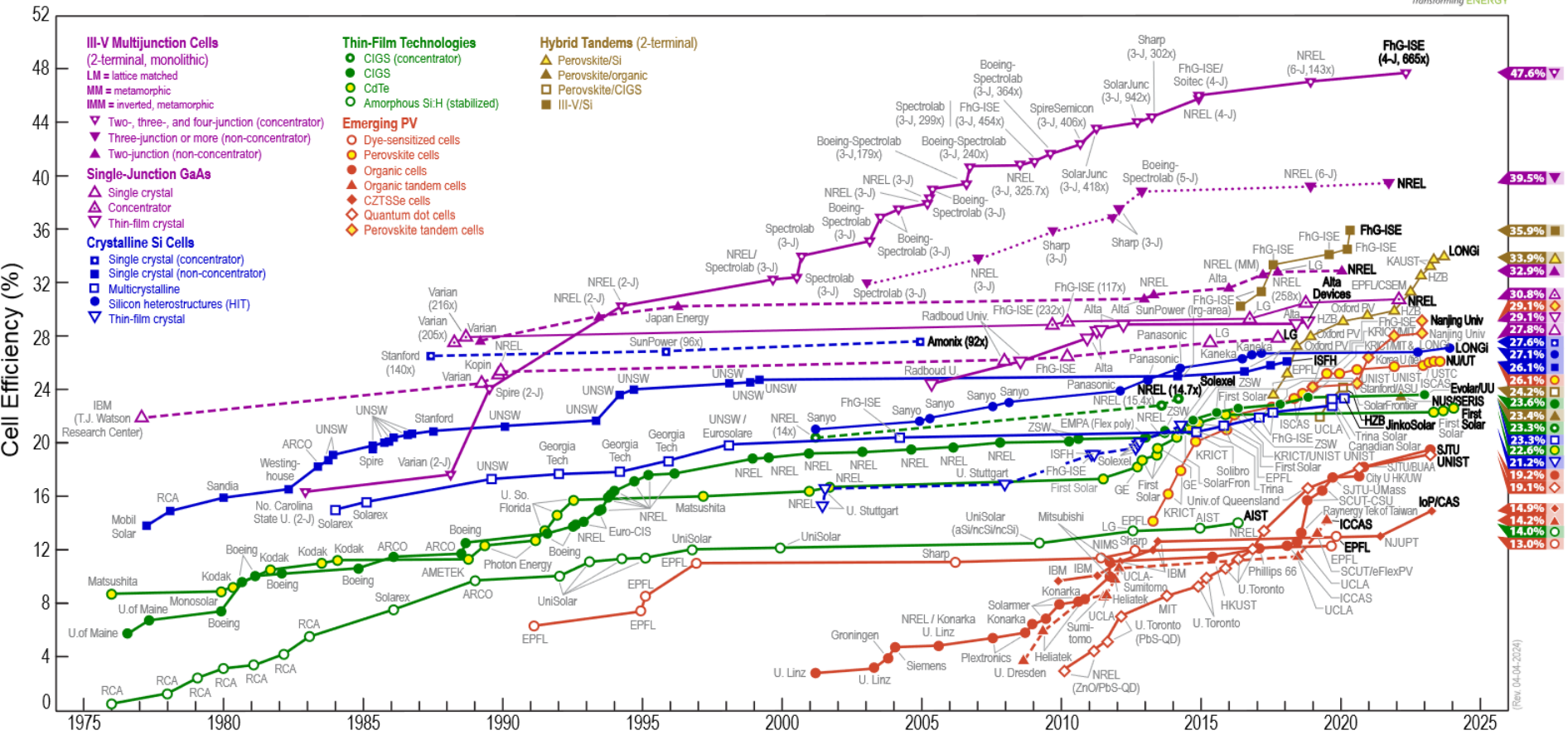
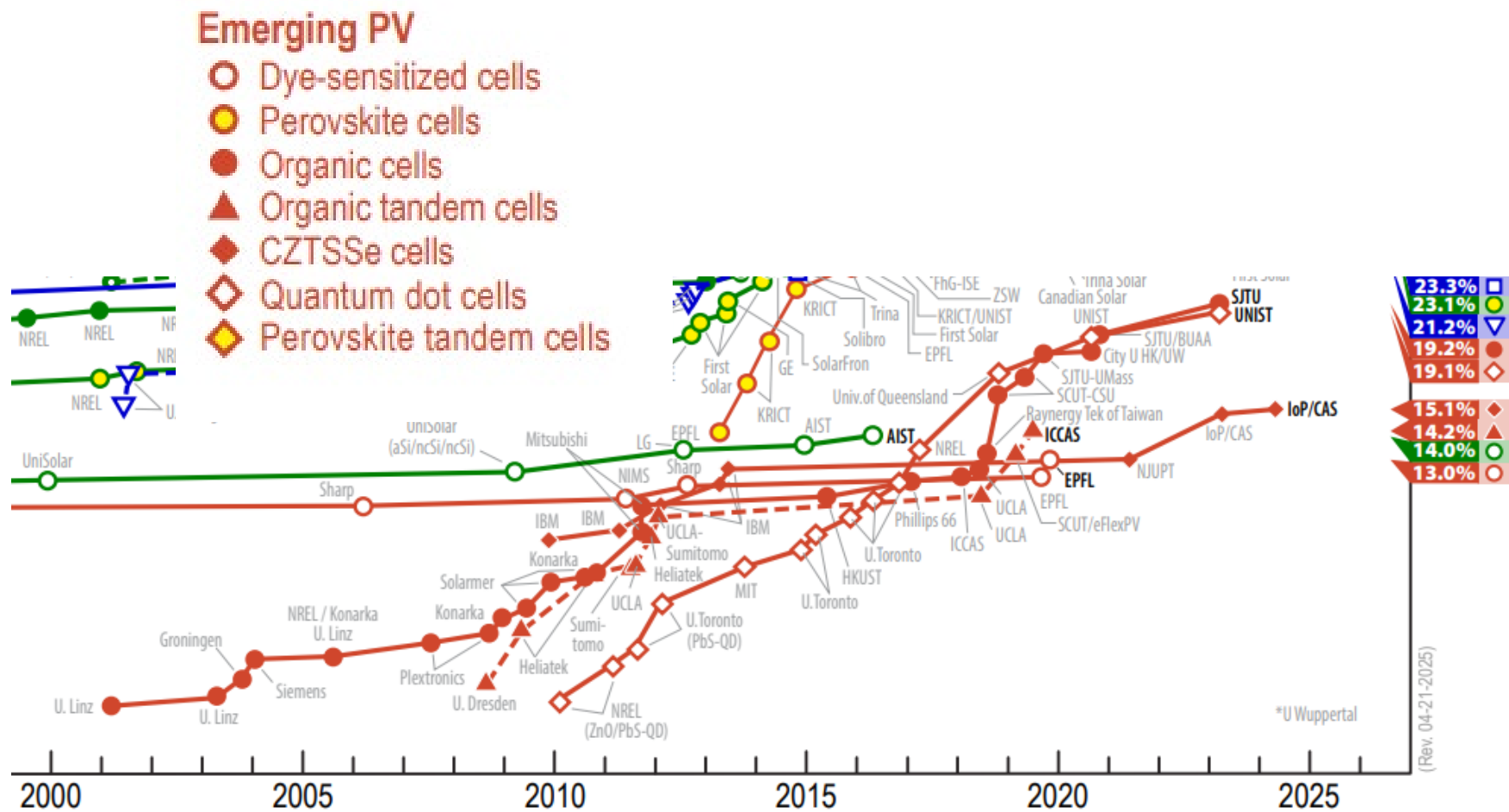


2.2A Organic Photovoltaics (OPV)

Best Research-Cell Efficiencies



2.2A Organic Photovoltaics (OPV)

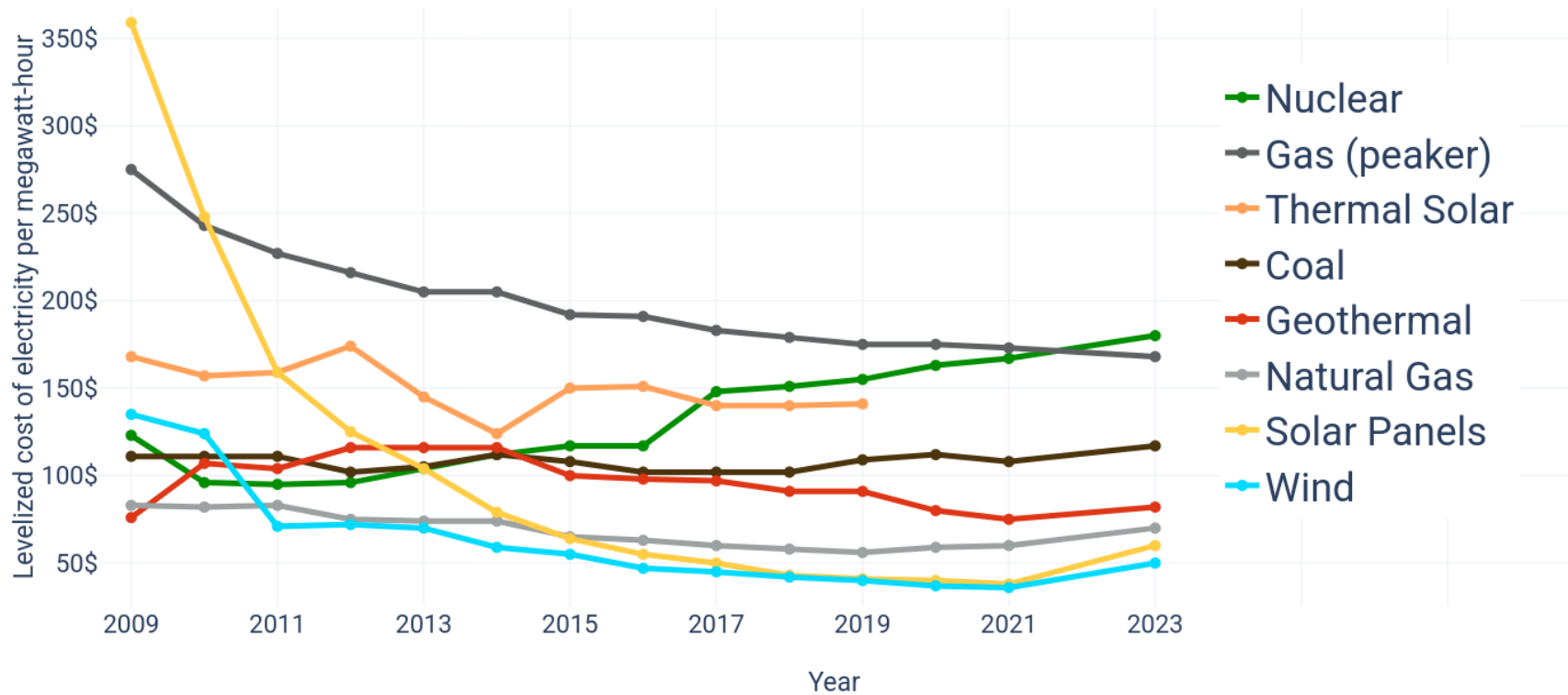


2.2A Organic Photovoltaics (OPV)

Learning goals

- ❑ Motivation / how competitive can it be?
- ❑ History: how it all started
- ❑ Properties of inorganic and organic semiconductors differ
 - ❑ What are the consequences for solar cell design?
- ❑ What strategies are followed to improve the efficiency?
 - ❑ It is a story of surpassing one bottleneck after the other
- ❑ State-of-the art
- ❑ Still fighting with stability
- ❑ Manufacturing
- ❑ Current research directions

Electricity cost (data from Lazard)



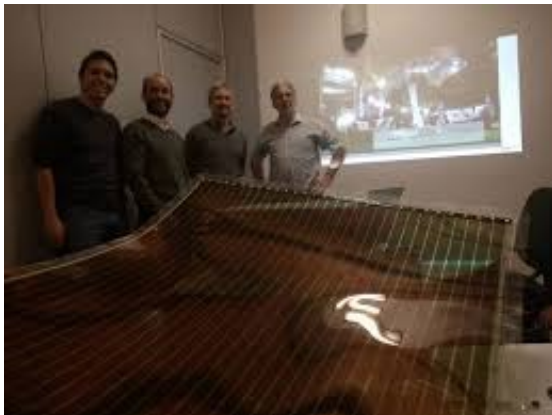
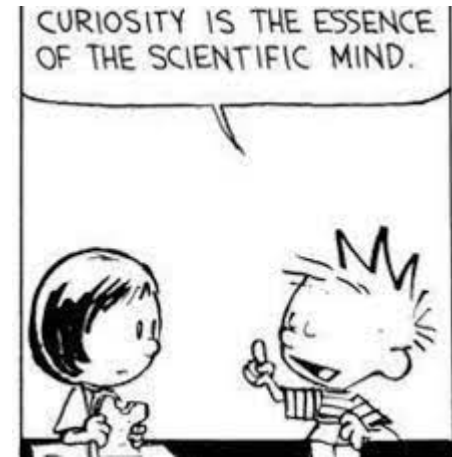
Driven mainly by cSi, electricity cost for Solar Panels dropped significantly.

Does an emerging technology have a chance to enter the market?

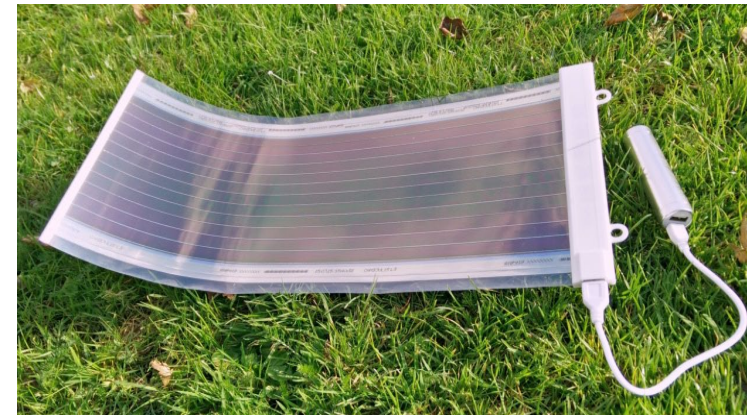
Why organic photovoltaics?

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

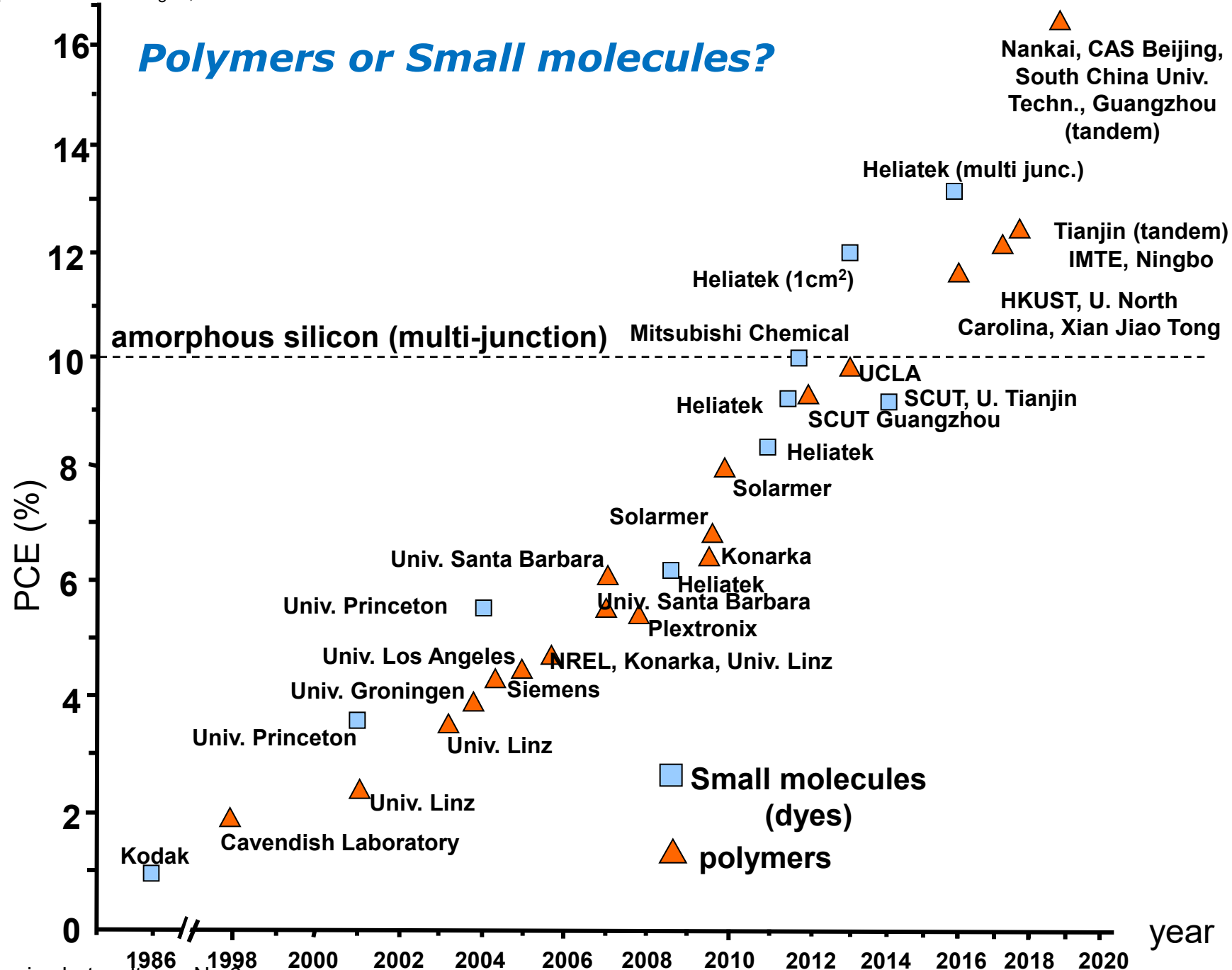
- ❑ **Low-cost manufacturing:** Soluble organic molecules enable roll-to-roll processing techniques
- ❑ **Abundant materials** may reduce supply and price constraints.
- ❑ **Lightweight** expands installation options
- ❑ **Flexible substrates** permits a wide variety of uses
- ❑ **Semitransparency** allows applications on windows



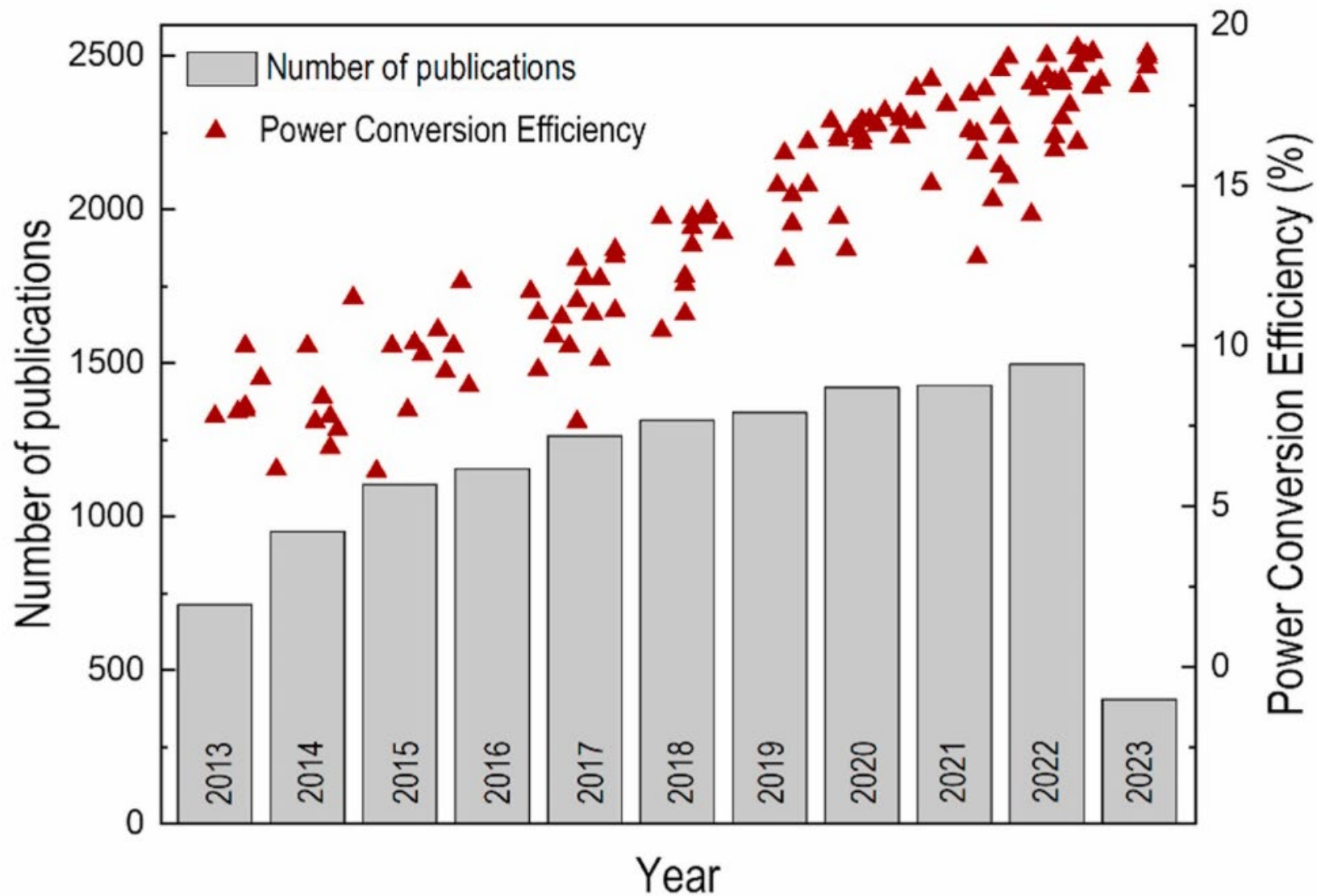
Fully printed oPV, CSEM Brazil



Light weight charger, Eight19 Cambridge



OPV: still an active field



Important milestones in OPV

Photoinduced charge generation:

- 1906 Pochettino: Photoconductivity in anthracene
- 1959 Kallmann, Popoe: PV effect in single cryst. Anthracene

Junction needed to dissociate "exciton":

- 1960 H. Meier et al.: PV-cells made of "p-n" heterojunctions
- 1978 K. Ghosh et al.: Merocyanine Schottky-barrier cells (0.5%)
- 1986 C. W. Tang: CuPc-perylene Heterojunction solar cell (1%)
- 1993 N. S. Sariciftci: Polymer / C60 heterojunction devices

Bulk heterojunction:

- 1994 G. Yu et al. "Bulk-heterojunction concept" between PPV and C60
- 2001 C. J. Brabec Bulk-heterojunction devices with 3%

Donor-acceptor polymers:

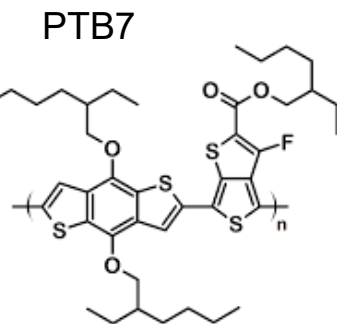
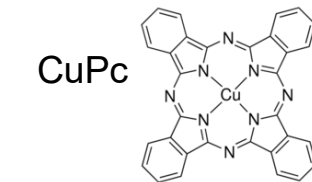
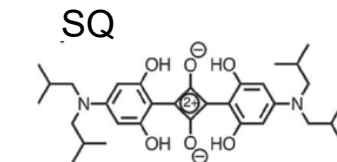
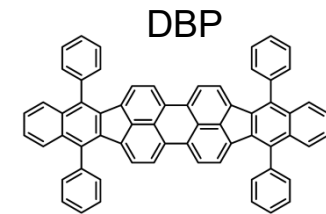
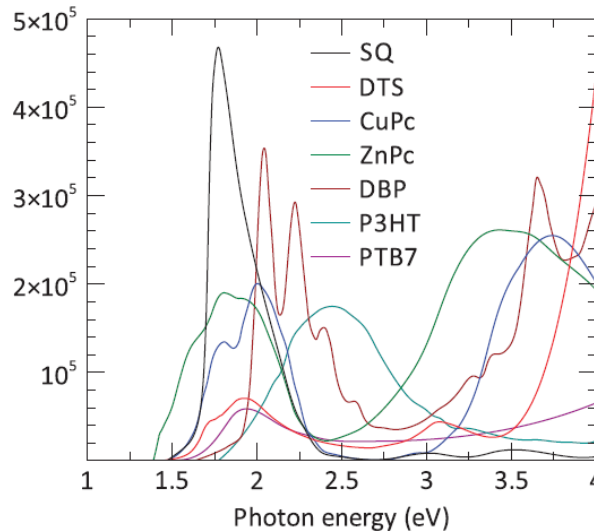
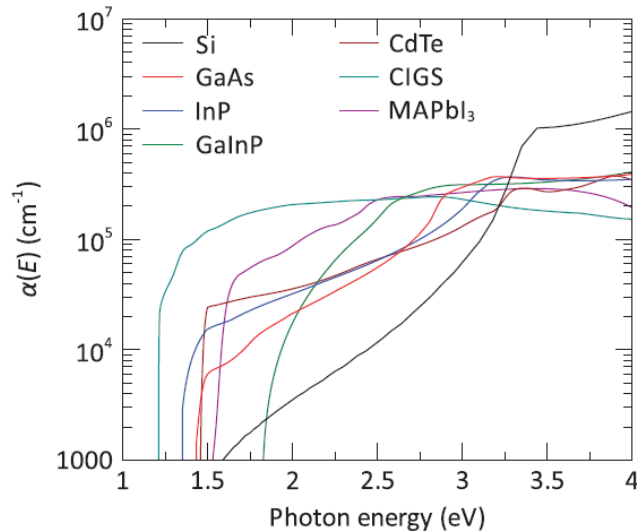
- 2009 H. Y. Chen et al.: PBDTTT polymer bulk-heterojunction (6.8%)

Non-fullerene acceptor:

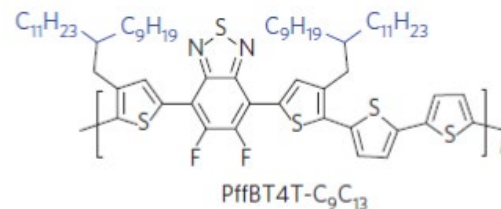
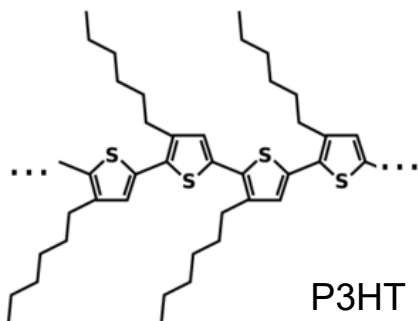
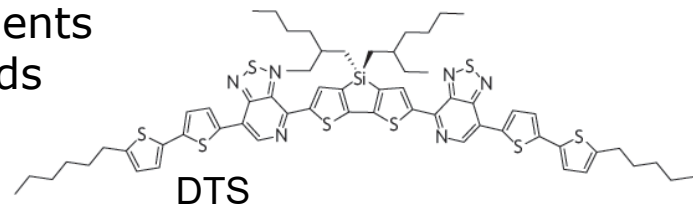
- 2019 Binary oPV with NIR-absorbing Non-fullerene acceptor (15.7%)

Fundamental differences in materials properties

Optical properties



- High absorption coefficients
- Narrow absorption bands
- High bandgap



Fundamental differences in materials properties

Charge carrier mobility

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

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

Organic semiconductors

Inorganic semiconductors

crystalline

crystalline

Anthracene	1.6 (e ⁻)	1.2 (h ⁺)
Pyrene	0.7 (e ⁻)	0.7 (h ⁺)
b-phthalocyanine	1.1(e ⁻)	1.4 (h ⁺)
Fullerene C ₆₀	1.1(e ⁻)	1.0 (h ⁺)

Si	1500 (e ⁻)	450 (h ⁺)
Ge	3900 (e ⁻)	1900 (h ⁺)
GaAs	8500 (e ⁻)	400 (h ⁺)
InAs	80000 (e ⁻)	1250 (h ⁺)

amorphous

amorphous

10⁻⁵ to 10⁻³ at high fields (1MV/cm)

Si ≈ 1

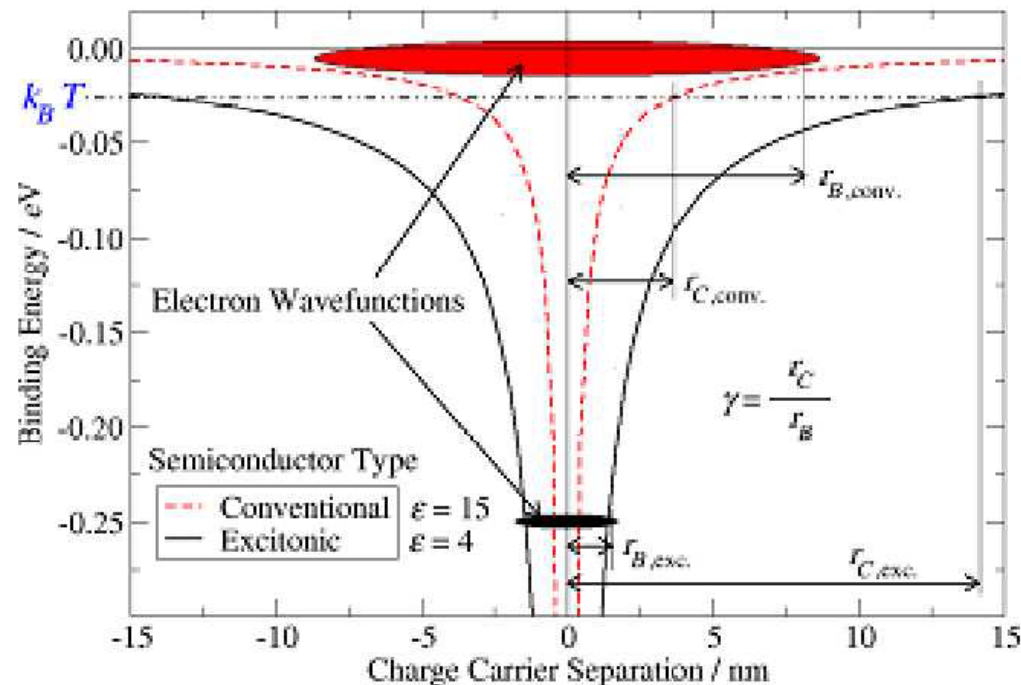
M. Pope, C. E. Swenberg, "Electronic Processes in Organic Crystals and Polymers", Oxford University Press, 1999

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 ($\epsilon = 3-4$) 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 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.

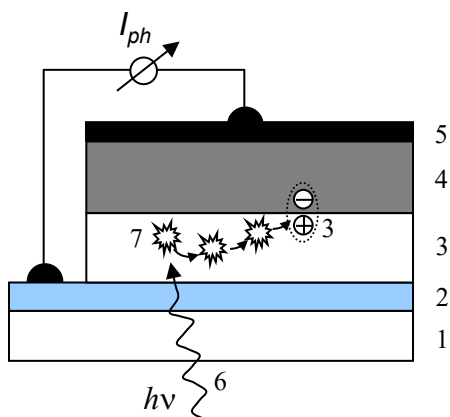
Working principle of organic solar cells

□ Response to exciton binding energy

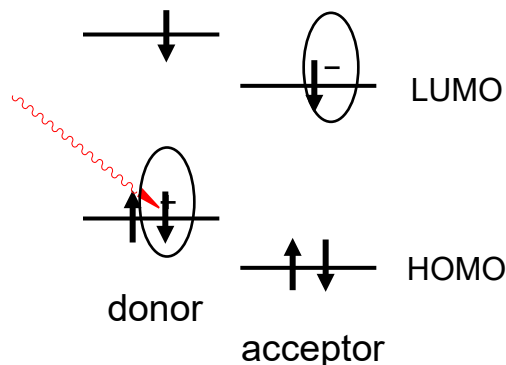
- (1) Transparent substrate
- (2) Transparent conductive anode
- (3) Electron donor
- (4) Electron acceptor
- (5) Cathode

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)

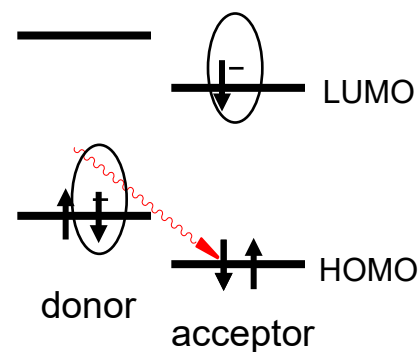
Issue: short exciton diffusion (about 10 nm)



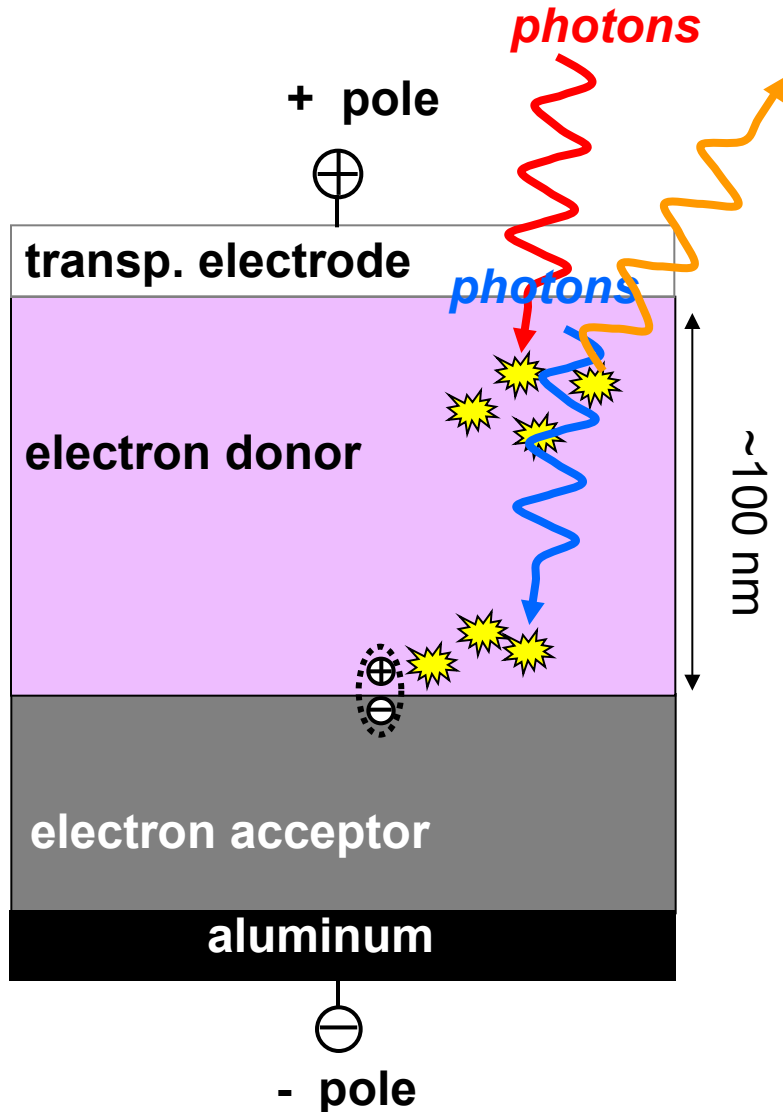
reductive electron transfer



oxidative electron transfer



The problem of the exciton diffusion length



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.

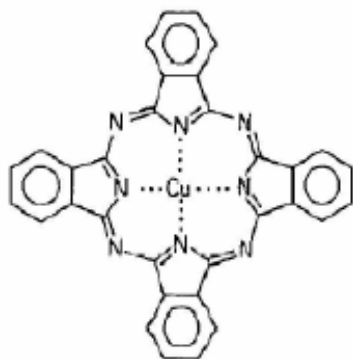
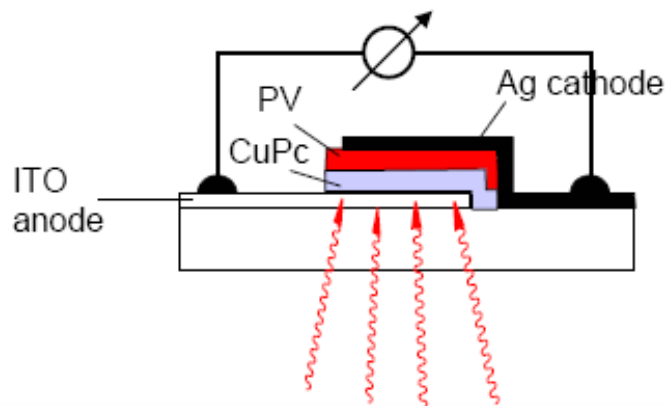
Excited states (excitons) have a lifetime of about 1 ns. During this lifetime, their diffusion length is about 5-20 nm.

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

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%

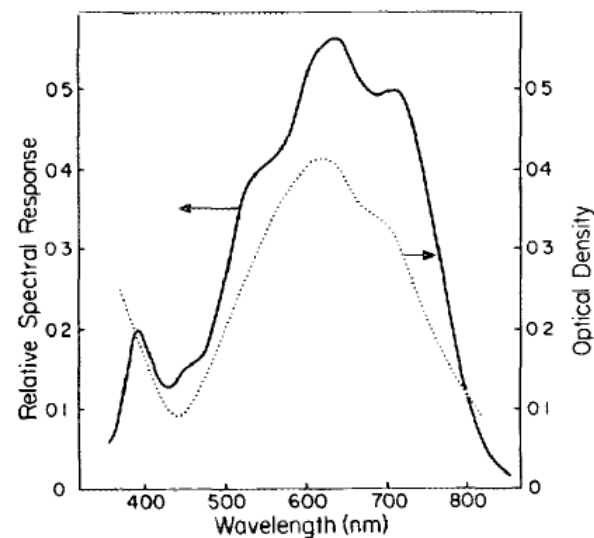
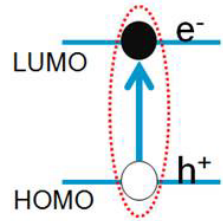


FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

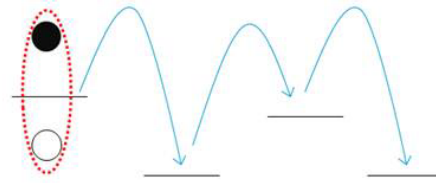
Q. Tang et al., Applied Physics Letters 48 (2), 183-185, 1986

The physics of the organic solar cell



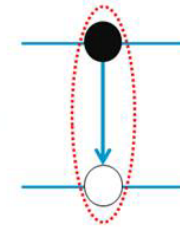
Exciton creation

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



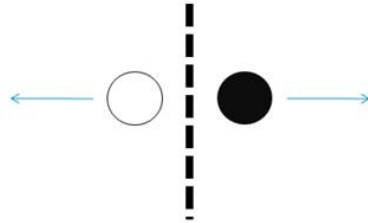
Exciton transport

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



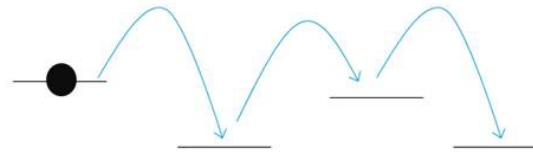
Loss mechanism: Geminate recombination

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



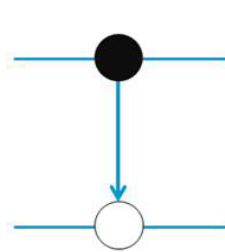
Exciton dissociation

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



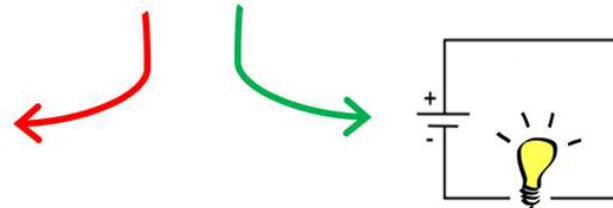
Charge transport

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



Loss mechanism: bimolecular recombination

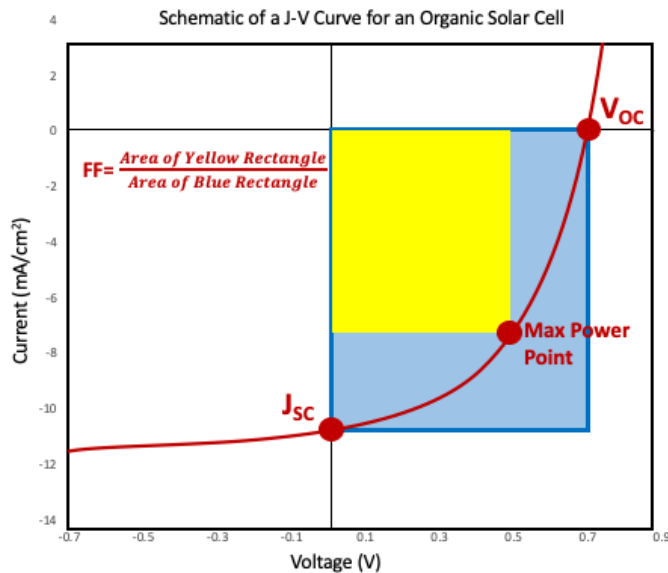
Free electrons and holes can still recombine depending on their proximity to each other.



Charge extraction

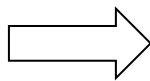
Charge carriers that reach their respective electrodes are considered extracted. An injection barrier can be included in the model.

How to design efficient organic solar cells?



