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FÉDÉRALE DE LAUSANNE

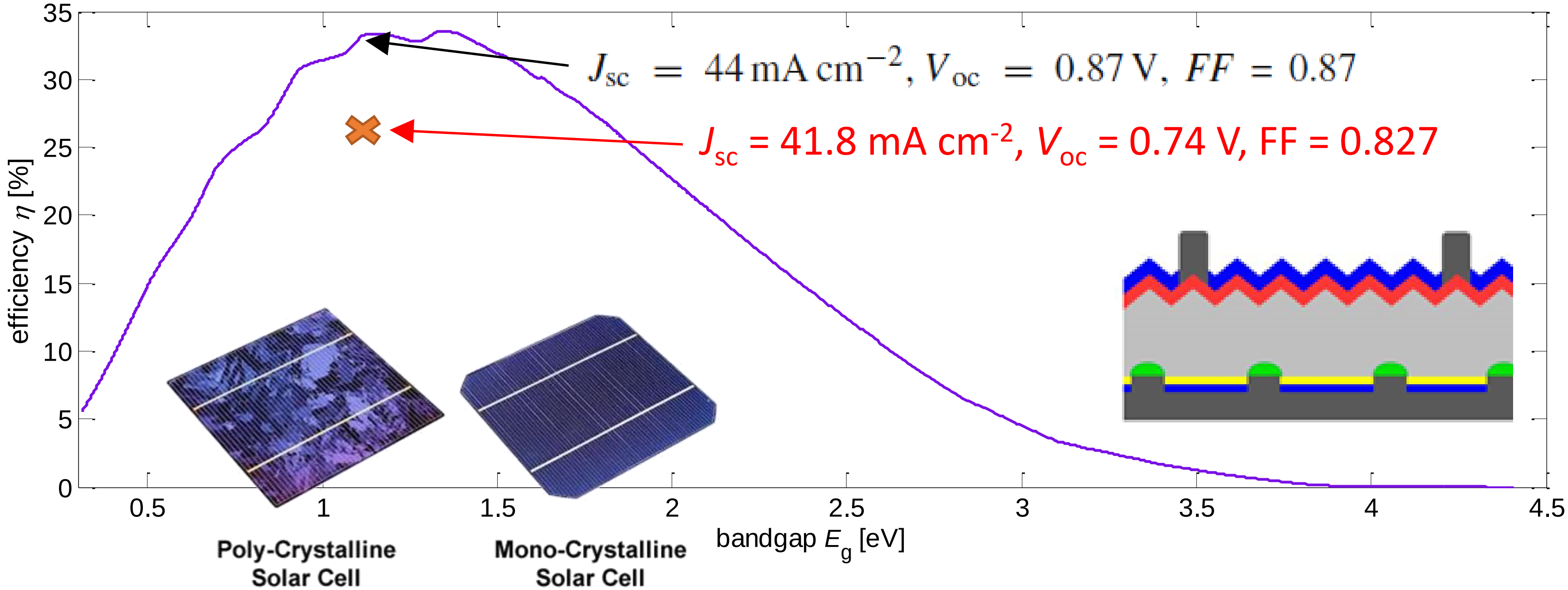
Solar Photovoltaics & Energy Systems

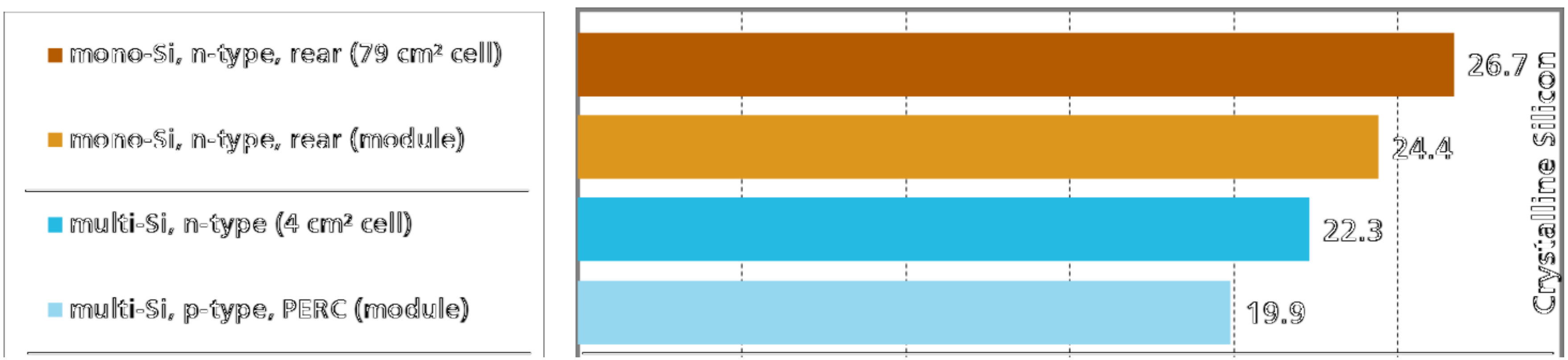
Lecture 4. III-V, Thin Film, and Organic Solar Cells

ChE-600

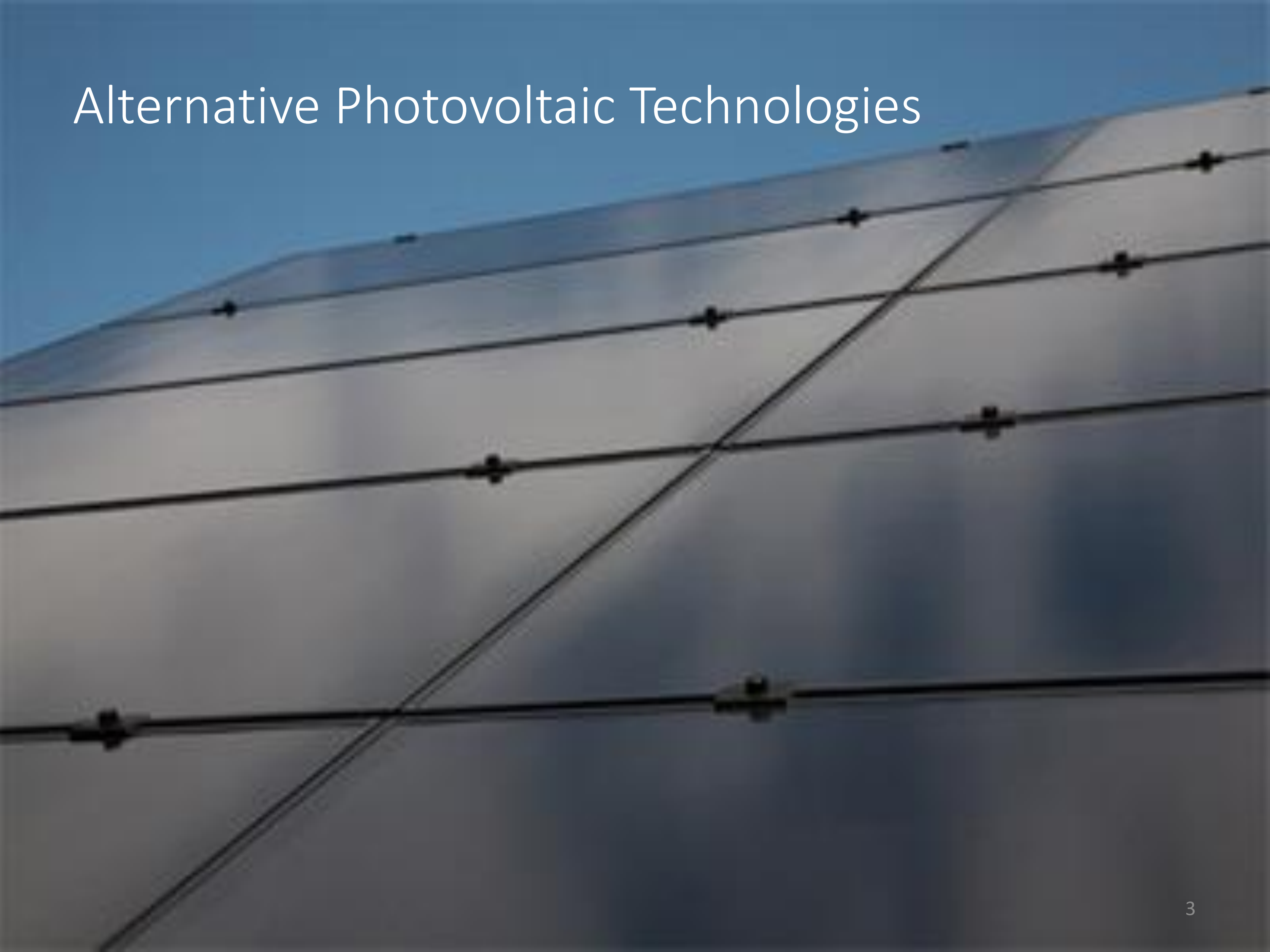
Wolfgang Tress, March 2018

Summary Crystalline Silicon Solar Cells





Alternative Photovoltaic Technologies



- Can we do better than Silicon?

- Can we do cheaper than Silicon?

- Can we do more than Silicon?

The Open Circuit Voltage

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- Ideally: $$V_{\mathrm{oc,rad}} = \frac{k_B T}{e} \ln\left(\frac{J_{\mathrm{ph}}}{J_{\mathrm{em},0}} + 1\right)$$

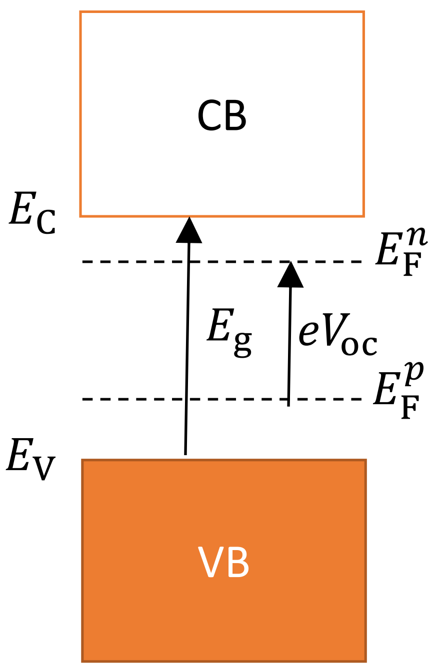
- Alternative expression: $$V_{\mathrm{oc}} = \frac{E_F^n - E_F^p}{e} = \frac{E_g}{e} - \frac{k_B T}{e} \ln\left(\frac{N_C N_V}{np}\right)$$

band gap

temperature

recombination

light intensity



$$n = N_C \exp\left(-\frac{E_C - E_F^n}{k_B T}\right)$$

$$p = N_V \exp\left(-\frac{E_F^p - E_V}{k_B T}\right)$$

Increasing the Open Circuit Voltage

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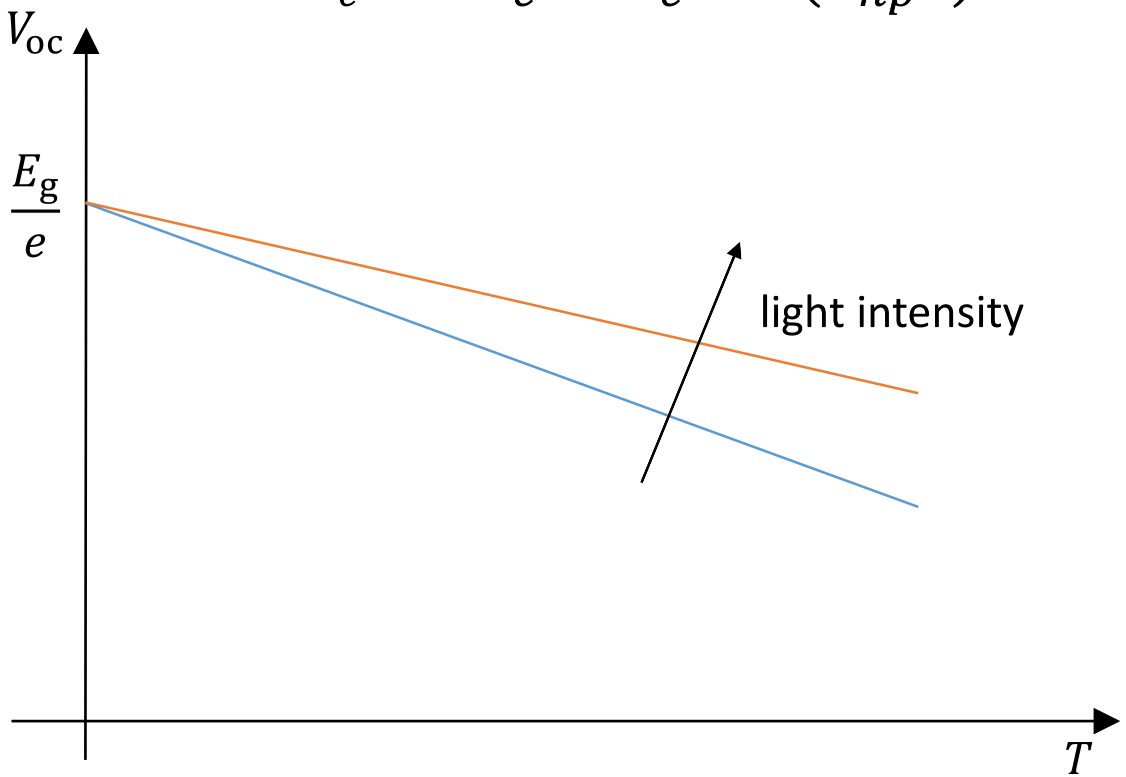
$$V_{\mathrm{oc}} = \frac{E_{\mathrm{F}}^{n} - E_{\mathrm{F}}^{p}}{e} = \frac{E_{\mathrm{g}}}{e} - \frac{k_{\mathrm{B}}T}{e} \ln\left(\frac{N_{\mathrm{C}}N_{\mathrm{V}}}{np}\right)$$



→ Cooling, concentration, high absorption, light trapping (thinner layers)

Recombination

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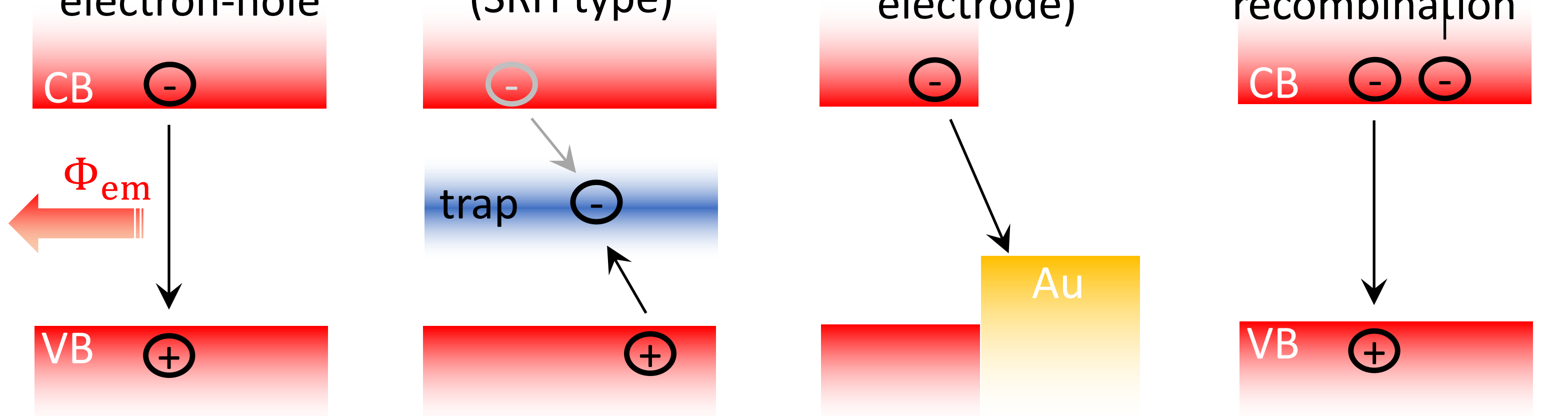
radiative electron-hole	via defects (SRH type)	at surfaces (wrong electrode)	Auger recombination



→ enters thermodynamic limit	→ pure, defect-free material	→ passivation, reduction of contact area	→ material property (indirect semiconductor)
unavoidable in absorber	to be avoided		

→ Decrease of minority carrier lifetime

Si is an Indirect Semiconductor

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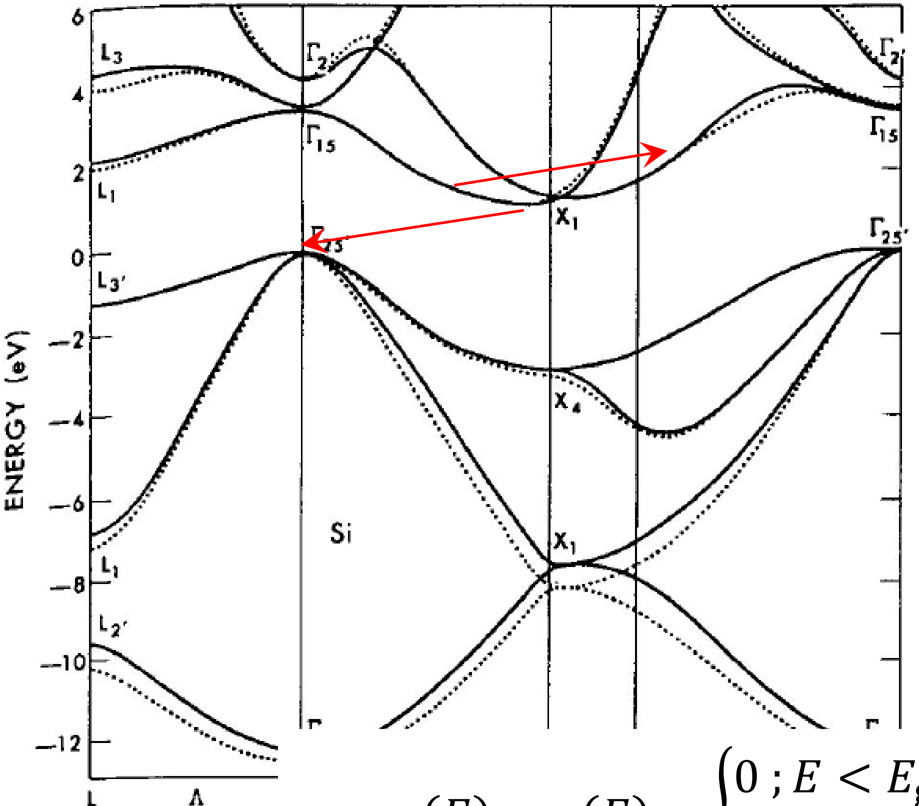

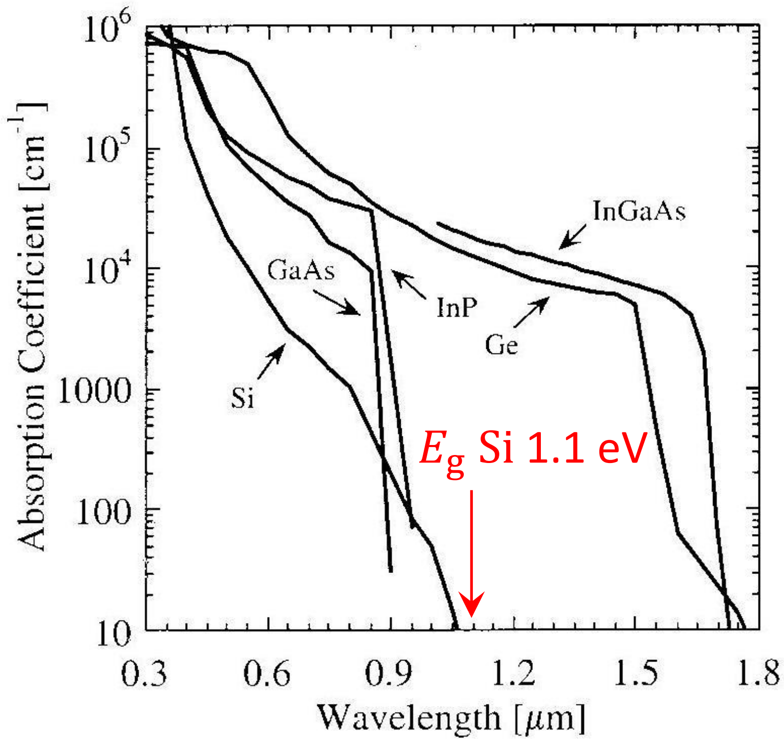

Handbook of Optical Constants of Solids, edited by Edward D. Palik, (1985), Academic Press NY.

$$a_{\text{ideal}}(E) = e(E) = \begin{cases} 0 \,;\, E < E_g \\ 1 \,;\, E \geq E_g \end{cases}$$

$$a_{\text{real}}(E) = 1 - r(E) - \exp(-\alpha d)$$

- Conservation of energy and momentum → Auger recombination
- Indirect transition → low absorption coefficient at E_g

