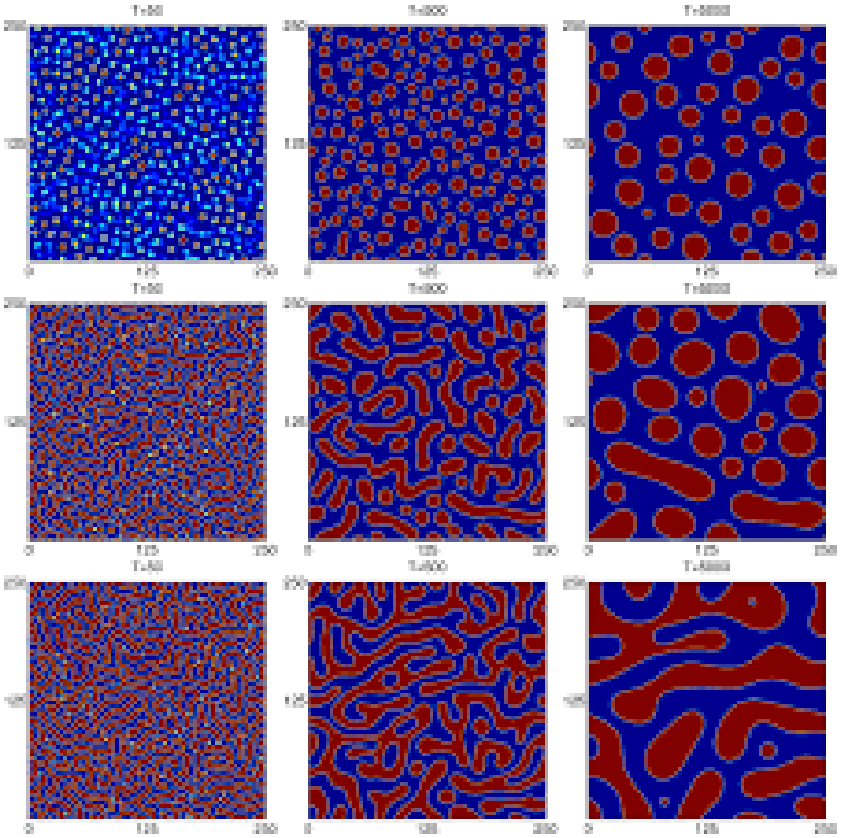


Evaporation of small molecules

How to design efficient organic solar cells?

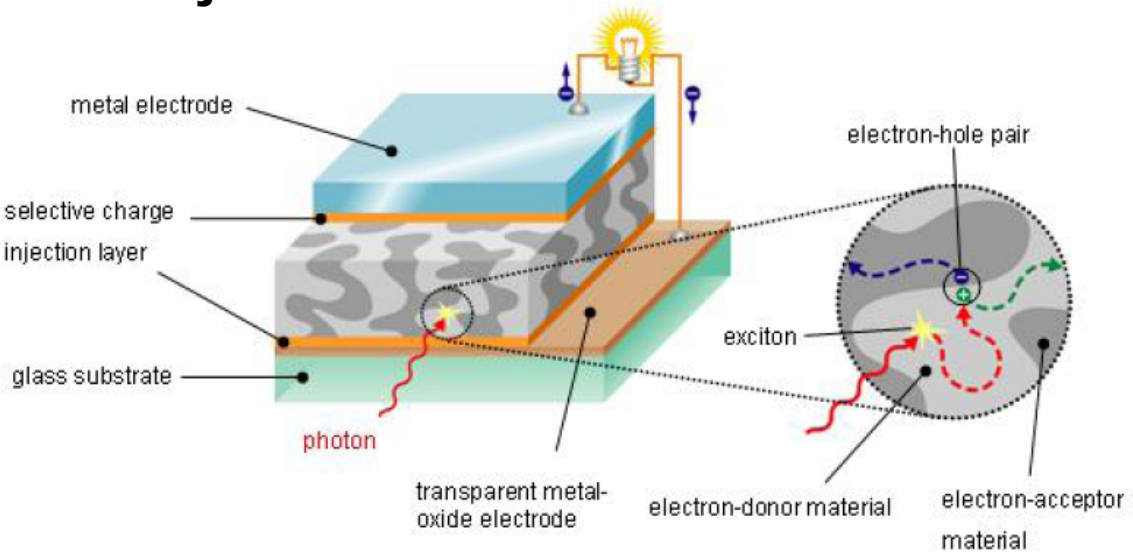
- **Bulk heterojunction solar cells: spinodal decomposition**





How to design efficient organic solar cells?

Bulk heterojunction solar cells

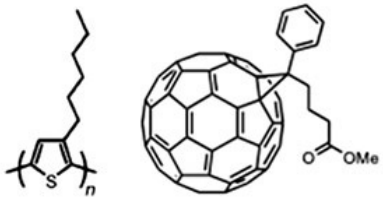


Allan Heeger, UCSB bulk-heterojunction using conjug. polym.

empirical estimation:

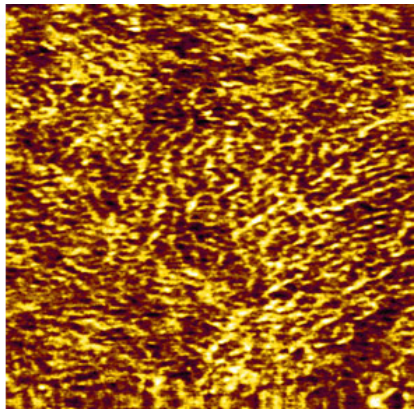
$$\eta = \frac{P_{max}(electric)}{P_{in}(light)} = FF \cdot \overline{IPCE} \cdot Abs \cdot \frac{eV_{OC}}{h\nu} = \frac{1}{2} \cdot \frac{3}{4} \cdot \frac{3}{4} \cdot \frac{1}{2} = 14\%$$

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).



P3HT
donor

PCBM
acceptor

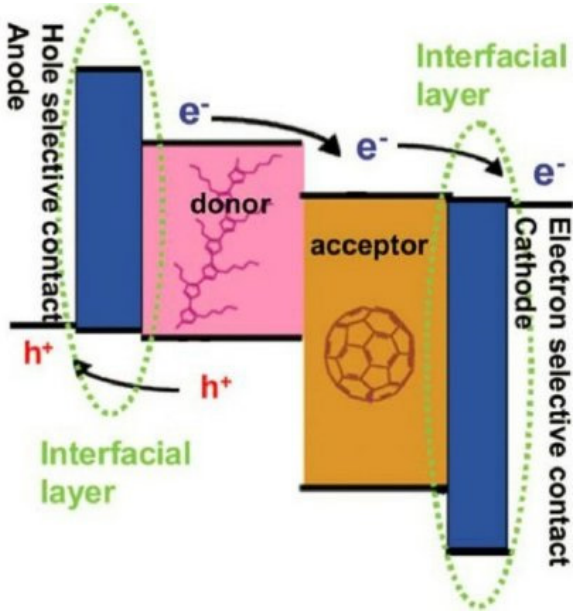


How to design efficient organic solar cells?

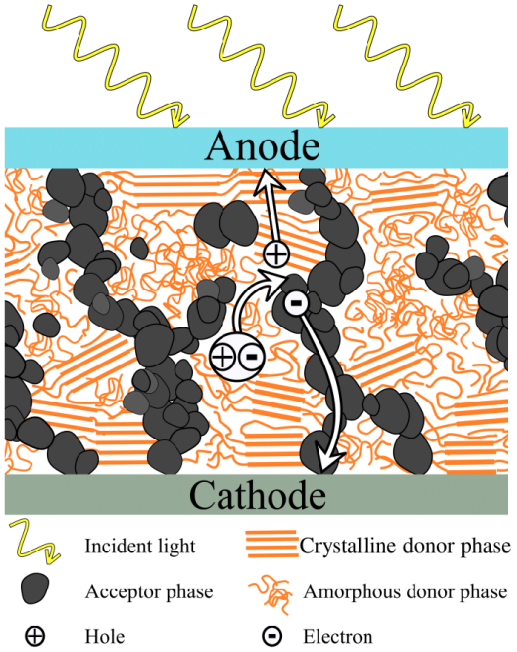
- **Energy levels of the electrodes?**

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.

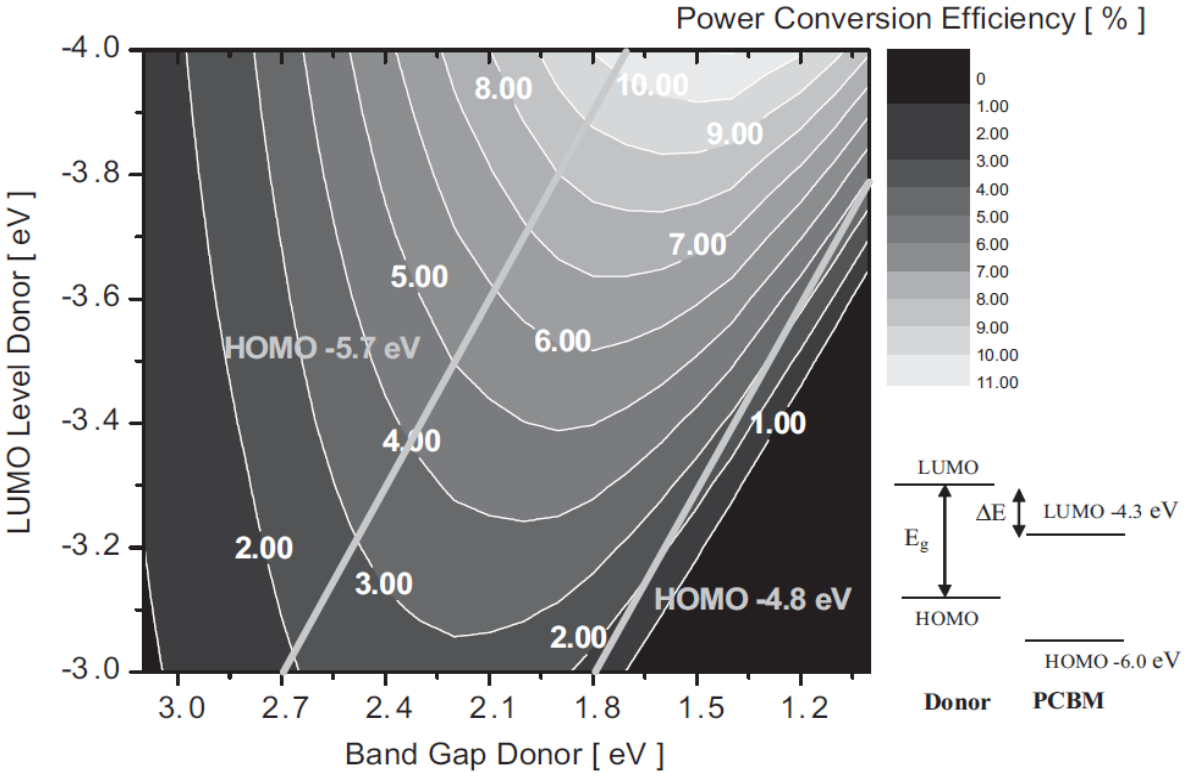


Impact of Solubility of Organic Semiconductors for Solution-Processable Electronics on the Structure Formation: a Real-Time Study of Morphology and Electrical Properties, Soft Matter, 2018, 14 (13).

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

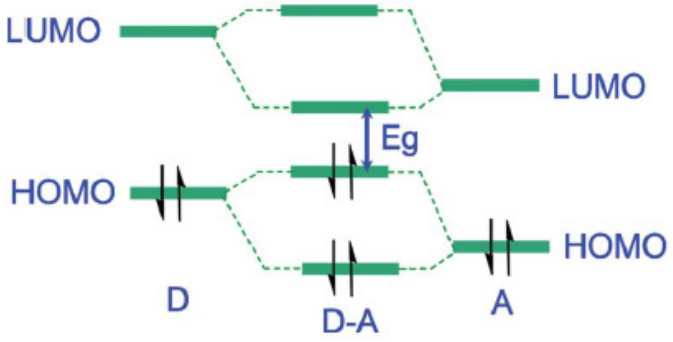


Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10 % Energy-Conversion Efficiency, Adv. Mater. 2006, 18, 789–794

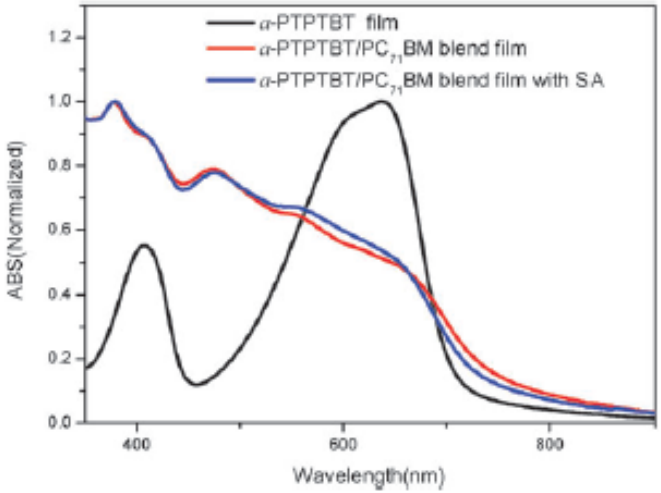
How to design efficient organic solar cells?