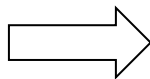
$$\eta = \frac{P_{max}}{I_{in}} = \frac{J_{mpp} V_{mpp}}{I_{in}} = \frac{J_{sc} V_{oc} FF}{I_{in}}$$

❑ Increase V_{oc} and FF



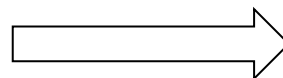
reduce recombination, optimize LUMO and HOMO levels

❑ Increase J_{sc}



increase absorption; match with solar spectrum

❑ Short exciton diffusion length

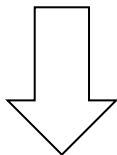
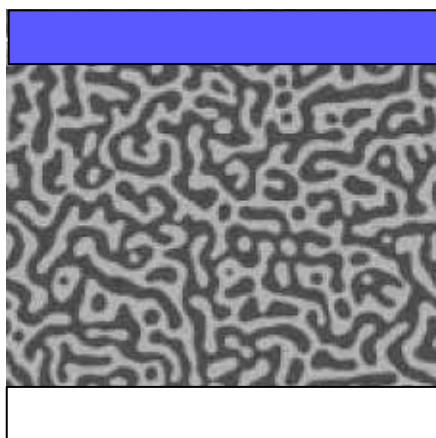


morphology

How to design efficient organic solar cells?

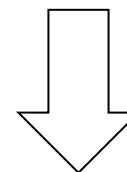
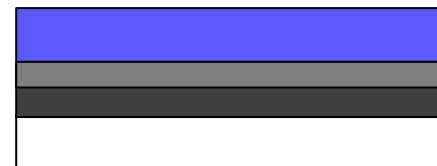
- Geometrical considerations: 2 options

Interconnected donor-acceptor phase



Phase separated bulk heterojunction
Solution processing from polymer
blends

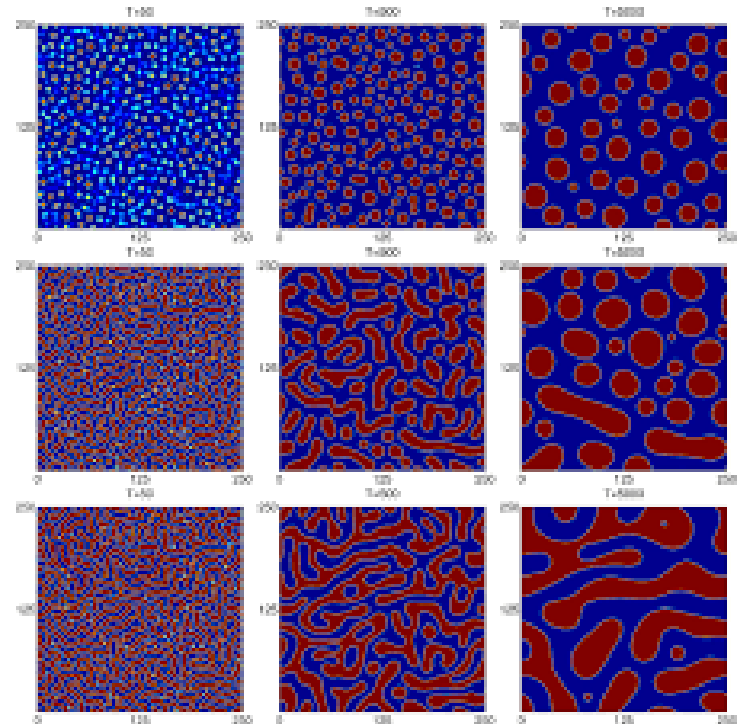
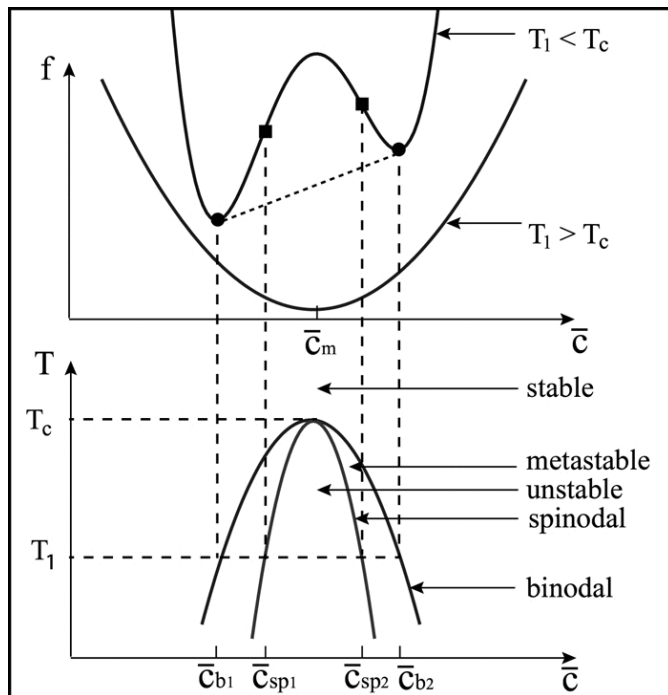
Thin films with very high
absorption coefficients



Evaporation of small molecules

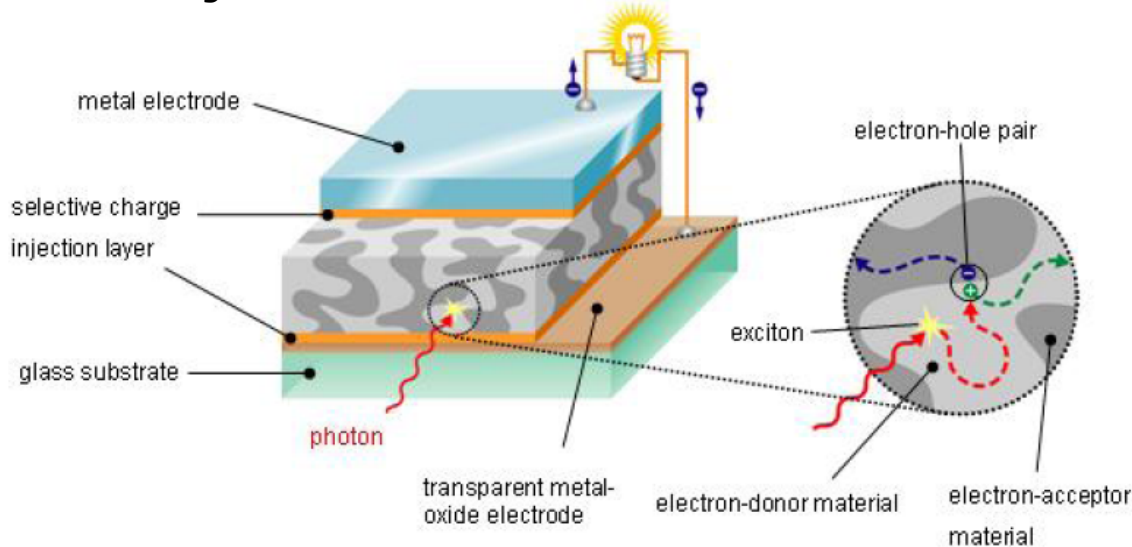
Bulk heterojunction solar cells: spinodal decomposition

- ❑ Mechanism by which a single thermodynamic phase spontaneously separates into two phases (without nucleation)
- ❑ E.g. during solvent evaporation, repulsive forces start dominating over entropic forces
- ❑ When the two phases emerge in approximately equal proportion (each occupying about the same volume or area), characteristic intertwined structures are formed that gradually coarsen



How to design efficient organic solar cells? $\eta = 4\%$

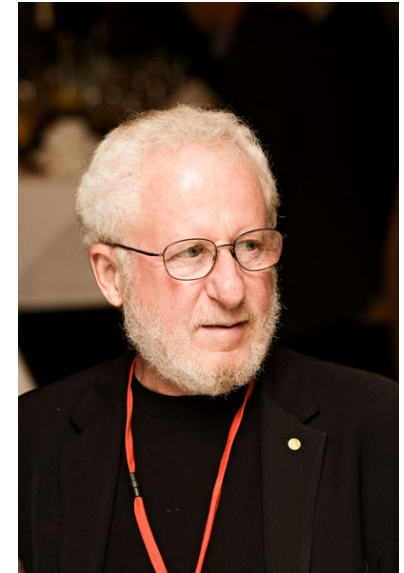
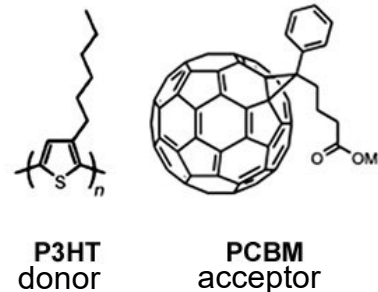
❑ Bulk heterojunction solar cells



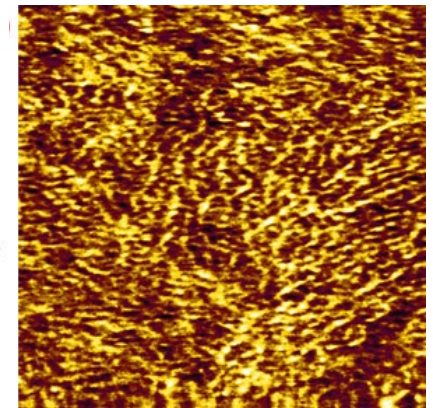
empirical estimation:

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

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.

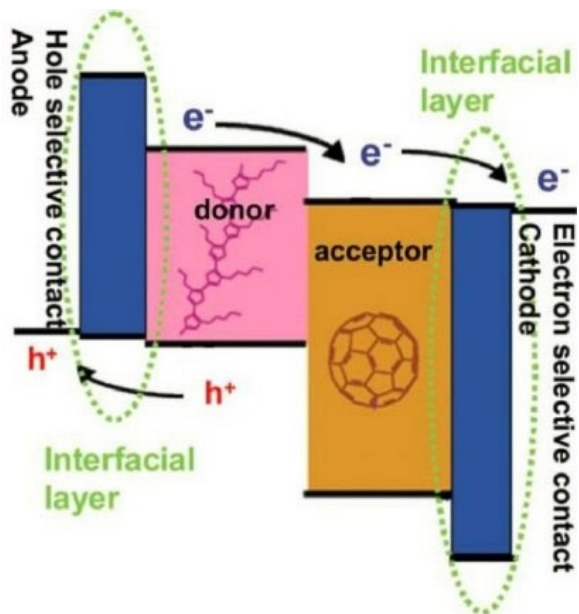


How to design efficient organic solar cells?

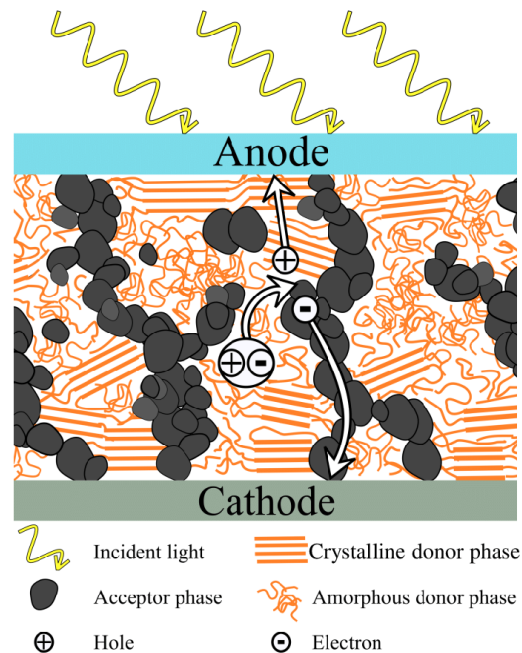
□ Energy levels of the electrodes?

Selectivity of electrode contacts is most important in bulk heterojunction.

Frequently blocking layers are introduced.



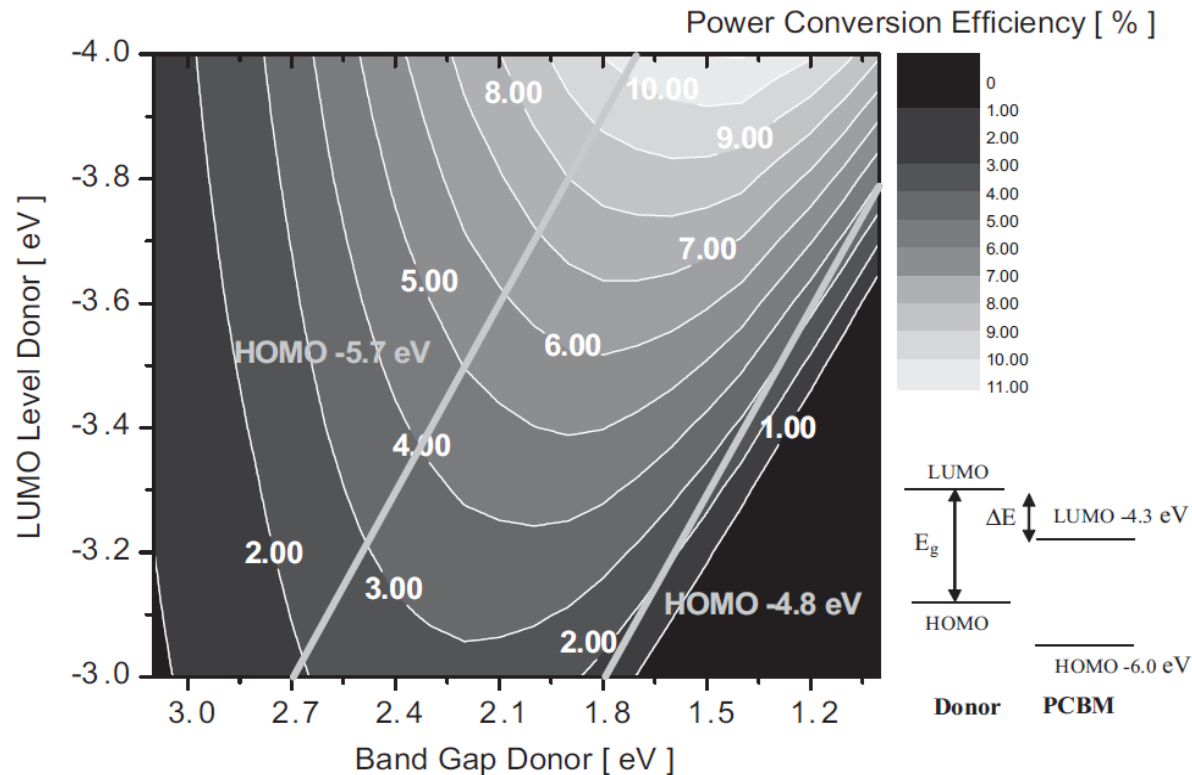
Interfacial Layer Engineering for Performance Enhancement in Polymer Solar Cells, *Polymers* 2015, 7(2), 333-372.



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? - $\eta = 10\%$

- ❑ **Challenge:** limited to PCBM: only available acceptor that is solution processible and forms bulk heterojunctions
- ❑ Optimize LUMO Level and Band Gap of donor for PCBM acceptor



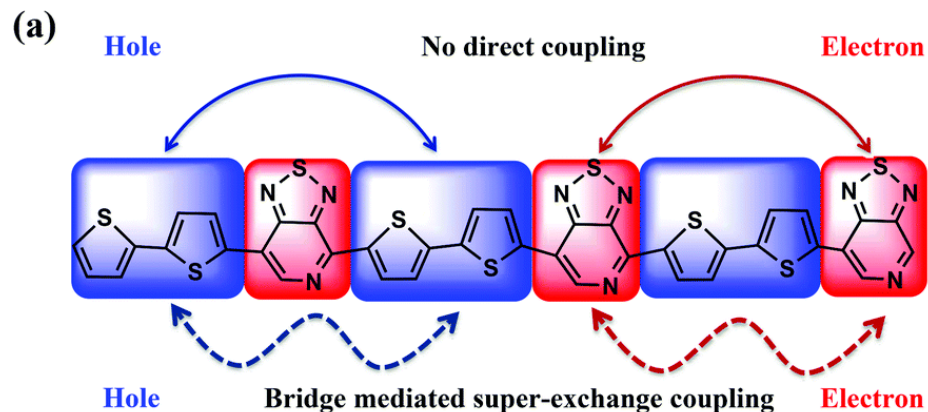
- ❑ Need for low bandgap donors!

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

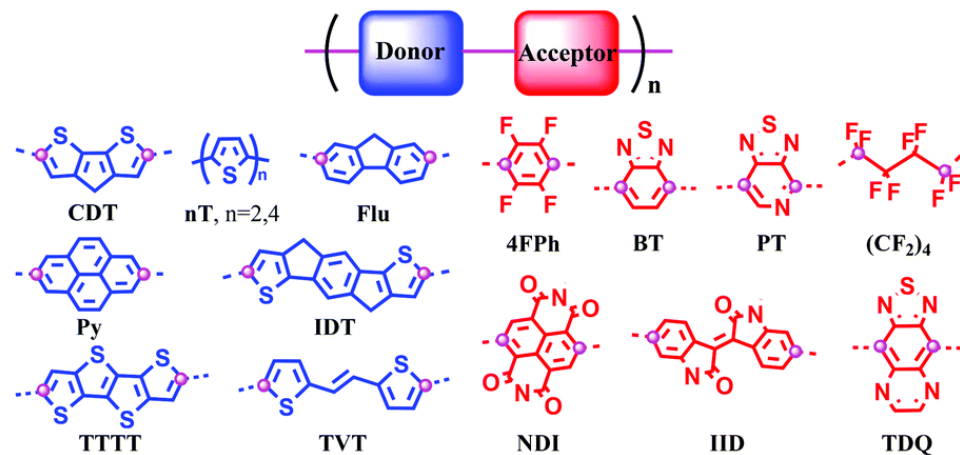
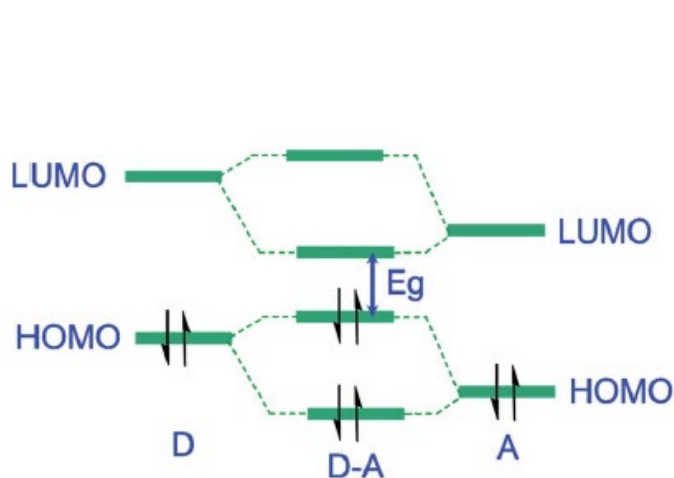
How to design efficient organic solar cells? $\eta = 13\%$

Donor-acceptor conjugated copolymers

- Designed for a blends with PC₇₁BM acceptor
- Not only the bandgap E_g is important, but also the microstructure of the blend films



(b)



PCBM bottleneck

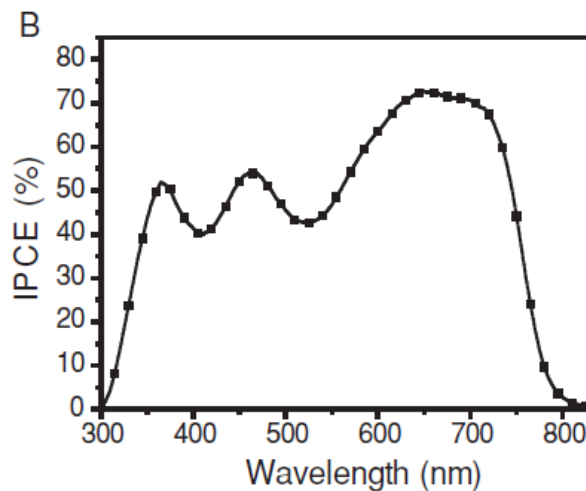
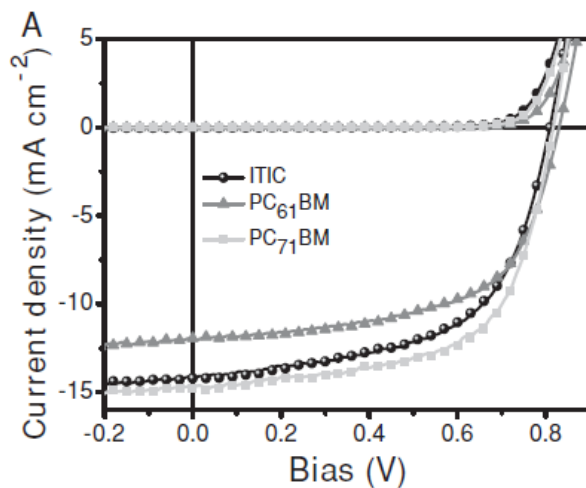
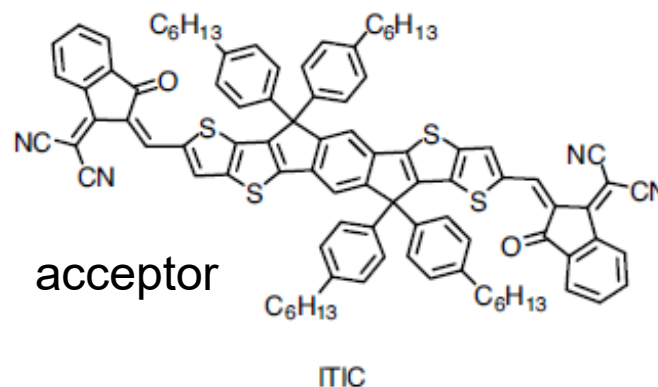
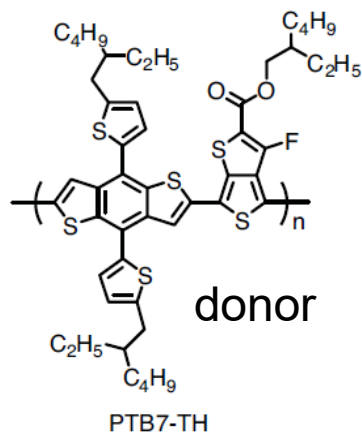
- ❑ Fullerene compounds offered certain advantages:
 - ❑ Ability to form nanoscale morphologies crucial for bulk heterojunctions
 - ❑ High electron affinity and mobility, which facilitated efficient electron capture and transport
- ❑ However, significant limitations
 - ❑ Weak absorption of solar radiation
 - ❑ High electron affinity that restricted the open-circuit voltage
 - ❑ Susceptibility to photo-oxidation
 - ❑ High synthesis and purification costs