III-V Semiconductors: GaAs

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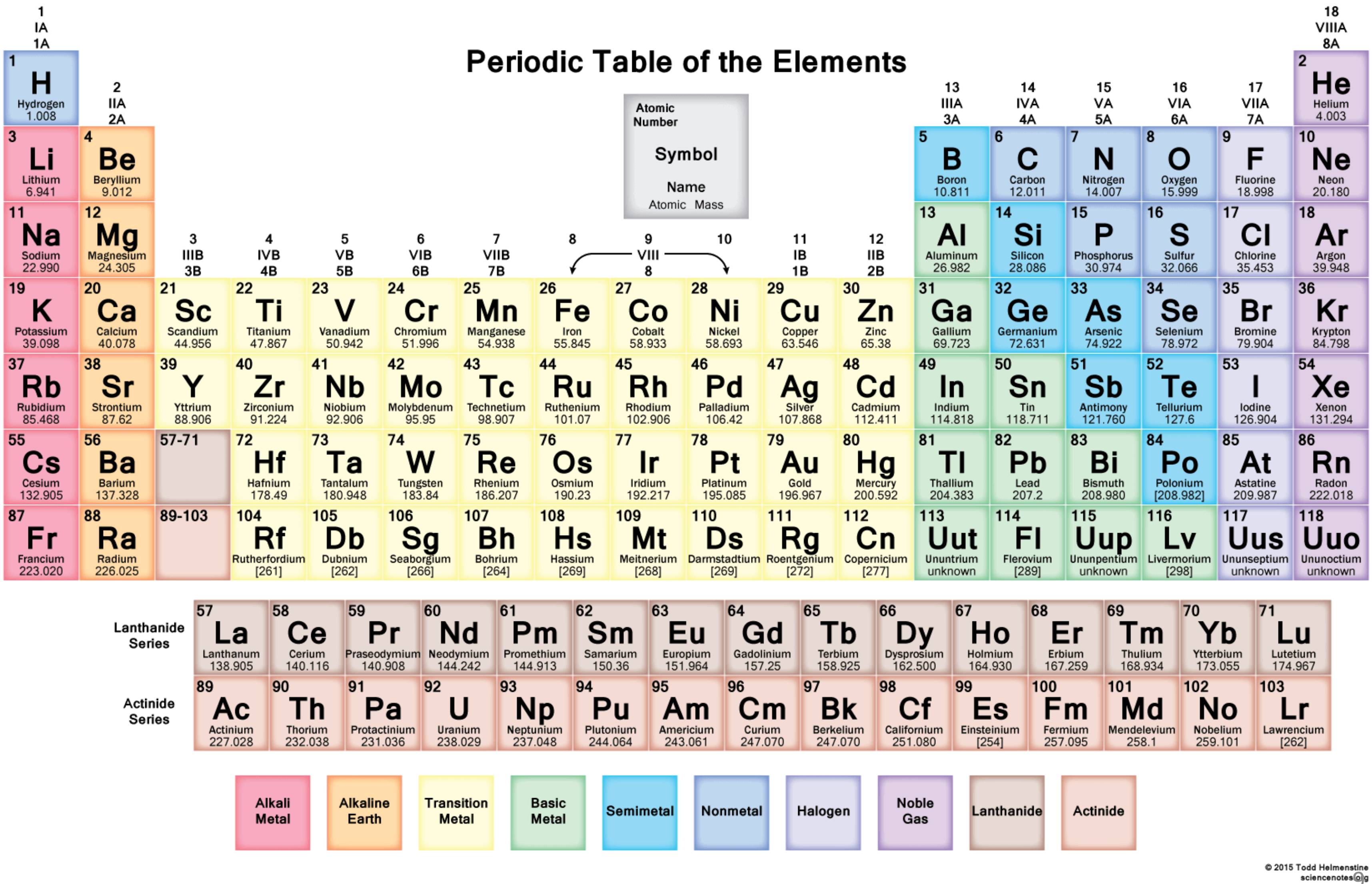
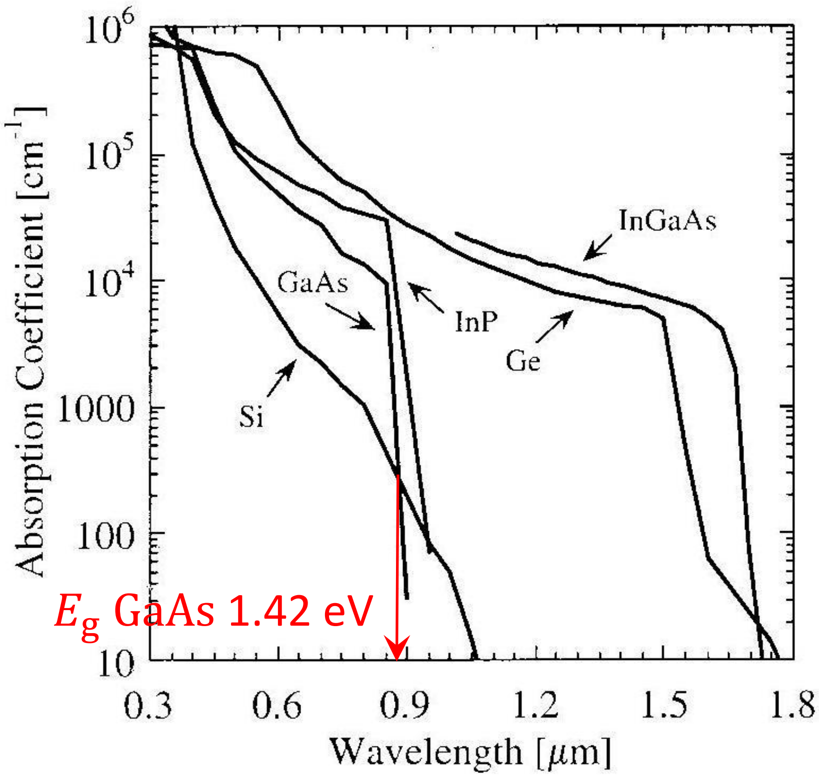


III-V Semiconductors: GaAs



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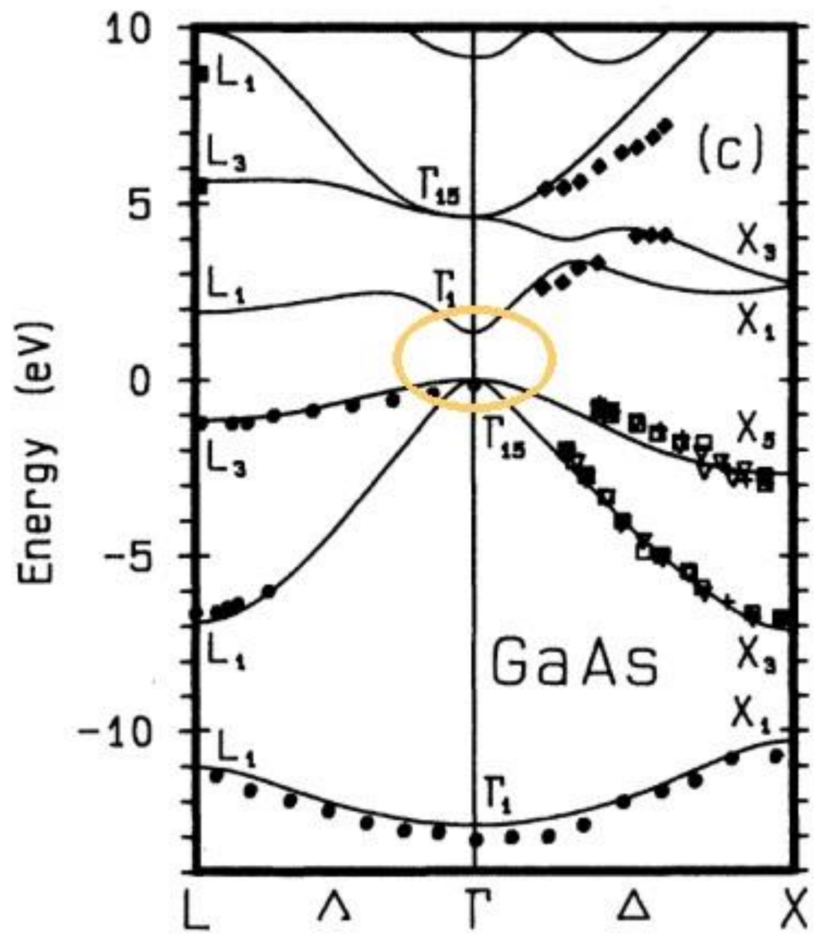
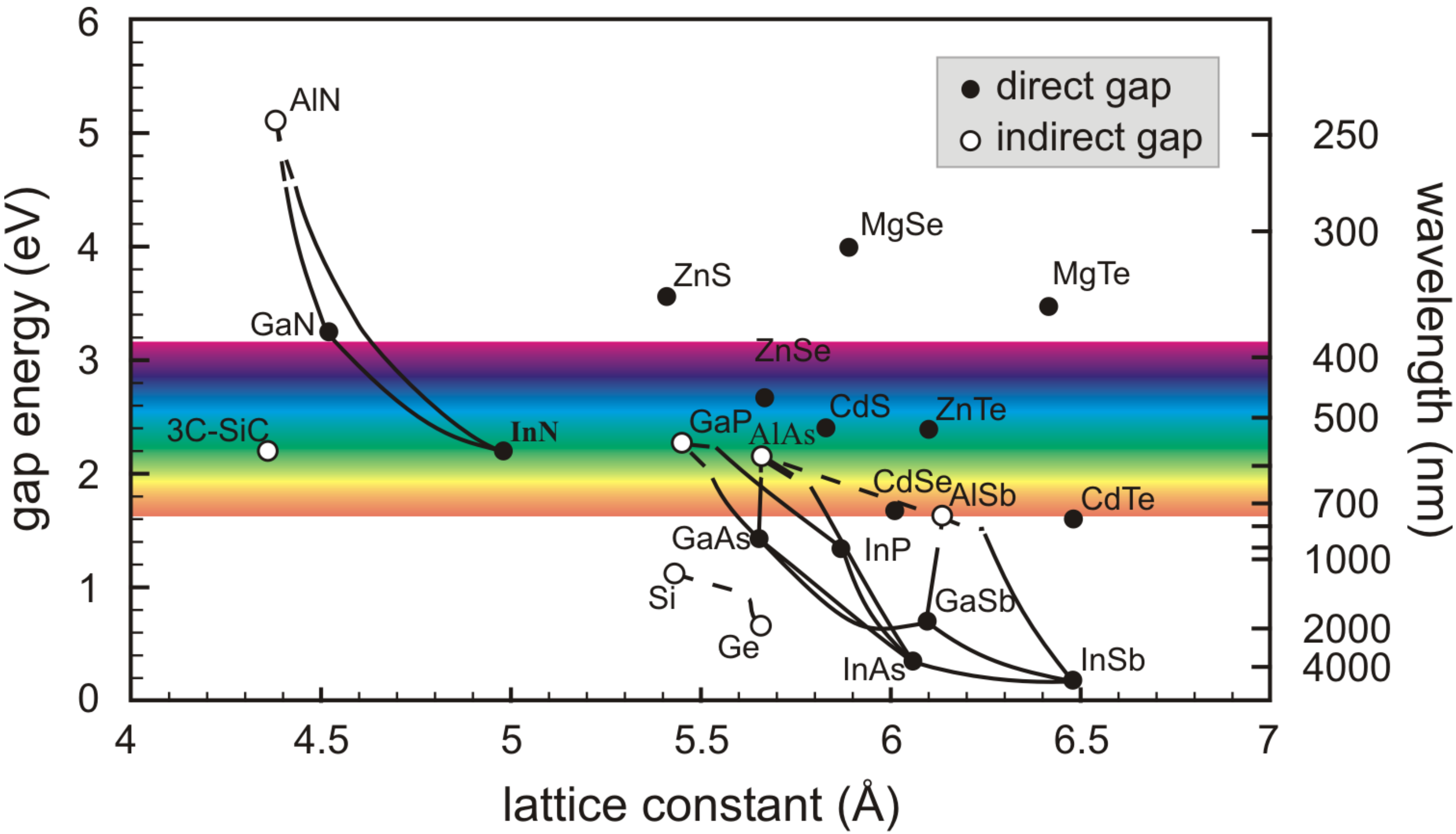


→ η = 28 % reached

Michael Rohlfing, Peter Krüger, and Johannes Pollmann: *Quasiparticle band-structure calculations for C, Si, Ge, GaAs, and SiC using Gaussian-orbital basis sets*, Phys. Rev. **B48** (1993) 17791-17805 (doi: 10.1103/PhysRevB.48.17791), Fig. 3.

III-V SC: Band Gap Engineering

http://gorgia.no-ip.com/phd/html/thesis/phd_html/node4.html



III-V SC: Multi Junction Solar Cells

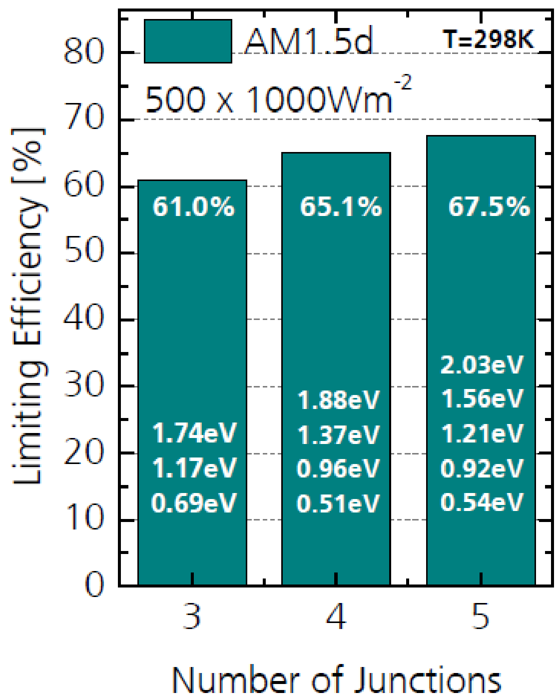


Figure 1: Detailed balanced limit calculations for 3J, 4J and 5J MJ cells under concentrated light, with the optimum bandgap combination shown [5].

ISE, Freiburg Presented at the 29th European PV Solar Energy Conference and Exhibition, 22-26 September 2014, Amsterdam, The Netherlands

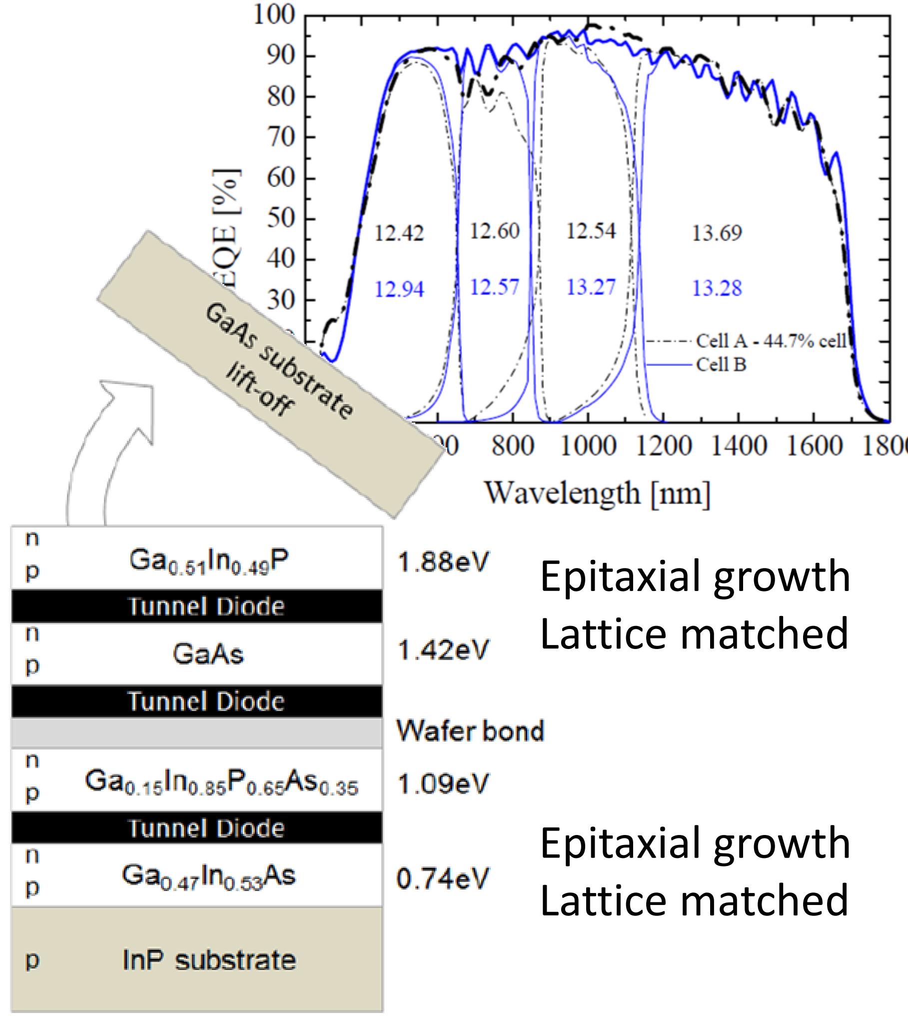


Figure 2: Schematic of a wafer-bonded GaInP/GaAs//GaInPAs/GaInAs 4J solar cell.

III-V SC: Multi Junction Solar Cells

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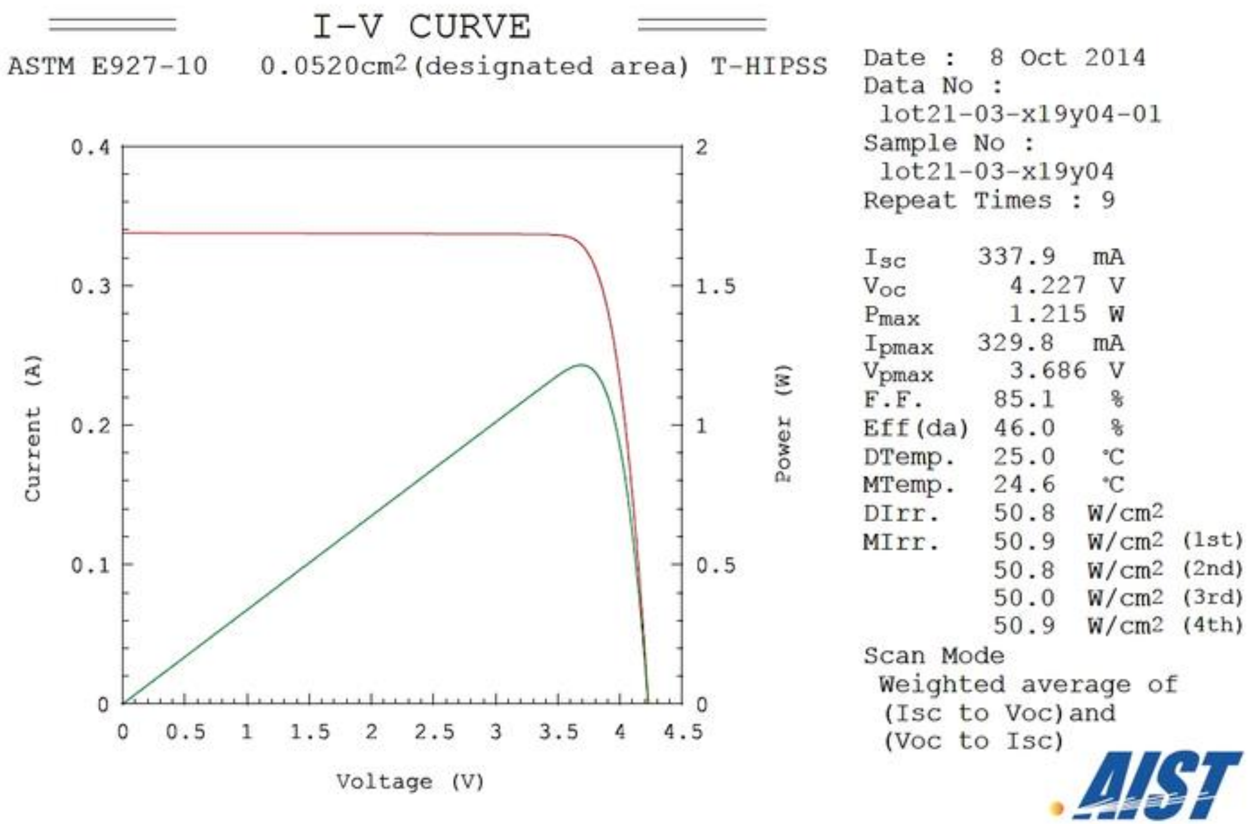


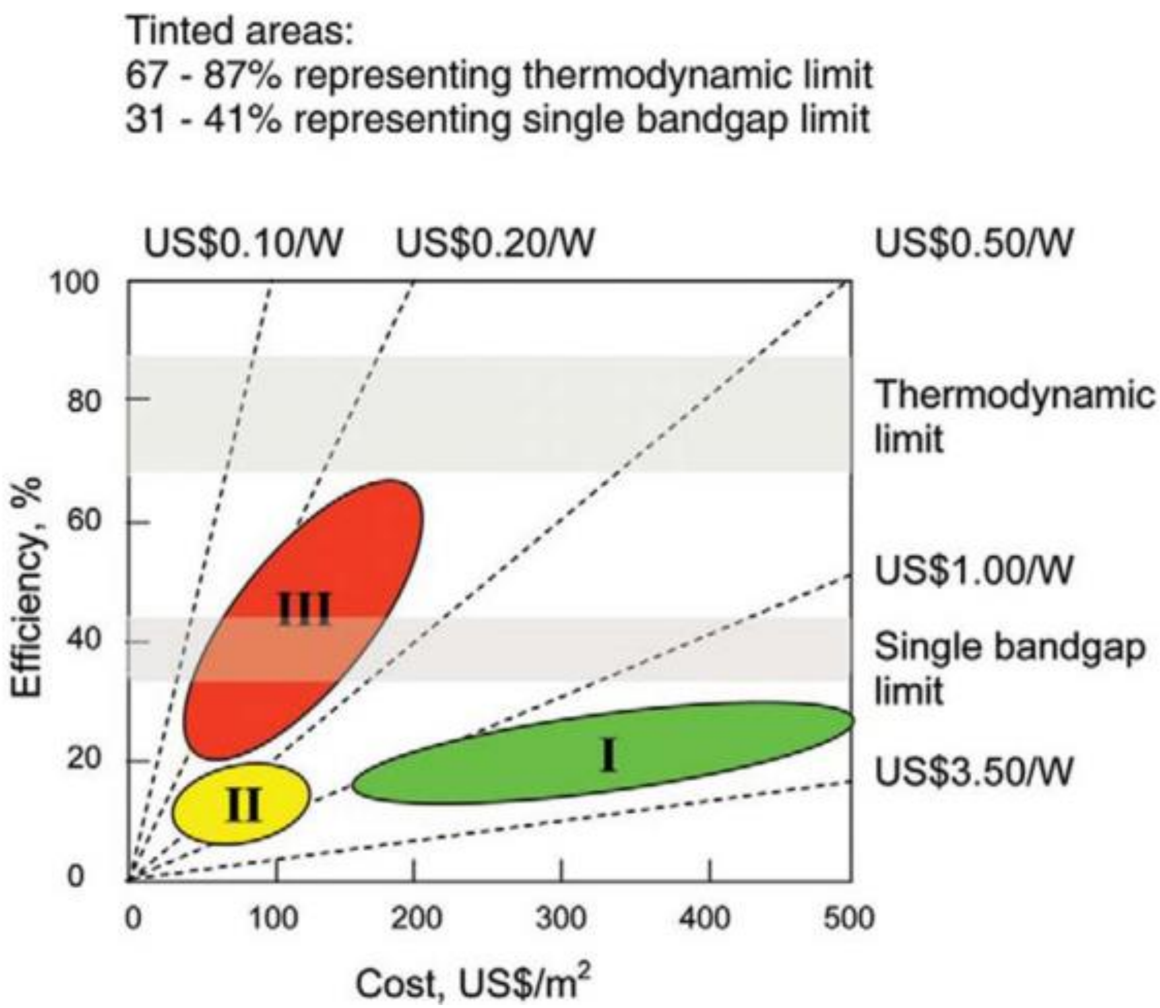
→ World record four-junction solar cell η = 46 %