❑ Donor-acceptor conjugated copolymers

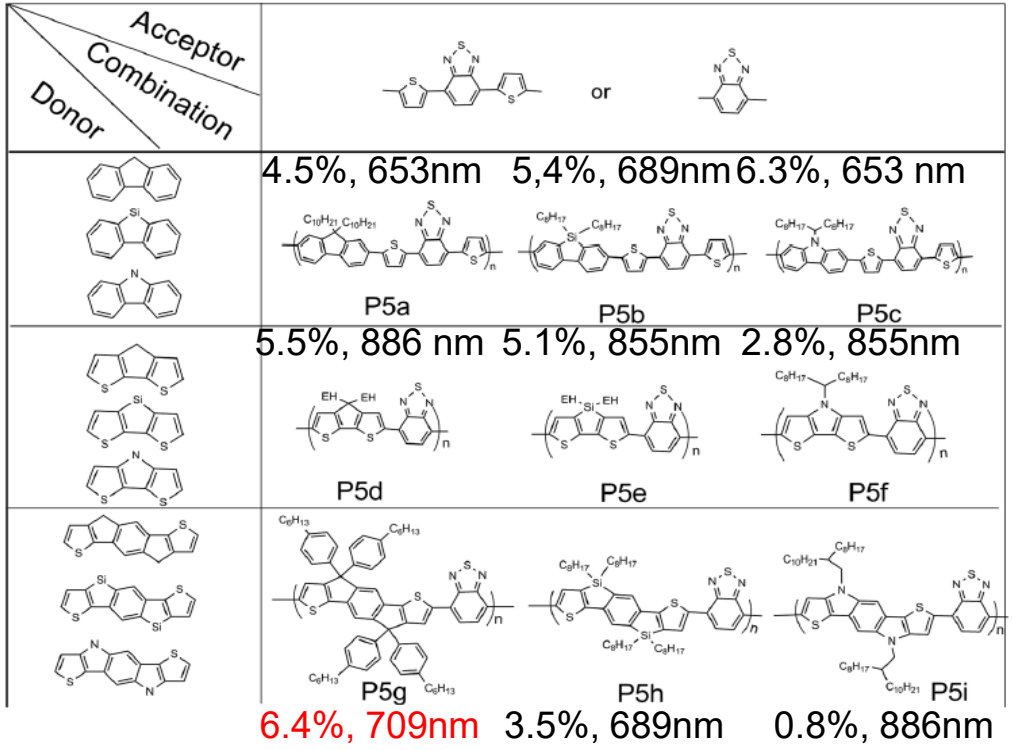
- Donor-acceptor co-polymers are the best performing organic semiconductors for OPV today
- Most of the films are blends with $PC_{71}BM$ (see next slide)
- Not only the bandgap E_g is important, but also the microstructure of the blend films



P5g and blend absorption



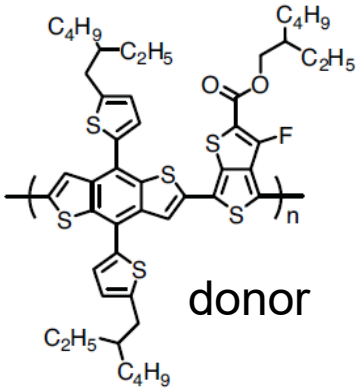
C. C. Yi et al, *Chem. Commun.,* 2010, **46**, 6503–6505
Z. Guo et al., J. Mater. Chem., 2012, 22, 4178



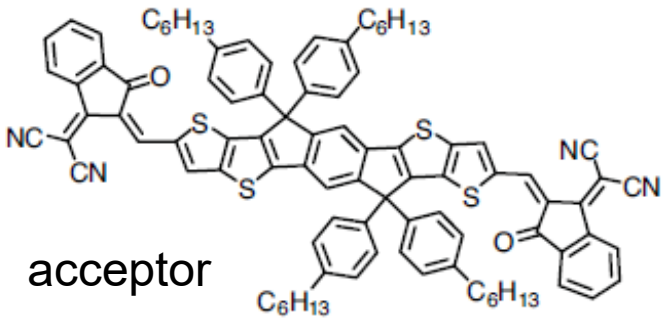
How to design efficient organic solar cells?

- Acceptor absorption complementary to donor absorption

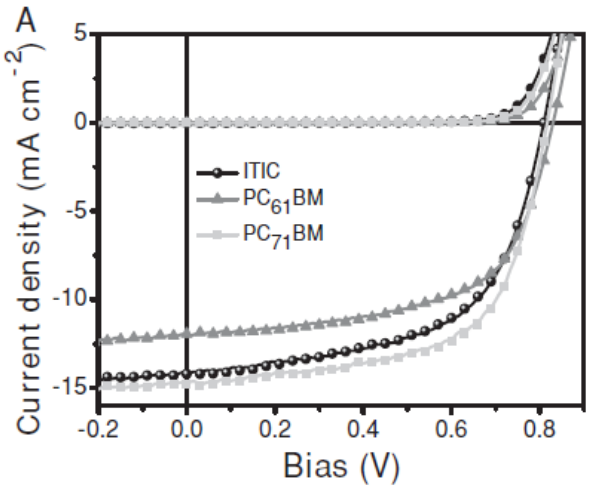
6.8% organic solar cell using non-fullerene acceptors

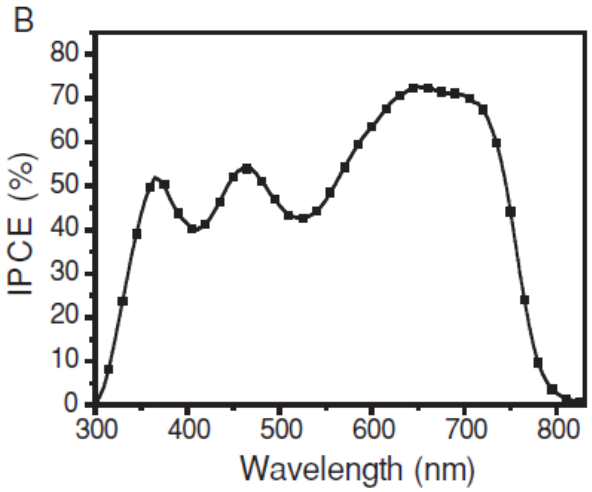


PTB7-TH



ITIC



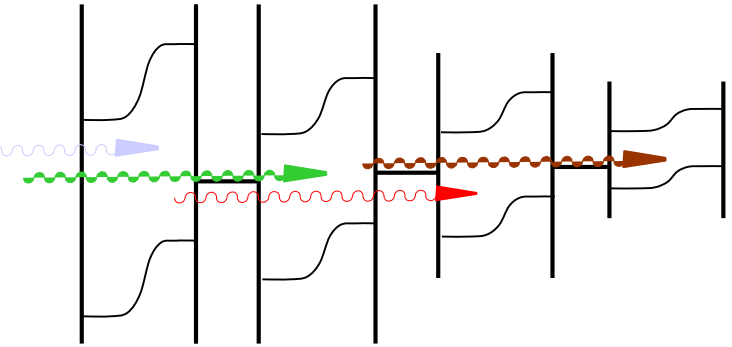


Y. Lin et al., *Adv. Mater.* **2015**, *27*, 1170–1174

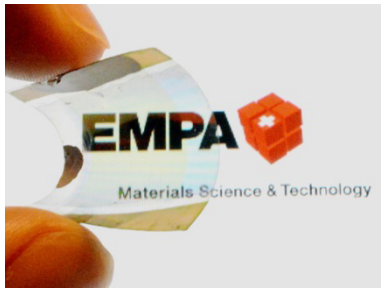
How to design efficient organic solar cells?

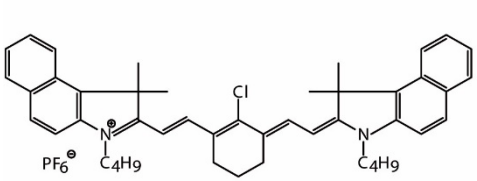
- Multi-junctions

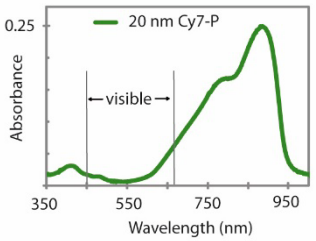
- Allows for increased photon harvesting, enhanced efficiency
- Need for NIR absorbing donors



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%



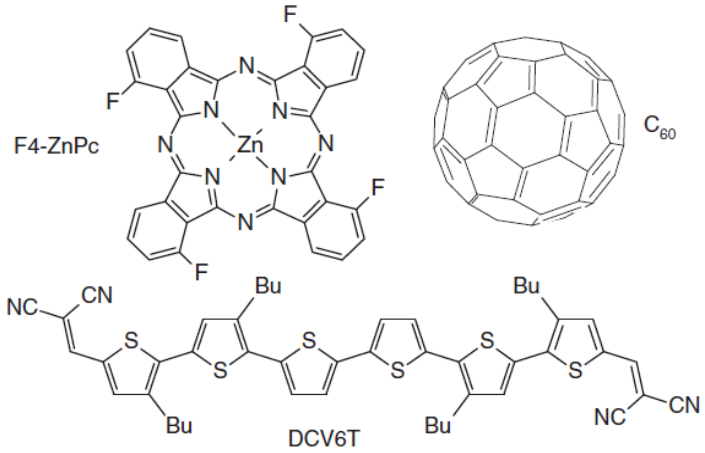


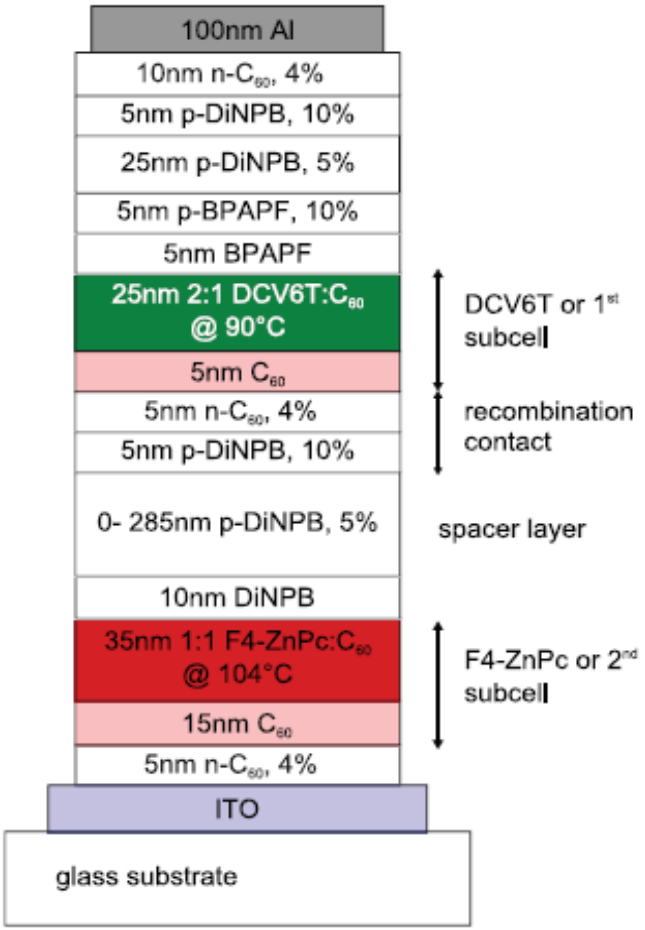


The solar cell absorbs solely in the NIR domain

How to design efficient organic solar cells?