Non-fullerene acceptors

- ❑ Easier to synthesize
- ❑ Flexible molecular design, tune active layer morphology and absorption range by incorporating:
 - ❑ Electron-deficient units (which introduce electron affinity and influence molecular packing)
 - ❑ Electron-rich units (which support charge carrier mobility and increase intermolecular interactions)
 - ❑ Side chains (crucial for tuning solubility and controlling molecular aggregation)
 - ❑ Bridging atoms (which can provide electron-donating character and modulate HOMO energy levels)

Non-fullerene acceptors? $\eta = 6.8\%$

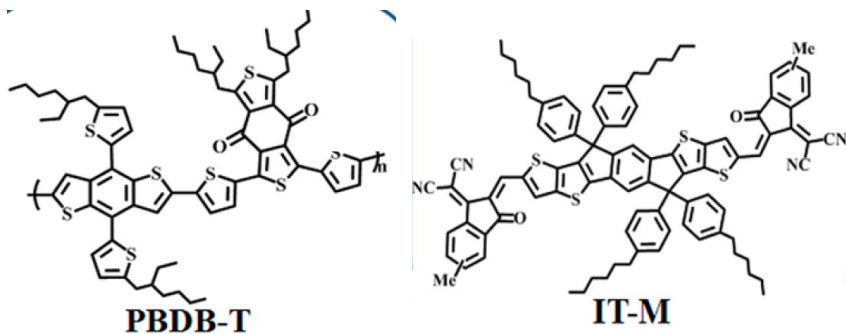
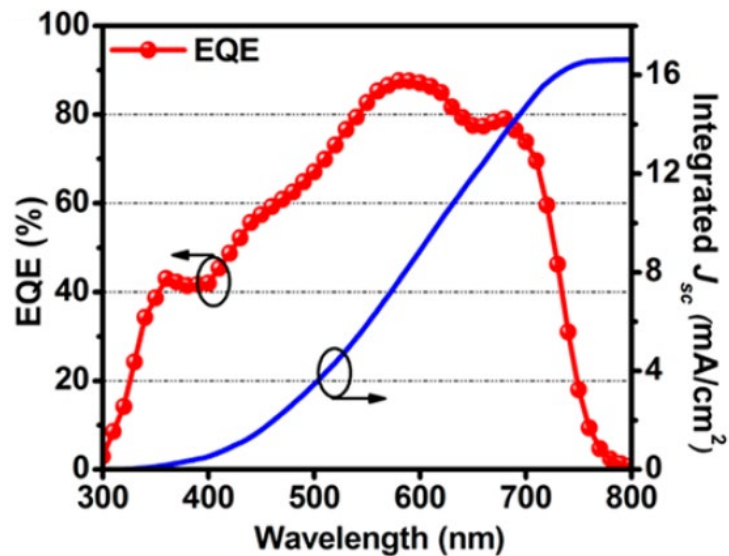
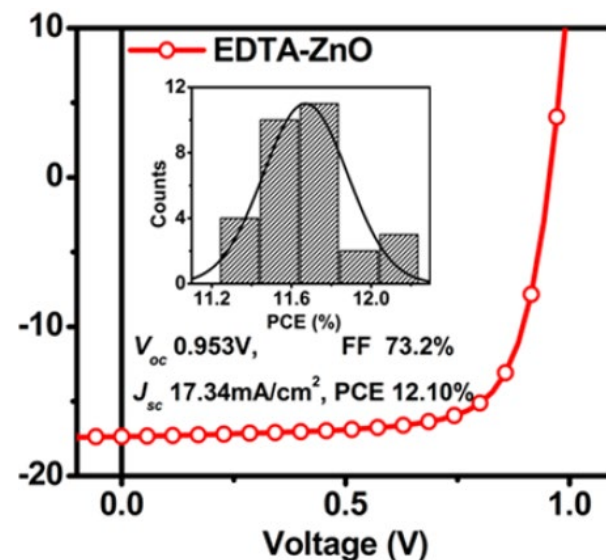
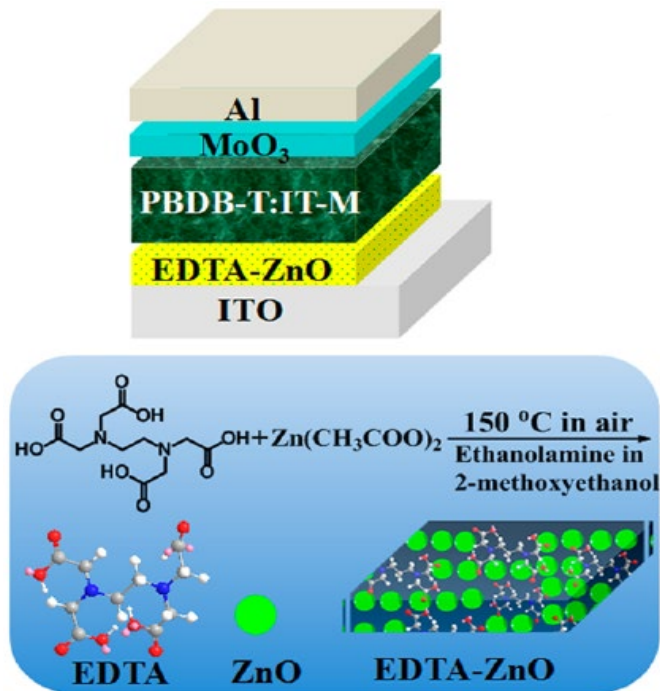
- First success story with ITIP: broad absorption between 500 – 800 nm



- As a consequence: large band-gap donors needed

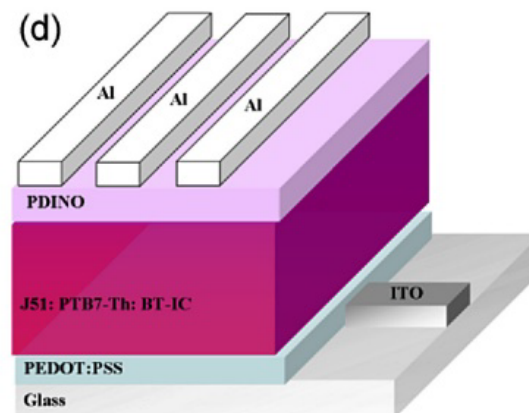
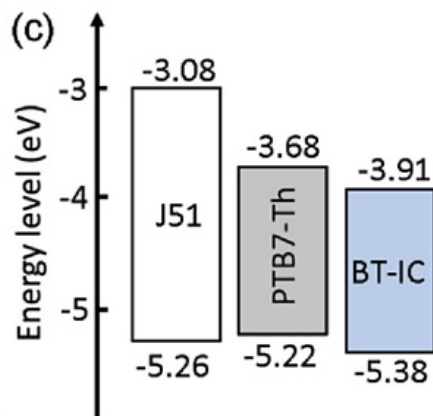
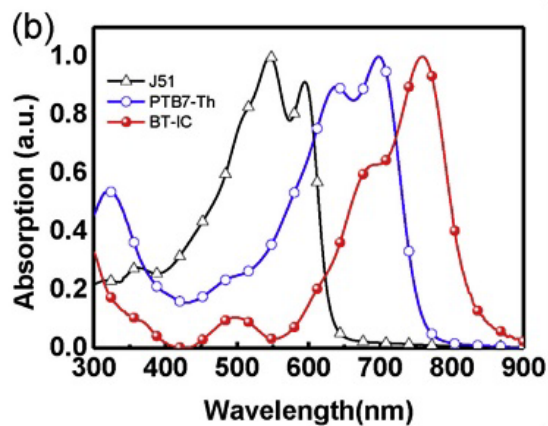
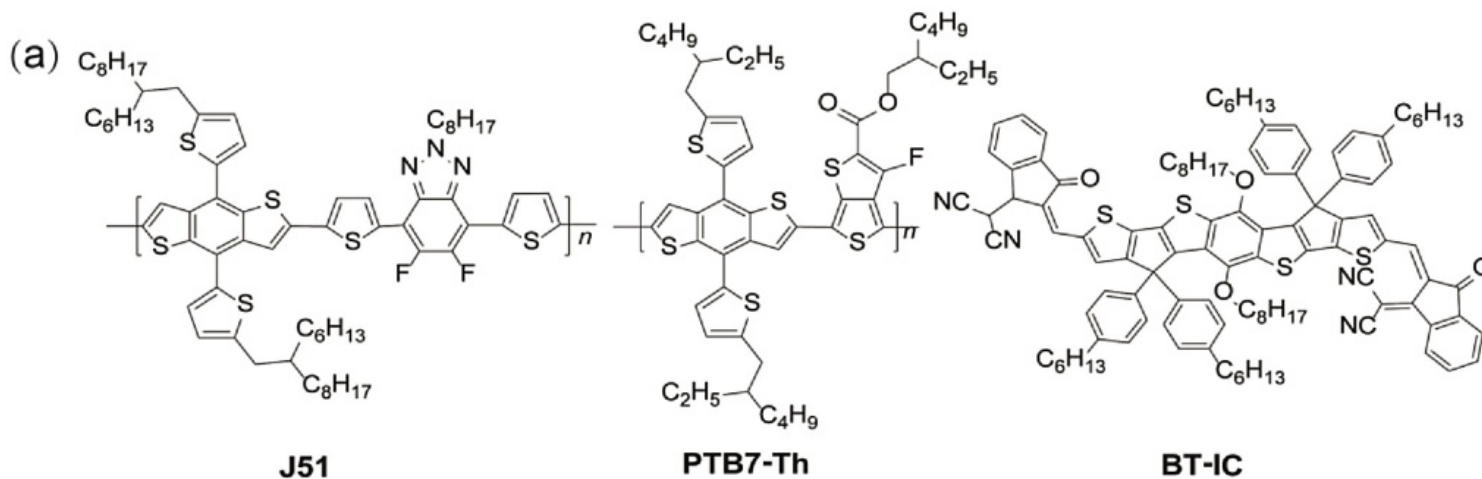
Non-fullerene acceptors expand absorption into the NIR

$\eta > 12\%$



How to design efficient organic solar cells? $\eta = 10.3\%$

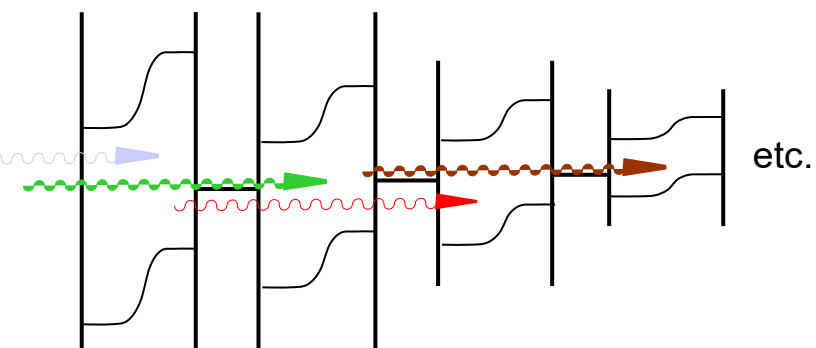
□ Ternary blends – can expand the absorption range



How to design efficient organic solar cells?

Multi-junctions

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



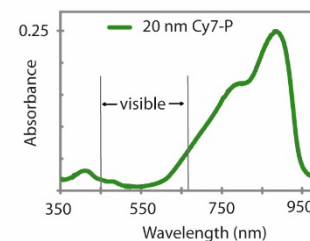
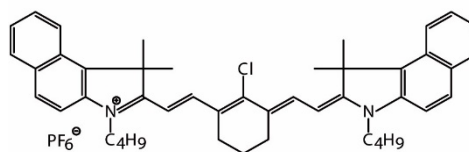
Ideal bandgaps:

1 junction (1.35 eV): 31%

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

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

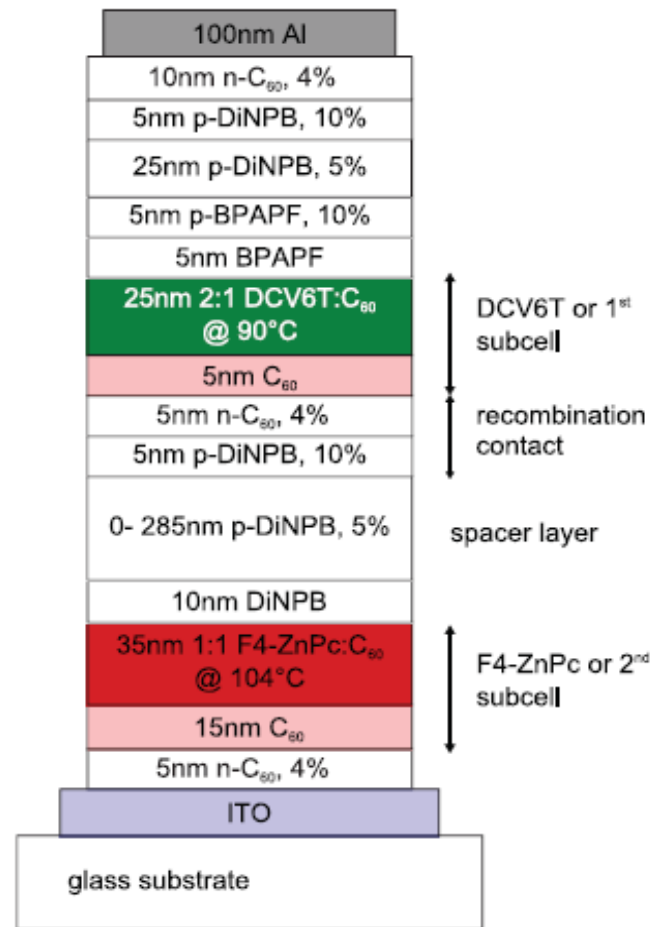
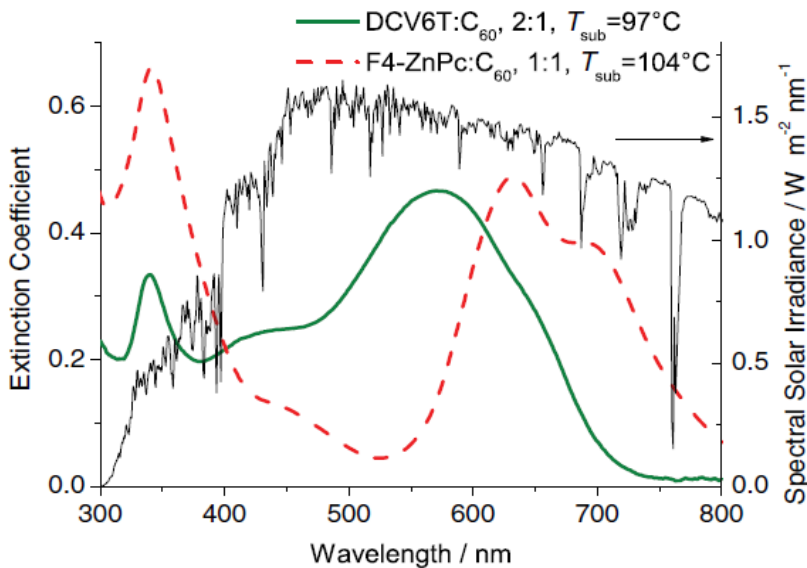
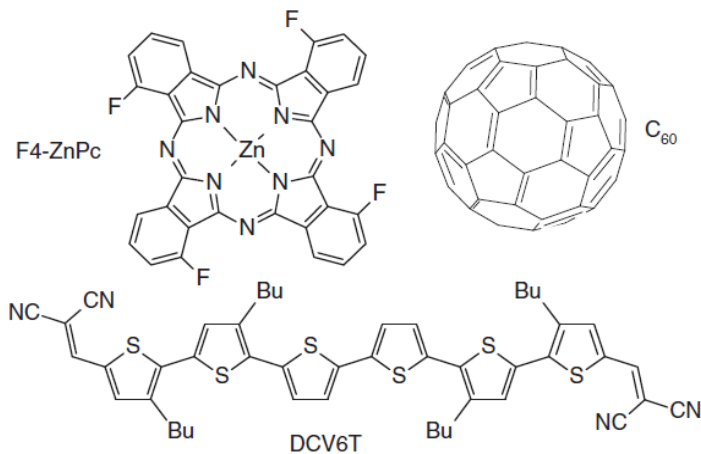
36 junctions: 72%



The solar cell absorbs solely in the NIR domain

How to design efficient organic solar cells? $\eta = 6.1\%$

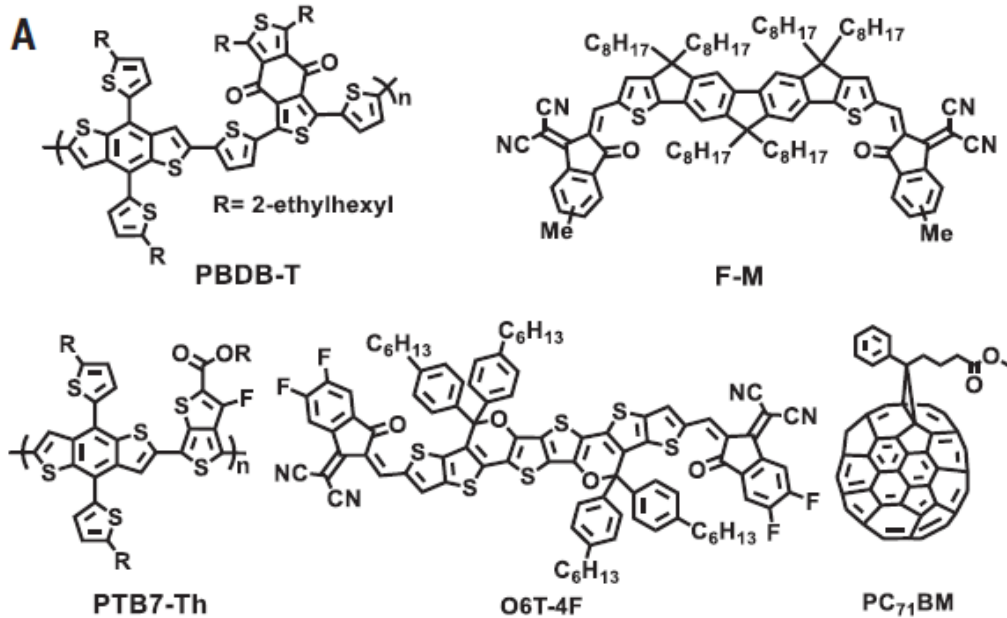
Match solar spectrum – small molecule multijunction cell



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

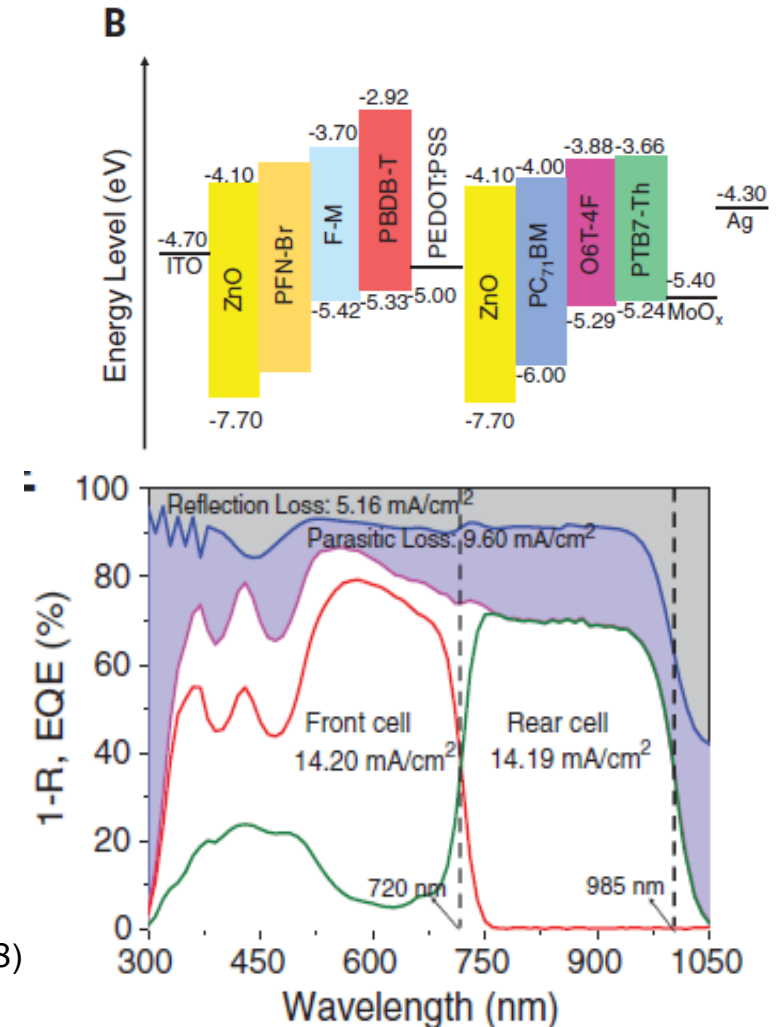
How to design efficient organic solar cells? $\eta = 17.3\%$

Organic and solution-processed tandem solar cells



- Broad band absorption
- Perfect current matching
- Optical optimization

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



Record cells?