Multi Junction Concentrator Solar Cells

- 500 x concentration
- Cooling
- Direct light

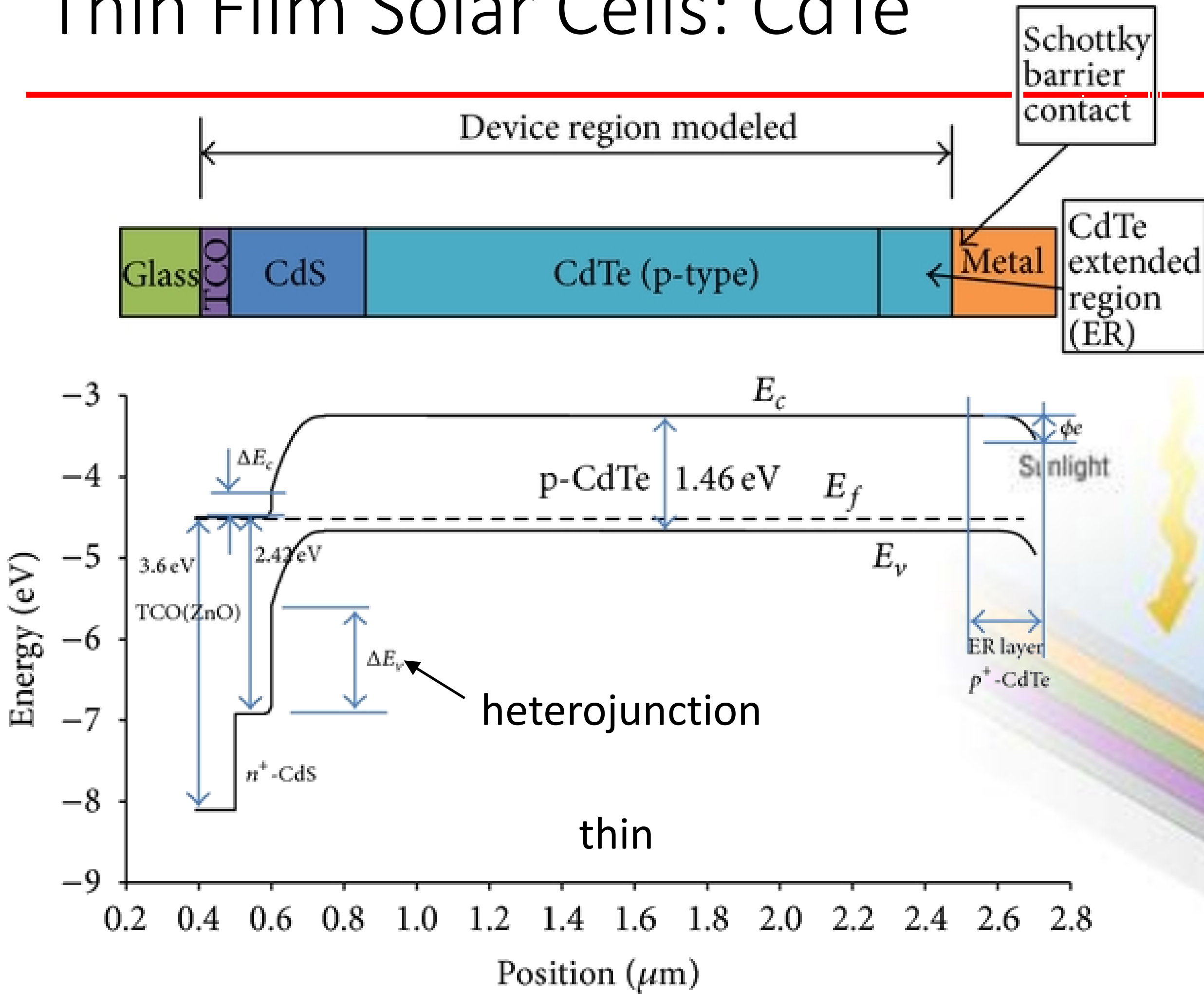
→ Sun tracking

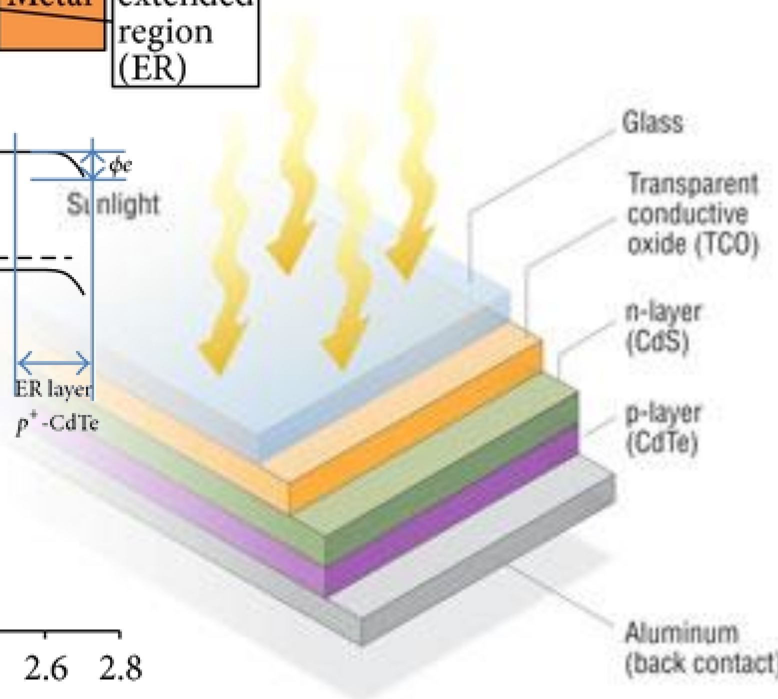
Generations of Solar Cells



http://www.intechopen.com/books/solar-cells-research-and-application-perspectives/optimization-of-third-generation-nanostructured-silicon-based-solar-cells

Thin Film Solar Cells: CdTe



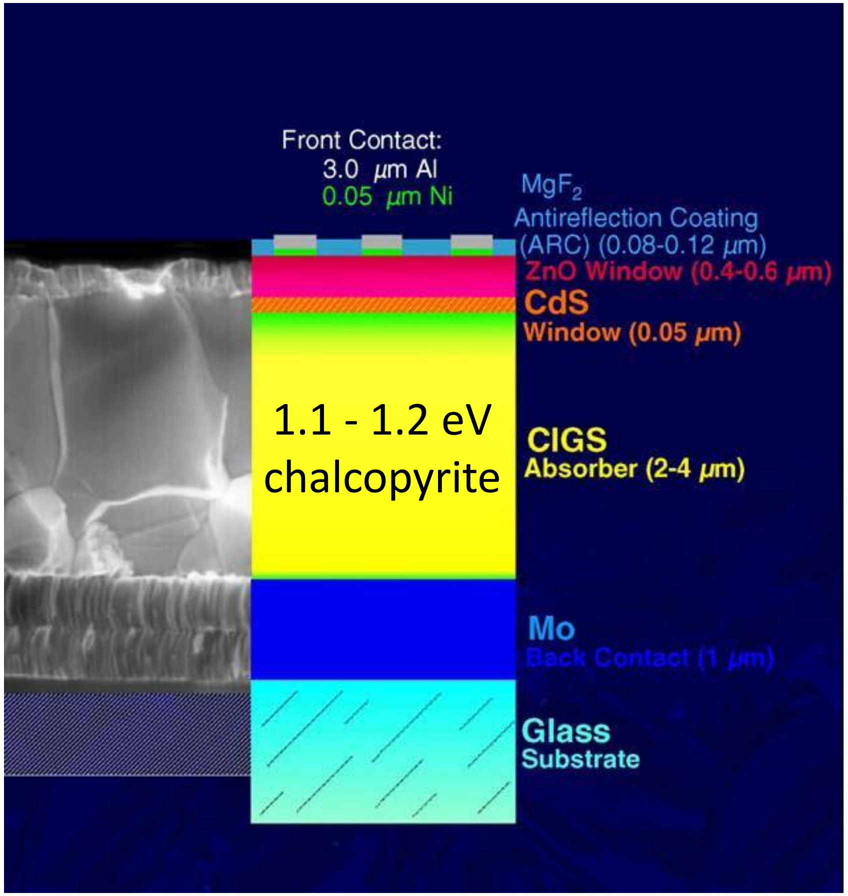


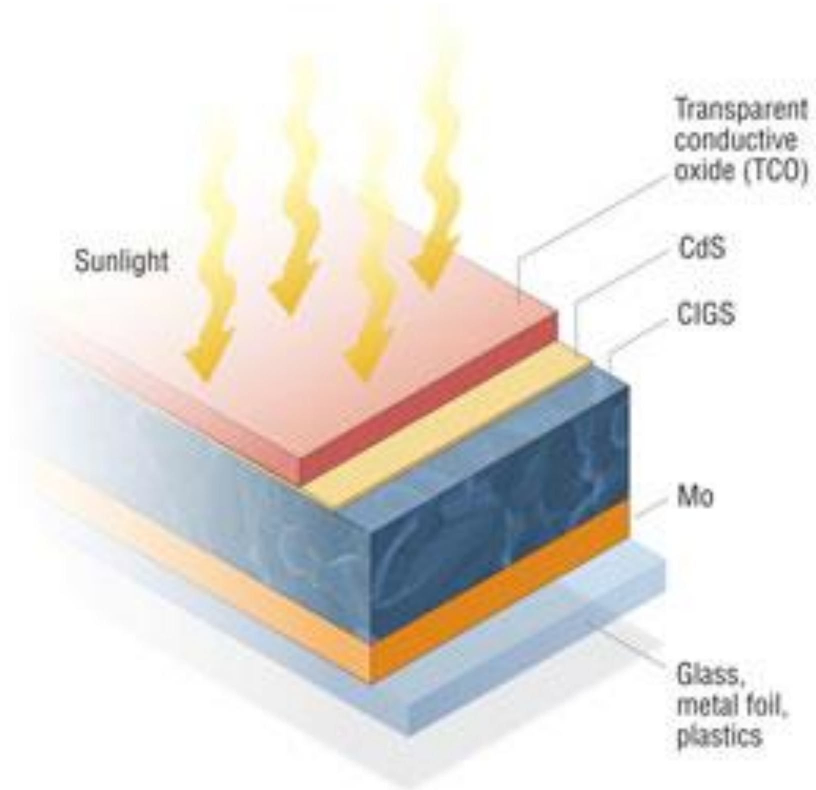
International Journal of Photoenergy
Volume 2013 (2013), Article ID 576952, 6 pages
http://dx.doi.org/10.1155/2013/576952

http://energyinformative.org/best-thin-film-solar-panels-amorphous-cadmium-telluride-cigs/

Thin Film Solar Cells: CIGS

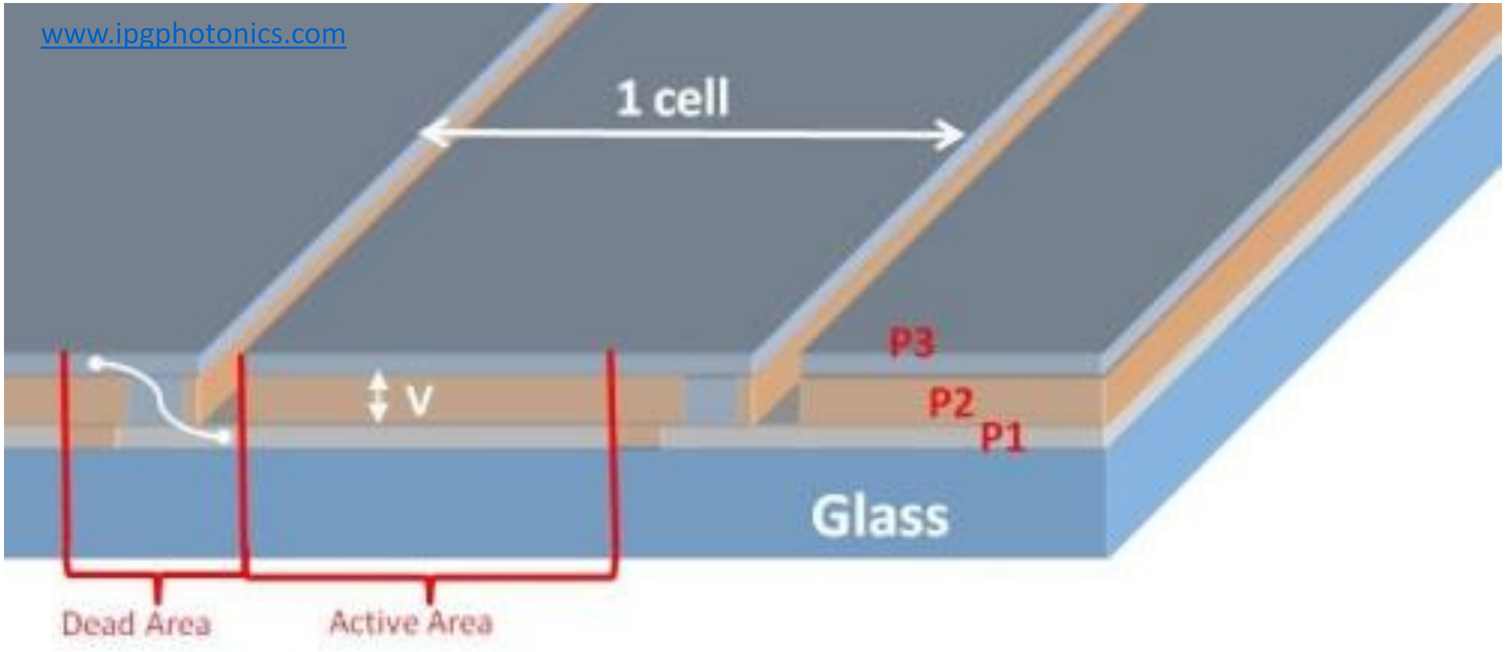
- Alloying of CIS ($CuInSe_2$) with CGS ($CuGaSe_2$) to tune band gap



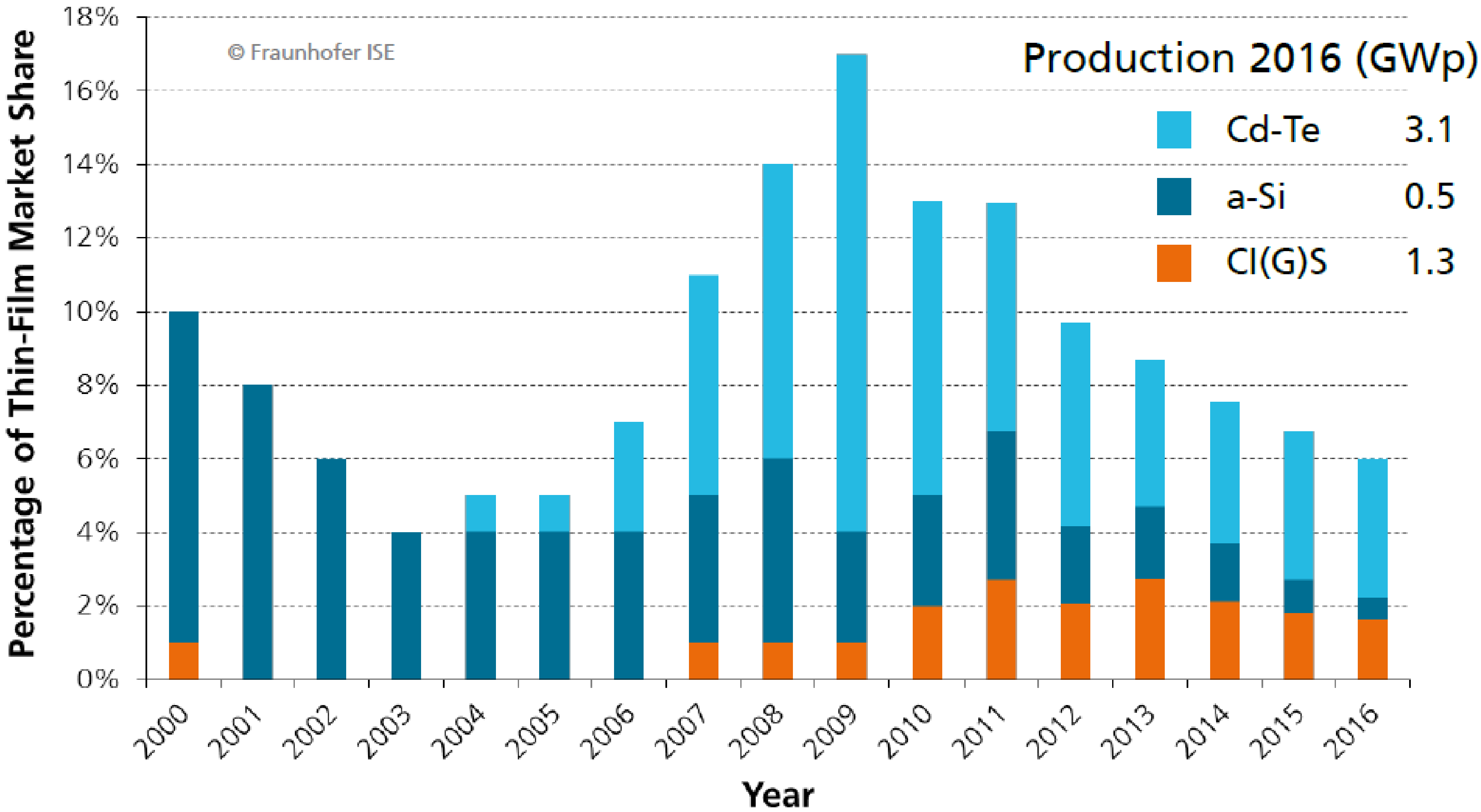


Thin Film Solar Cells: Module

Glass substrate → thin film deposition → laser scribing → series connection of stripes

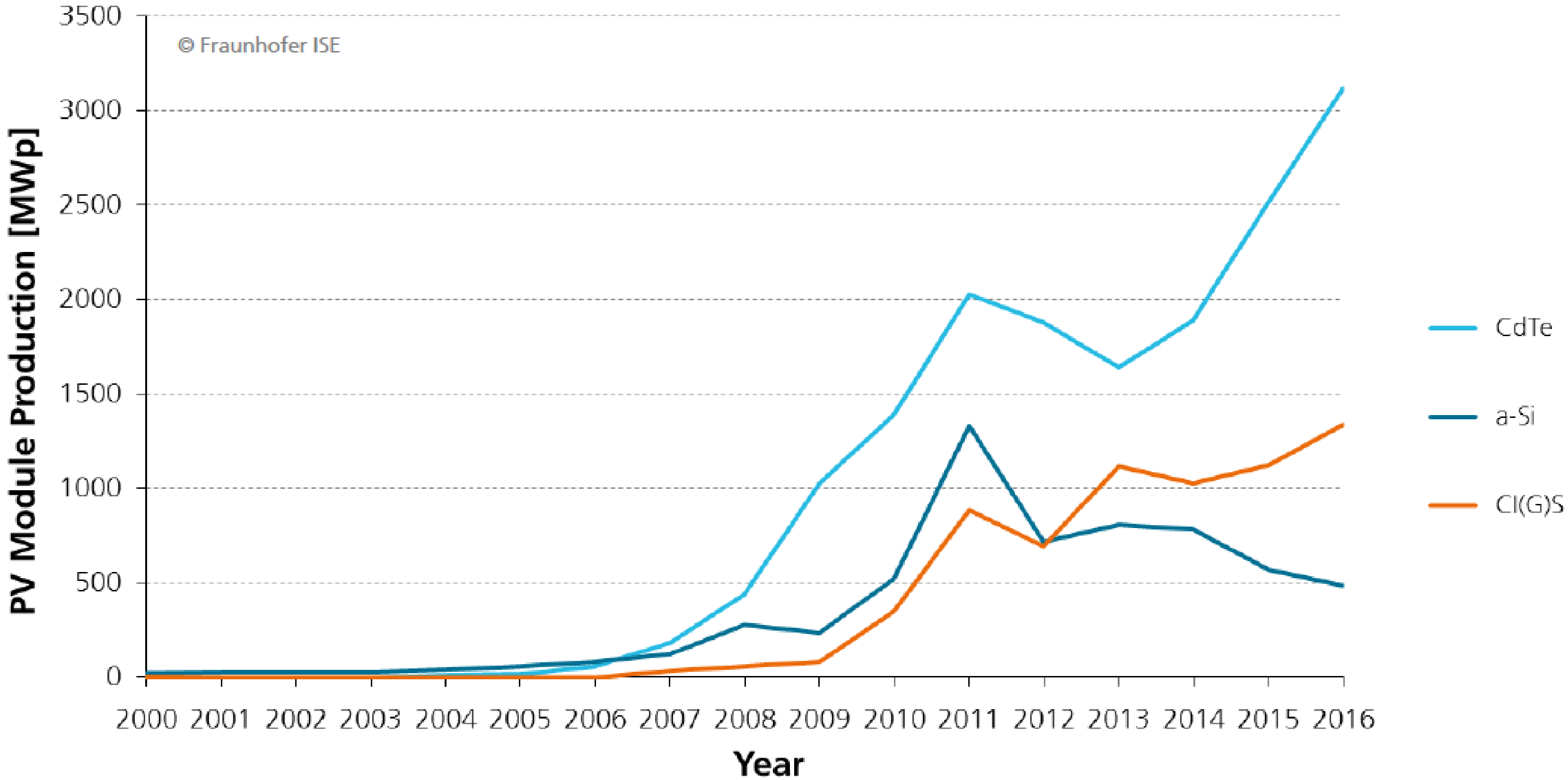


Thin Film Solar Cells: Market Share



Data: from 2000 to 2010: Navigant; from 2011: IHS. Graph: PSE 2017

Thin Film Solar Cells: Production



Data: from 2000 to 2010: Navigant; from 2011: IHS. Graph: PSE 2017

Energy Payback Time (EPBT)