Match solar spectrum – 6.1 % in small molecule multijunction cell

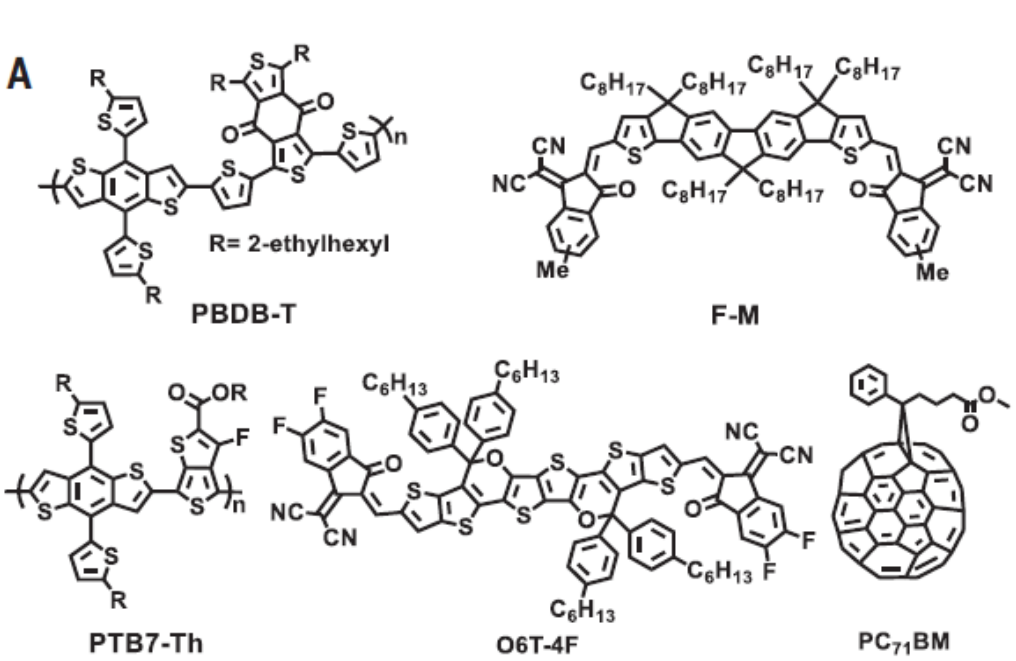


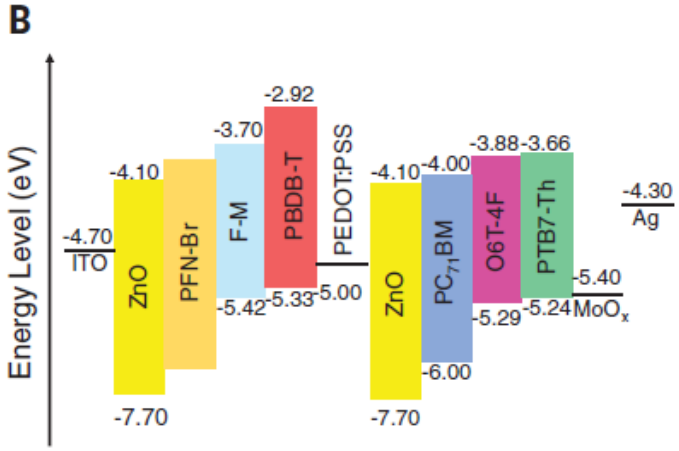


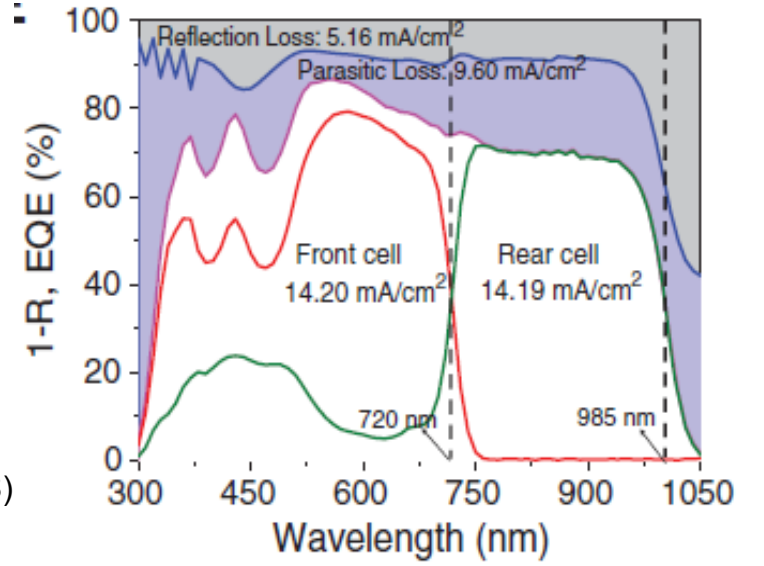
Adv. Funct. Mater. 2011, 21, 3019–3028

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 (still true in 2023)

Received: 29 October 2020 | Accepted: 5 November 2020

DOI: 10.1002/pip.3371

ACCELERATED PUBLICATION

PROGRESS IN PHOTOVOLTAICS WILEY

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 Wm^{-2}) at 25°C (IEC 60904-3: 2008 or ASTM G-173-03 global)

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

How to design efficient organic solar cells?

Record cells

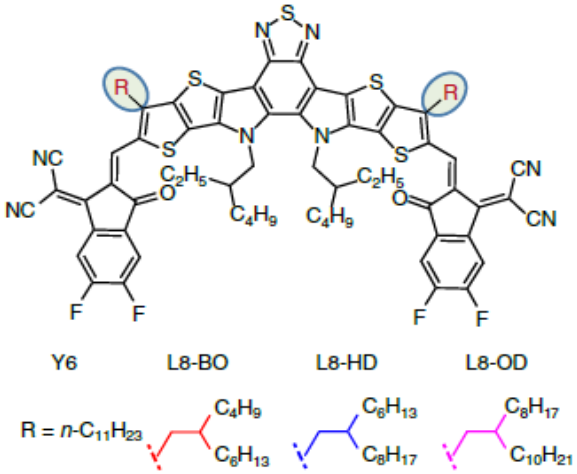
nature energy

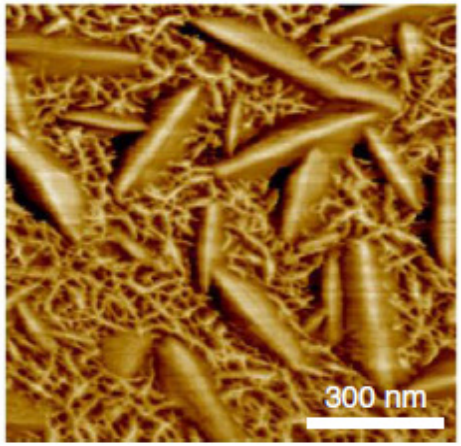
ARTICLES

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

Check for updates

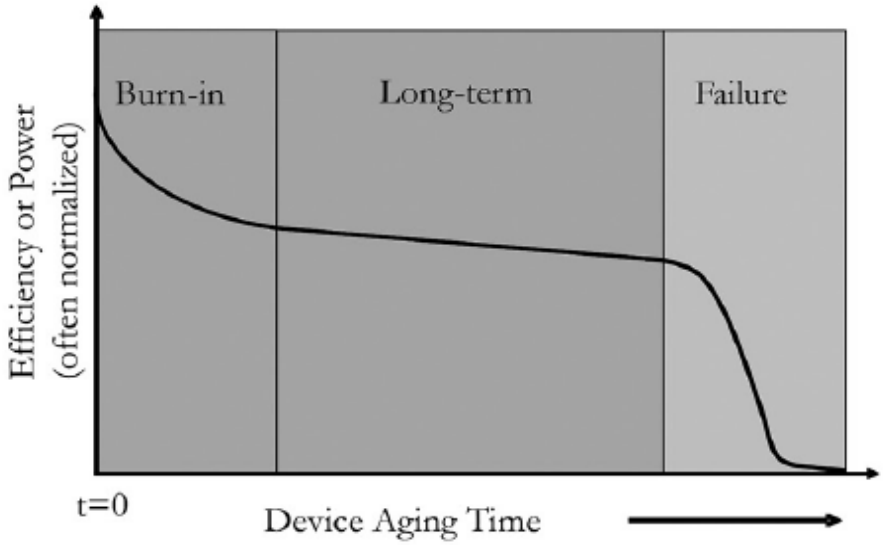
Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells





Stability / degradation

- Three different regimes



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

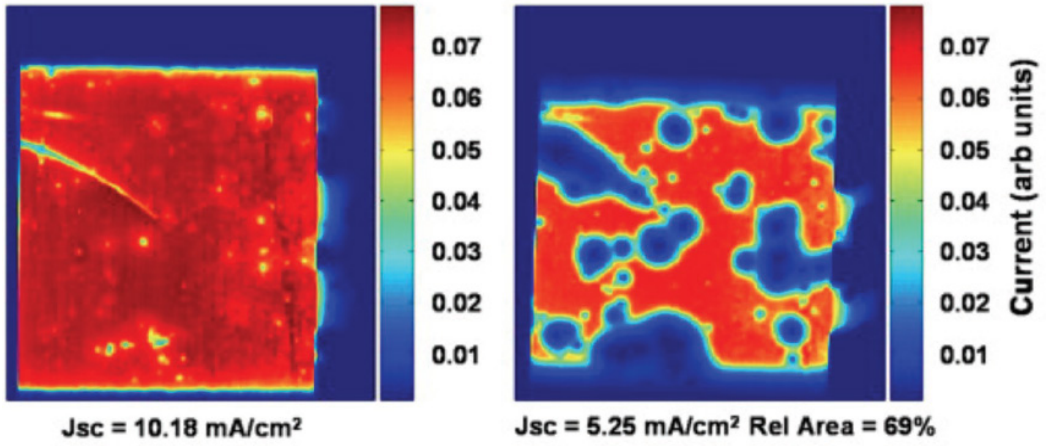
- Different stress factors

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

W. Mateker et al., Advanced Materials 29,1603940 (2017)

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)

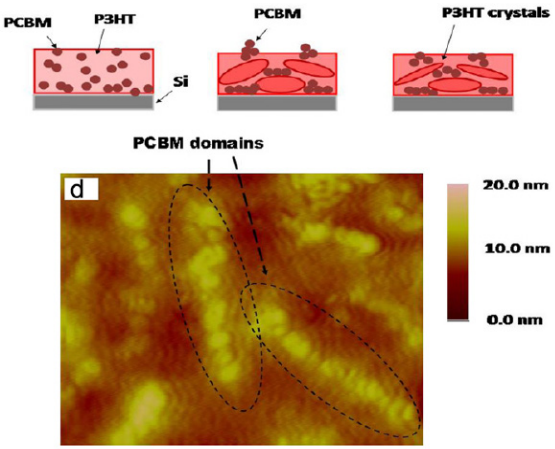


Laser beam induced current (LBIC) map of a solar cell before (left) and after (right) prolonged illumination in ambient conditions. In the degraded solar cell, dead zones clearly form around pinhole defects and there is significant ingress around the edges of the device.

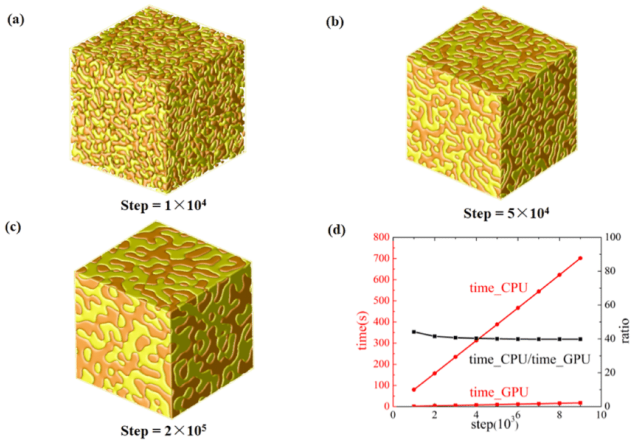
W. Mateker et al., Advanced Materials 29,1603940 (2017)

Stability / degradation

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



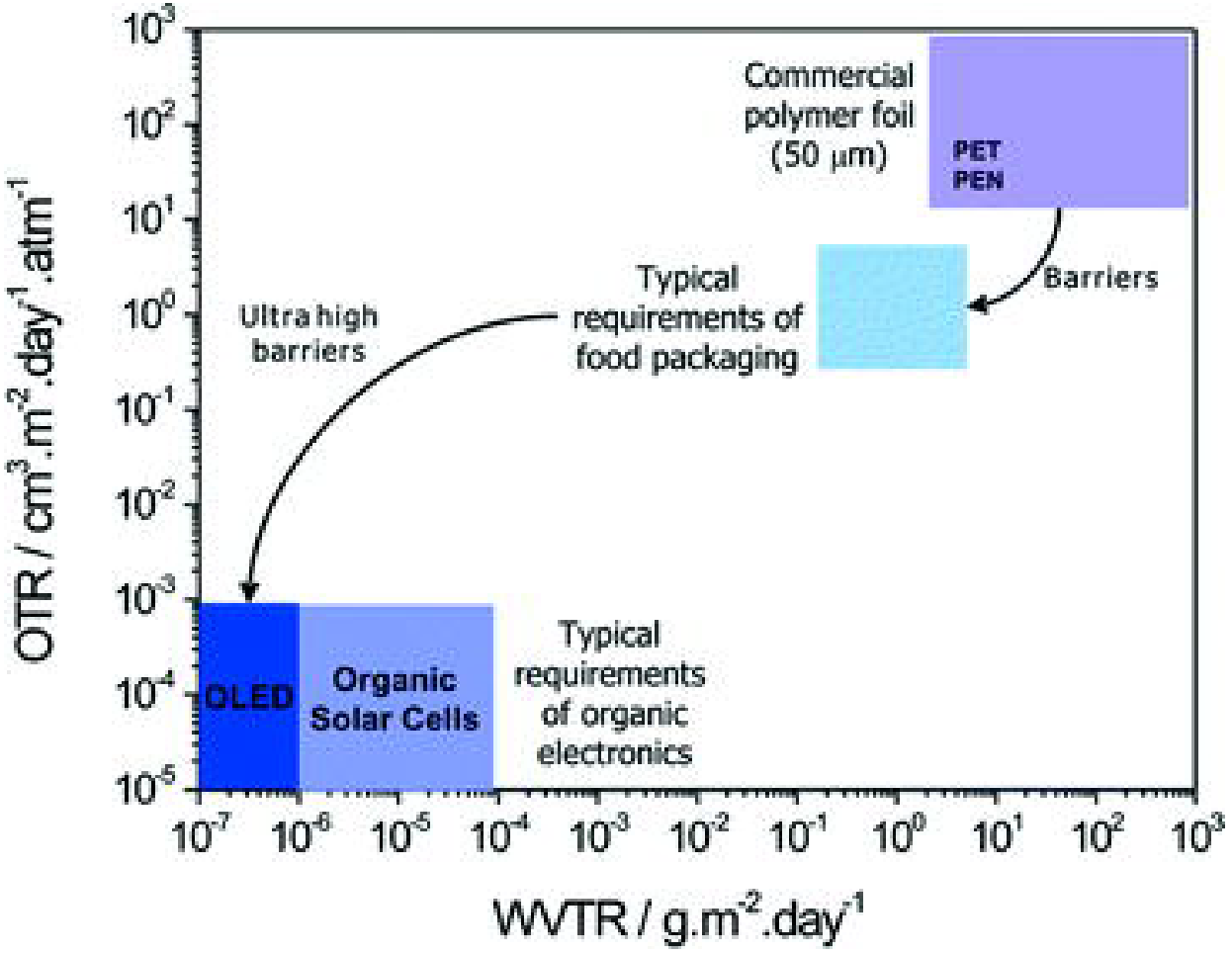
Solar Energy Materials & Solar Cells 107 (2012) 112–124