Received: 9 October 2023

Accepted: 17 October 2023

DOI: 10.1002/pip.3750

SHORT COMMUNICATION



Solar cell efficiency tables (Version 63)

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.
Organic (thin-film)	19.2 ± 0.3^q	0.0326 (da)	0.9135	26.61^m	79.0	NREL (3/23)	SJTU ⁴¹

How to design efficient organic solar cells? $\eta = 18.0\%$

Record cells

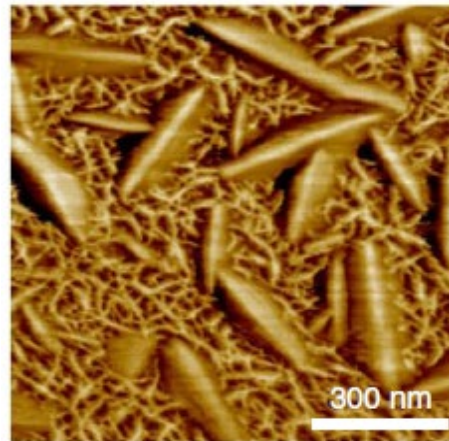
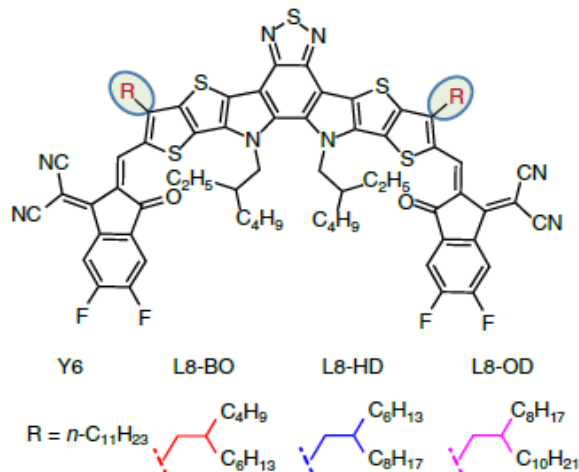


ARTICLES

<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



How to design efficient organic solar cells? $\eta = 19\%$

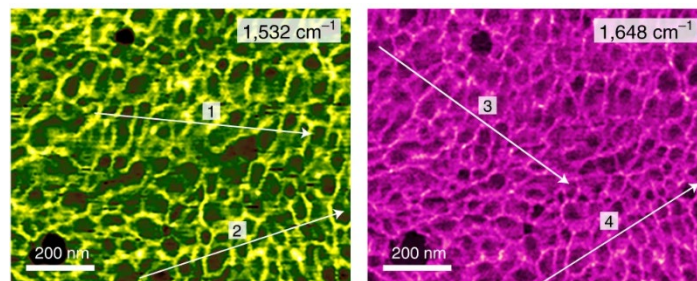
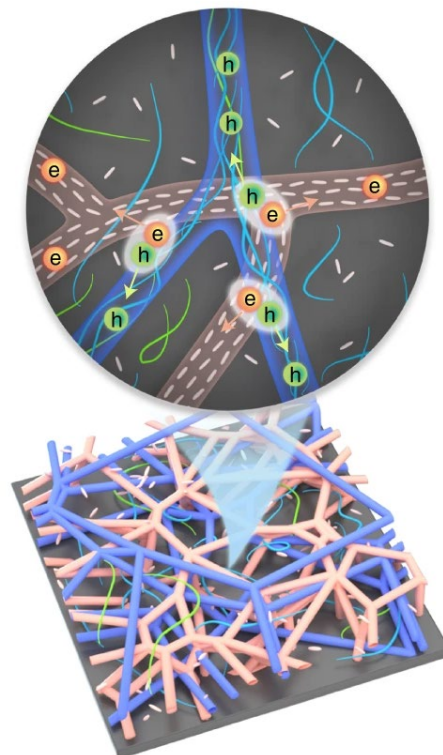
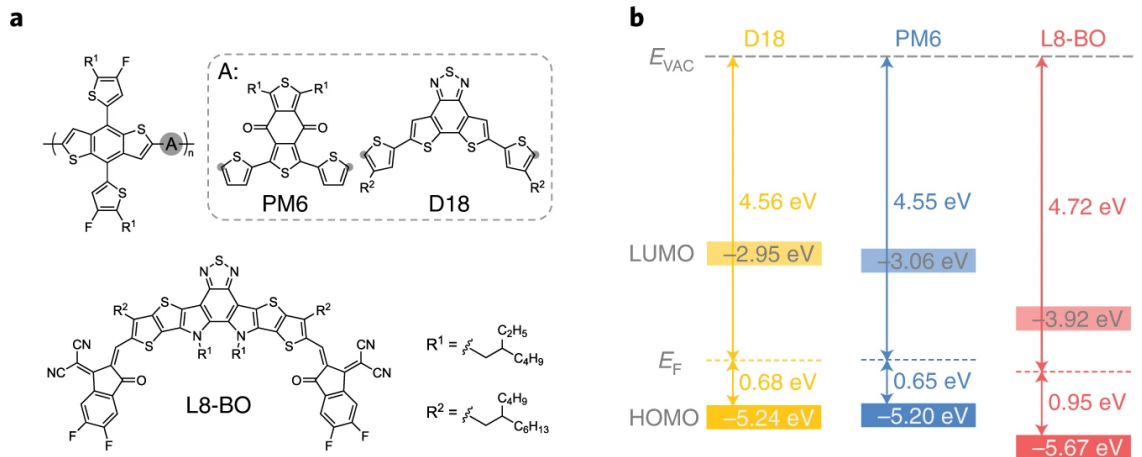
ARTICLES

<https://doi.org/10.1038/s41563-022-01244-y>

nature
materials

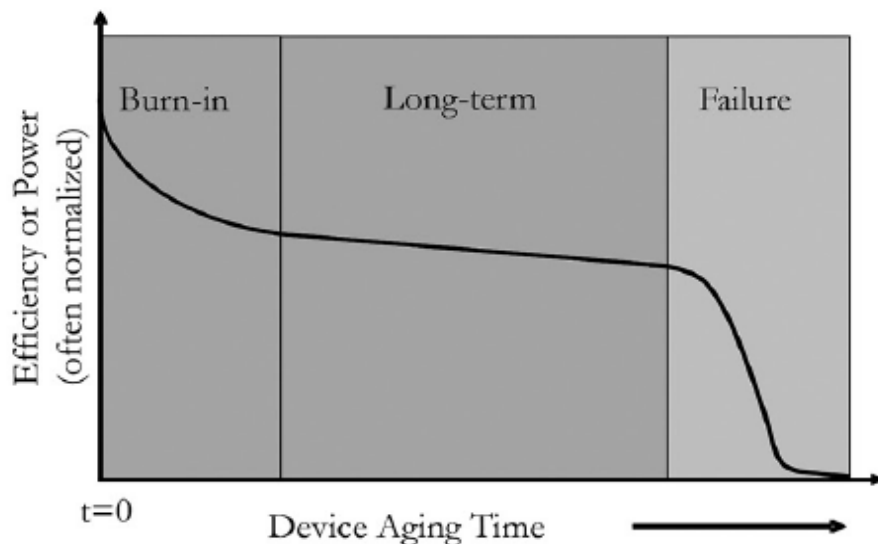
Check for updates

Single-junction organic solar cells with over 19% efficiency enabled by a refined double-fibril network morphology



Stability / degradation

□ Three different regimes



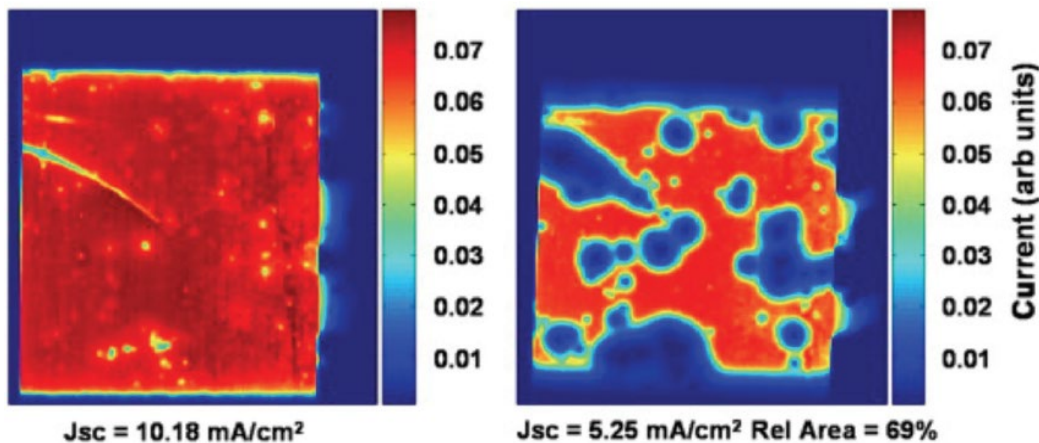
- Photo-induced burn-in: Initial exponential degradation
- Long-term regime: Continuing degradation
- Failure: Rapide and complete device degradation

□ Different stress factors

- Thermal and light stress (extrinsic)
- Water and oxygen from atmosphere (extrinsic)
- Mechanical stress (extrinsic)
- Morphological changes (intrinsic in the dark)
- Electrochemical reactions (intrinsic under light)

Stability / degradation

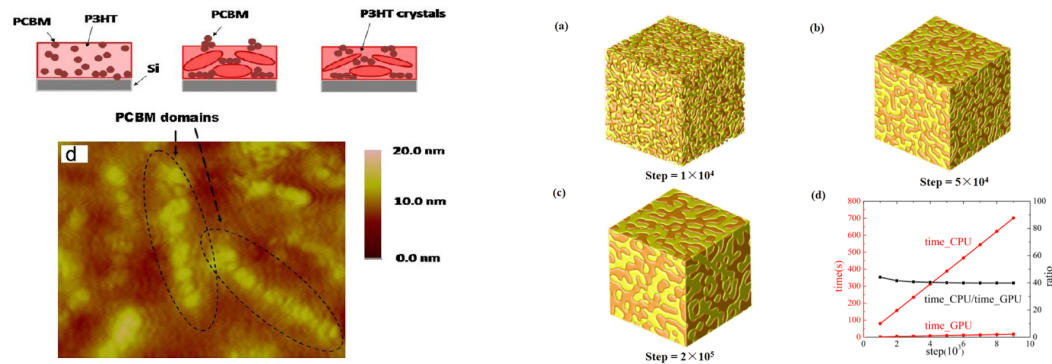
- ❑ Extrinsic degradation
 - ❑ Low work function metals oxidize when exposed to atmosphere (even in the dark)
 - => encapsulation, inverted geometry
 - ❑ Photooxidation causes organic films to loose optical density, via a free-radical reaction
 - => encapsulation
 - ❑ Mechanical failure (delamination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



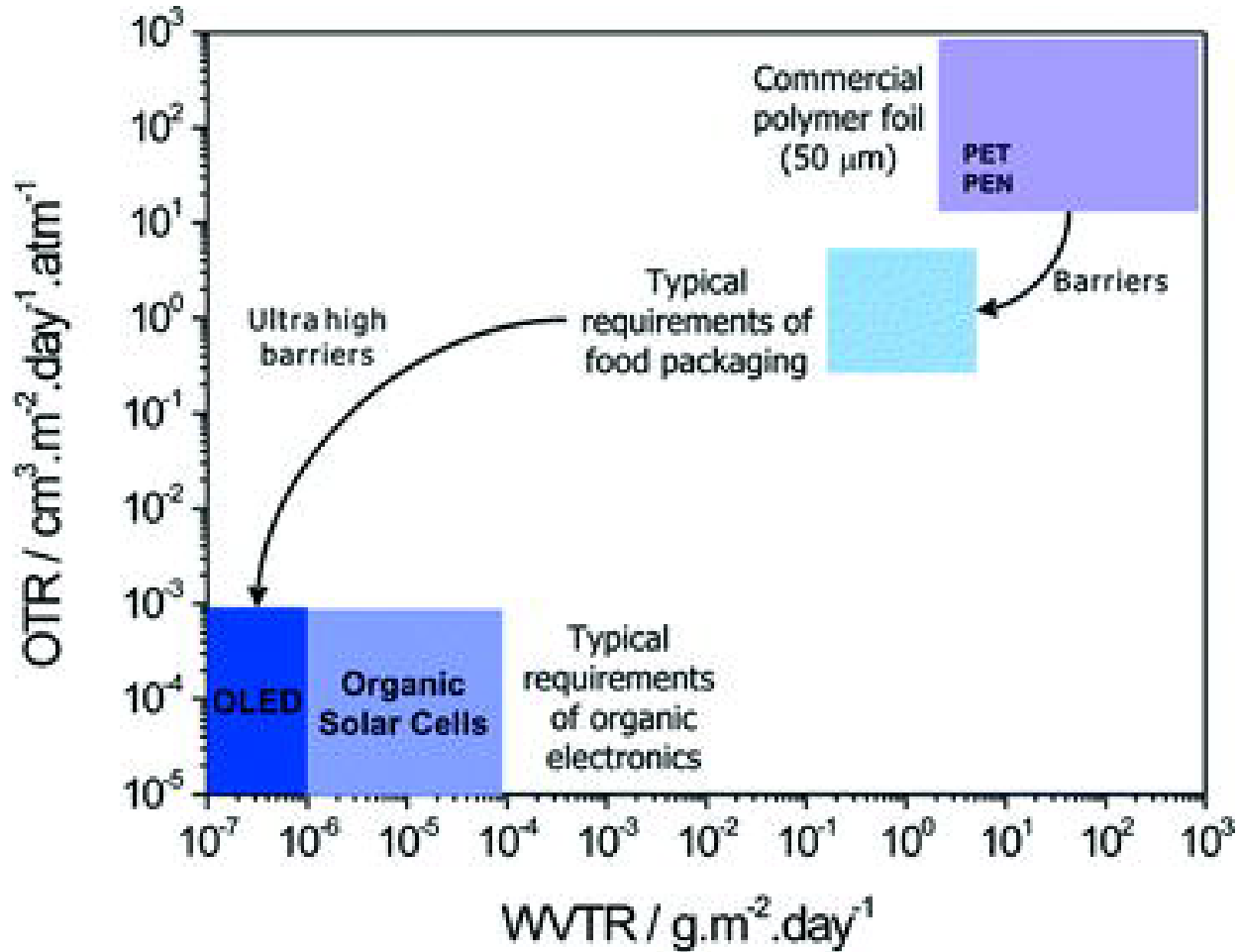
Solar Energy Materials & Solar Cells 107 (2012) 112–124

AIP Advances 7 (2017) 105216

⇒ Incorporation of specific cross-linking agents, such as the six-bridged azide cross-linker

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

Encapsulation

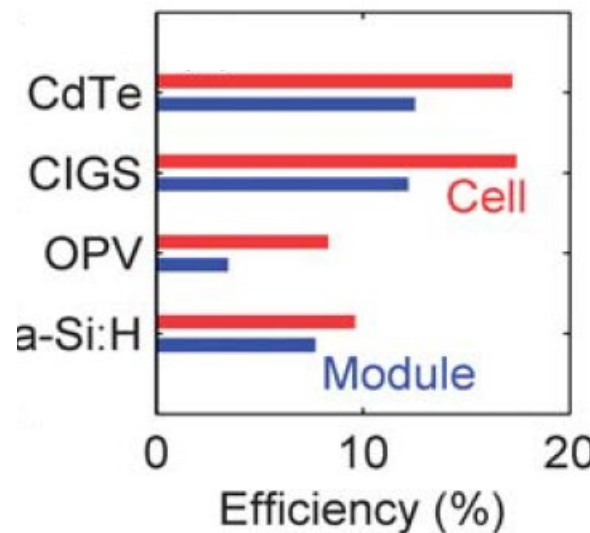
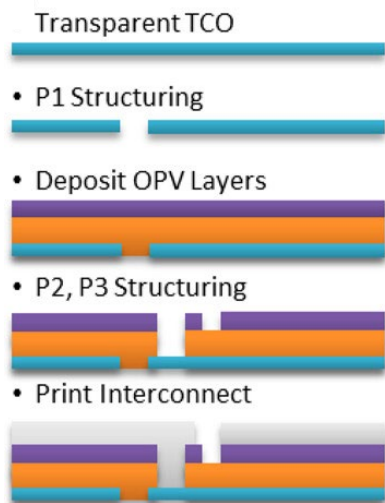
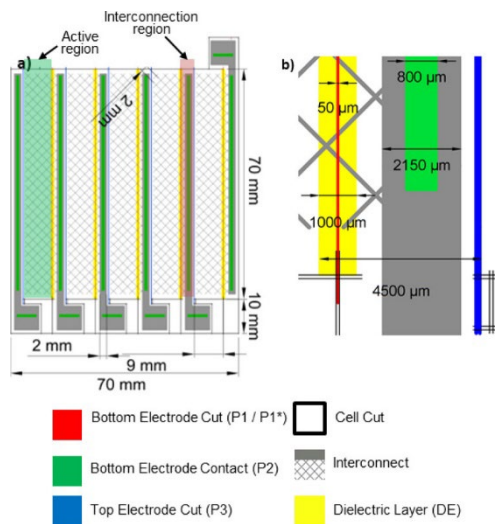


Waldauf C., et al. (2009) Bulk Heterojunction Solar Cells for Large-Area PV Fabrication on Flexible Substrates. In: Wong W.S., Salleo A. (eds) Flexible Electronics. Electronic Materials: Science & Technology, vol 11.