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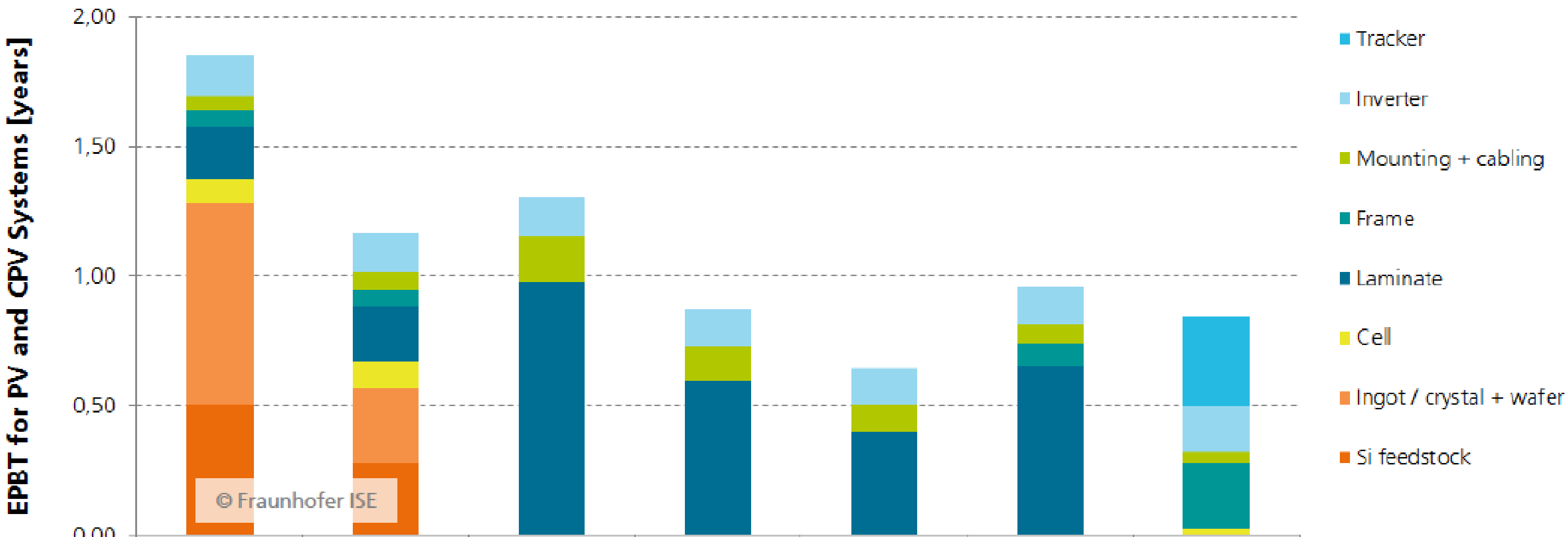
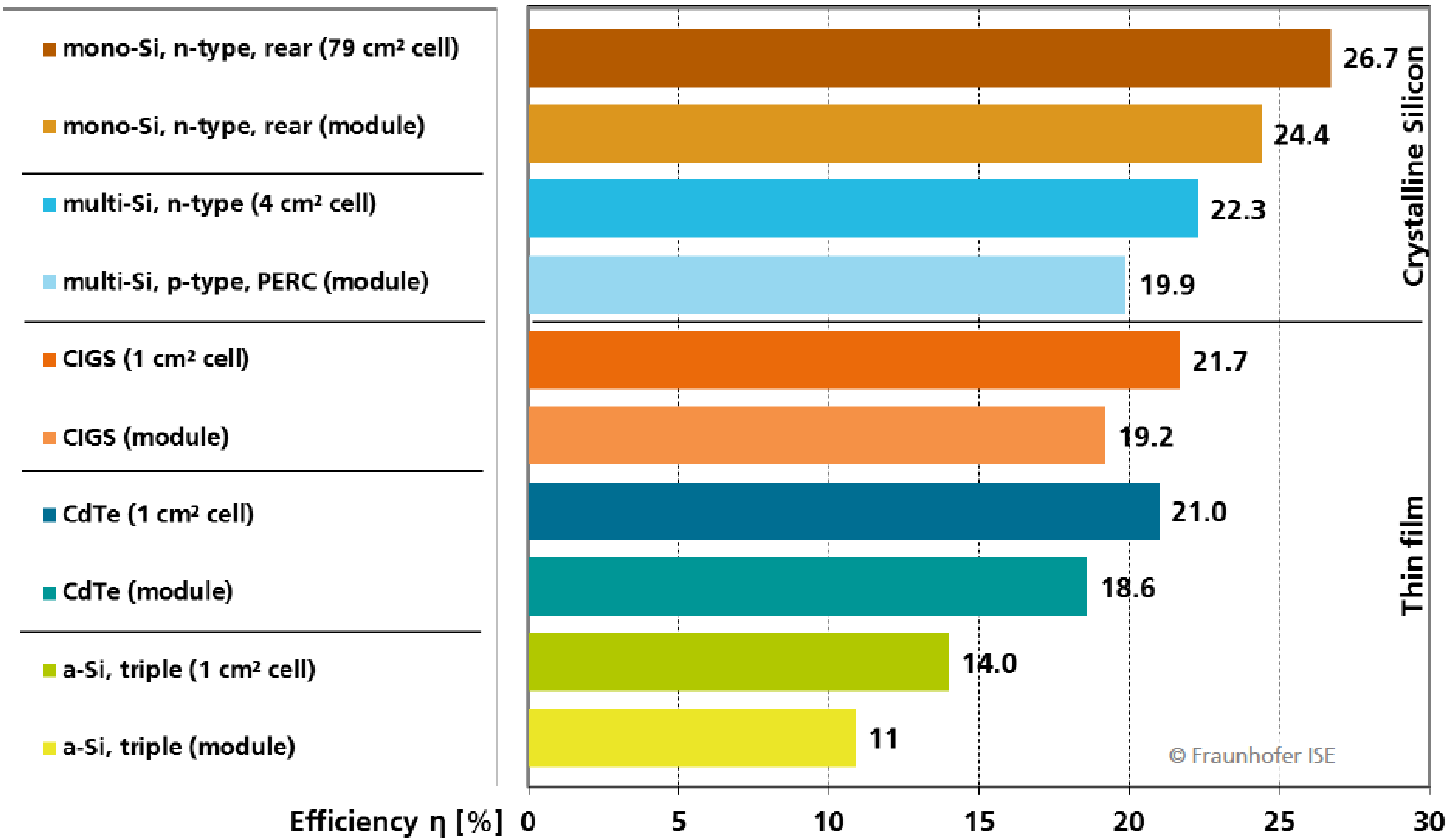
Global Irrad.: 1925 kWh/m²/yr, Direct Normal Irrad.: 1794 kWh/m²/yr



Technology	Mono-Si	Multi-Si	a-Si	µm-Si	CdTe	CIGS	CPV
Module composition	Glass-EVA-backsheet	Glass-EVA-backsheet	Glass-PVB-glass	Glass-EVA-glass	Glass-EVA-glass	Glass-EVA or PVB-glass	Flatcon CX-75 CPV-System
Status	2011	2011	2008-2011	2013 estimate	2010-2111	2011	2011
Efficiency	14,8%	14,1%	7,0%	10,0%	11,9%	11,7%	24,1%
Scale of production	~300 MWp	~300 MWp	33-45MWp	120MWp	963MWp	20-66MWp	-

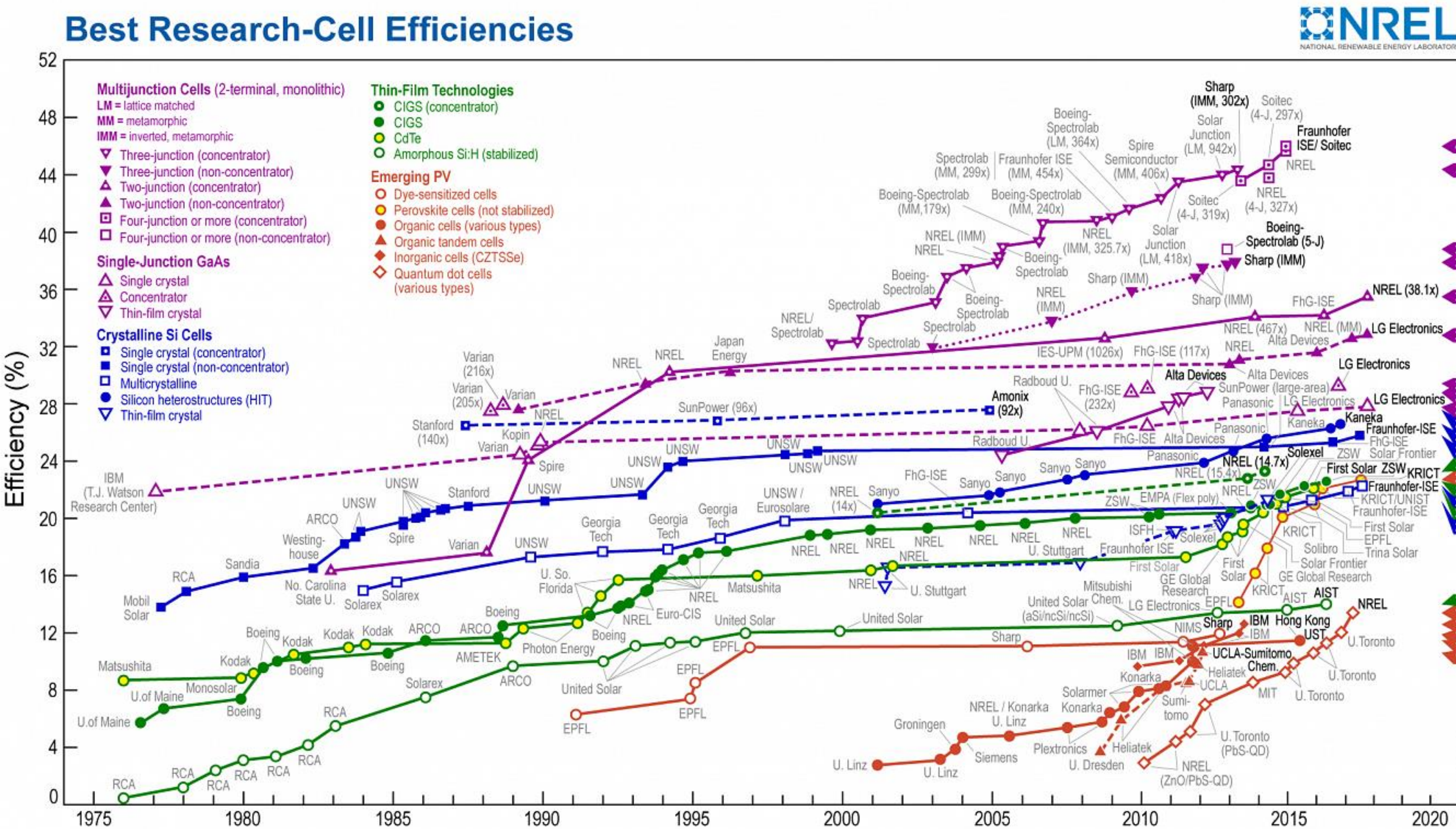
Data: M.J. de Wild-Scholten 2013; CPV data: "Environmental Sustainability of Concentrator PV Systems: Preliminary LCA Results of the Apollon Project" 5th World Conference on PV Energy Conversion. Valencia, Spain, 6-10 September 2010. Graph: PSE 2014

Record Efficiencies



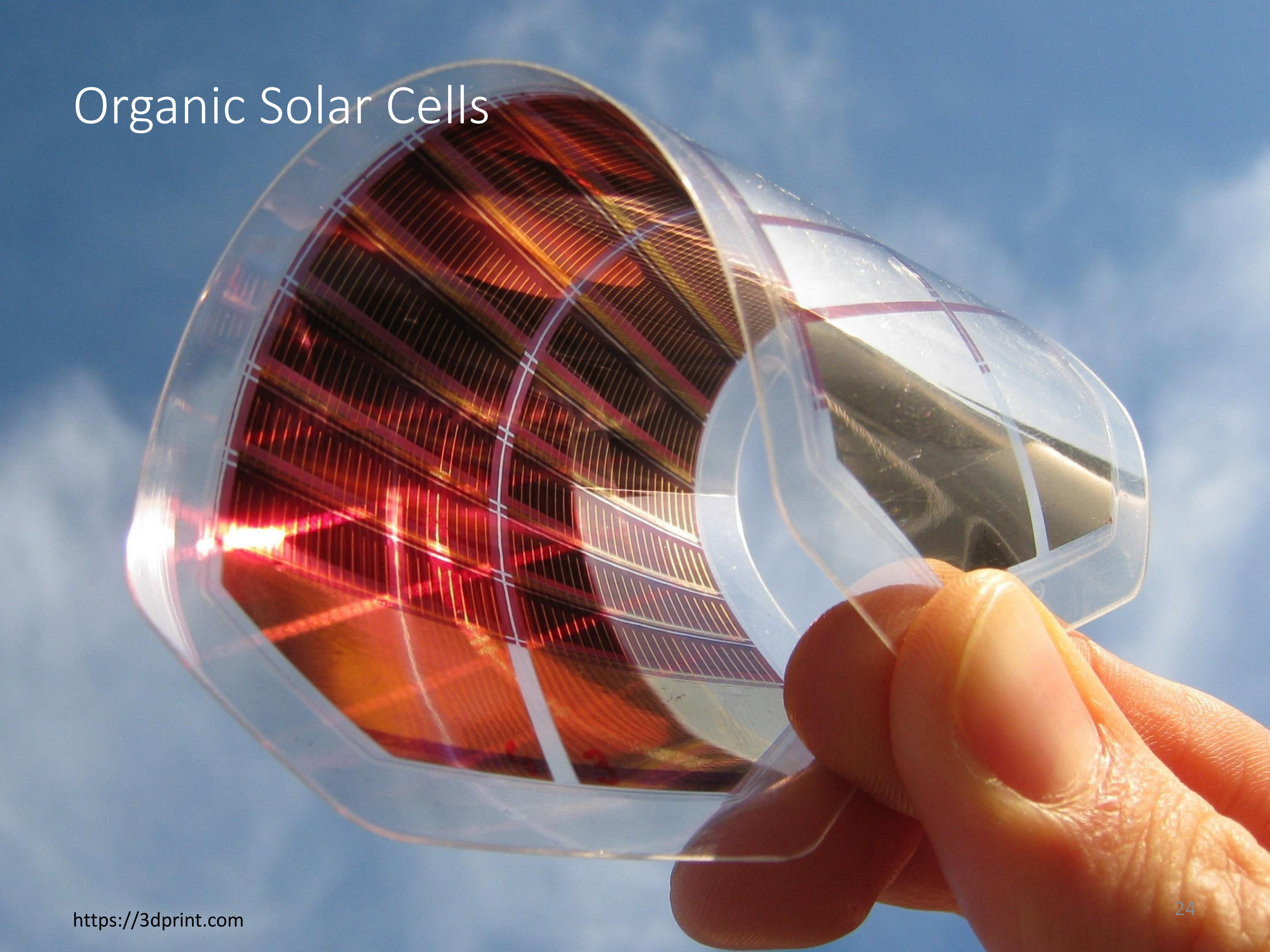
Data: Green et al.: Solar Cell Efficiency Tables (Version 51), Progress in PV: Research and Applications 2018. Graph: PSE 2018

NREL Chart



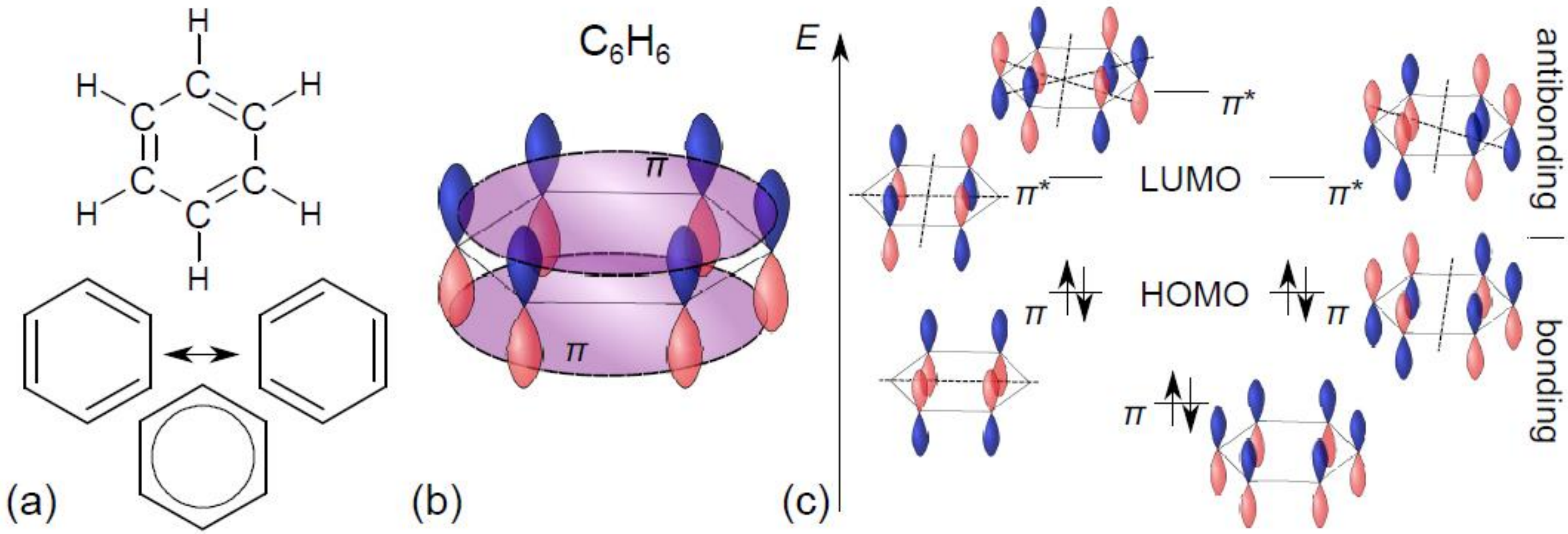
Best Research-Cell Efficiencies
NREL
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye-sensitized cells
Perovskite cells (not stabilized)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells (various types)
46.0%
44.4%
38.8%
37.9%
35.5%
32.8%
29.3%
28.8%
27.8%
27.6%
26.6%
25.8%
23.3%
22.7%
22.6%
22.3%
22.1%
21.2%
14.0%
13.4%
12.6%
11.9%
11.5%
10.6%