AIP Advances 7 (2017) 105216

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

Encapsulation



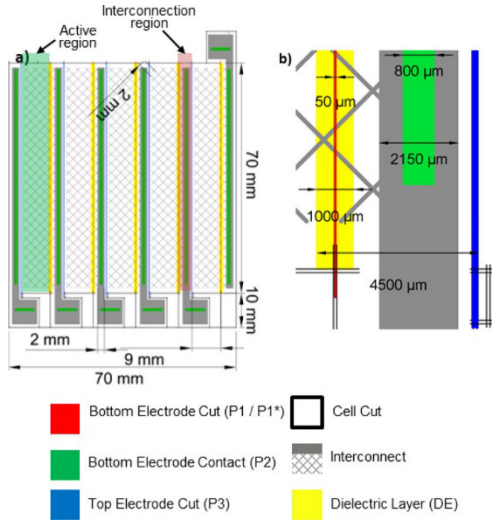
Waldauf C., et al. (2009) Bulk Heterojunction Solar Cells for Large-Area PV Fabrication on Flexible Substrates. In: Wong W.S., Salleo A. (eds) Flexible Electronics. Electronic Materials: Science & Technology, vol 11.

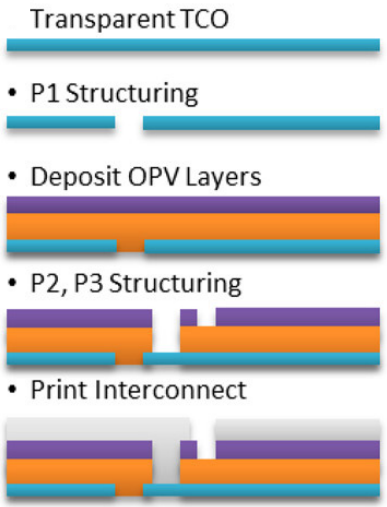
Efficiency loss when moving from laboratory cell to module

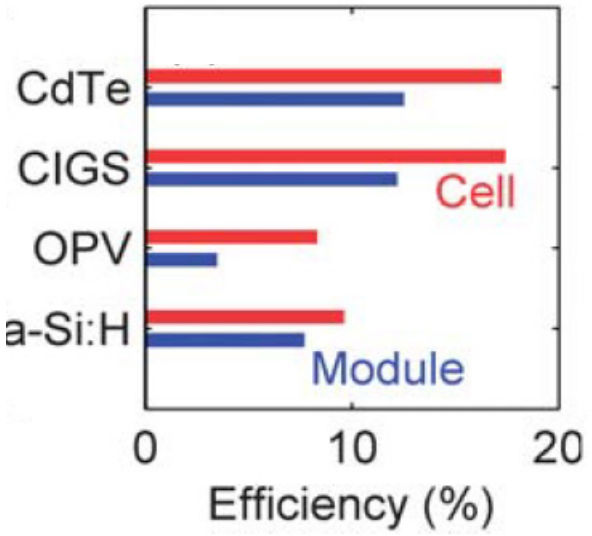
TABLE 1 Confirmed single-junction terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m^2) at 25°C (IEC 60904-3: 2008 or ASTM G-173-03 global)