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/m²) 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,l}	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,l}	69.3	FhG-ISE (10/19)	ZAE Bayern (33 cells) ²⁰

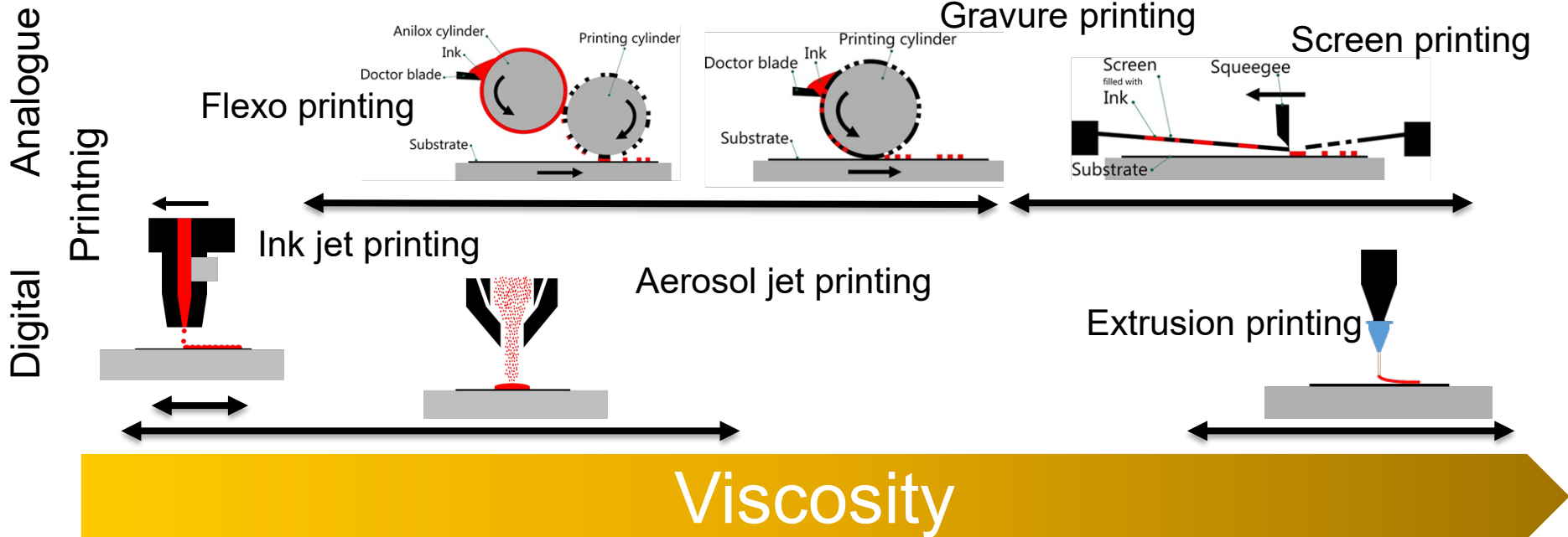
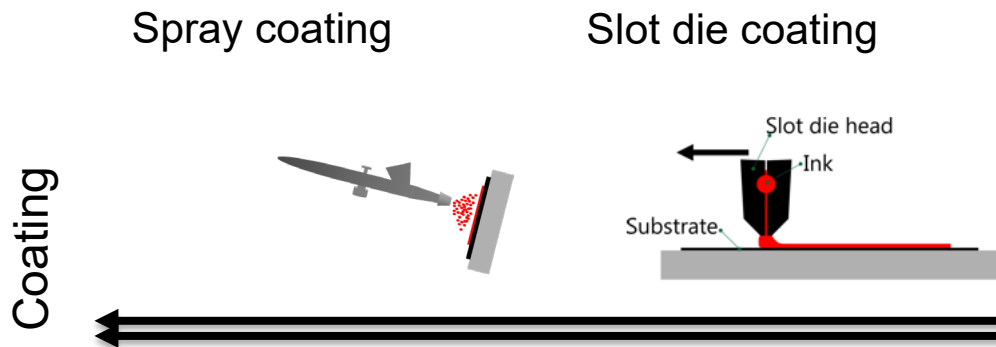
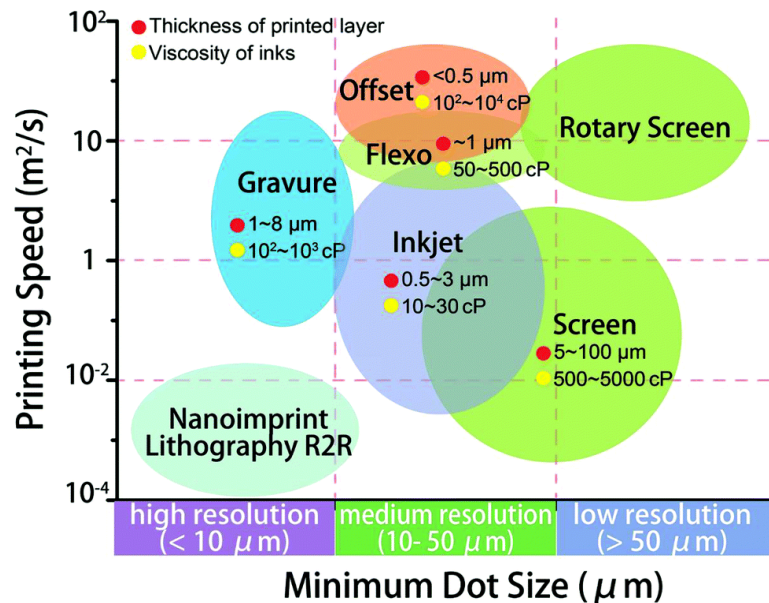


ACS Appl. Electron. Mater. 2020, 2, 756–762

Energy Environ. Sci., 2013, 6, 782

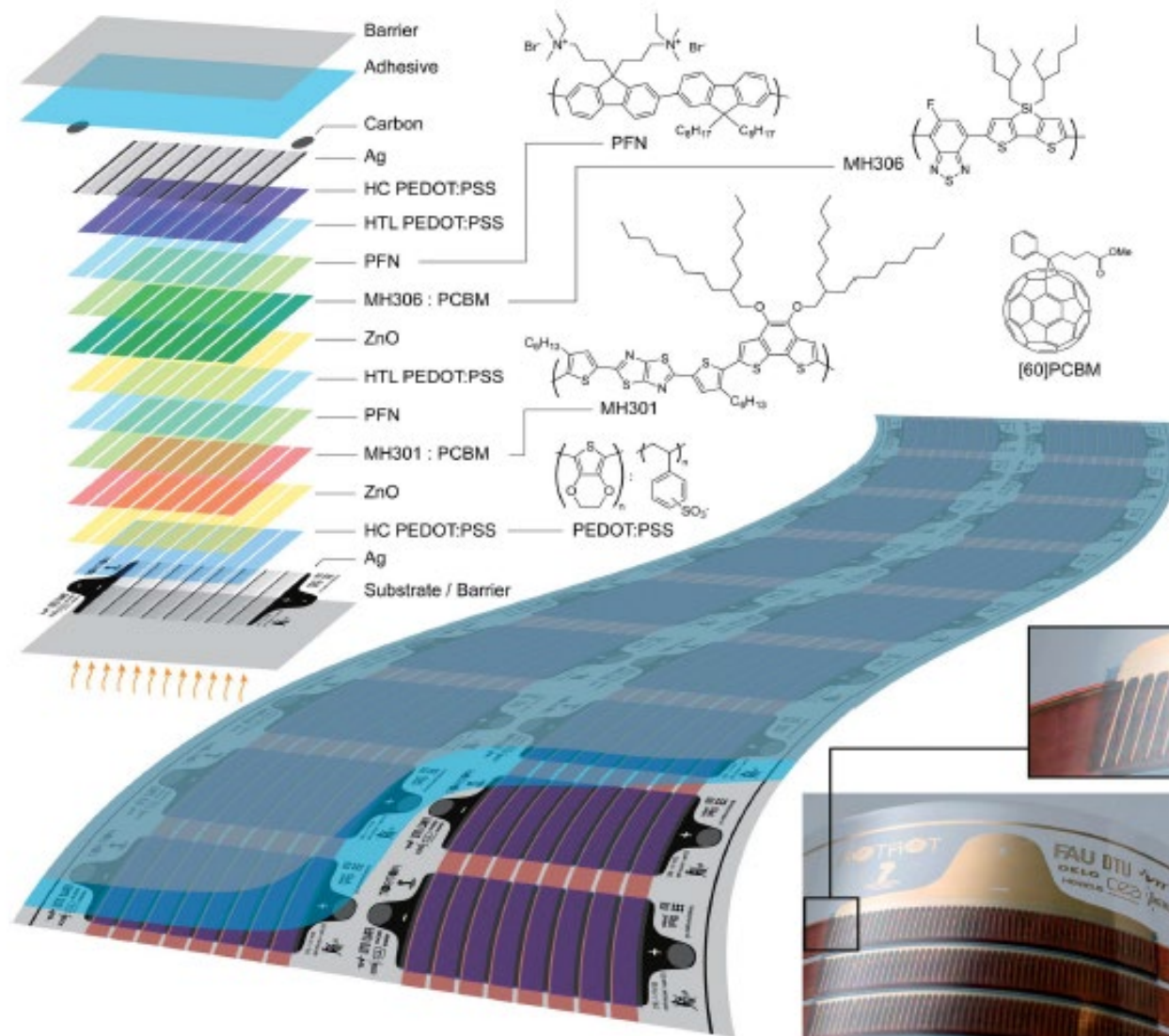
Printing and coating techniques

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

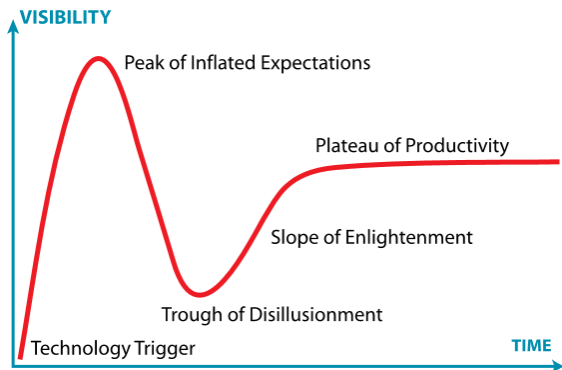


Scalable, ambient atmosphere roll-to-roll manufacture of encapsulated large area, flexible organic tandem solar cell modules

Energy Environ. Sci., 2014, 7, 2925



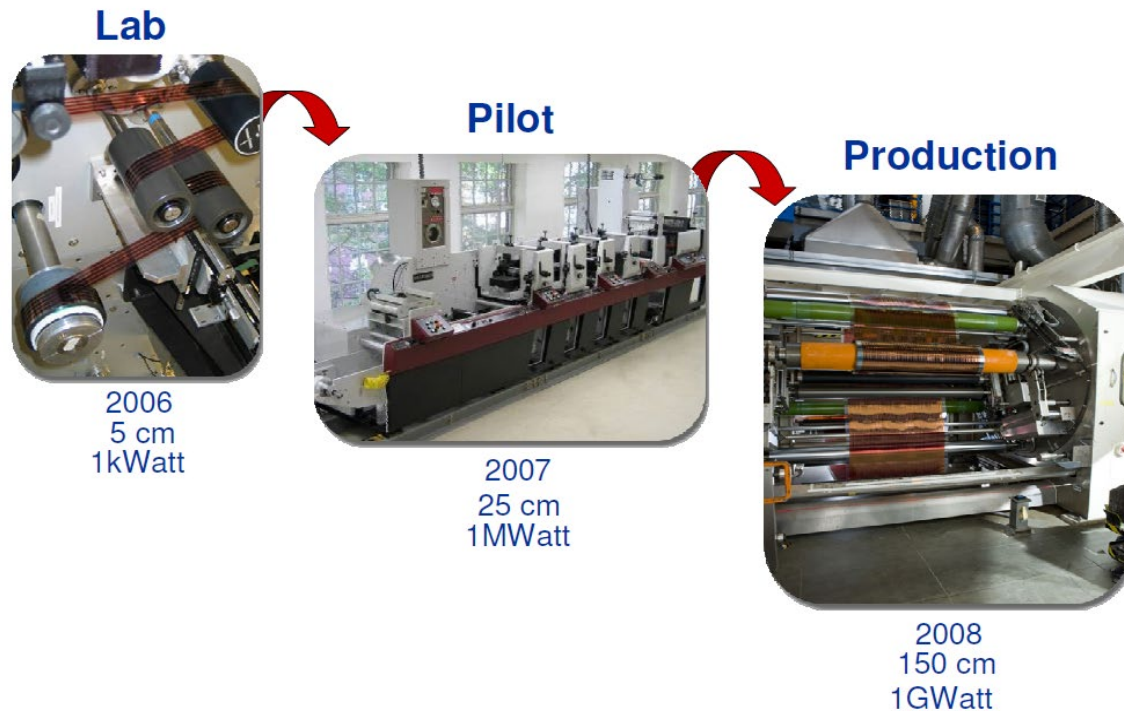
Printed organic solar cells: Trough of Disillusionment



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.

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



Solar Power Standard 2W



Rollable power supply



Shading elements

A look at the market

- Any market research report will give you some numbers



Applications

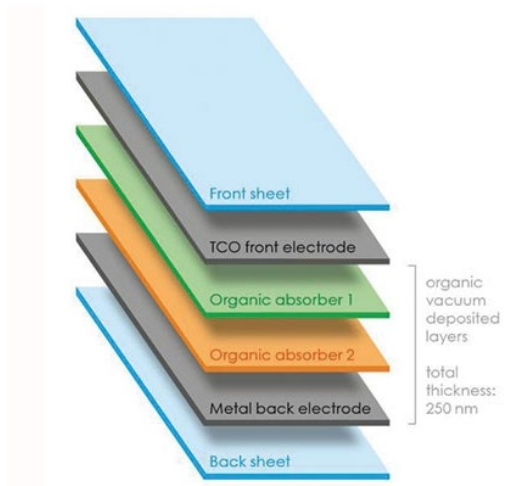
- ❑ **Emerging Niche Applications:** OSCs are uniquely suited for producing thin-film devices, which enables highly flexible designs and semi-transparent window coverings. This versatility has led to their adoption in a wide array of emerging niche applications:
 - ❑ **Building-Integrated Photovoltaics (BIPV):** A prominent application segment, accounting for 35.09% of the market share in 2023.¹⁶ Semi-transparent OSCs (ST-OSCs) are particularly ideal for photovoltaic windows, capable of generating electricity while allowing light transmission
 - ❑ **Flexible/Wearable Electronics:** Their lightweight and mechanical flexibility make OSCs highly suitable for integration into wearable devices, including smart textiles and skin-compatible sensors.
 - ❑ **Portable Devices:** OSCs are also being developed for portable electronic devices and off-grid power solutions.
 - ❑ **Indoor Applications:** A significant niche is indoor applications, where OSCs are optimized for low-light conditions, powering devices such as sensors, electronic shelf labels (ESLs), and remote controls.

Companies

Company Name	Market Share (%) (Est.)	Estimated Revenue (2023)	Key Applications/Innovations
Heliatek GmbH	20%	USD 250 million	Flexible, ultra-thin solar films for BIPV, automotive, consumer electronics; low manufacturing costs, small carbon footprint
BELECTRIC OPV GmbH	15%	USD 190 million	Customizable OPV modules for smart textiles, automotive surfaces, architectural designs; adaptable, lightweight, curved, semi-transparent
Disa Solar	12%	USD 150 million	Off-grid power solutions, portable solar applications, urban infrastructure; pioneers roll-to-roll production for lower costs
Epishine	N/A	USD 9.6 million (Annual)	Indoor solar cells for sensors, smoke detectors, asset trackers, remote controls, electronic shelf labels; enables self-powered products, cuts battery waste

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”



Needed for lab-to-fab transfer of OPV technology

- ❑ **Upscaling of ITO-based single cells** and interconnection into large area modules: There is a need for strategies to upscale individual cells and modules of serially connected cells while minimizing performance losses.
- ❑ **Alternatives to vacuum processing:** Top (back) metal electrodes are commonly deposited by thermal evaporation under vacuum, which restricts high-throughput manufacturing and increases costs.
- ❑ **Alternatives to ITO-based substrates:** Indium-tin-oxide (ITO) is widely used but is expensive, scarce, and has modest conductivity and mechanical flexibility, making it unsuitable for flexible and large-area applications.
- ❑ **Improving lifetime of large area cells and modules:** The operational lifetimes of large area devices are currently significantly lower than the market requirement of ≥ 10 years, necessitating new encapsulation strategies.
- ❑ Use of **green solvent formulations:** Upscaling requires replacing toxic halogenated solvents (typically used in small-scale development).
- ❑ Development of **new molecularly engineered donor and acceptor materials**

Before achieving full commercial viability

- ❑ **Enhancing long-term durability and reliability:** Bridging the performance gap with traditional silicon PV (which offers 25-year warranties) remains a significant hurdle. This necessitates continued research into encapsulation, intrinsic material stability, and mechanical robustness under prolonged environmental exposure.
- ❑ Achieving **cost-effective scalability** for mass production: Overcoming manufacturing complexities such as the need for alternatives to ITO and vacuum processing, ensuring film homogeneity over large areas, and transitioning to widespread use of green solvents are crucial for reducing production costs.
- ❑ Optimizing **efficiency for large-area devices:** Maintaining high PCEs achieved at laboratory scale when translating to larger modules is an ongoing challenge due to electrical losses and film quality variations.
- ❑ Deeper **understanding of degradation mechanisms:** Continued fundamental research into the precise chemical and physical pathways of degradation is essential to design more intrinsically resilient materials and devices.
- ❑ **Bridging the "valley of death":** The transition from laboratory breakthroughs to industrial-scale production without sacrificing performance remains a critical barrier.

2.2A Organic Photovoltaics (OPV)

Learning outcome

❑ Motivation

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

❑ History

- *Long development phase, tackle one bottleneck after the other*

❑ 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 devices*

❑ What strategies are followed to improve the efficiency

- Donor-acceptor polymers, complementary absorption donor-acceptor, expand to NIR, non-fullerene acceptors, tandem cells

❑ State-of-the art

- 19.2% efficiency, pilot plants for printing

❑ Current research directions

- Stability and upscaling

2.2B Dye sensitized solar cells (DSSC)

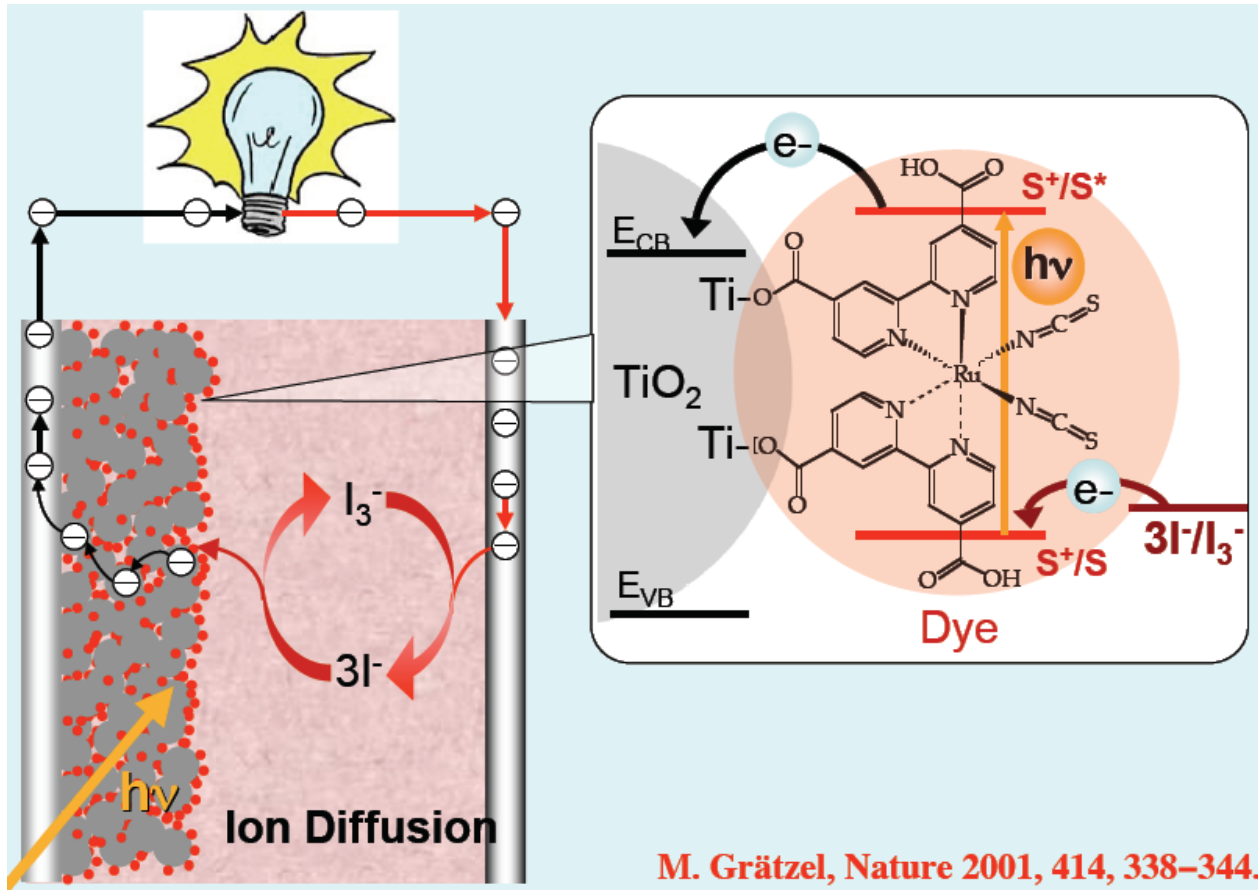
Learning goals

- ❑ 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 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

Working principle of DSSC



*M. Grätzel, EPFL
Dye sensitized
Solar cells*

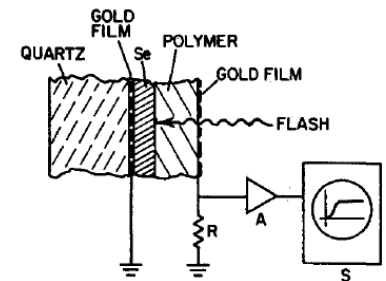
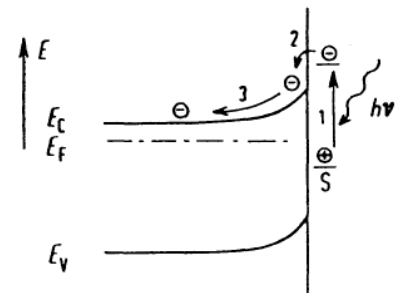
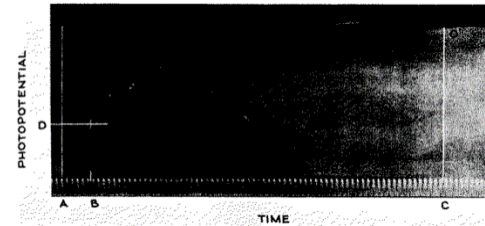
Important milestones in dye sensitization and DSSCs

1839 Bequerel discovers the photovoltaic effect

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

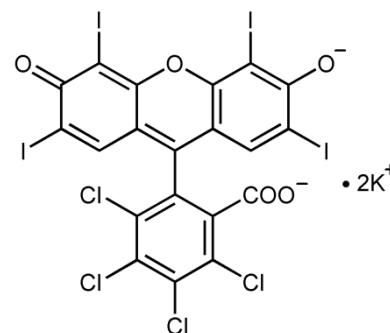
1940 S. E. Sheppard, W. Vanselow, G. P. Happ
Photovoltaic cells with AgBr Electrodes, J. Phys. Chem., 44, 4, 411-421

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



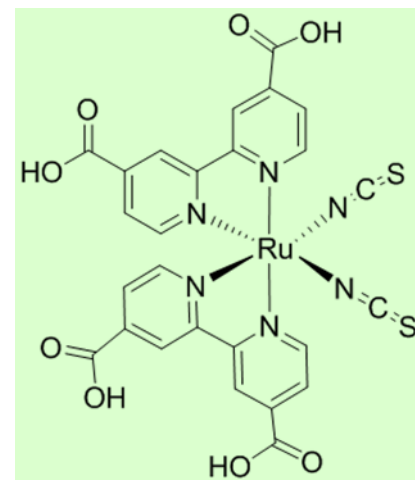
Important milestones in dye sensitization and DSSCs

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 TiO₂ surfaces.