Organic Solar Cells



https://3dprint.com

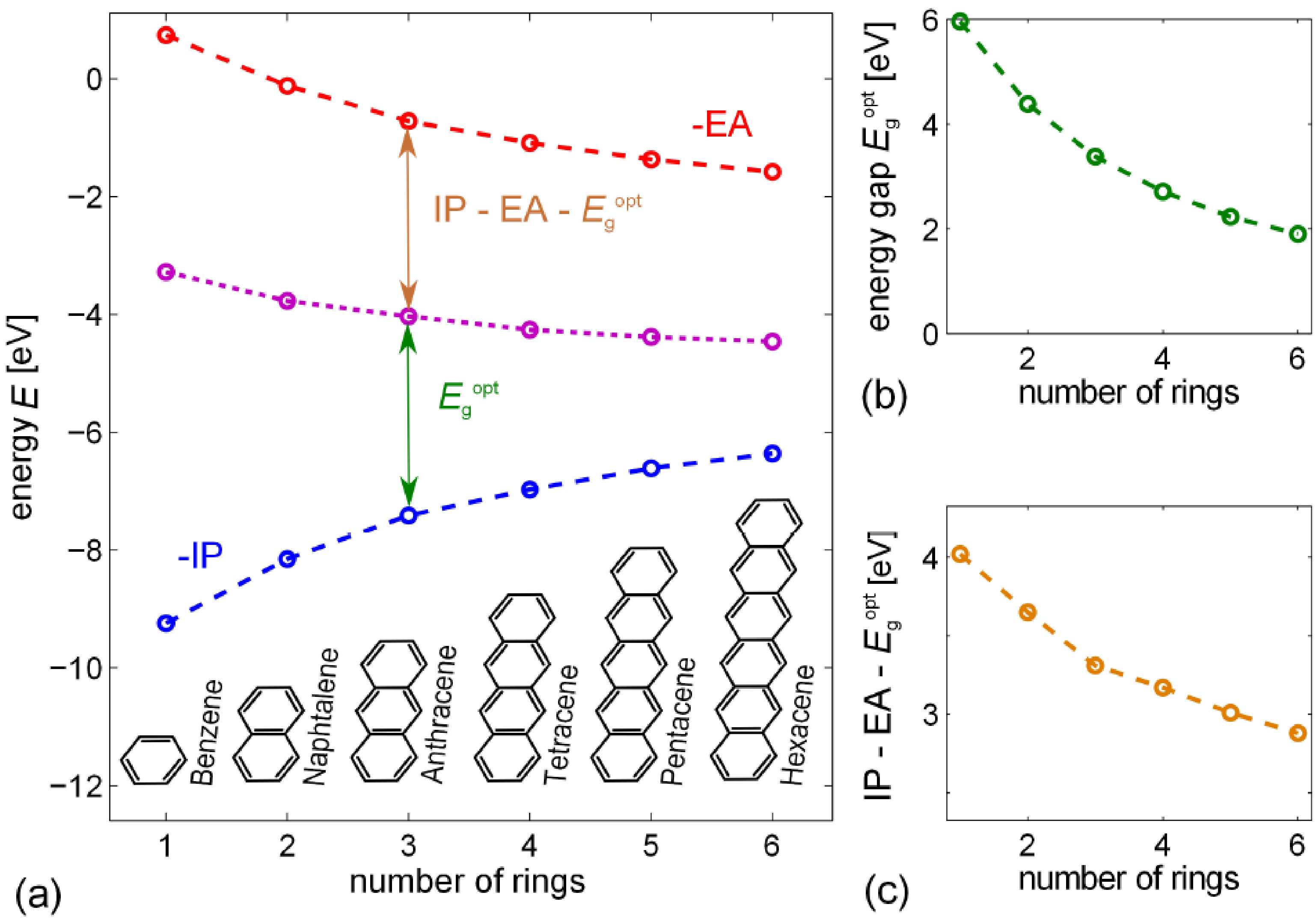
Pi-Conjugated Molecules: LCAO



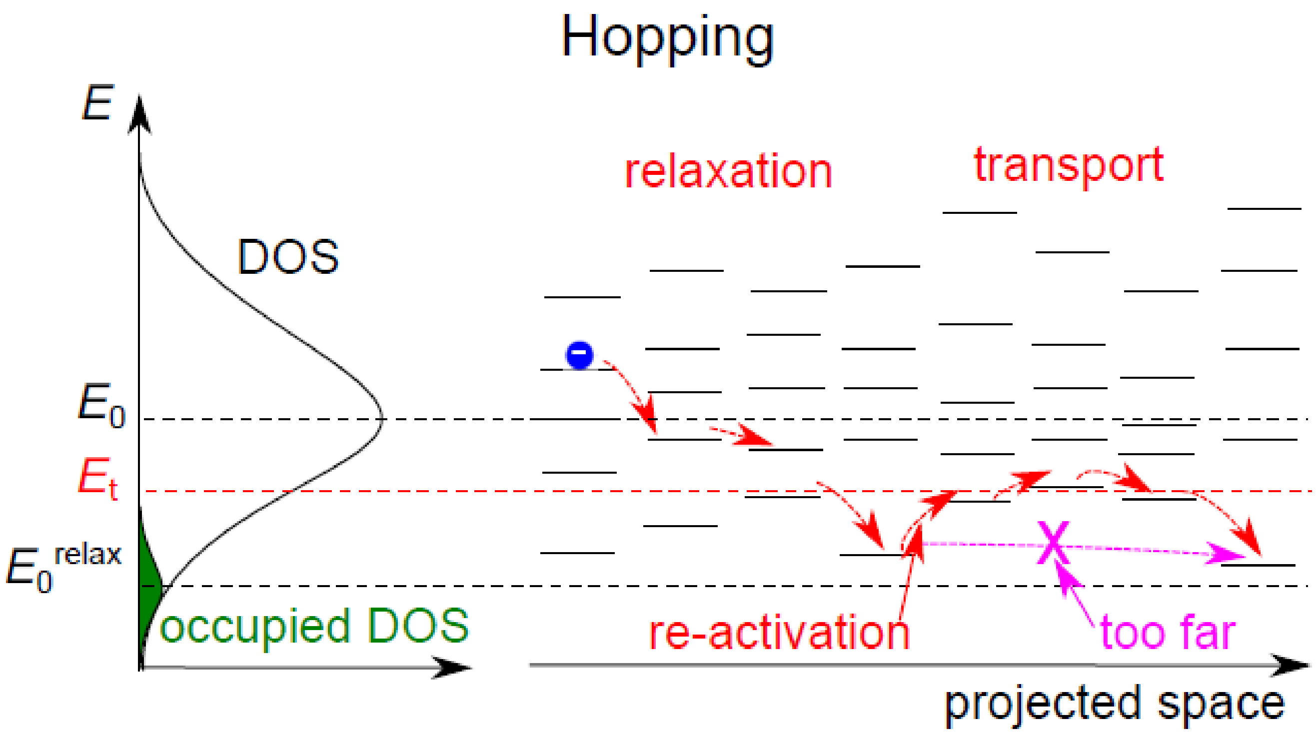
- Frontier orbitals:
  - Highest Occupied Molecular Orbital (HOMO)
  - Lowest Unoccupied Molecular Orbital (LUMO)

→ HOMO LUMO transitions can be in visible range

Frontier Orbitals of Oligoacetenes

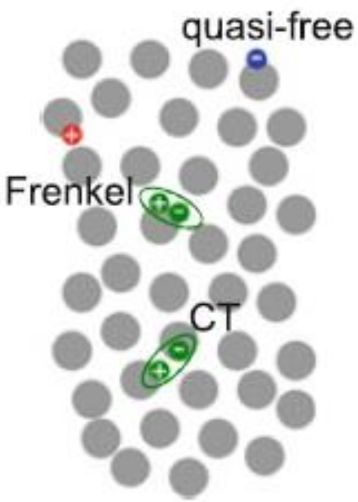


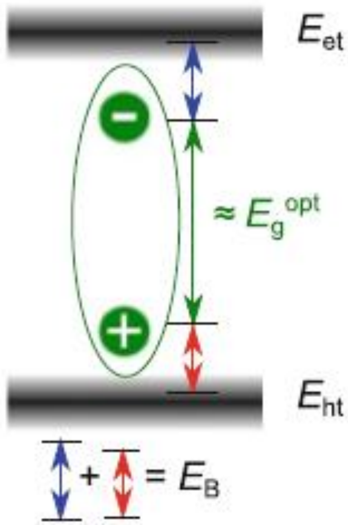
Charge Transport and Disorder

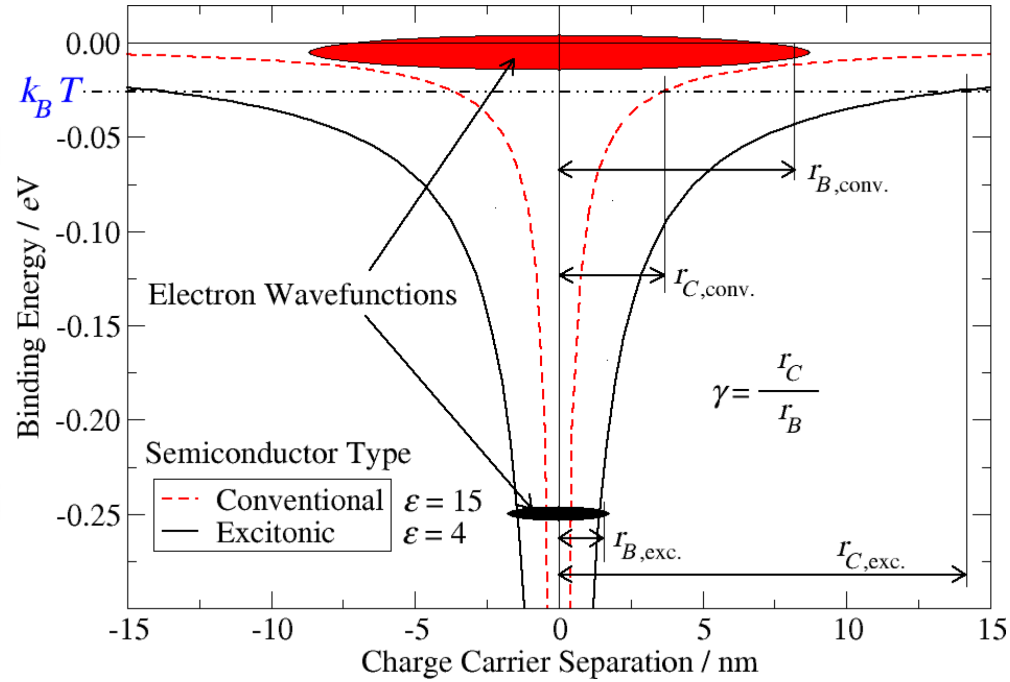


Amorphous film → distribution of sites → low mobility

Excitonic Semiconductors



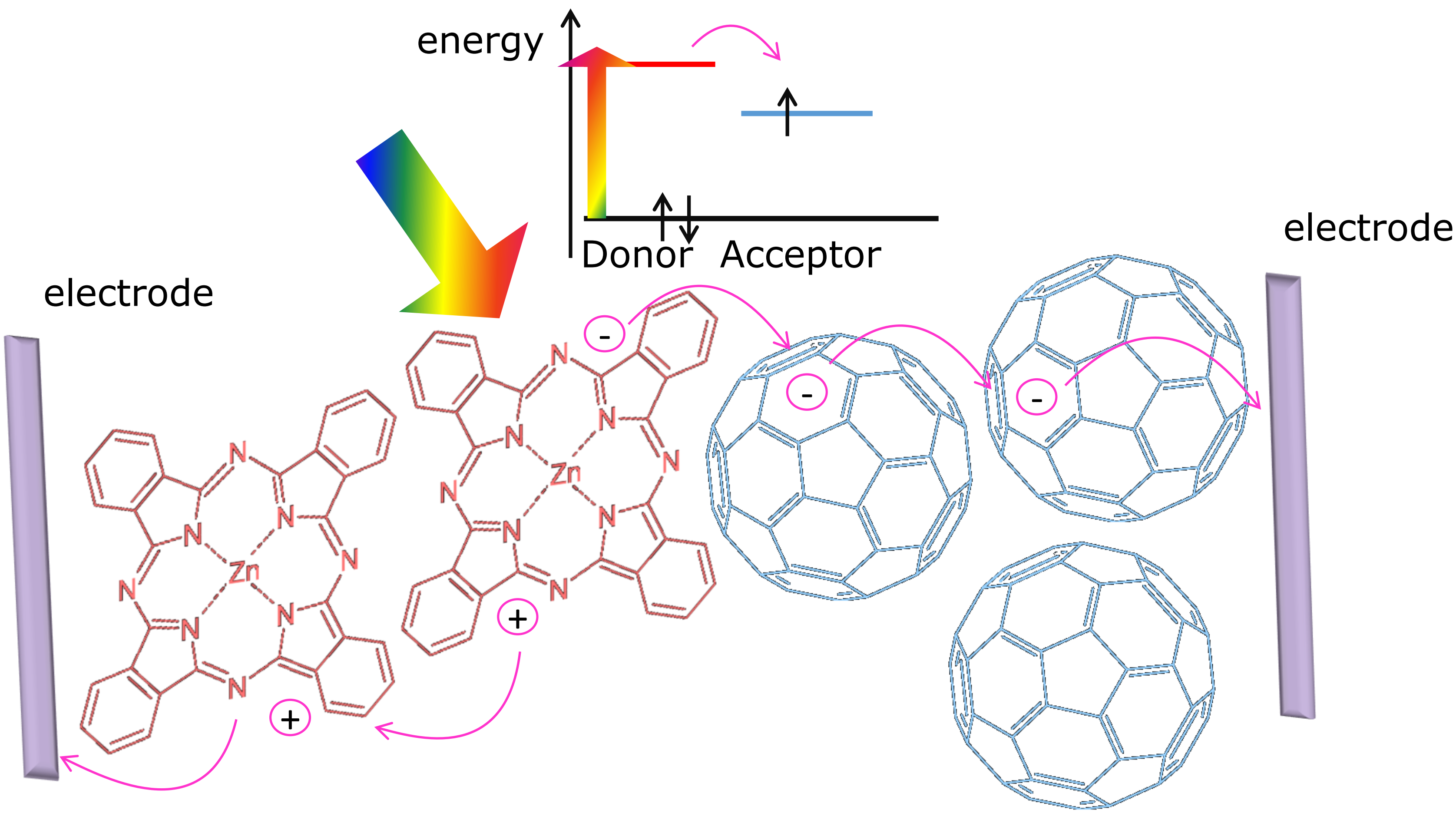




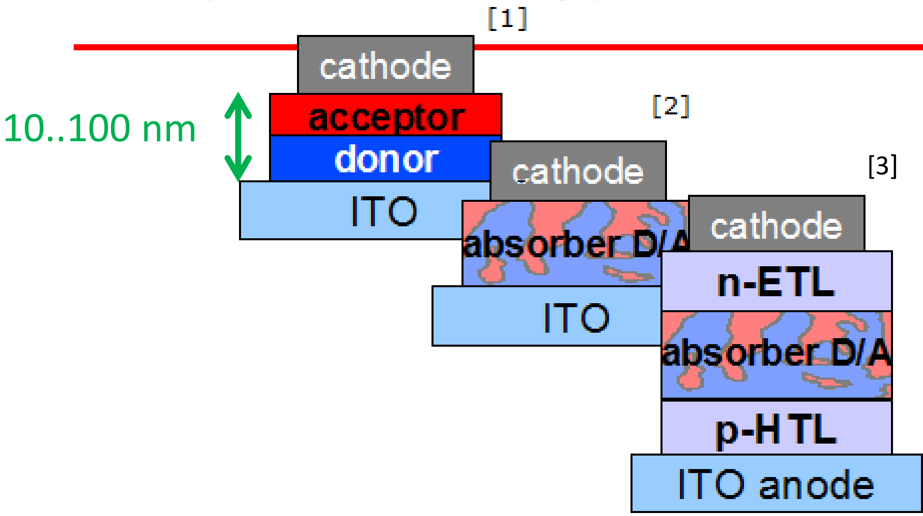
S. E. Gledhill *et al.* J. Mat Res. 20, 3167 (2005) P. Würfel, CHIMIA 61, 770 (2007)

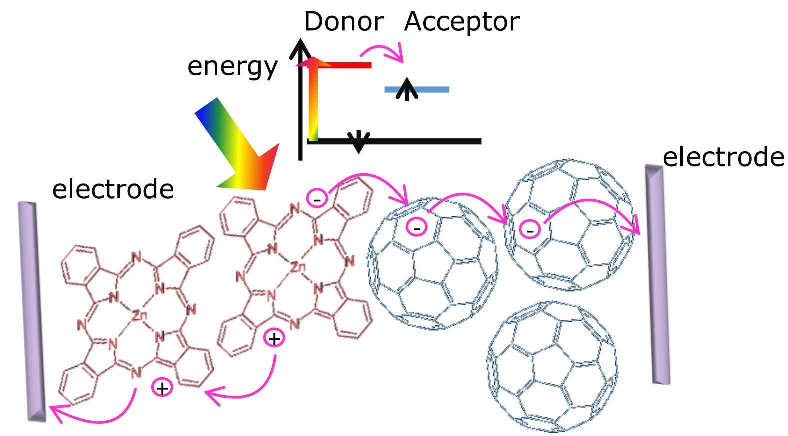
- Molecular film: low interactions between Van-der-Waals bound molecules → molecular properties remain
- Low dielectric constant → high exciton binding energy

Donor-Acceptor Concept



Steps of Energy Conversion

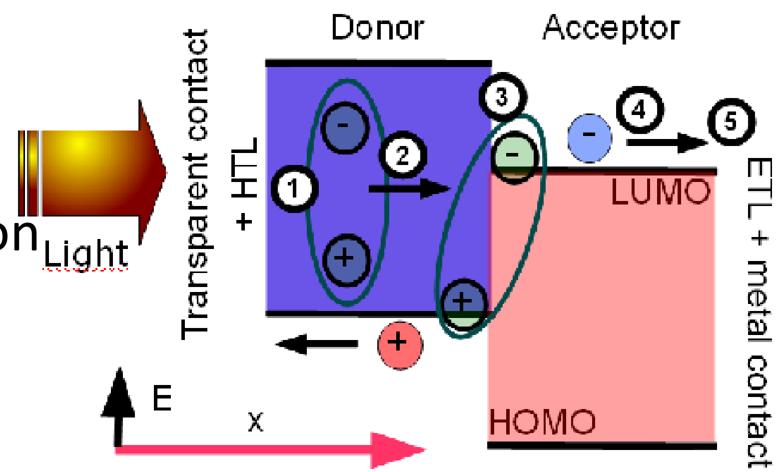




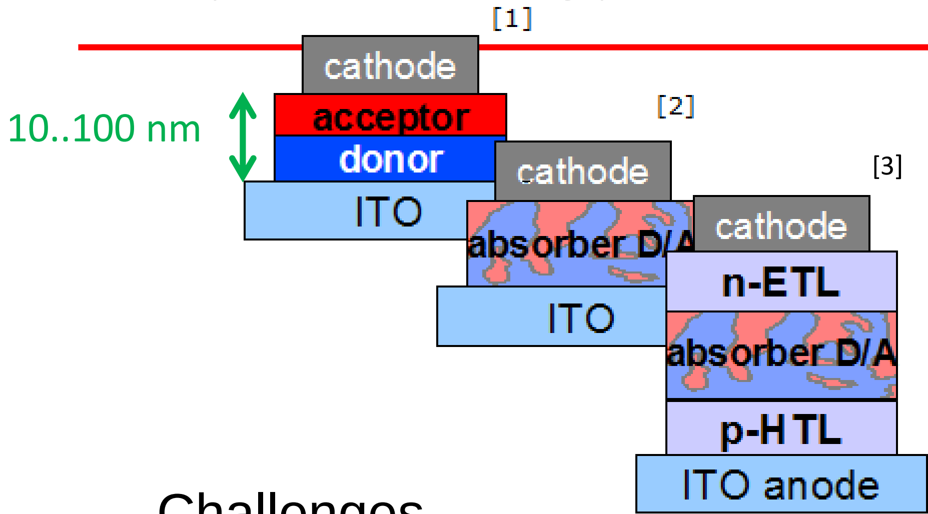
[1] Tang, Appl. Phys. Lett. 48, 183 (1986)
[2] Hiramoto et al. Appl. Phys. Lett. 58, 1062 (1991)
[3] B. Maennig et al., Appl. Phys. A 79, 1 (2004)

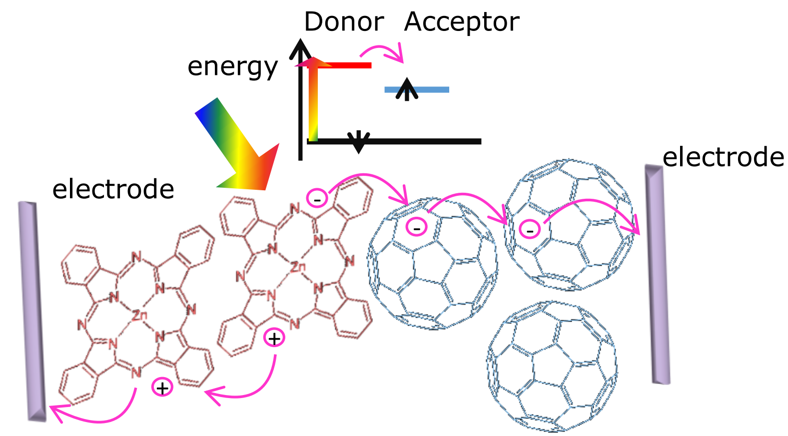
Steps of energy conversion

1. Exciton generation via light absorption
2. Exciton migration (diffusion)
3. Exciton separation and dissociation
4. Charge carrier transport
5. Charge carrier collection/injection



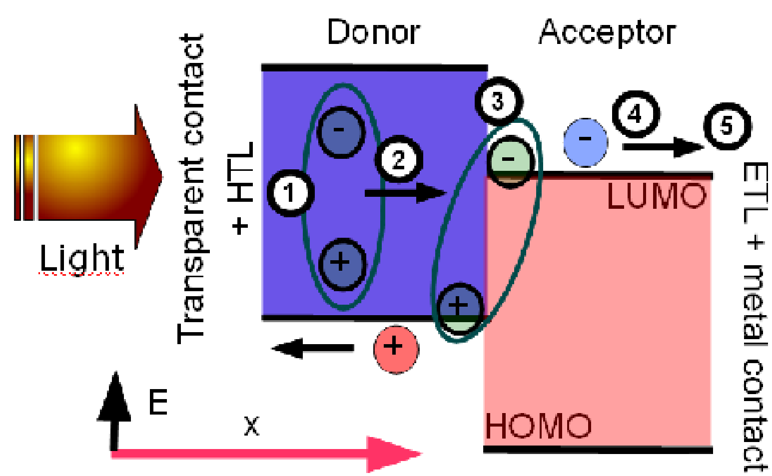
Steps of Energy Conversion





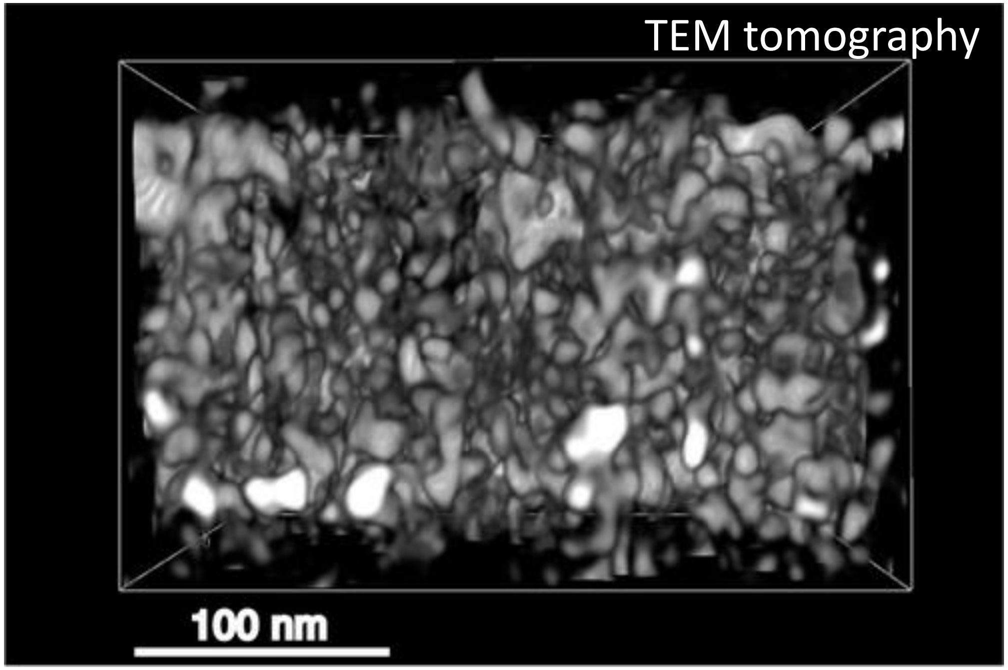
Challenges

- Disorder, poor charge transport
- Excited states hard to split
- Low fill factor
- High recombination, low voltage
- Narrow absorption, but broad onset
- Low long-term stability