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

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



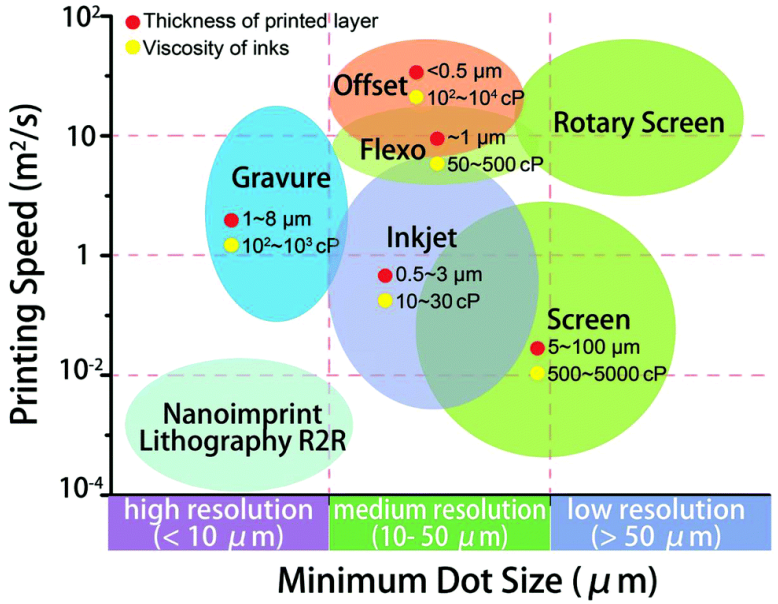




Energy Environ. Sci., 2013, 6, 782

Printing and coating techniques

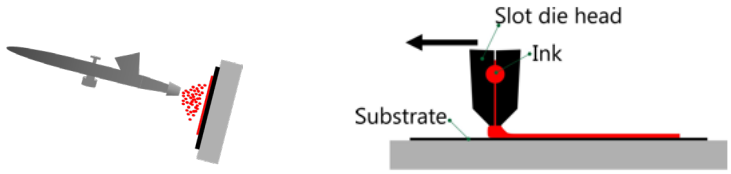
Wu, Nanoscale, 2017, 9, 7342-7372



Coating

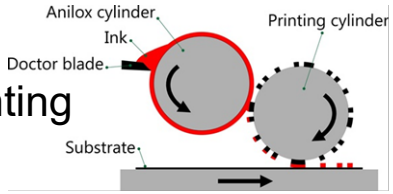
Spray coating

Slot die coating

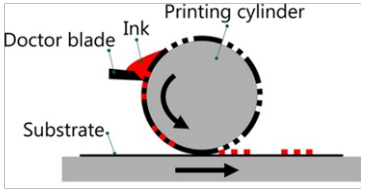


Analogue Printnig

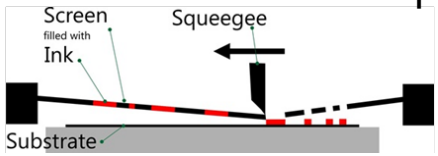
Flexo printing



Gravure printing

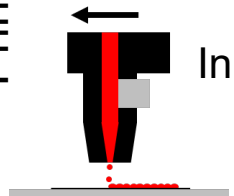


Screen printing



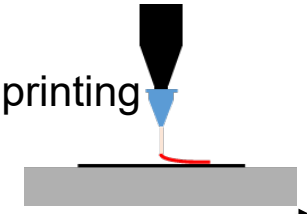
Digital

Ink jet printing



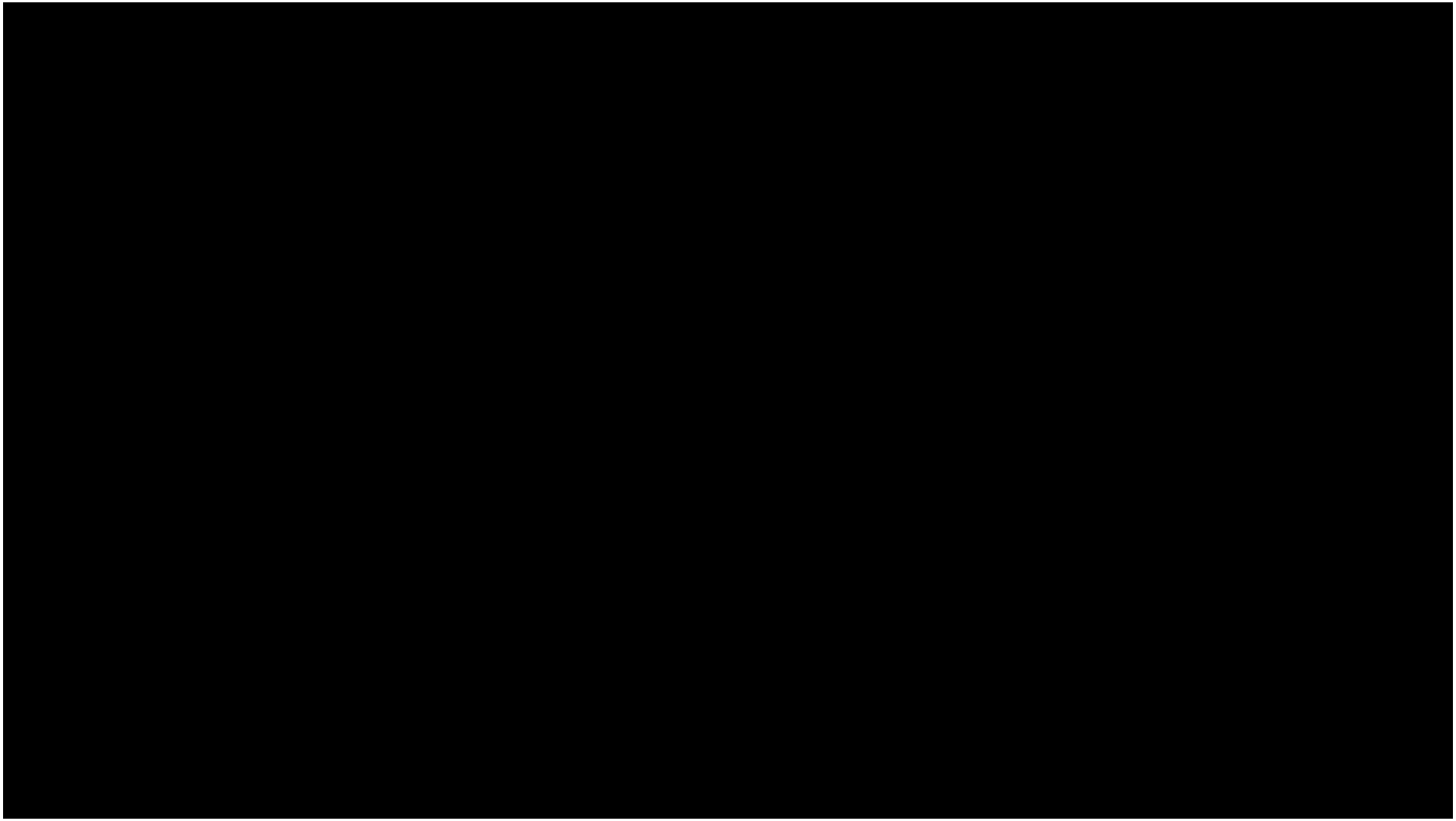
Aerosol jet printing

Extrusion printing



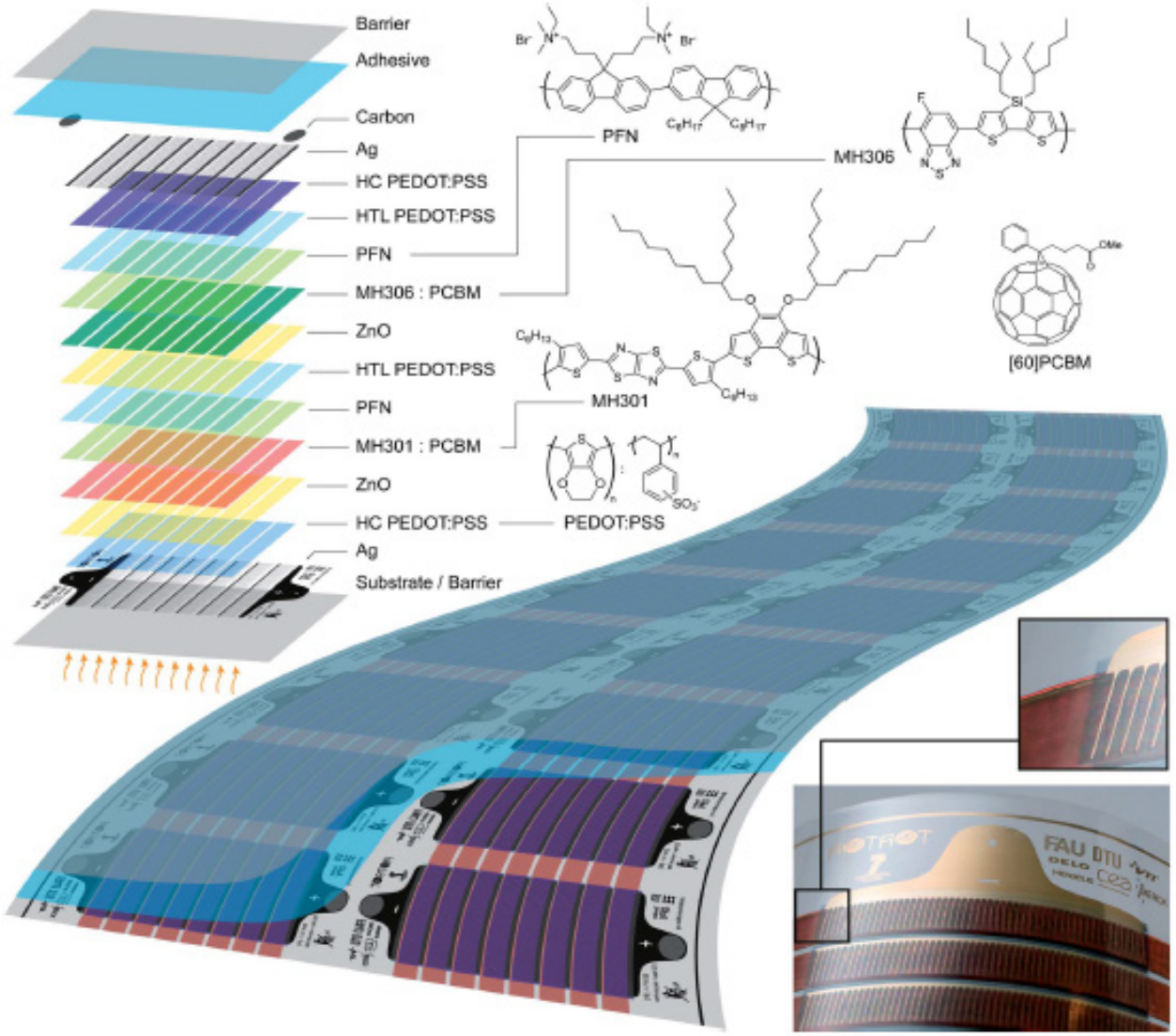
Viscosity

Printing at Empa

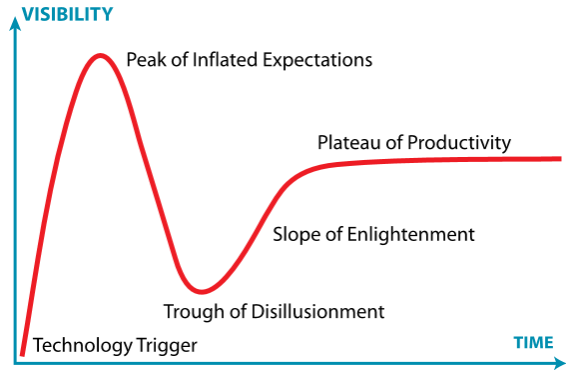


Scalable, ambient atmosphere roll-to-roll manufacture of encapsulated large area, flexible organic tandem solar cell modules

Energy Environ. Sci.,2014, 7, 2925

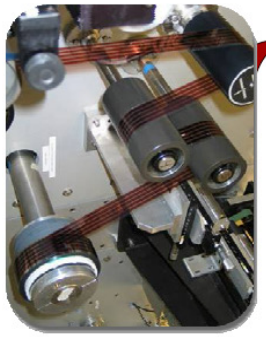


Printed organic solar cells: Trough of Disillusionment



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

Lab



2006
5 cm
1kWatt

Pilot

2007
25 cm
1MWatt

Production

2008
150 cm
1GWatt

2021: Konarka files for bankruptcy

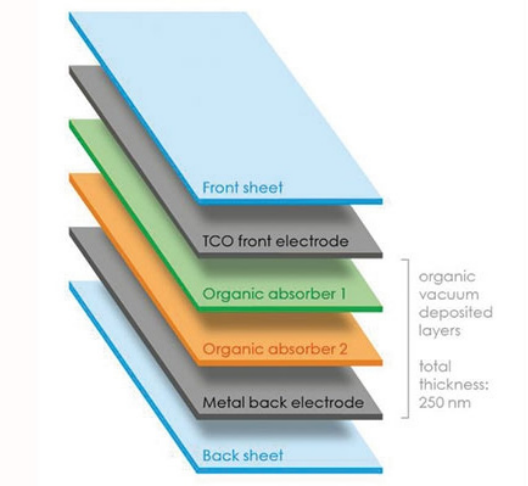
Organic solar film manufacturer, Konarka Technologies, Inc. is the latest solar company to file for bankruptcy protection under chapter 7 of the U.S. Federal bankruptcy laws.

Rollable power supply

Shading elements

Evaporated roll-to-roll modules at Helithek

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”



www.heliathek.com

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

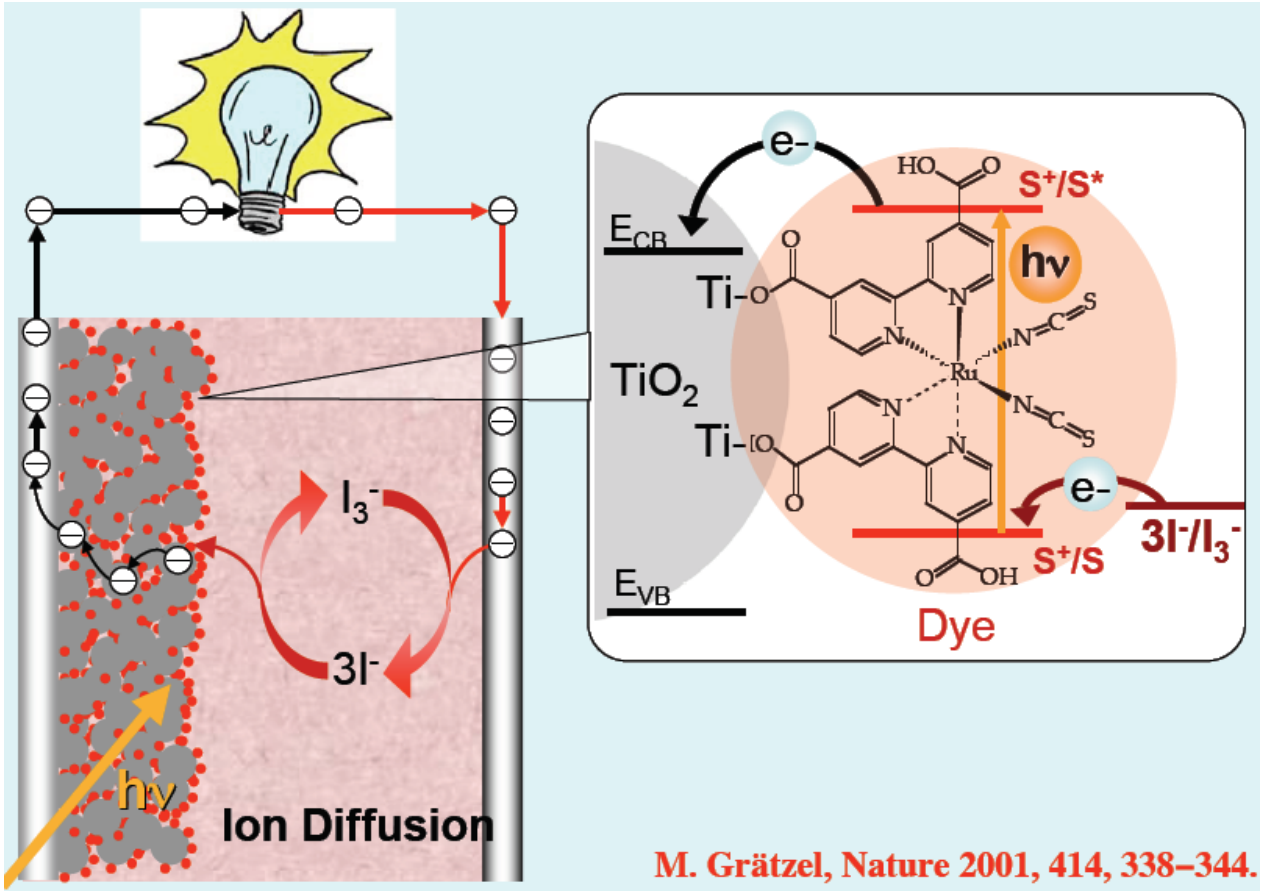
- Motivation
  - *Chemical synthesis of materials, cheap manufacturing, design freedom*
- History
  - *Long development phase*
- Materials properties compared to inorganic semiconductors
  - *Formation of excitons with short diffusion lenght, narrow absorption band*
- Consequences for solar cell design
  - *Bulk heterojunction or thin film tandem devices*
- What strategies are followed to improve the efficiency
  - Donor-acceptor polymers, complementatary 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

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

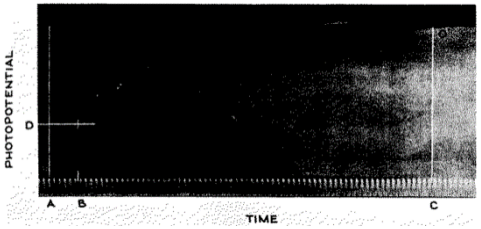
- In a DSSC, one of these interfaces is a semiconductor

- A DSSC is a unipolar device (electrons only), because the semiconductor is not directly excited (wideband semiconductor) => reduced recombination

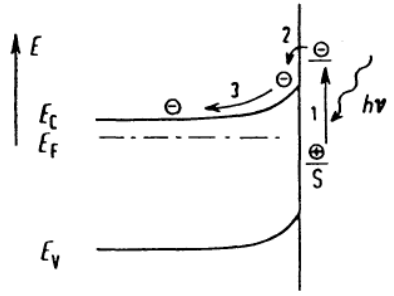
Important milestones in dye sensitization and DSSCs

1839 Bequerel discovers the photovoltaic effect

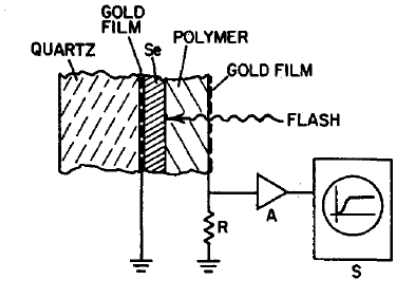
1887 Moser (Vienna University) reported the first dye sensitized photoelectric effect on chlorinated silver plates.



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

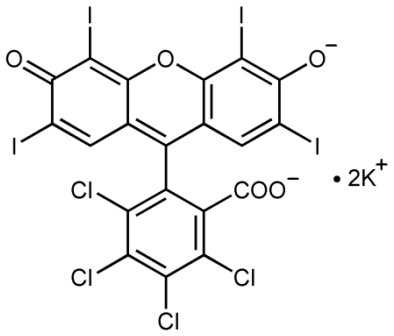


1968 H. Gerischer and H. Tributsch, Mechanism of dye-sensitization. Rose bengal on ZnO, Ber. Bunsenges. Phys. Chem. 72 (1968) 437.



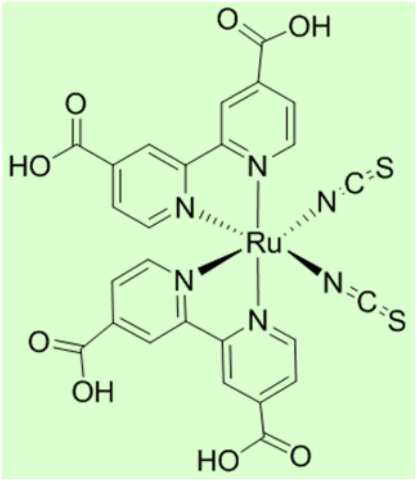
Important milestones in dye sensitization and DSSCs

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_2 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

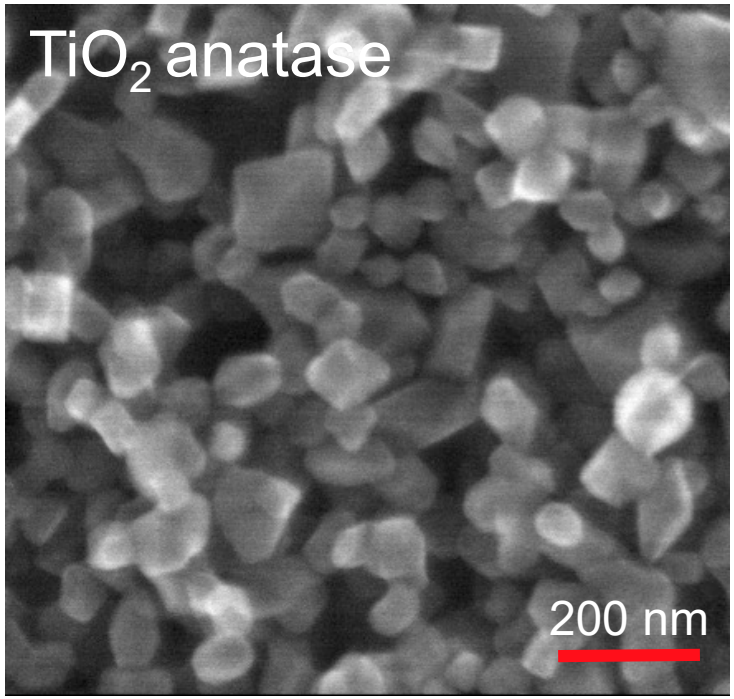


The real break-through came with the development of nanoporous photoanodes

1990 B. O'Regan, B. Moser, J. Anderson, M.Grätzel, M. 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'Reagan, 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