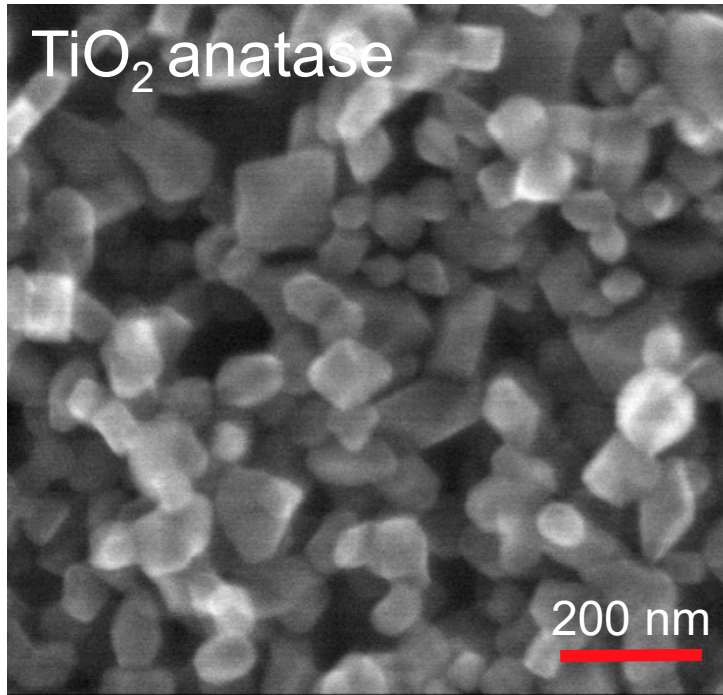
1985 Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. Highly Efficient Sensitization of Titanium Dioxide. Colloidal Nanoparticles, *J. Am. Chem. Soc.* 1985, 107, 2988–2990



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

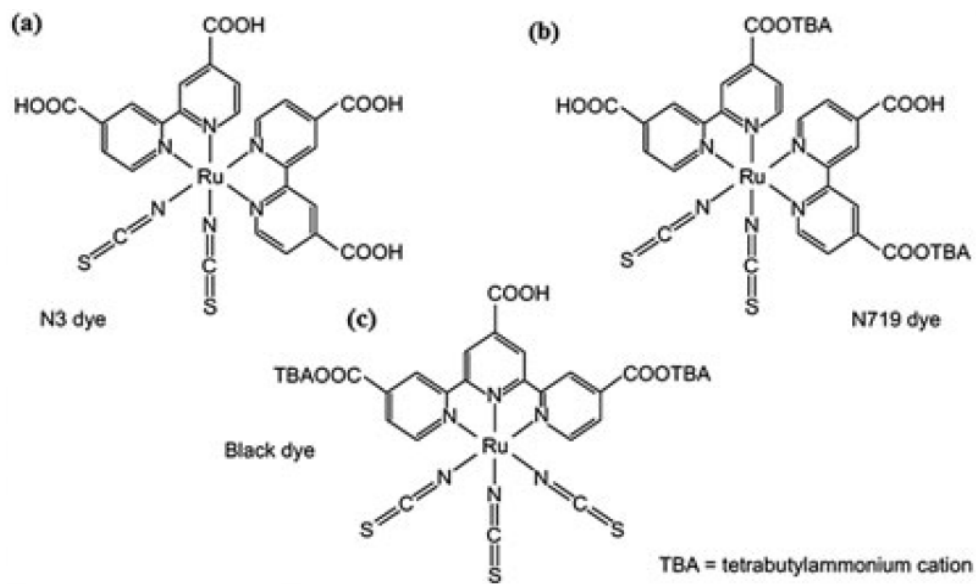
3. The insulating nature of the oxide nanocrystals prevents energy transfer quenching of the excited sensitizer by conduction band electrons

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

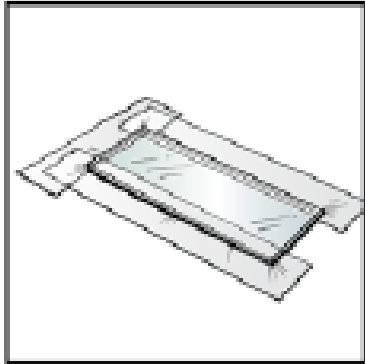


Abb. 1

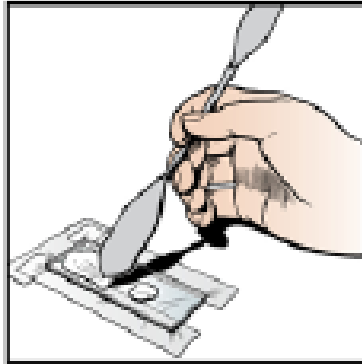


Abb. 2

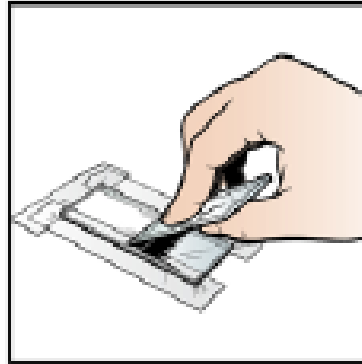


Abb. 3



Abb. 4

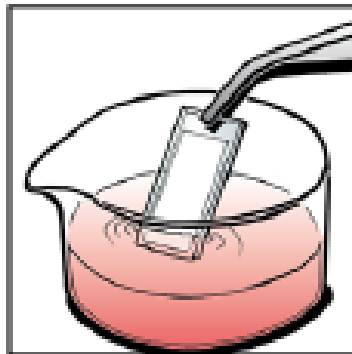


Abb. 5



Abb. 6

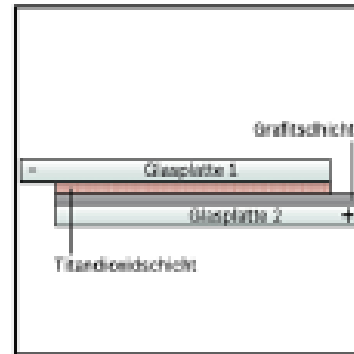


Abb. 7

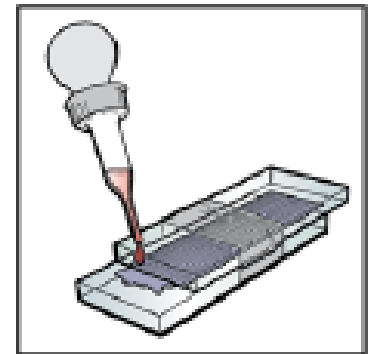


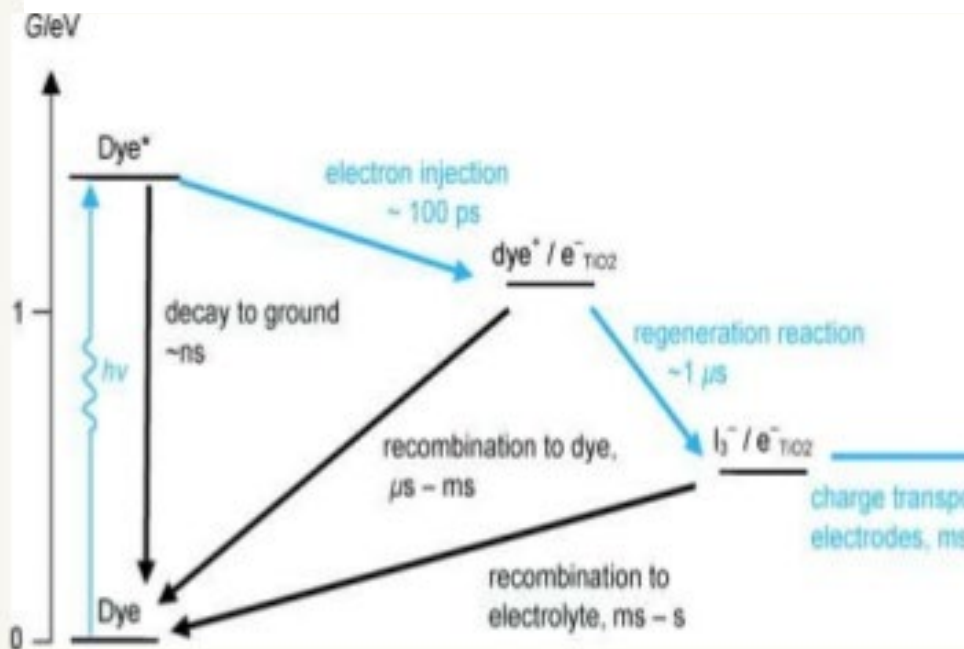
Abb. 8

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 μs)
 $\text{Dye}^* + e^-_{\text{TiO}_2} \rightarrow \text{Dye}$ ($\mu\text{s} - \text{ms}$)
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)

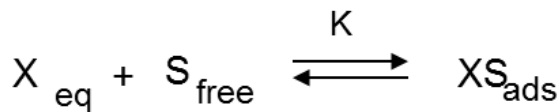
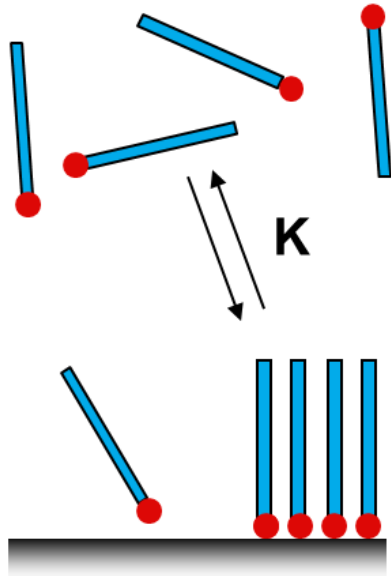


$$\eta_{\text{collection}} = 1 / (1 + \tau_{\text{trans}} / \tau_{\text{rec}}) \cong 1$$

τ_{trans} : transport through TiO_2
 τ_{rec} : recombination

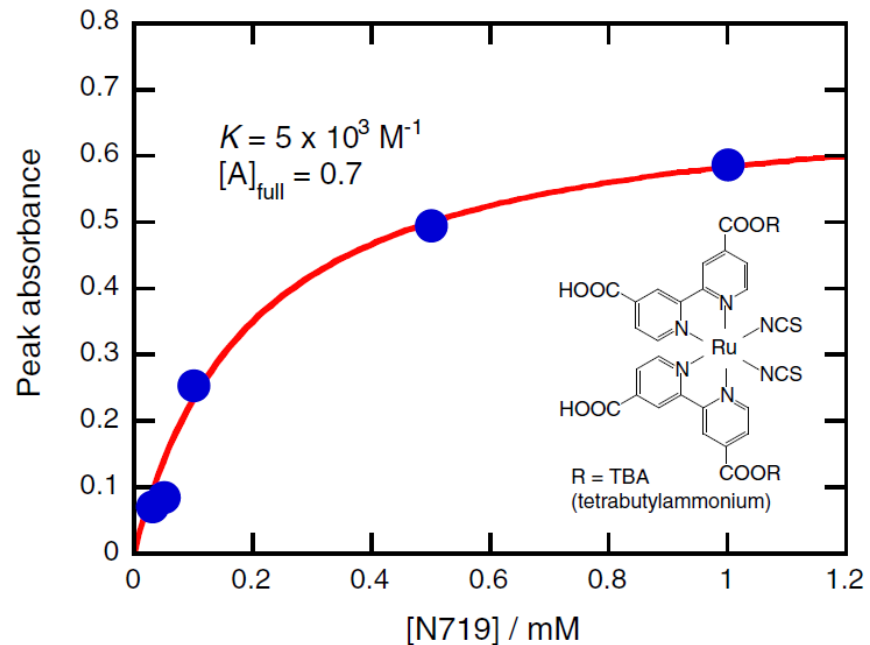
Adsorption of dye onto surface:

- Dye work most efficiently when chemisorbed onto the surface



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

Adsorption thermodynamics of N719 on TiO₂



- 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 1cm² of porous TiO₂, the effective surface area is 1000 cm²

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

Full sunlight intensity 100 mW/cm²

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

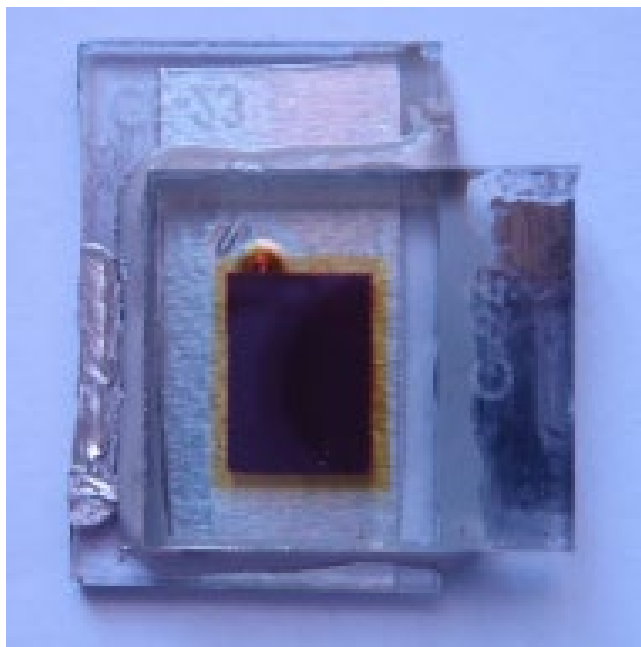
20 years are about 3 years of steady, full sunlight irradiation:

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

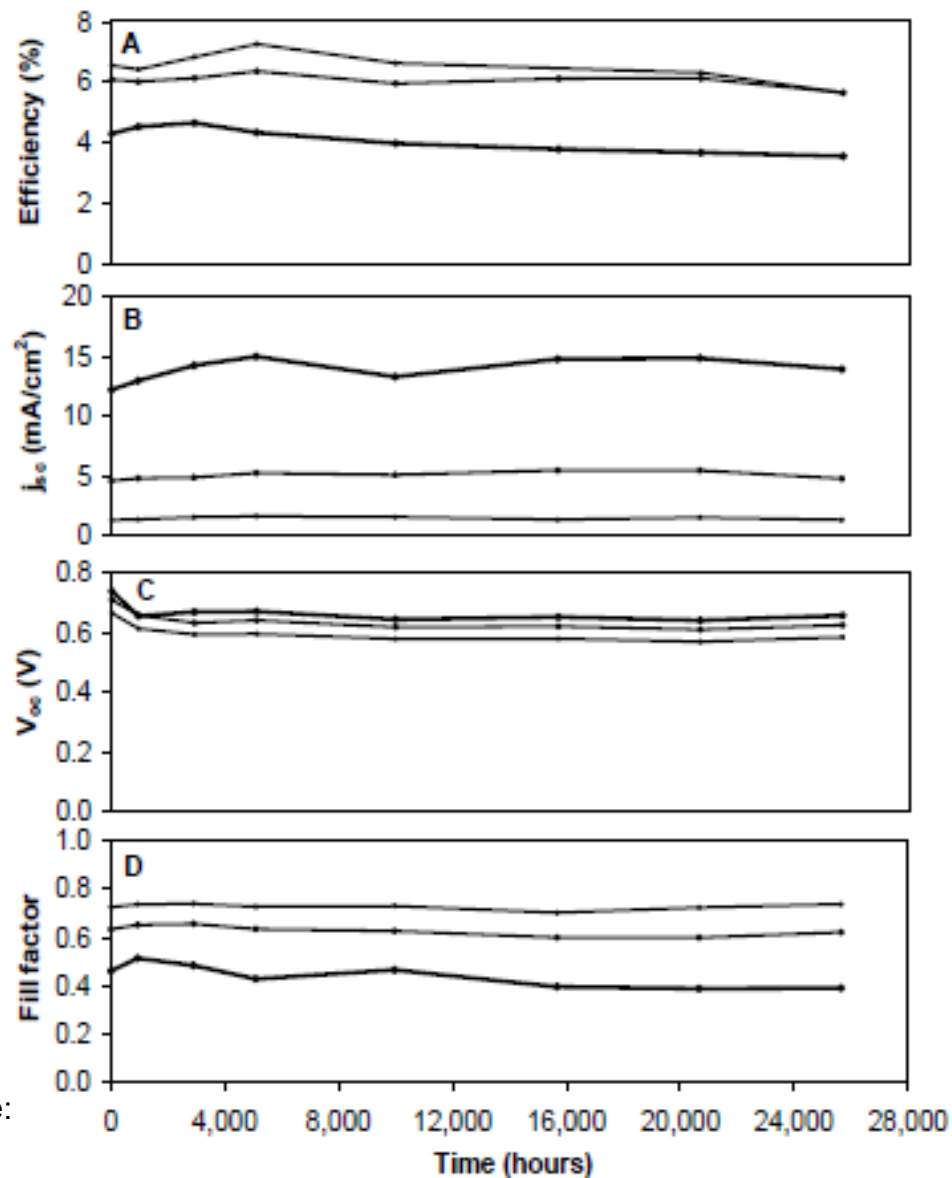
Number of cycles / molecule: $\frac{9.46 \times 10^7 \times 1.7 \times 10^{17} \text{ s}^{-1}}{10^{17}} = 1.6 \times 10^8$

Long term stability of DSSCs

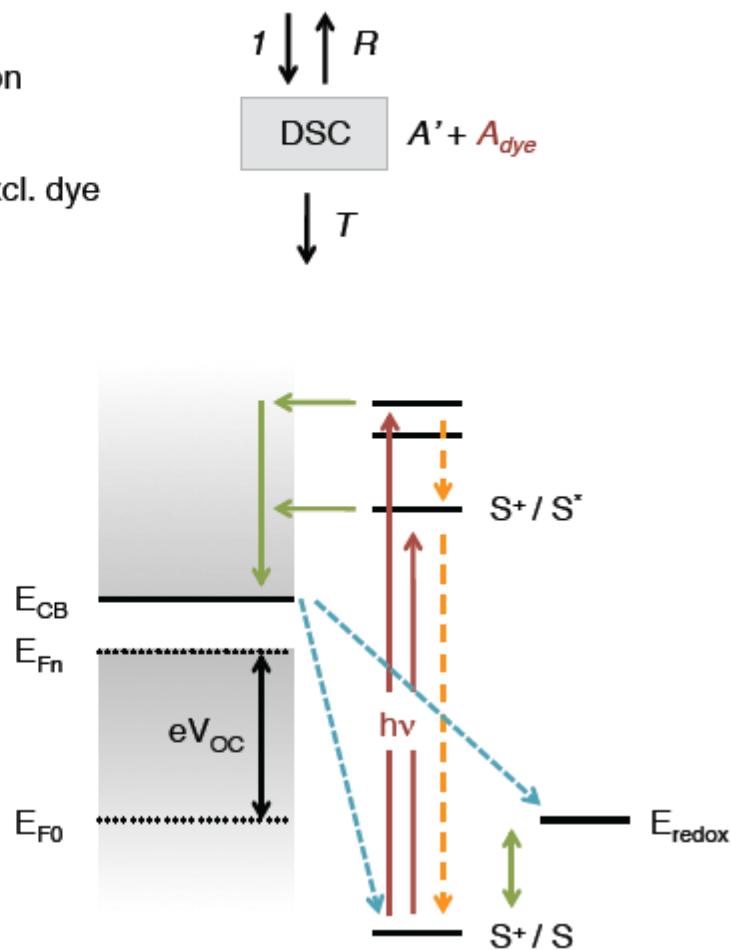
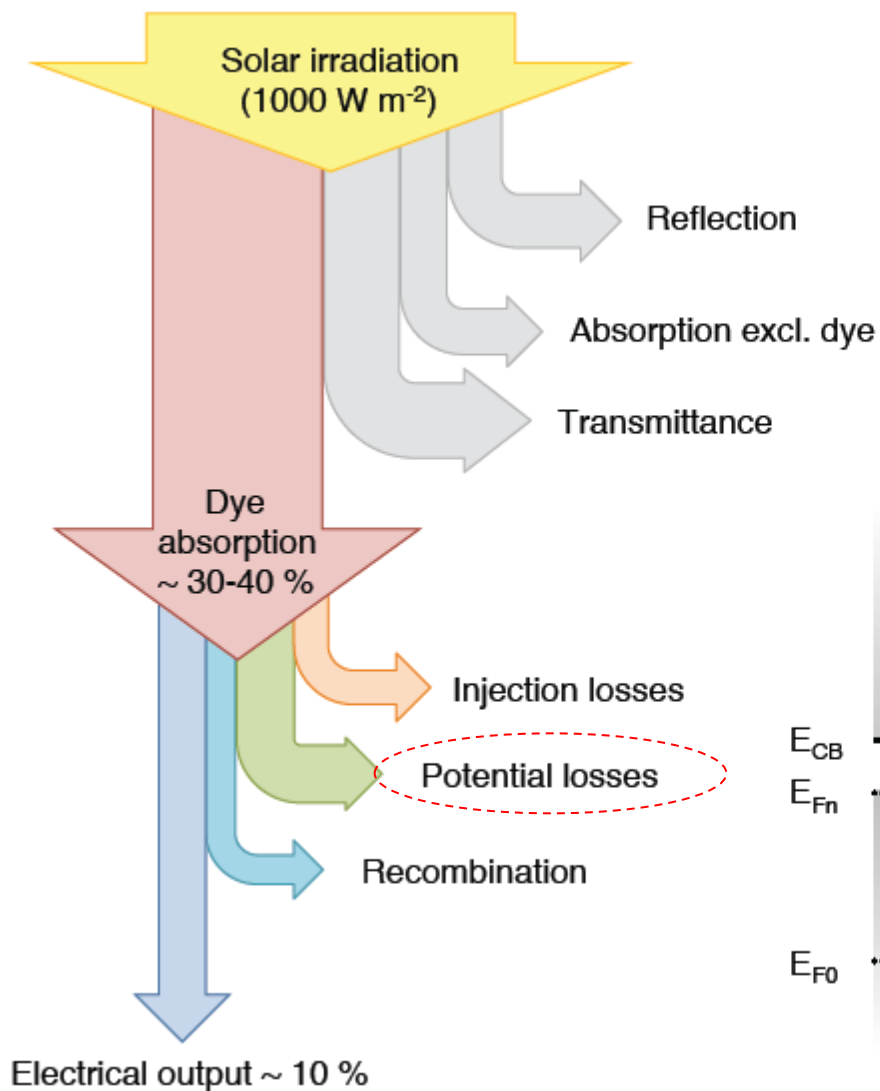
Dye Z907