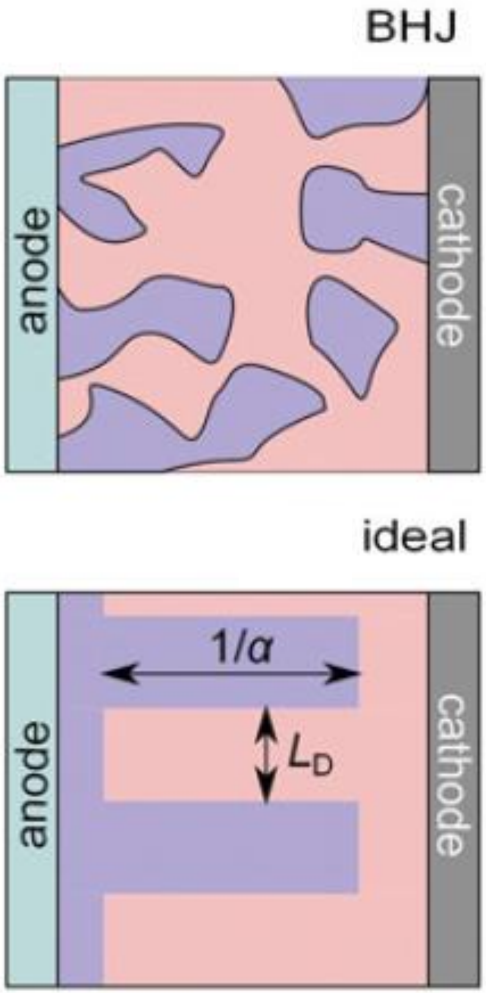


Bulk Heterojunction: Morphology

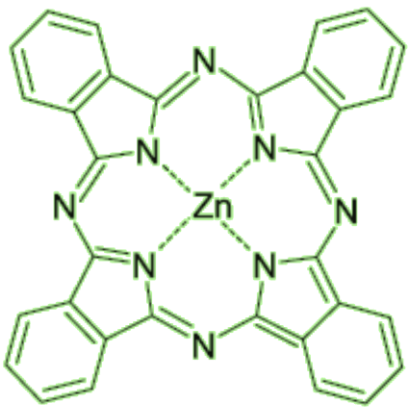
- Tune amount of mixing/demixing
  - Energy vs. entropy
  - Annealing
  - Solvents

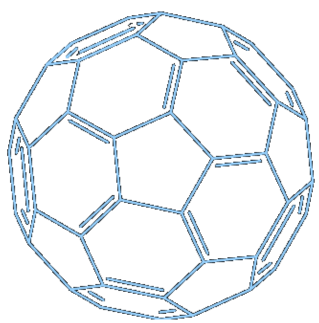


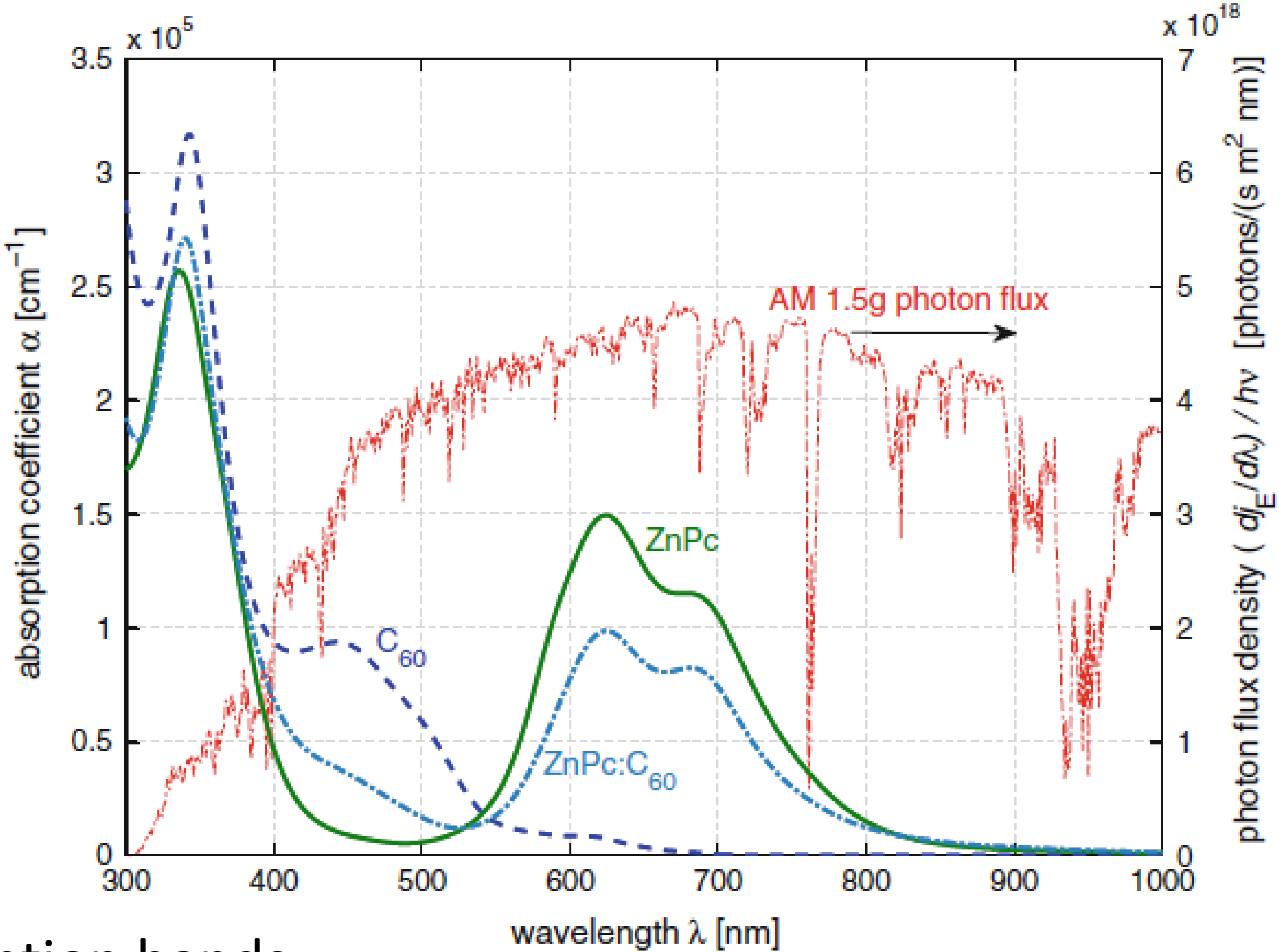
Nano Lett., 2009, 9 (2), pp 853–855 **DOI:** 10.1021/nl803676e



Absorption and EQE

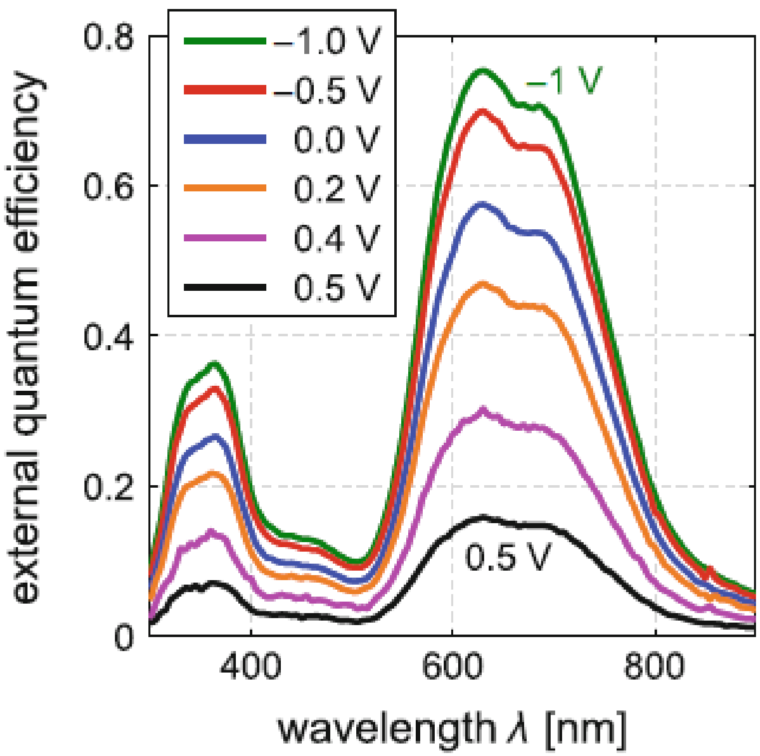


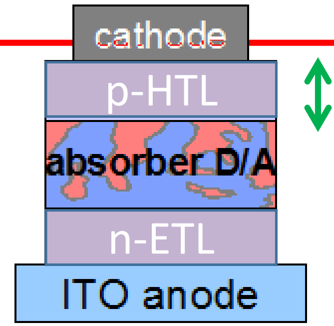


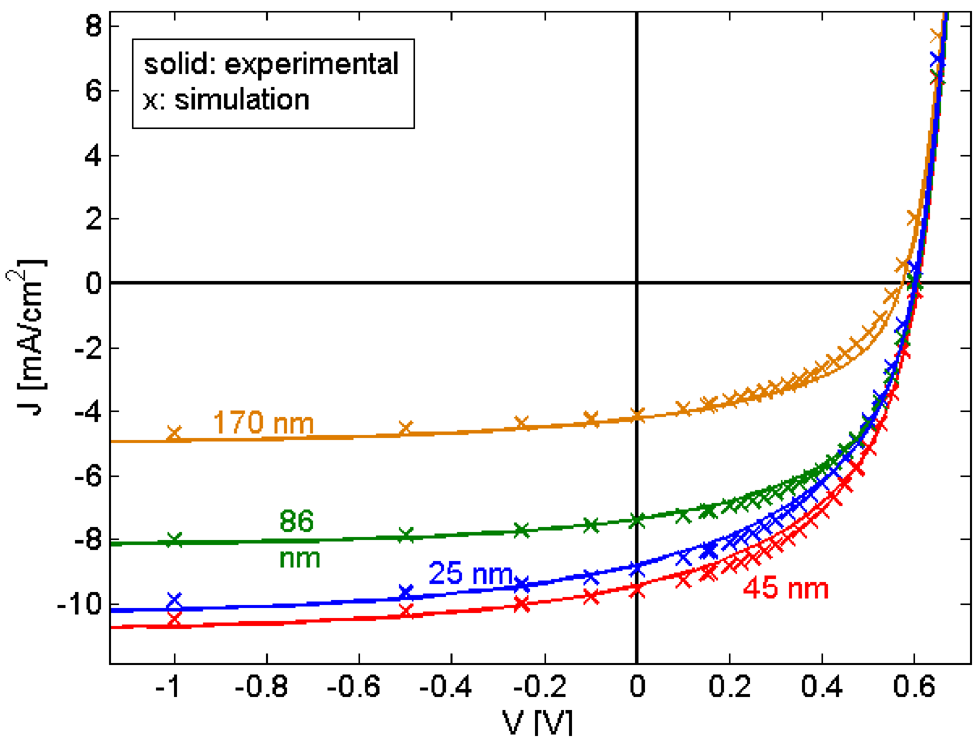


- Narrow absorption bands

EQE and JV-curve





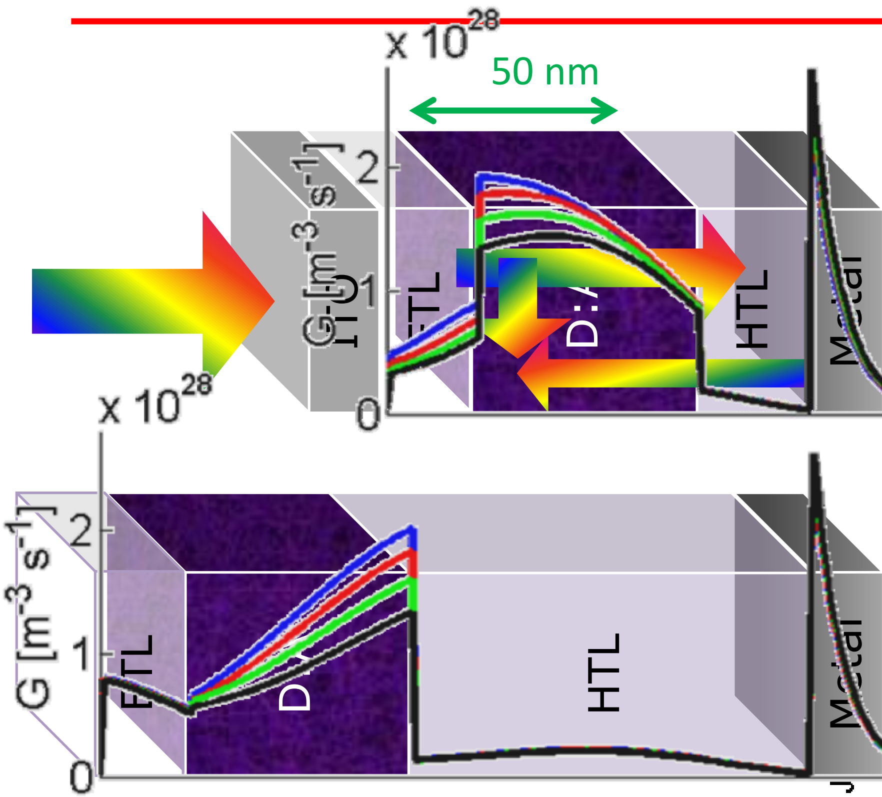


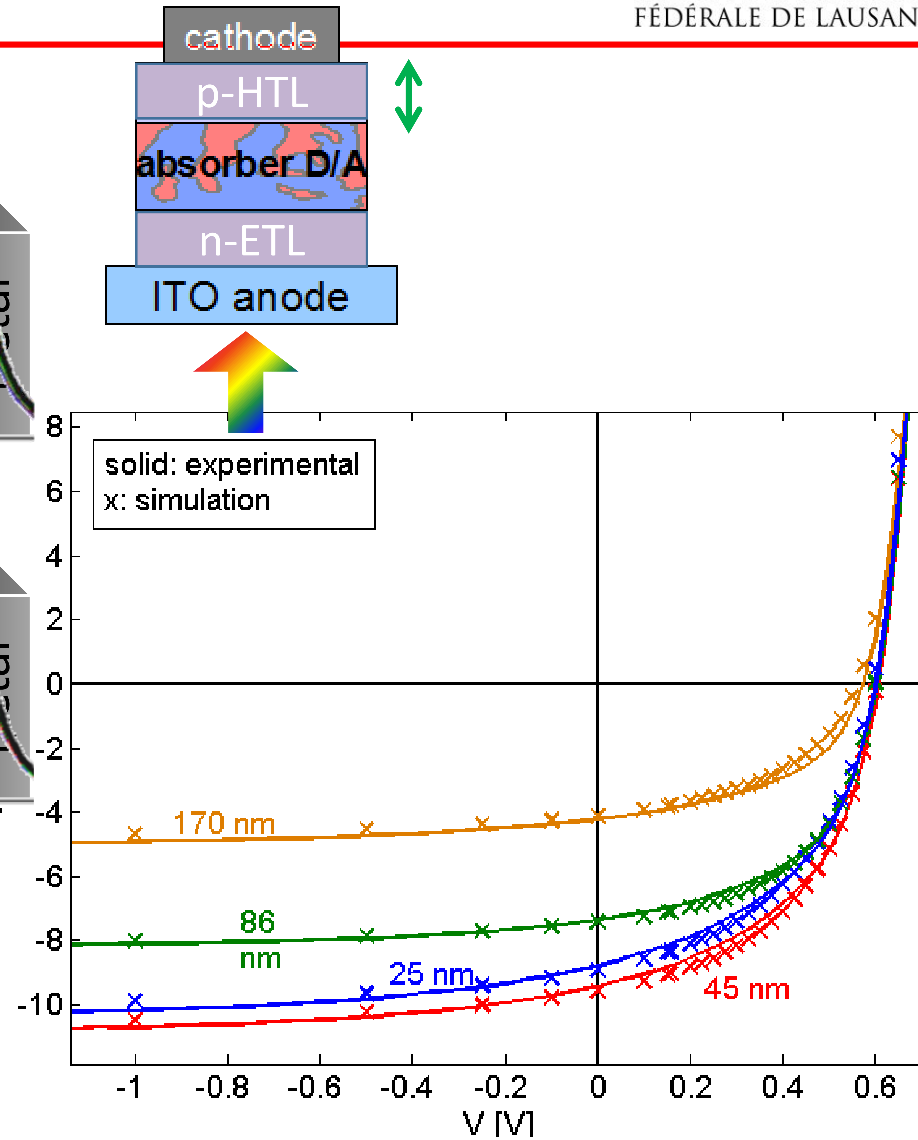
J_{ph} depends on voltage

→ Charge collection problem

→ Reduces fill factor

Light Management



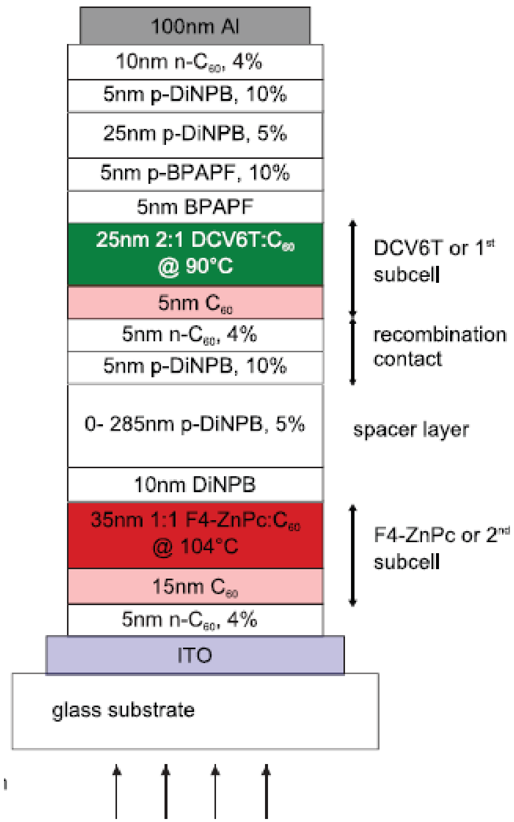


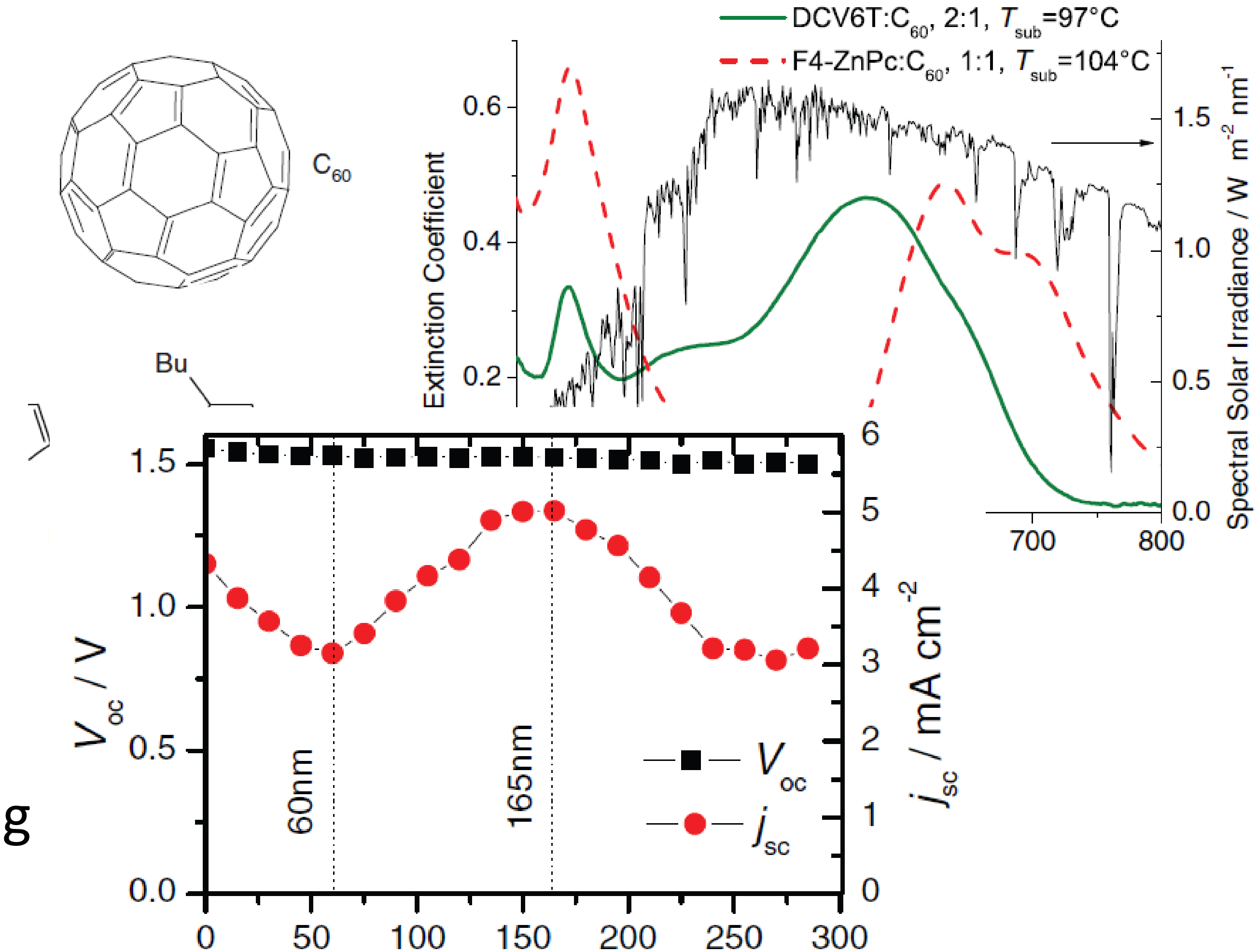
Thin film optics: interference

→ Beer-Lambert law does not apply

Tandem Solar Cells

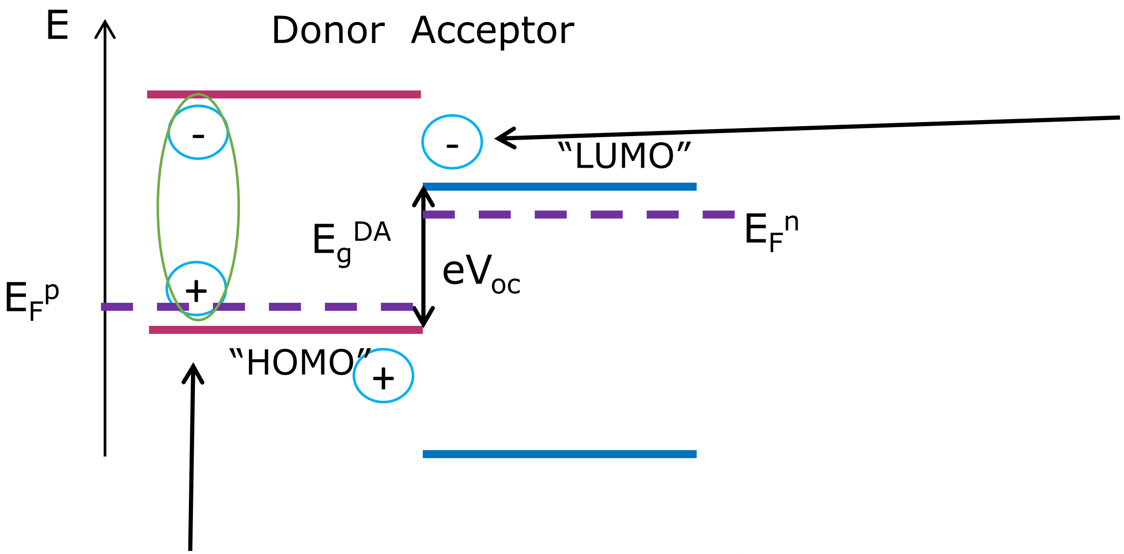
Adv. Funct. Mater. **2011**, *21*, 3019–3028