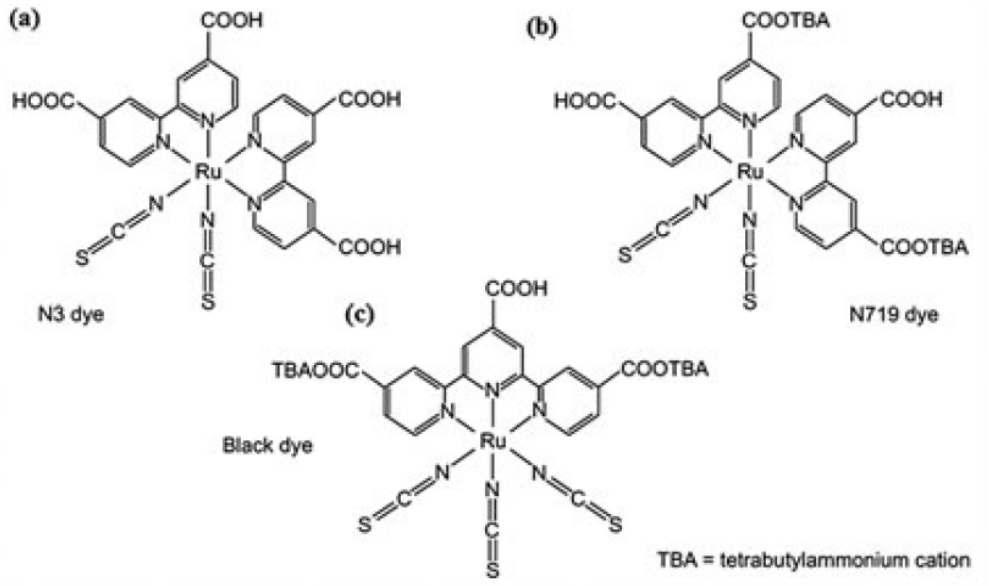
3.The insulating nature of the oxide nanocrystals prevents energy transfer quenching of the excited sensitizer by conduction band electrons

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: η= 10.3 % with dye N3 (Cis- bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II))
2005: η= 11.2 % with dye N719

- Ruthenium is very expensive; search for alternatives

It is easy to fabricate a DSSC

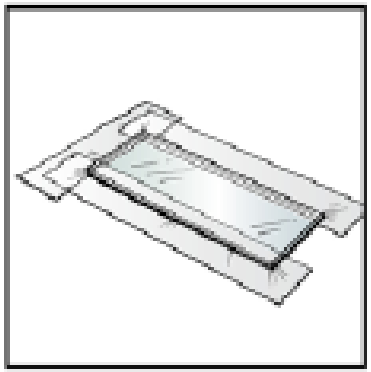


Abb. 1

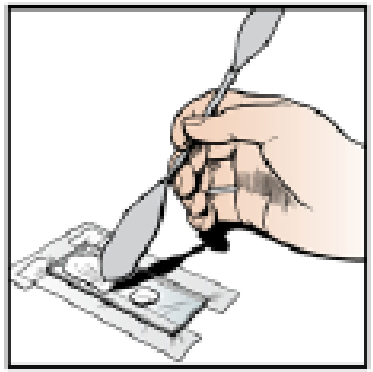


Abb. 2

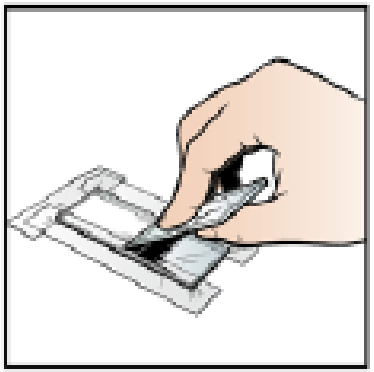


Abb. 3


Abb. 4

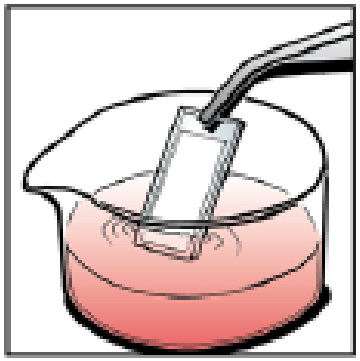


Abb. 5


Abb. 6

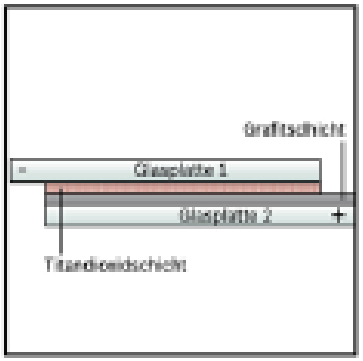


Abb. 7

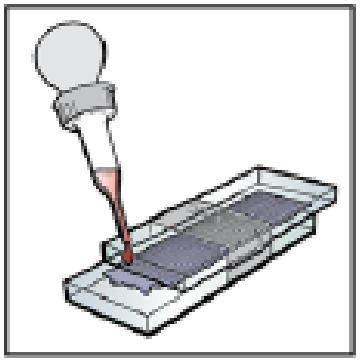


Abb. 8

DSSC kinetics

- Kinetic competition drives charge separation

1. **Absorption**

   $Dye + hv \rightarrow Dye^*$

2. **Electron Injection**
   v. Decay to Ground

   $Dye^* \rightarrow e^-_{TiO2} + Dye^+$ (100 ps)

   $Dye^* \rightarrow Dye + hv$ (~ns)

3. **Regeneration Reaction**
   v. Recombination to Dye

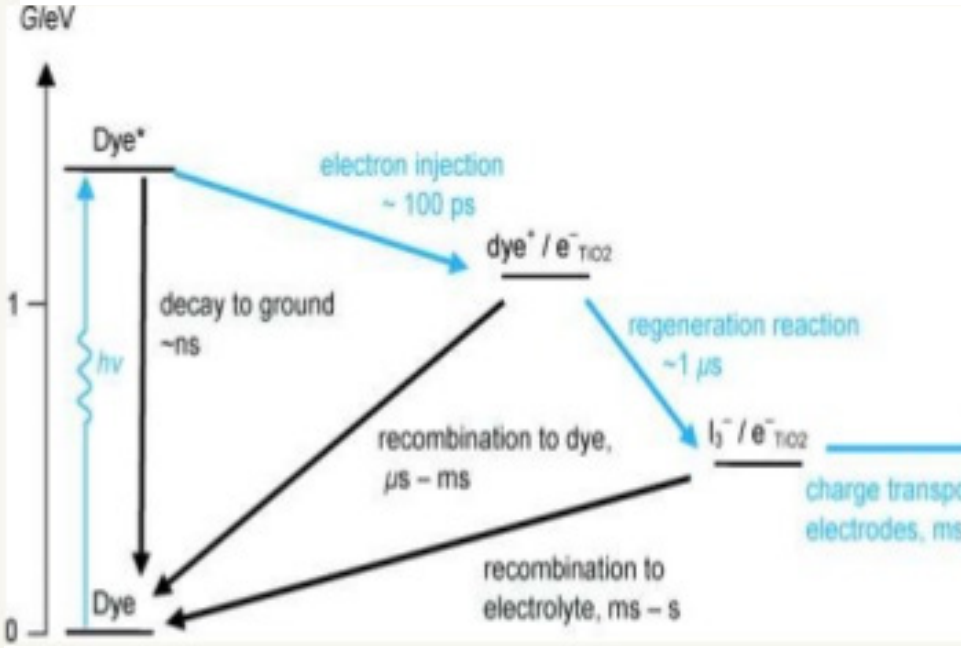
   $Dye^+ + I^- \rightarrow Dye + I_3^-$ (~1 µs)

   $Dye^+ + e^-_{TiO2} \rightarrow Dye$ (µs – ms)

4. **Charge Transport**
   v. Recombination to Electrolyte

   $I_3^- + e^-_{Pt} \rightarrow I^-$ (ms – s)

   $I_3^- + e^-_{TiO2} \rightarrow I^-$ (ms – s)



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

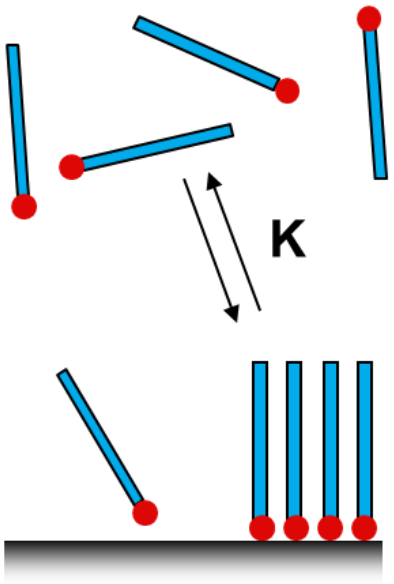
τ_{trans}: transport through TiO_2

τ_{rec} : recombination

Listarti, A.; O'Regan, B.; Durrant, J., Chem. Mater. 2011, 23, 3381

Adsorption of dye onto surface:

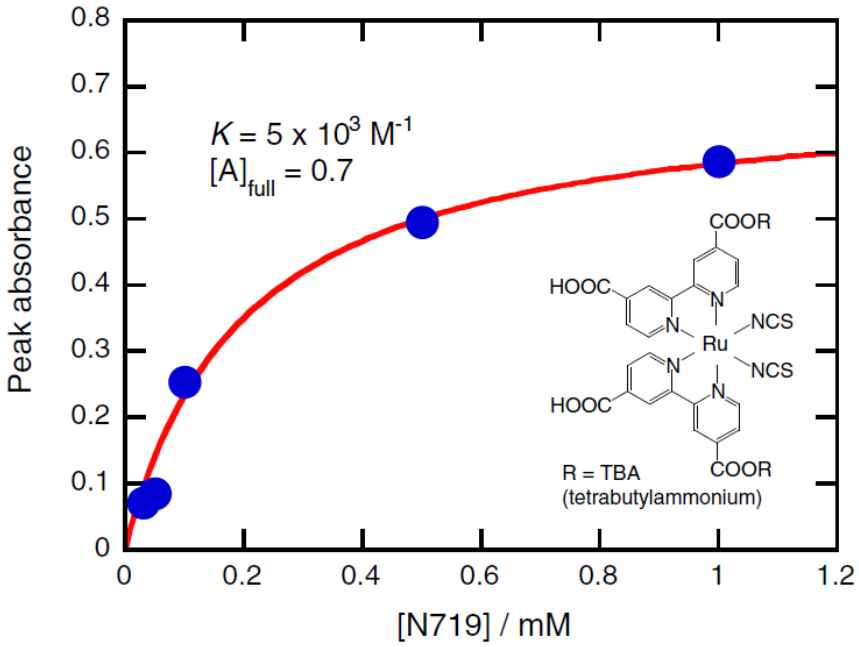
- Dye work most efficiently when chemiosorbed onto the surface



$$X_{eq} + S_{free} \underset{}{\overset{K}{\rightleftharpoons}} XS_{ads}$$

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

Adsorption thermodynamics of N719 on TiO_2



- surface area / molecule: 1nm²
- 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^2 of porous TiO_2, the effective surface area is 1000 cm^2

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

Full sunlight intensity 100 mW/cm^2
yields (half of the photons are absorbed, average wavelength =700 nm) number of photons/s.