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

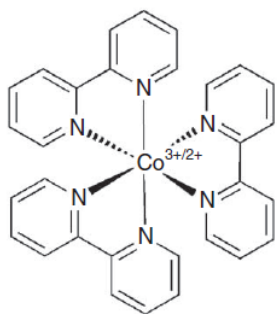
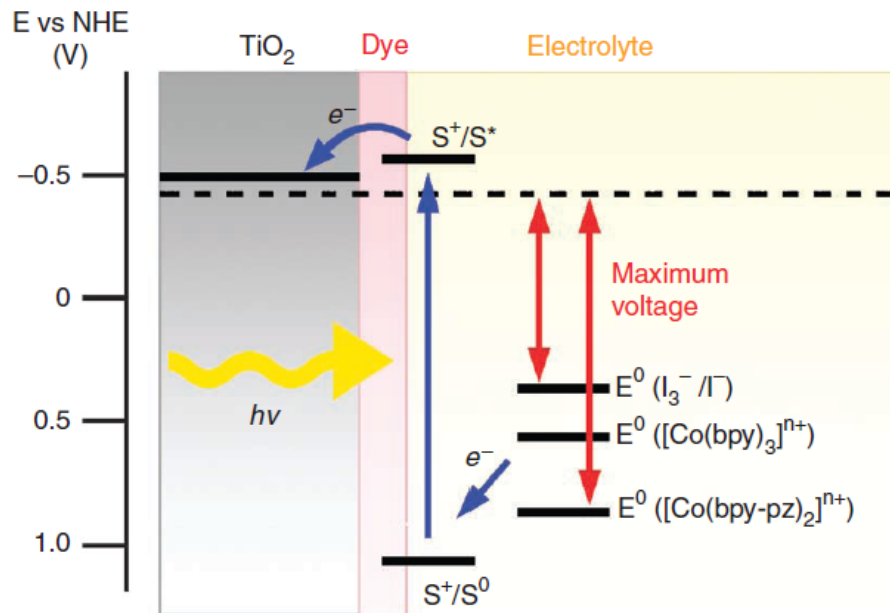


Challenges in DSSCs

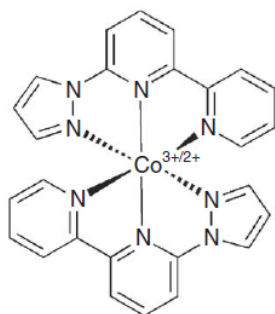


S. Wenger, thèse No. 4805 (2010), Epfl, Lausanne

New redox mediators

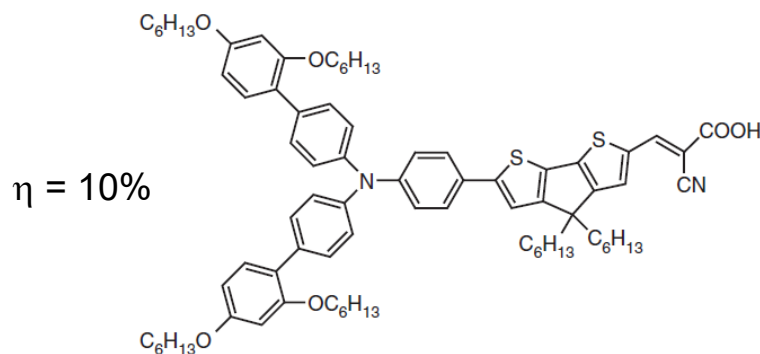
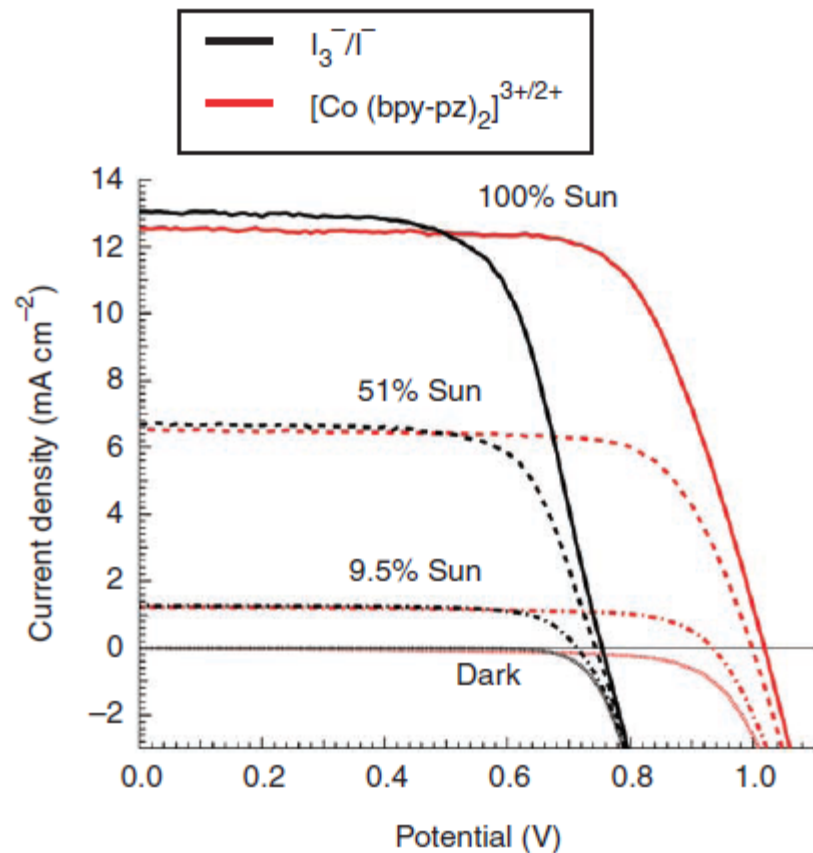


Co(bpy)₃

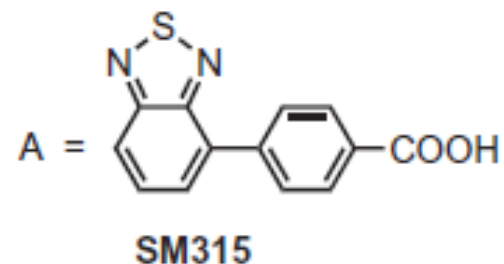
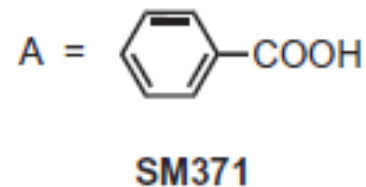
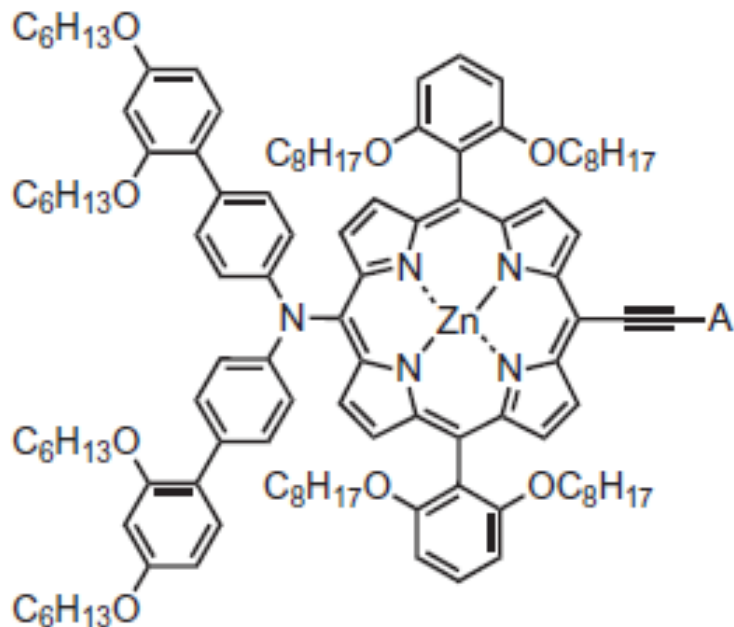


Co(bpy-pz)₂

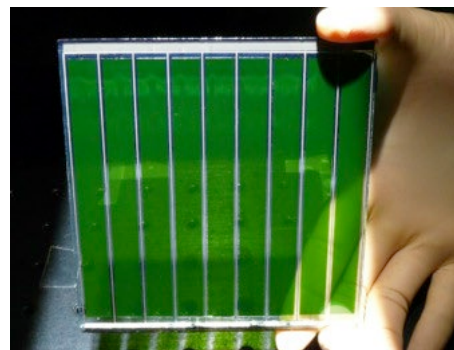
Jun-Ho Yum et al., Nature communications, 3:631, 2011



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, 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)

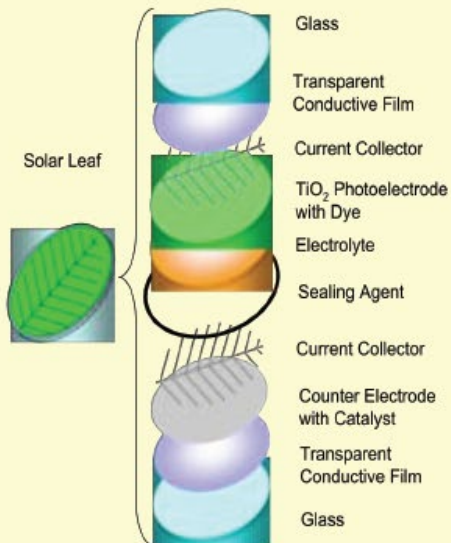
Classification	Efficiency (%)	Area (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill factor (%)	Test centre (date)	Description
<i>Dye sensitized</i>							
Dye (cell)	11.9 ± 0.4n	1.005 (da)	0.744	22.47 ^o	71.2	AIST (9/12)	Sharp ¹⁷
Dye (minimodule)	10.7 ± 0.4n	26.55 (da)	0.754 ^c	20.19 ^c p	69.9	AIST (2/15)	Sharp, seven serial cells ¹⁸
Dye (submodule)	8.8 ± 0.3n	398.8 (da)	0.697 ^c	18.42 ^c 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





Courtesy Sony Inc

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

 **Fraunhofer**
ISE

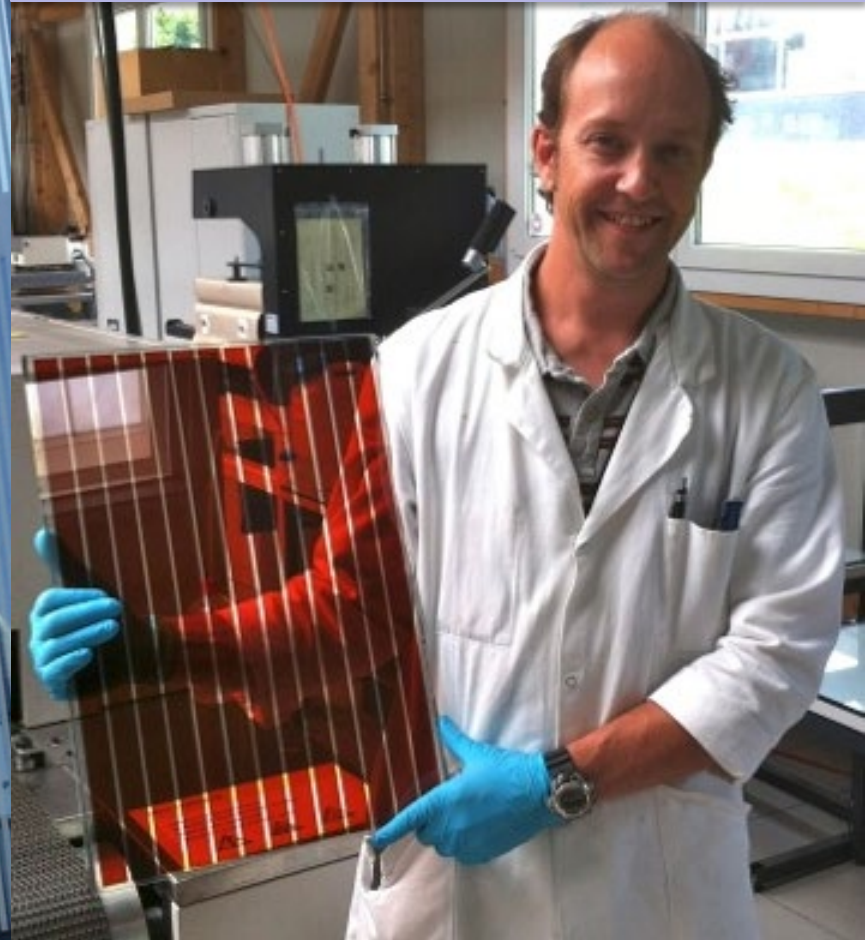


<http://www.ise.fraunhofer.de/presse-und-medien/presseinformationen/presseinformationen-2011/auf-dem-weg-in-die-fassade-fraunhofer-ise-praesentiert-weltweit-groesstes-farbstoffsolarmodul-in-siebdruck>



2.2B Dye sensitized solar cells Nr.22

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



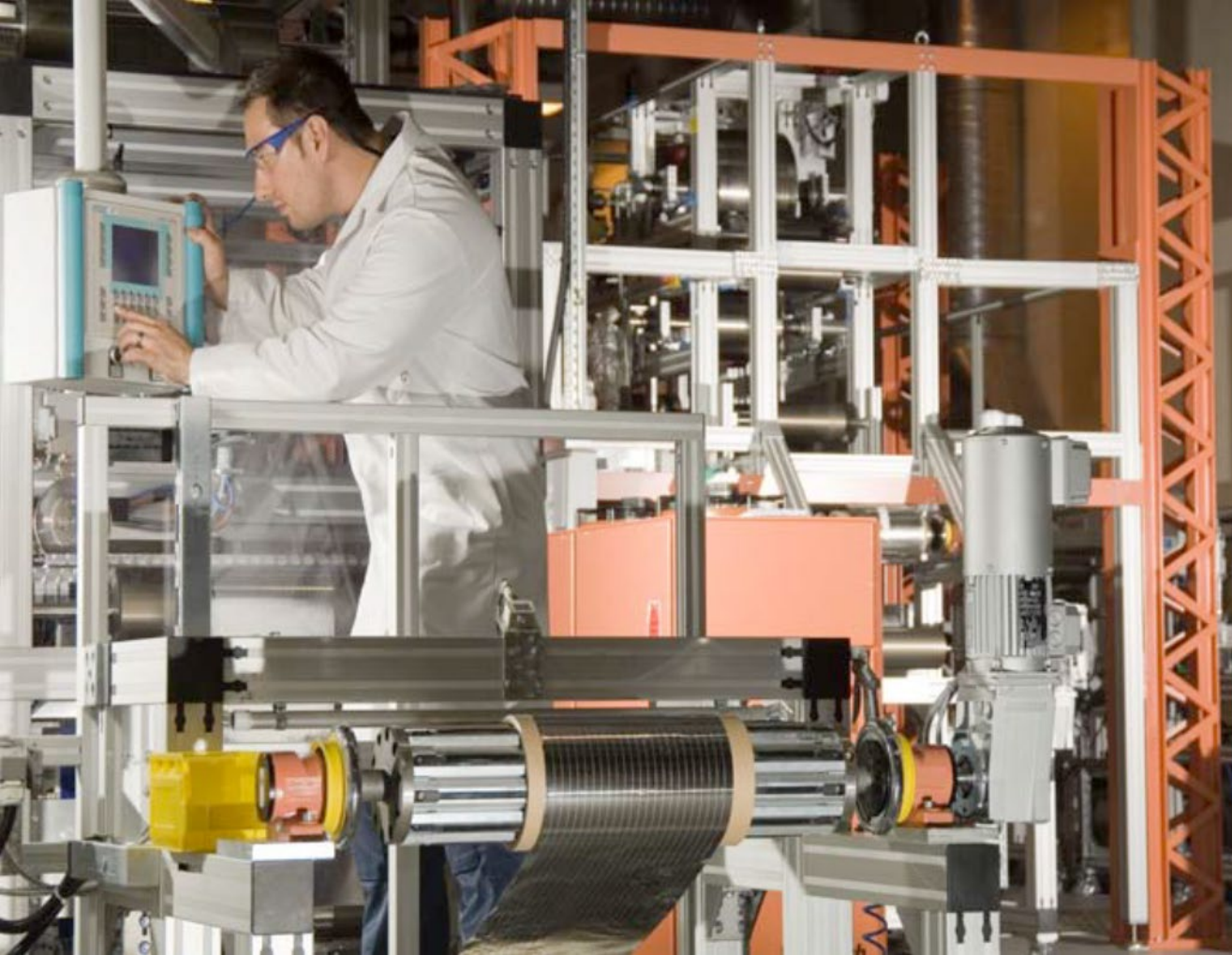
SOLARONIX

« efficiently innovative »

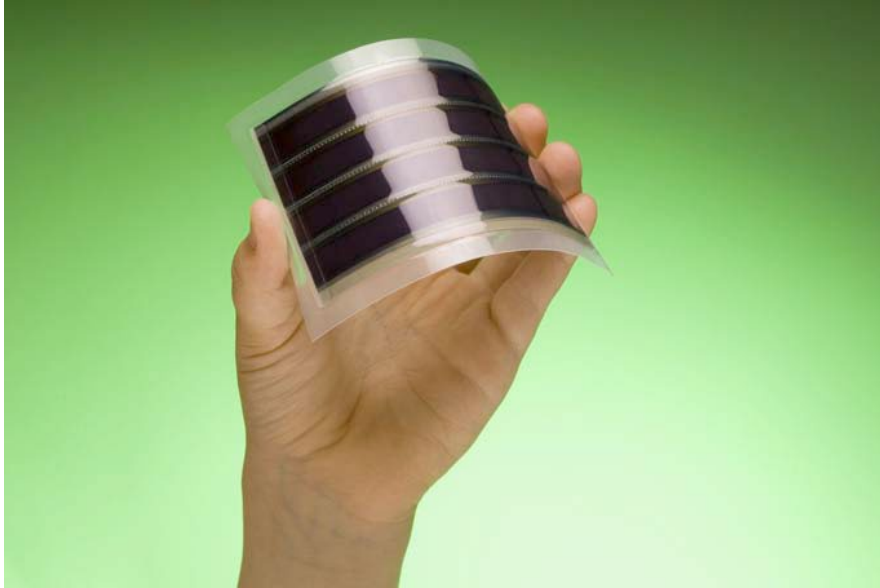


New Congress center at EPFL to be opened in May 2014 uses glass panels featuring dye sensitized solar cells for electricity production

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*