- Current matching

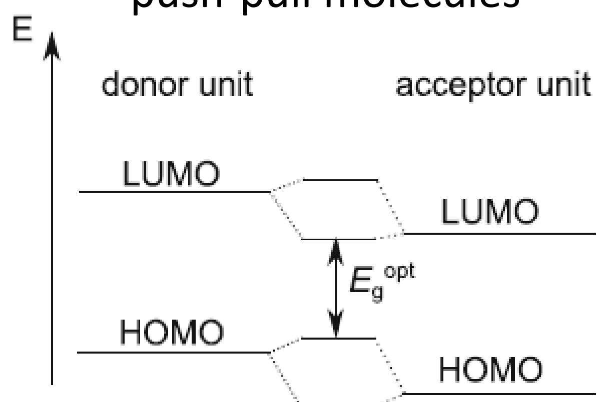
How to Increase Current and Voltage



Voltage:
→ Reduce "offset" energies
→ Combination of donor and acceptor

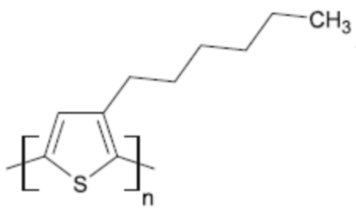
Current:
→ Low band gap materials
→ Complementary absorption of donor and acceptor

push-pull molecules

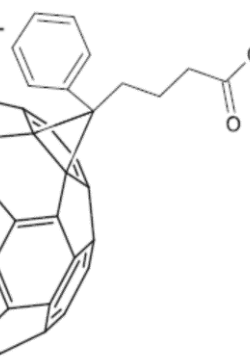


Tuning Absorption in Polymers

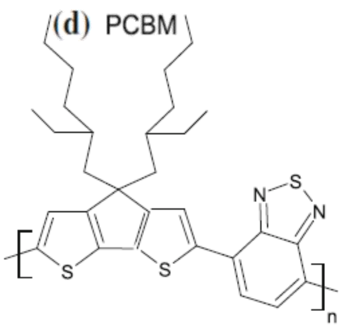
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE



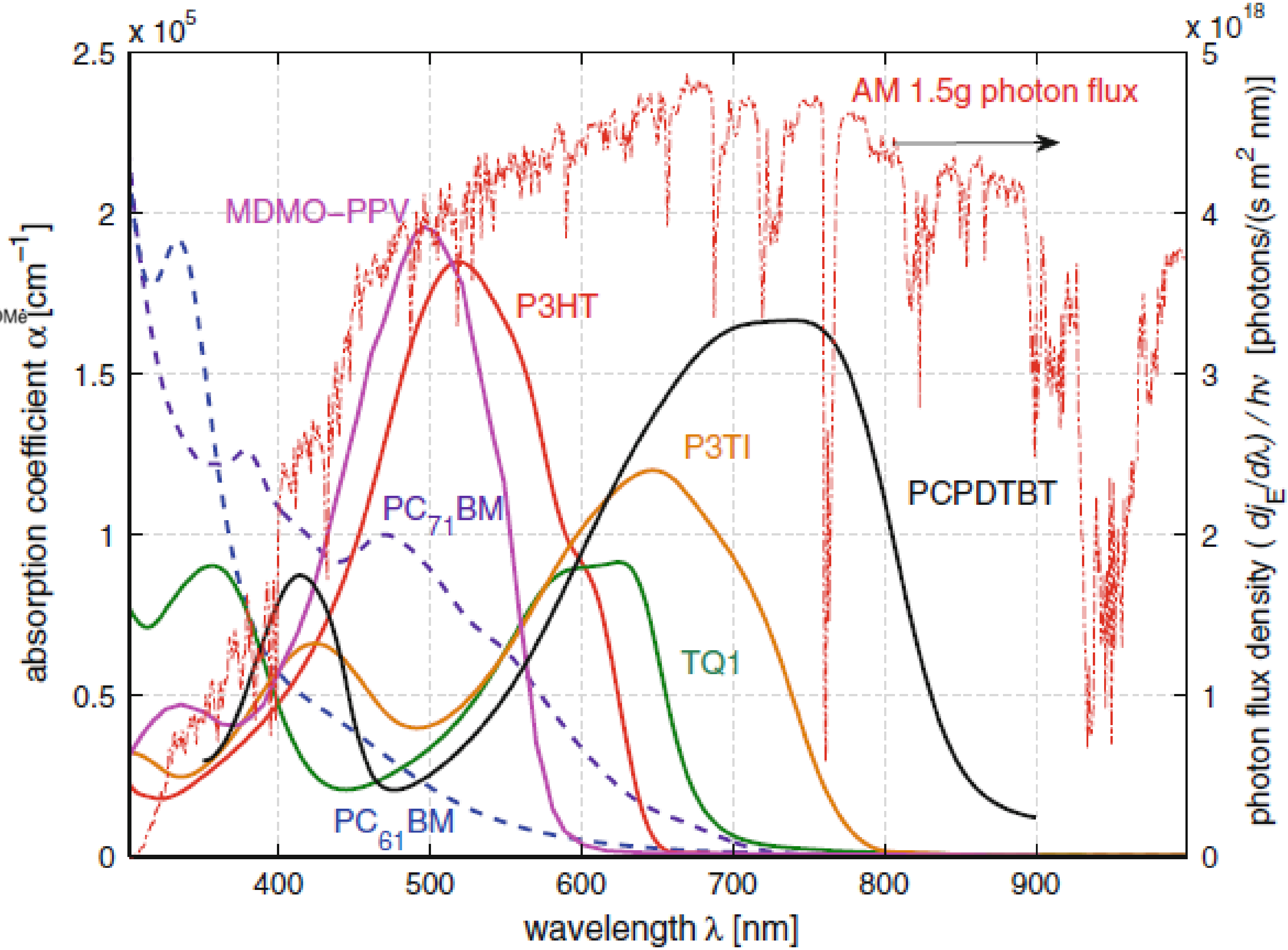
(c) P3HT



(d) PCBM

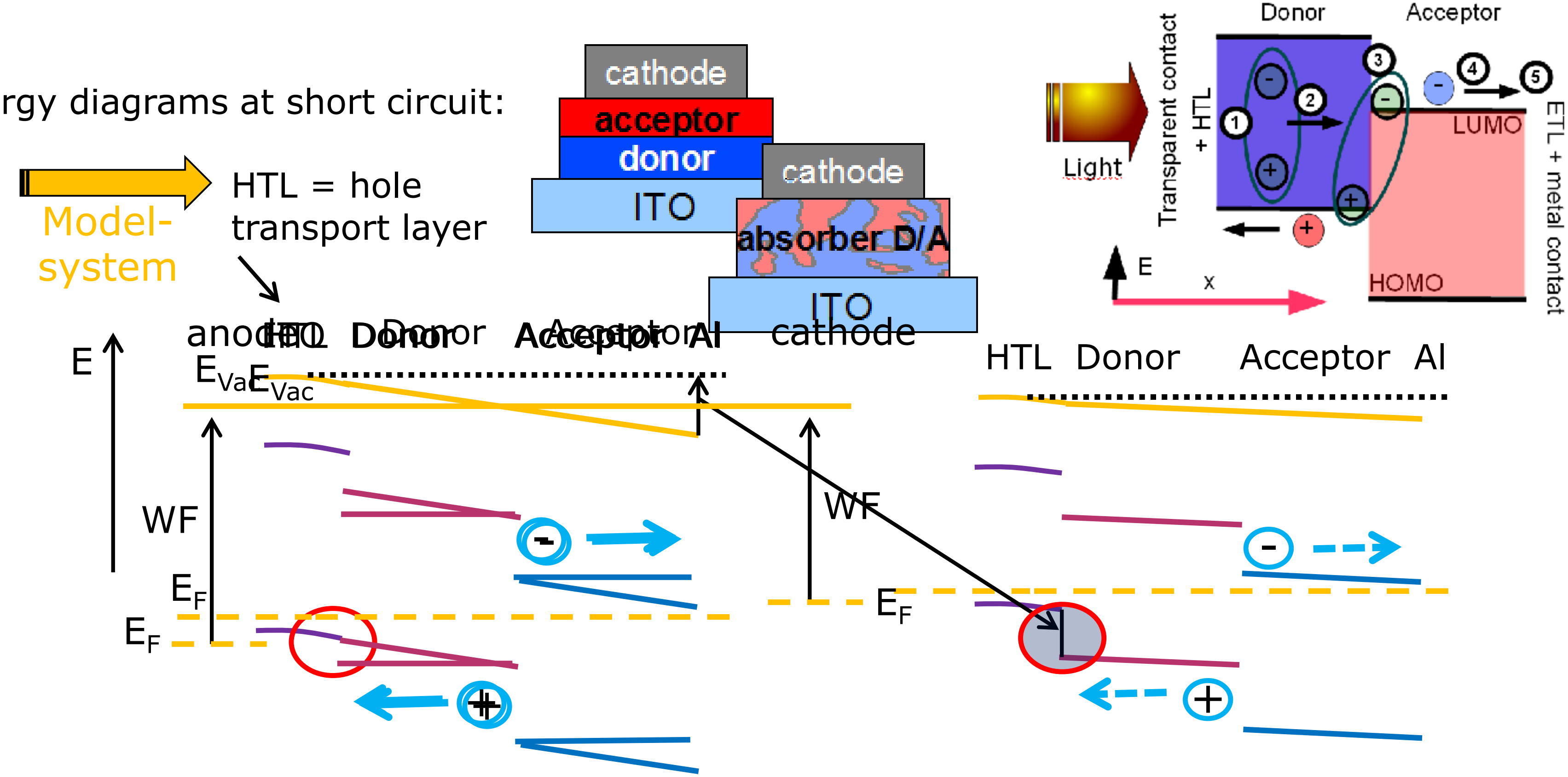


(e) PCPDTBT



Working Principle and Role of Contacts

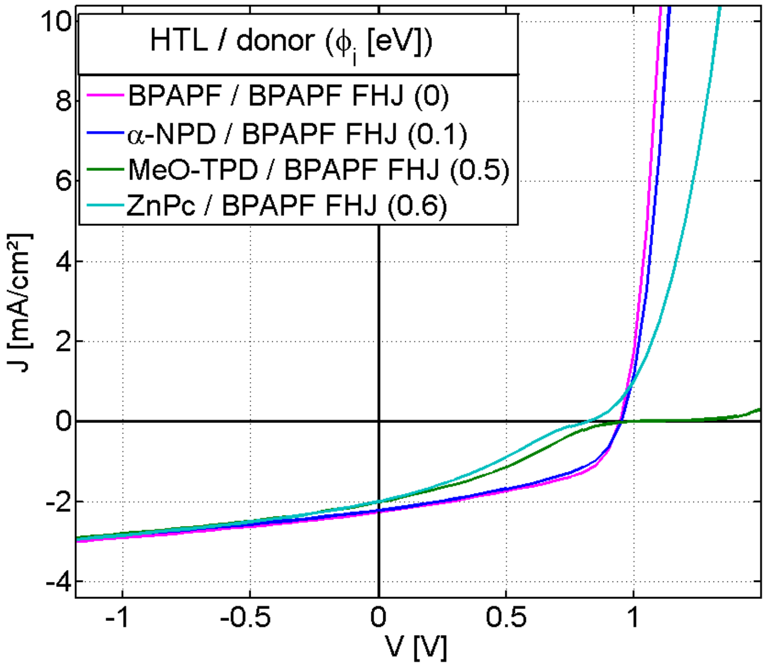
Energy diagrams at short circuit:



→ Provide built-in field due to difference in work functions

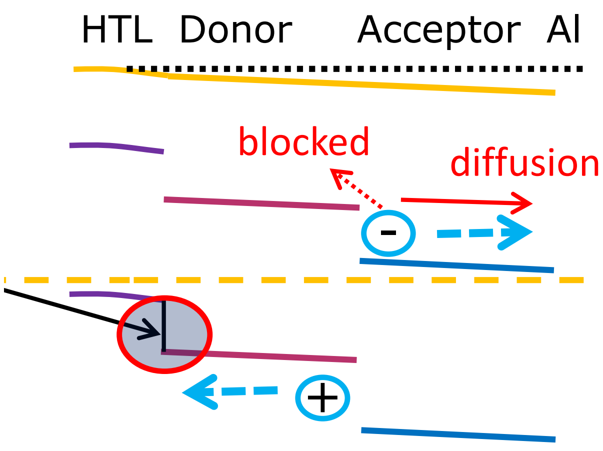
Flat vs. Bulk Heterojunction

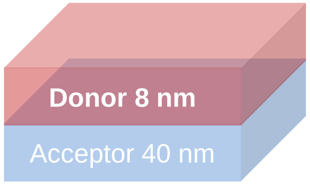
Energy diagrams at short circuit:



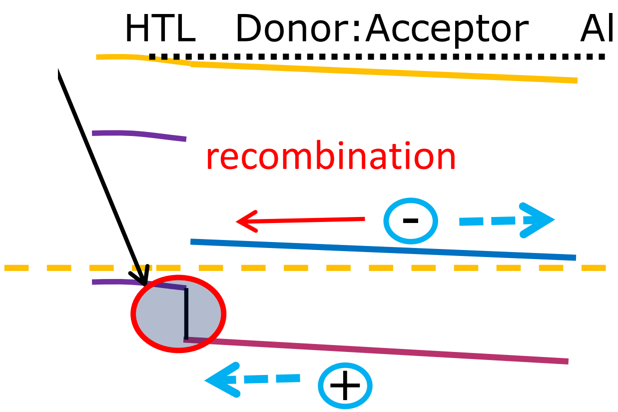
Missaligned contacts → S-Shape

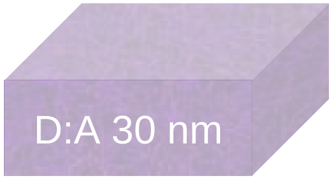
→ Build selective device!