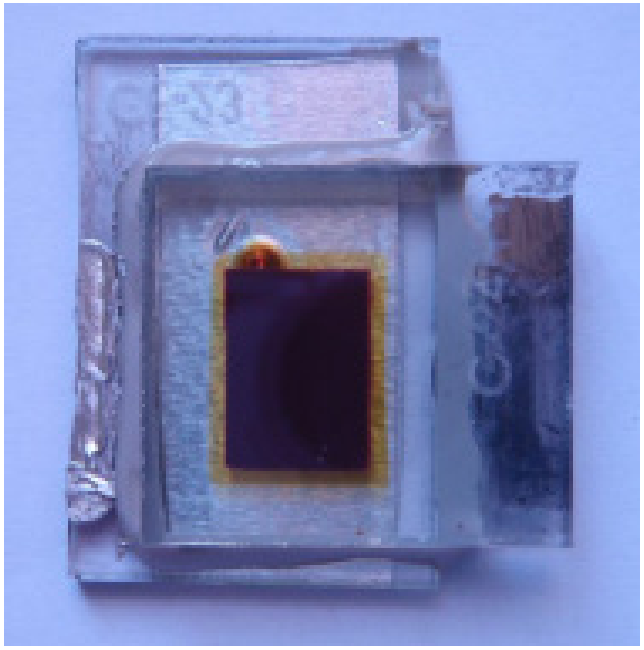
$$\frac{50\ mW cm^{-2}}{2.8.\times 10^{-19} J} = 1.7 \times 10^{17} s^{-1}$$

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

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

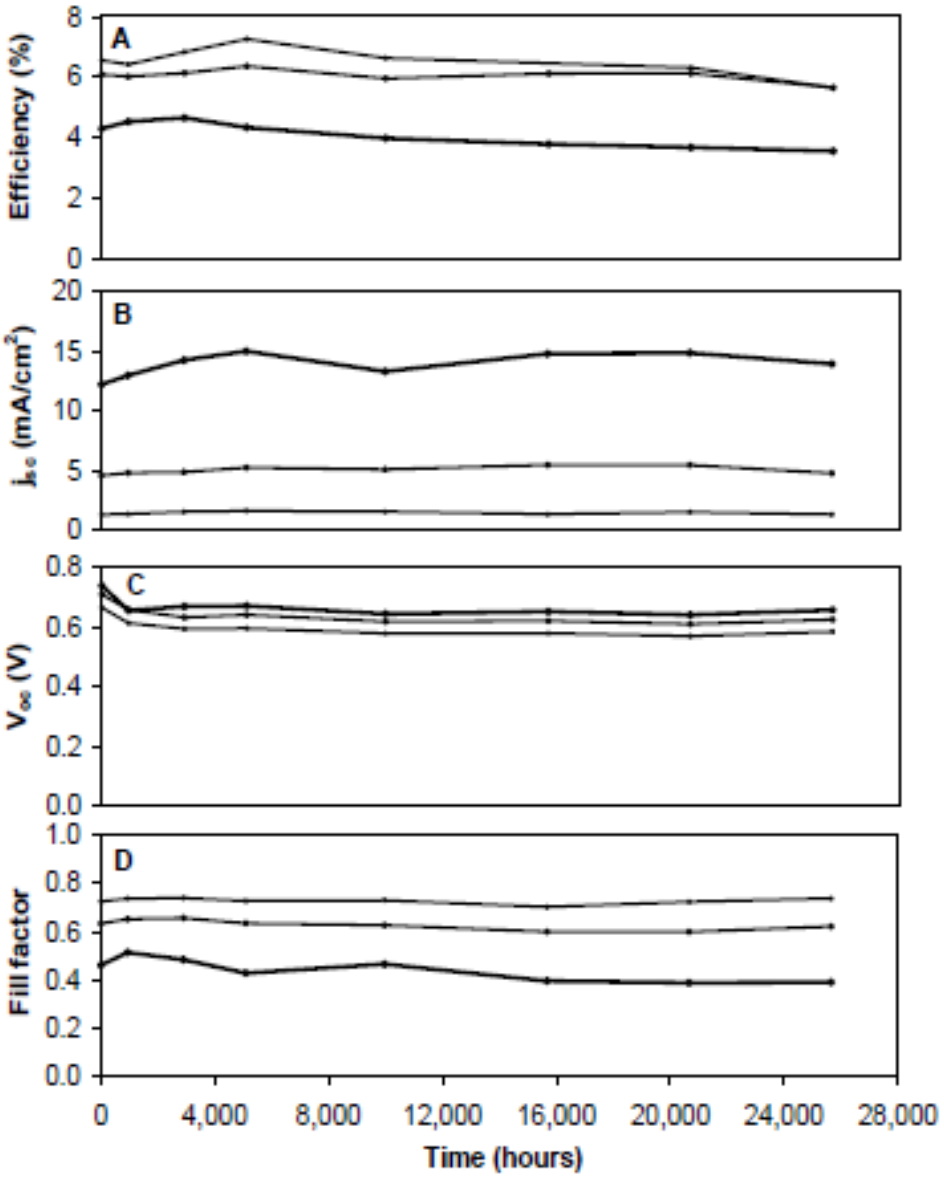
Number of cycles / molecule: $\frac{9.46 \text{ x } 10^7 \times 1.7 \times 10^{17} s^{-1}}{10^{17}} = 1.6 \times 10^8$

Long term stability of DSSCs



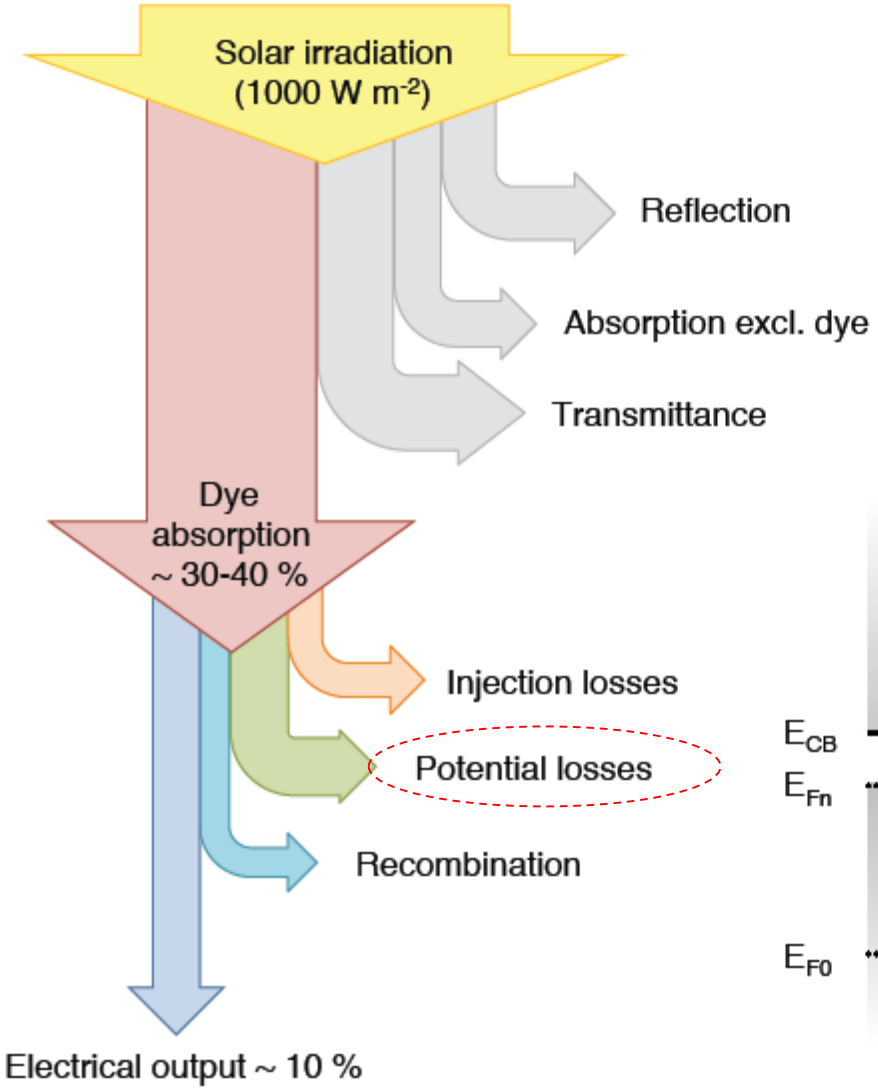
Efficiencies (A), short circuit currents (B), open circuit voltages (C) and fill factors (D) of solvent based cell, periodically assessed at 1 sun (bold lines), 0.33 sun (intermediate line width) and 0.1 sun (thin lines), as a function of light soaking time at 0.8 sun, with cell temperature maintained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

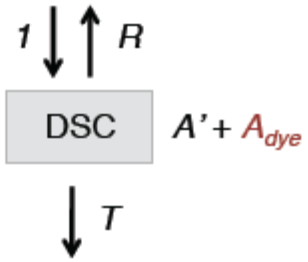
Dye Z907

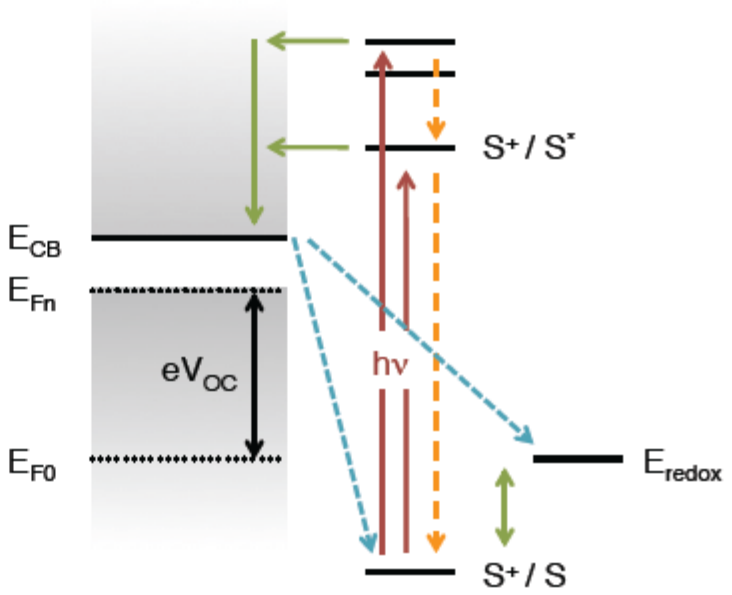


Harikisun, Ravi, Desilvestro, Hans, SOLAR ENERGY Volume: 85 Issue: 6 Special Issue: Pages: 1179-1188 (2011)

Challenges in DSSCs

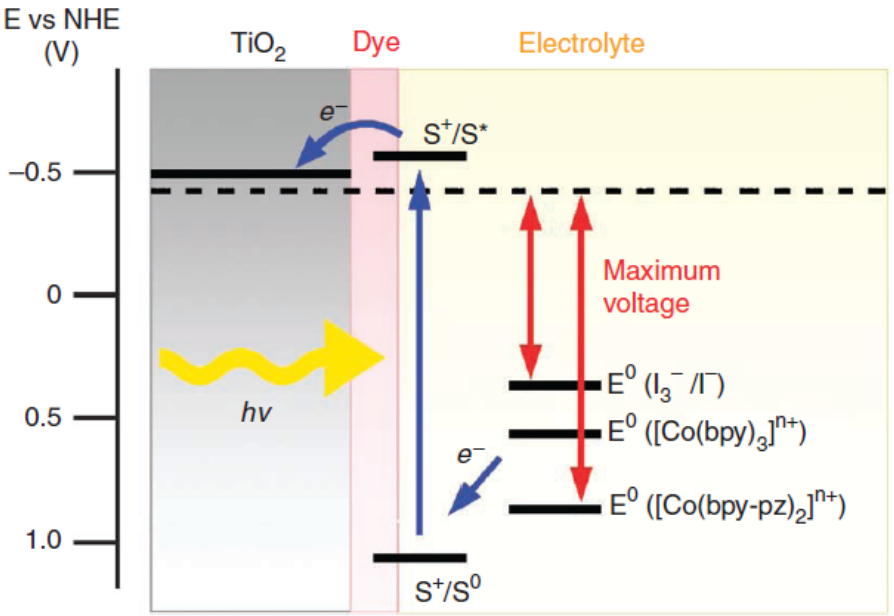


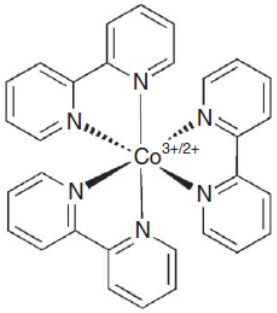




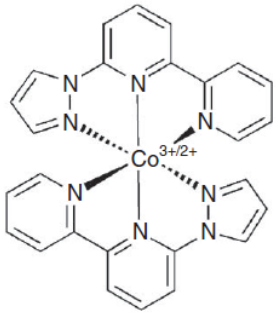
S. Wenger, thèse No. 4805 (2010), Epfl, Lausanne

New redox mediators

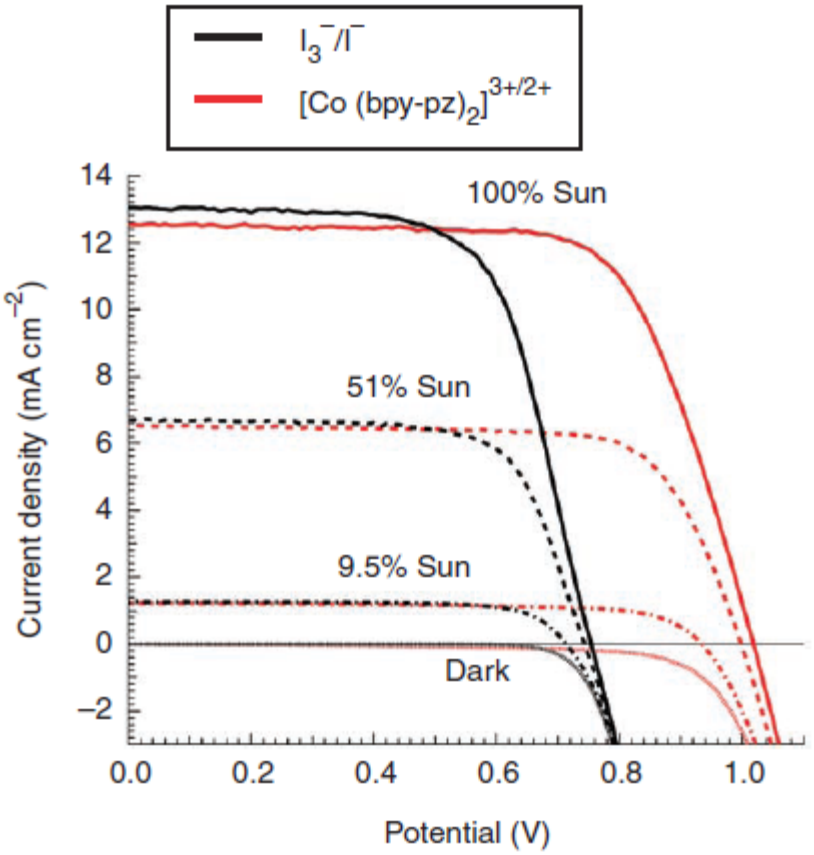




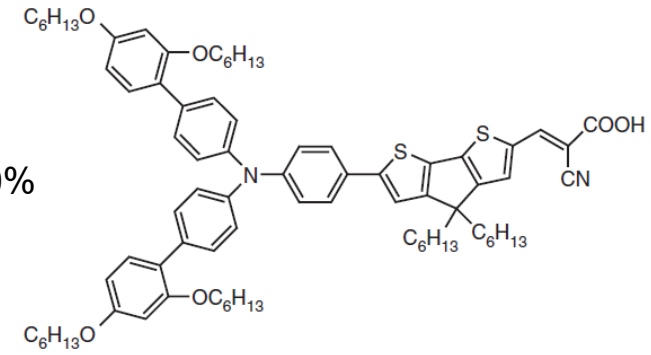
Co(bpy)$_3$



Co(bpy-pz)$_2$

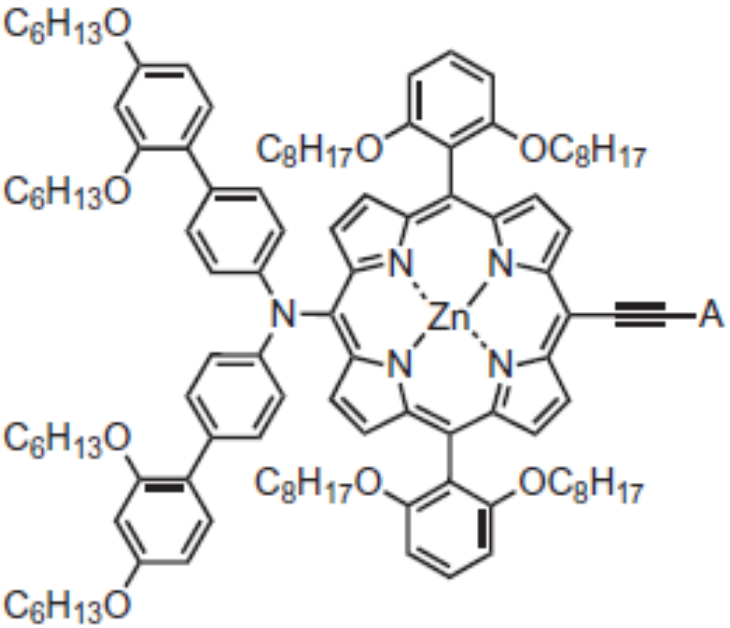


η = 10%



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

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



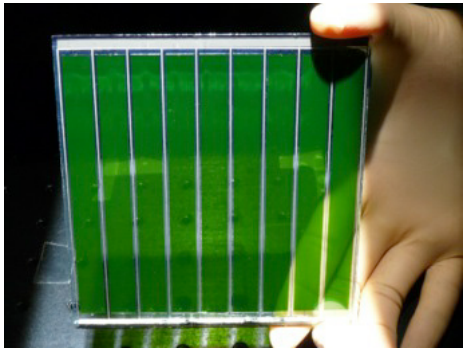
A = COOH

SM371

A =

SM315

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, 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

PROGRESS IN PHOTOVOLTAICS WILEY

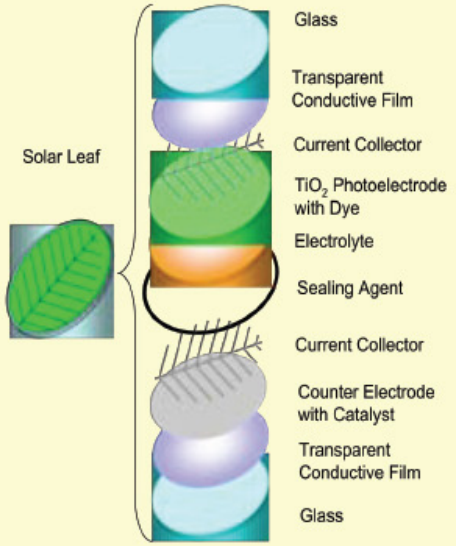
Solar cell efficiency tables (version 57)

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

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

SC DEVELOPMENT GROUP, ENERGY DEVELOPMENT DEPT.

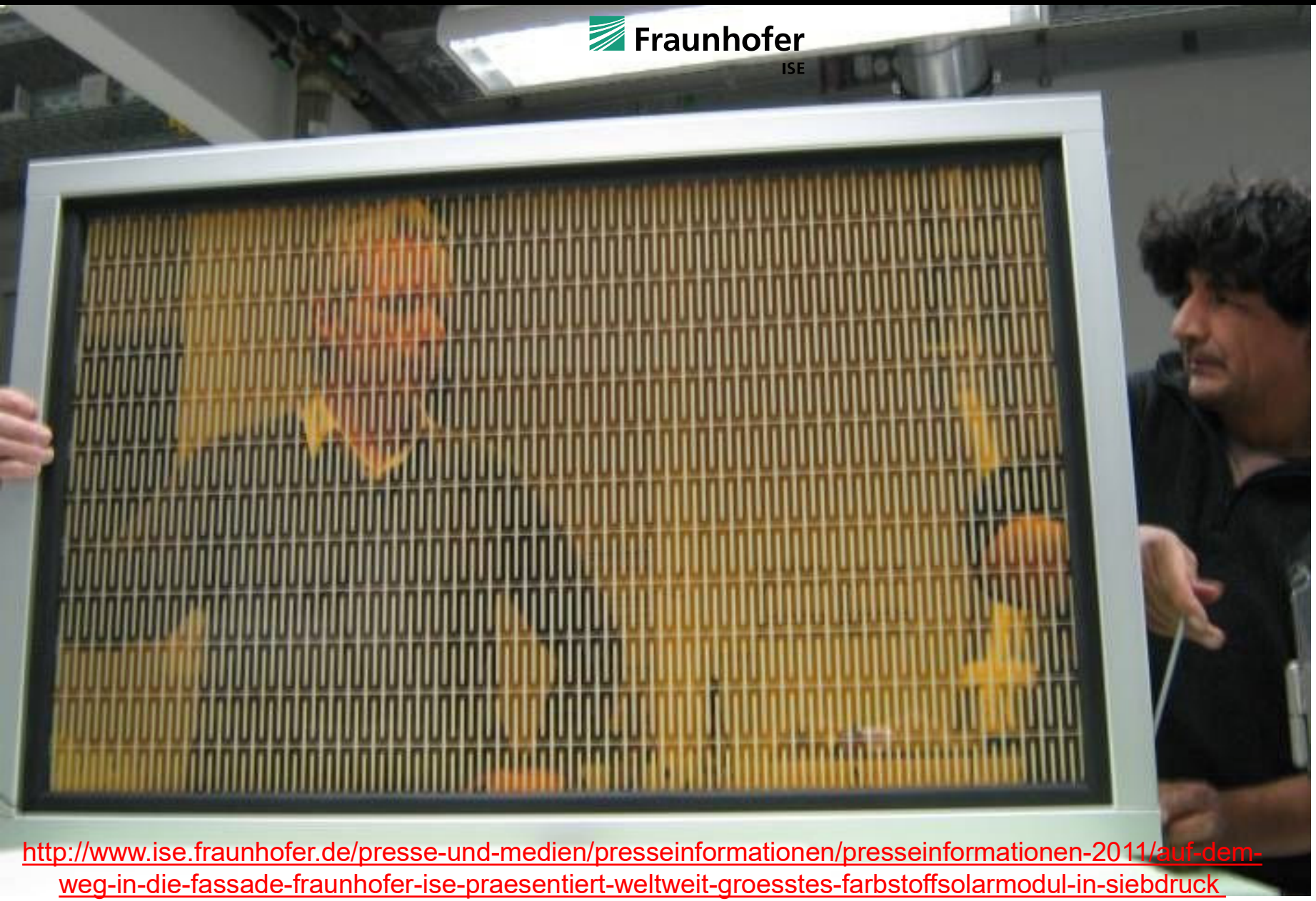
AISIN

AISIN SEIKI CO.,LTD.

6th SEPTEMBER, 2006

Courtesy Sony Inc

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



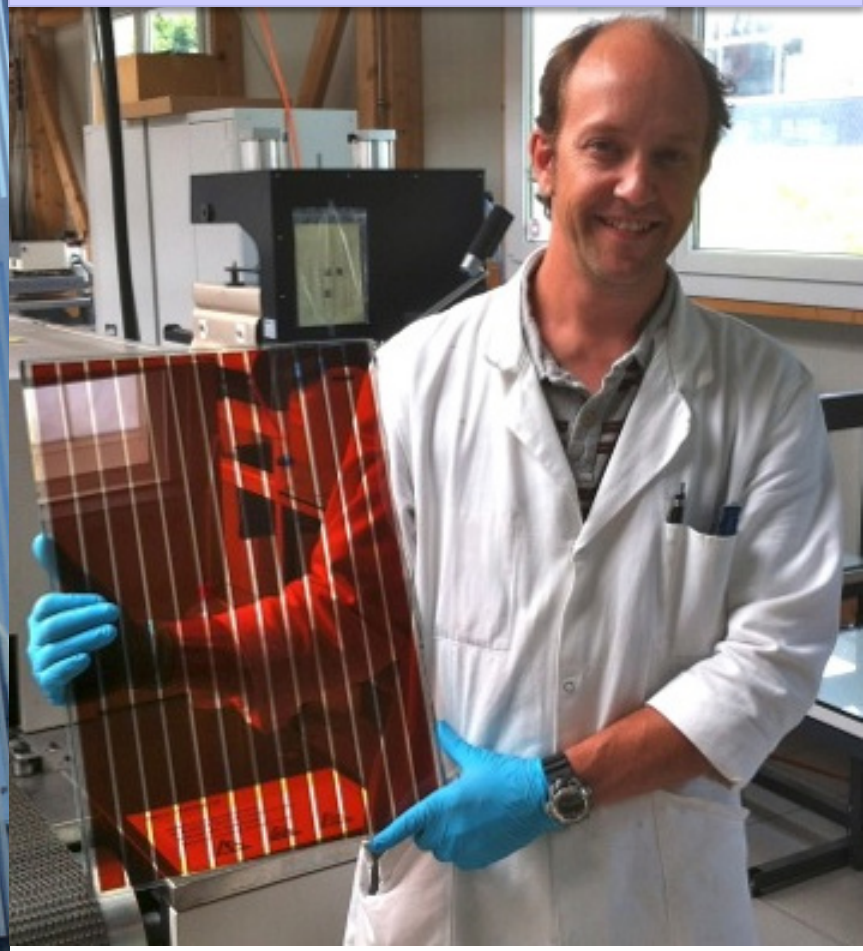
http://www.ise.fraunhofer.de/presse-und-medien/presseinformationen/presseinformationen-2011/auf-dem-weg-in-die-fassade-fraunhofer-ise-praesentiert-weltweit-groesstes-farbstoffsolarmodul-in-siebdruck

Swiss Museum of Transport

SOLARONIX « efficiently innovative »

Empa Materials Science and Technology

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



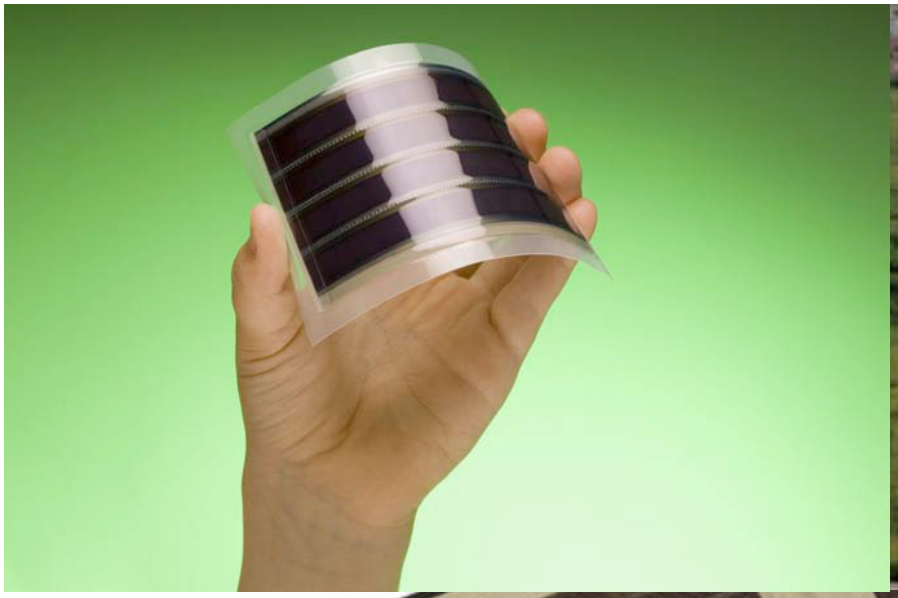
SOLARONIX

« 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*