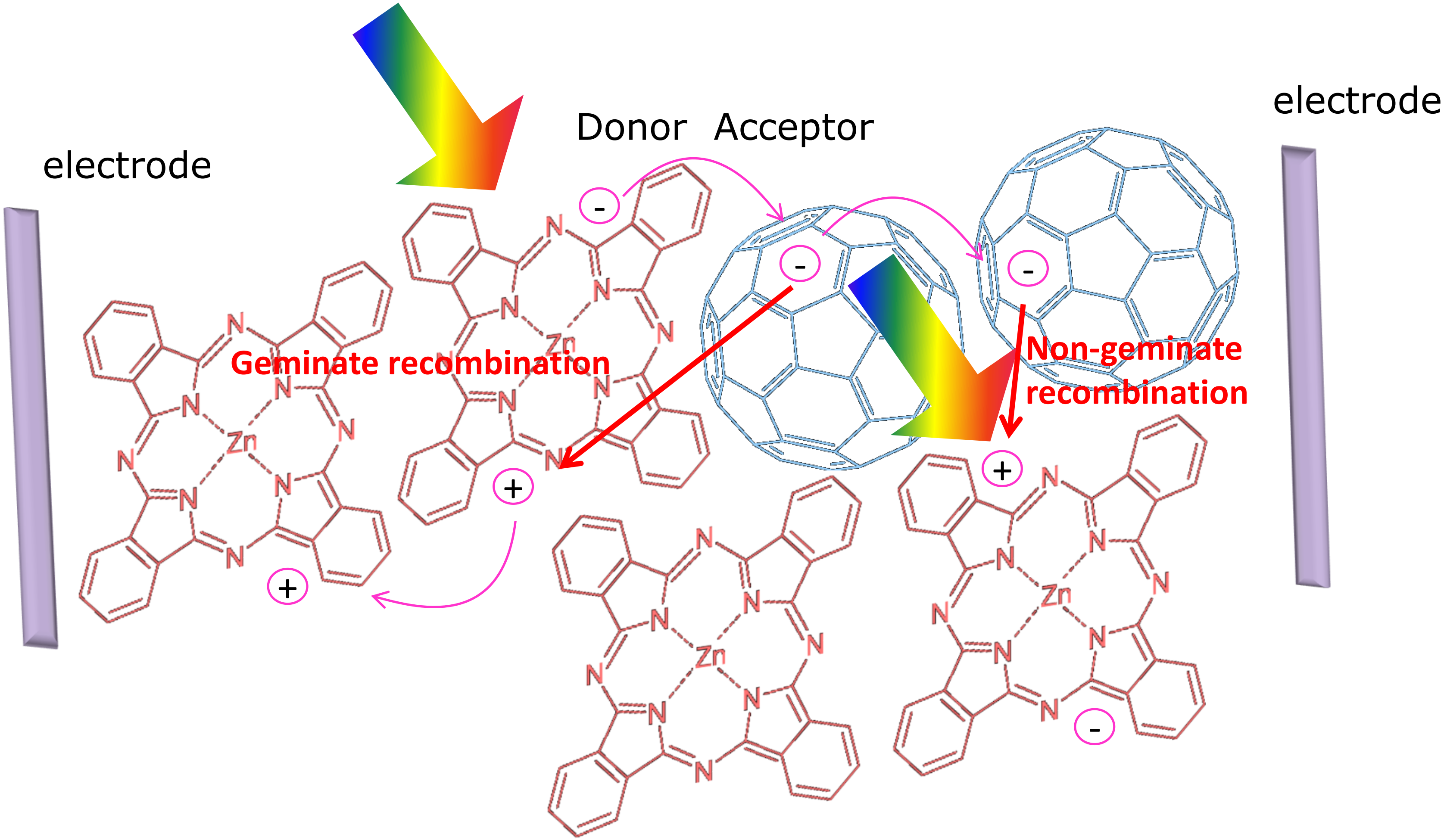
no changes of V_{oc}



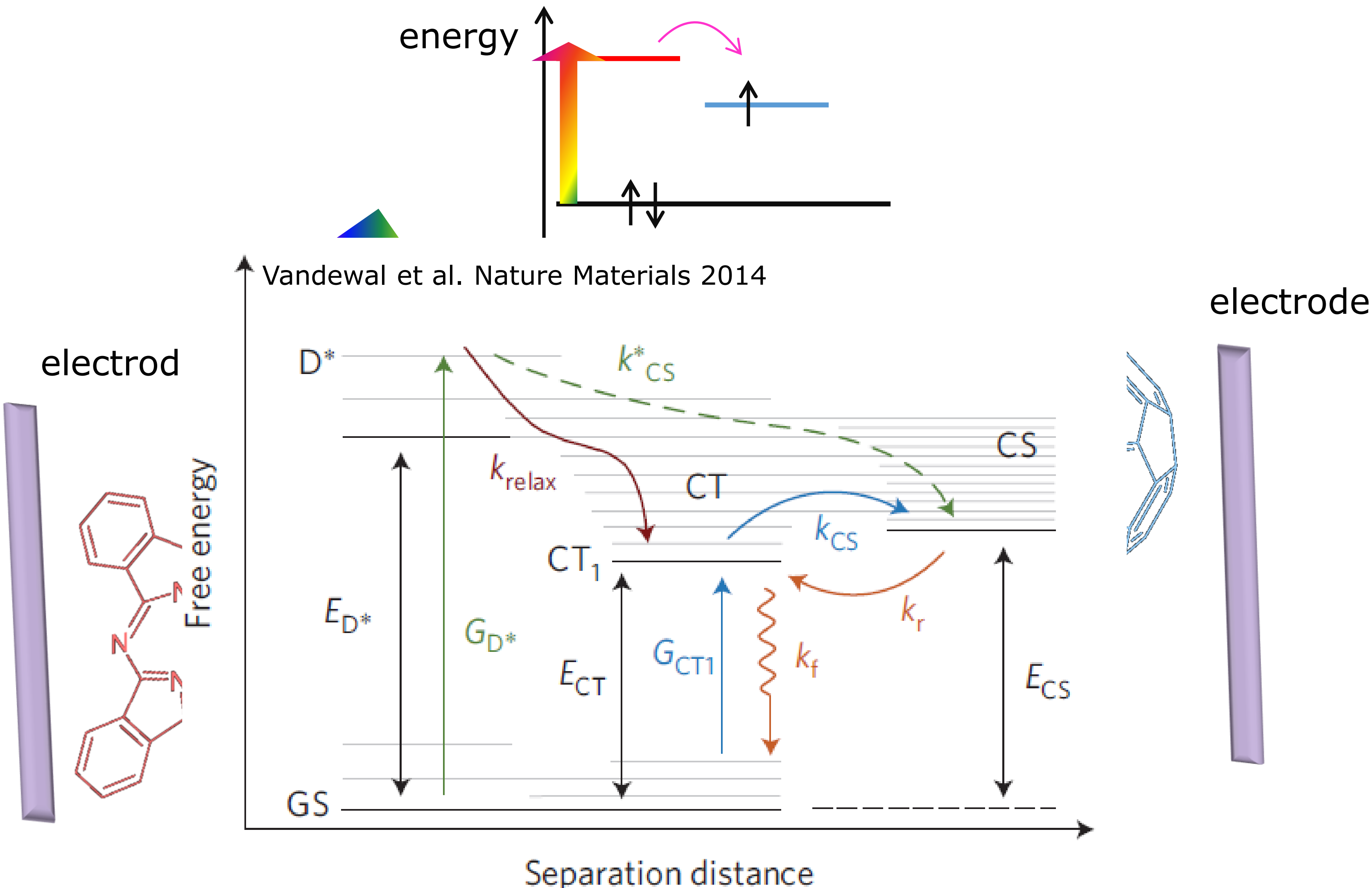


decrease of V_{oc}

Geminate Recombination

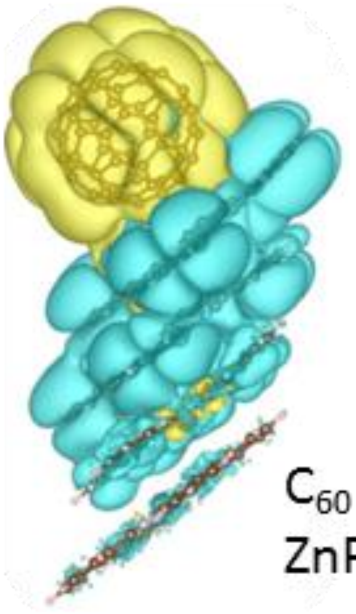


Charge Transfer States: hot, (de)localized?



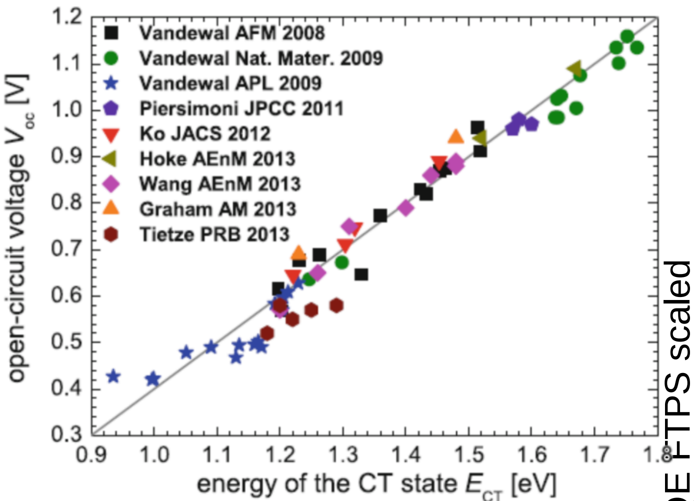
Charge Transfer State: Delocalized?

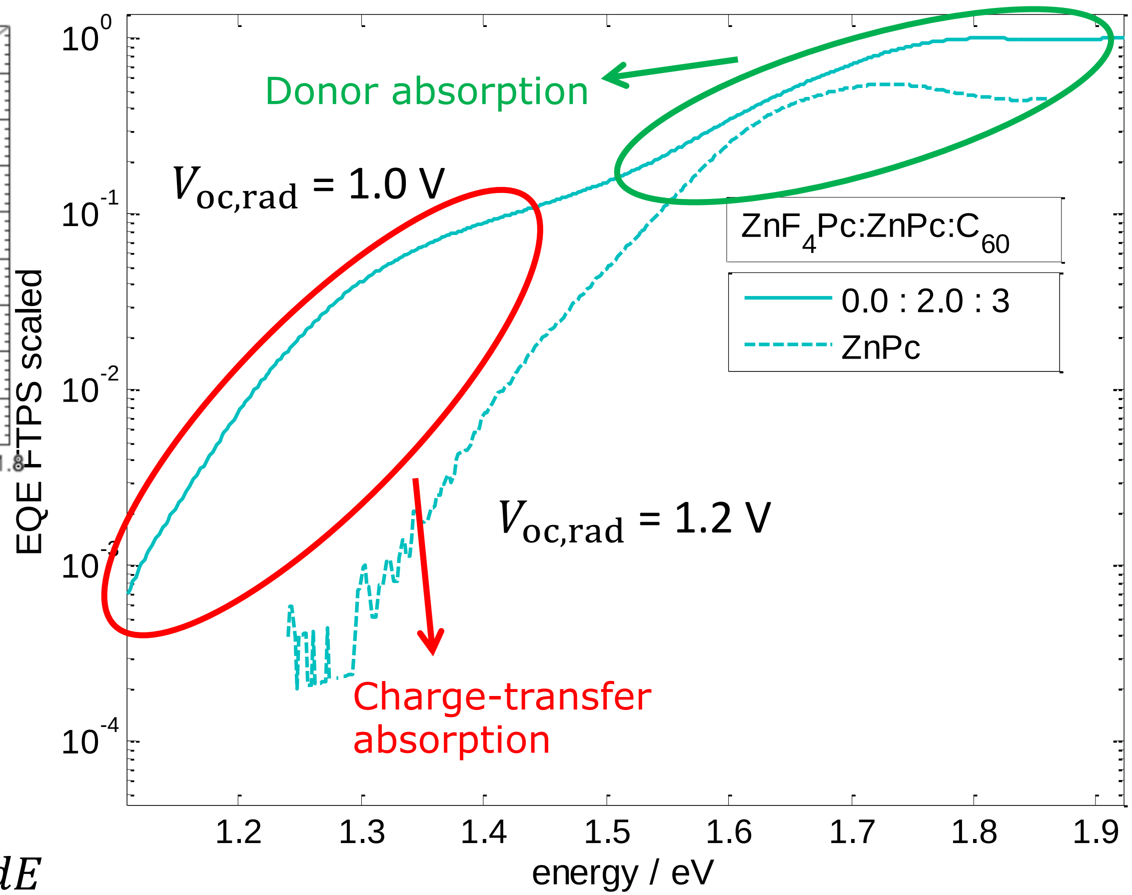
Compare to **TD DFT simulations**



In collaboration with U. Roethlisberger, EPFL

Charge Transfer State and V_{oc}





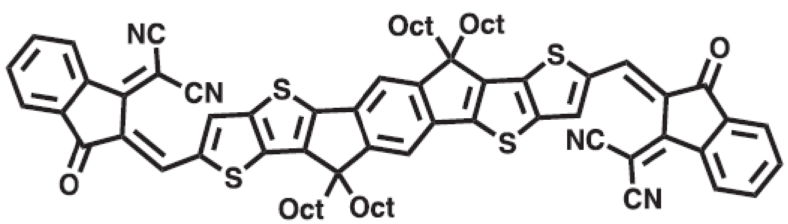
$$V_{oc,rad} = \frac{k_B T}{e} \ln\left(\frac{J_{ph}}{J_{em,0}} + 1\right)$$

$$J_{ph} = e \int \mathrm{EQE}(E) \Phi_{AM1,5g}(E) dE$$

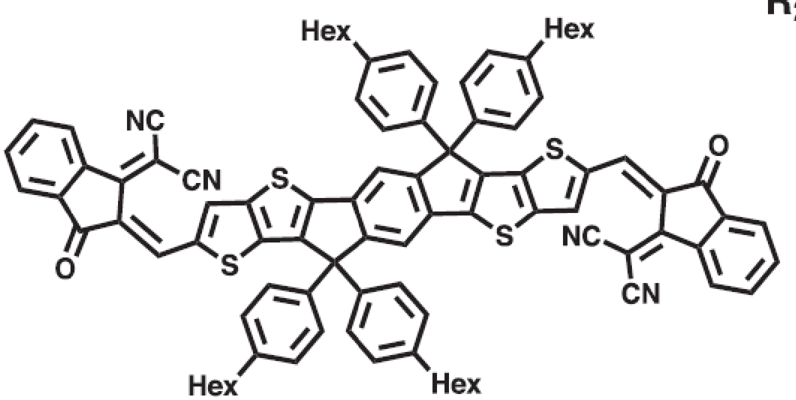
$$J_{em,0} = e \int \mathrm{EQE}(E)\, \phi_{BB}(T_0) dE$$

State-of-the-Art Materials and Efficiencies

small-molecule acceptors

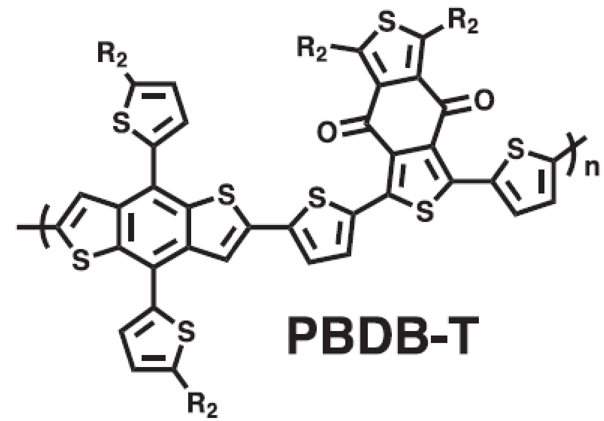


C8-ITIC



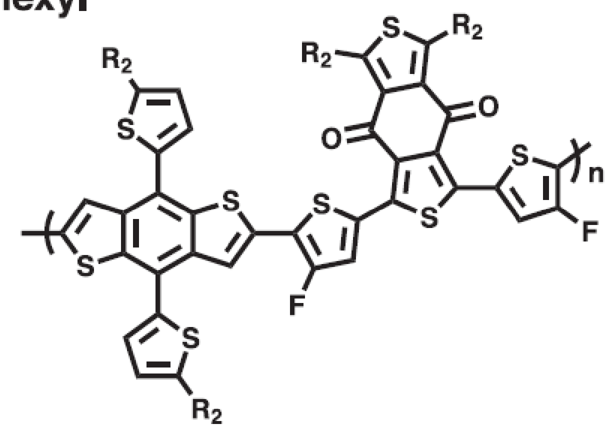
ITIC

donor polymers



PBDB-T

R_1 = octyl
R_2 = 2-ethylhexyl

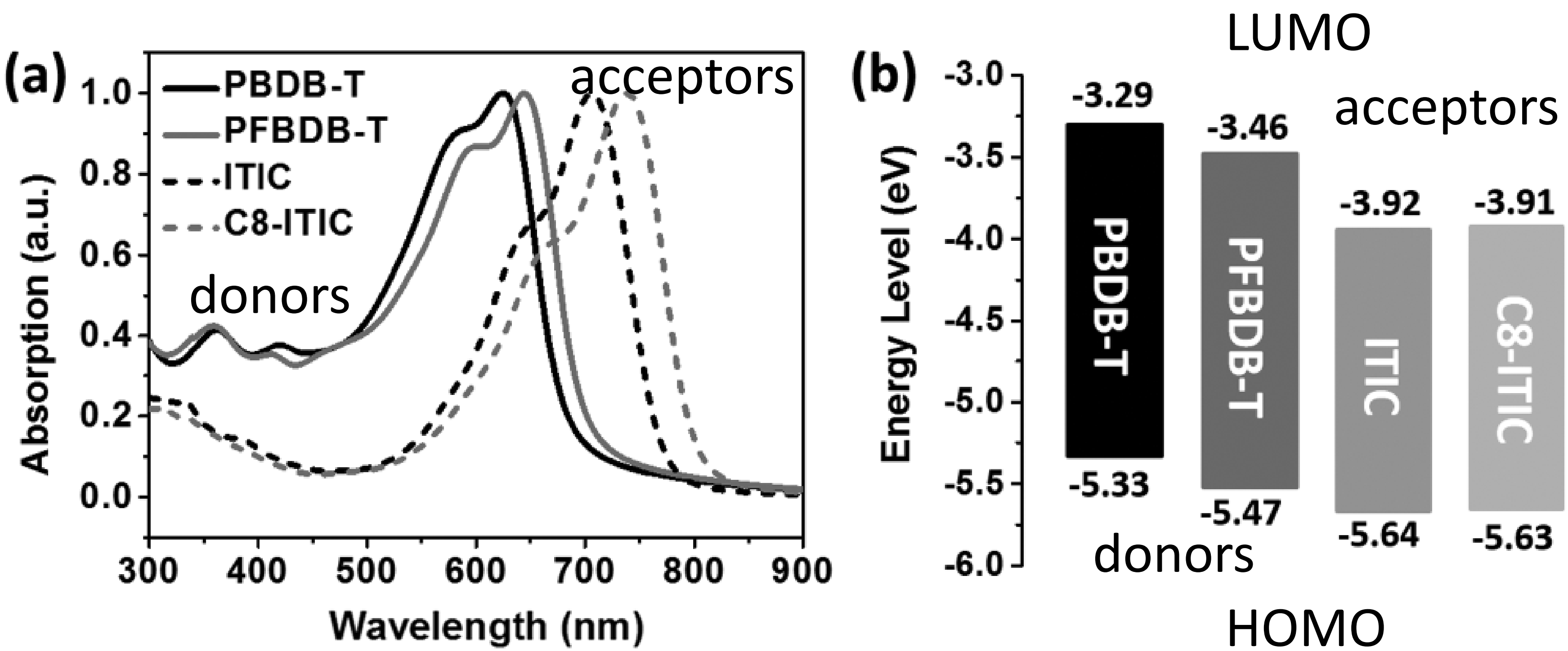


PFBDB-T

Adv. Mater. **2018**, *30*, 1705209

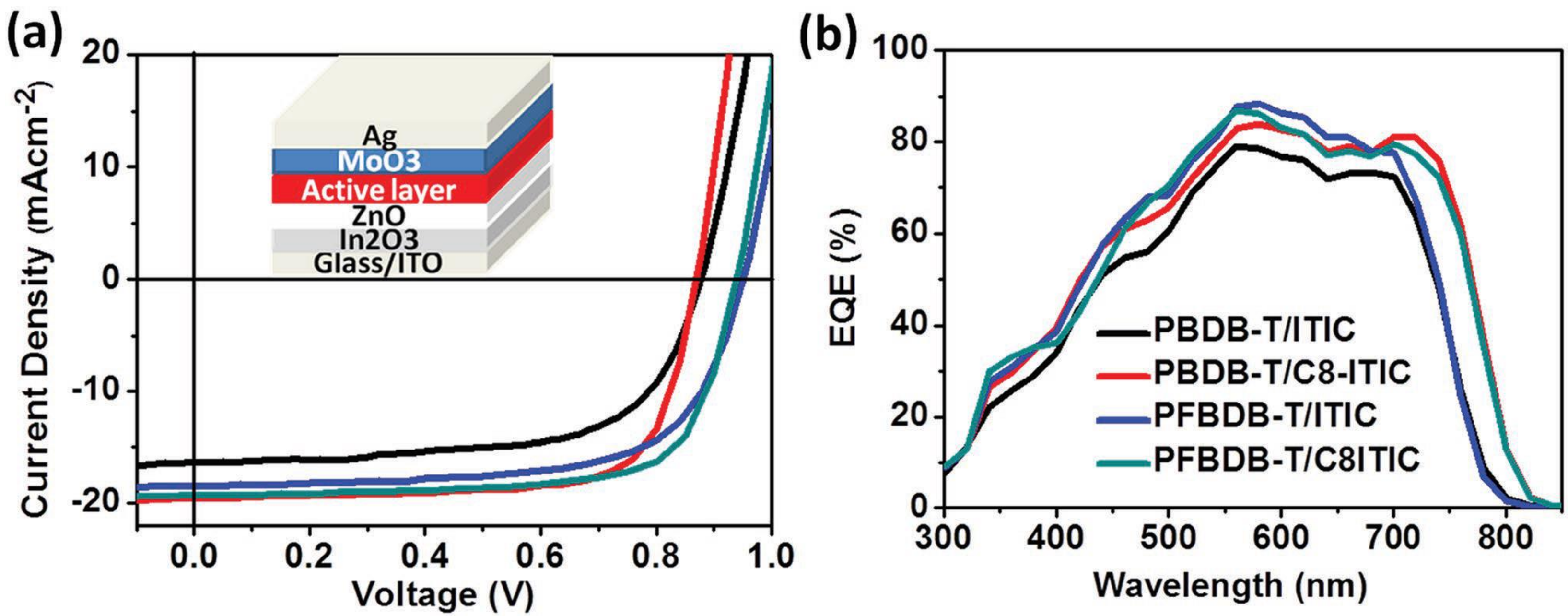
State-of-the-Art Materials and Efficiencies

Adv. Mater. **2018**, *30*, 1705209



State-of-the-Art Efficiencies

Adv. Mater. **2018**, *30*, 1705209



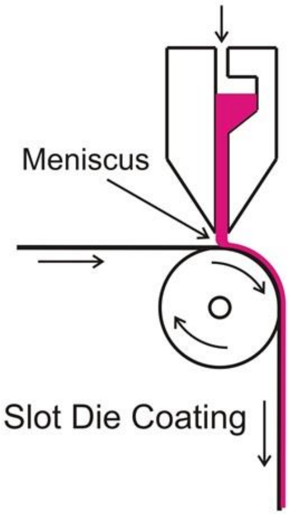
power-conversion efficiency > 13 %

See also: *J. Am. Chem. Soc.*, 2017, 139 (21), pp 7148–7151

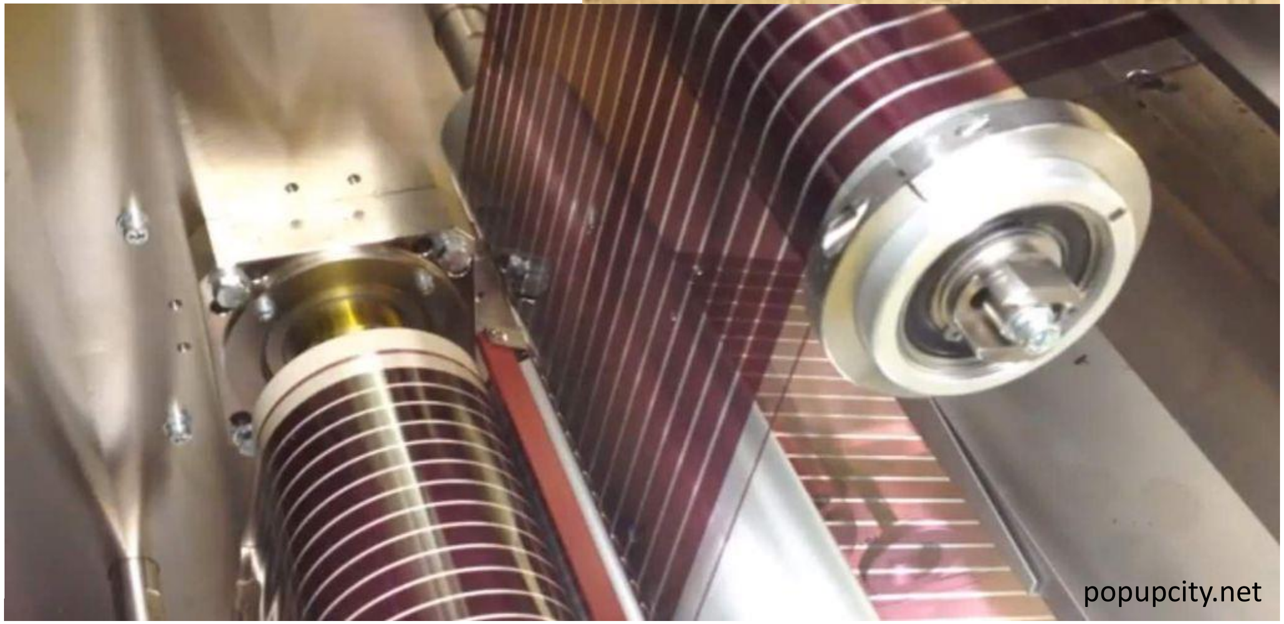
Fabrication

- Low-Cost: Roll-to-roll
  - Printing
  - Slot die coating
  - Evaporation

penscetriaru.5hark.net



https://www.tu-ilmenau.de/



popupcity.net

Organic Photovoltaics State of the Art

ÉCOLE POLYTECHNIQUE
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- ✓ Building integrated, Flexible, Colorful, **Semitransparent**
- ✓ Record 13.2 %

- o Stability

- In module/film 7%
- Not really in market yet
- Low efficiency

Heliatek®
The future is light

Future applications







Summary: Organic semiconductors

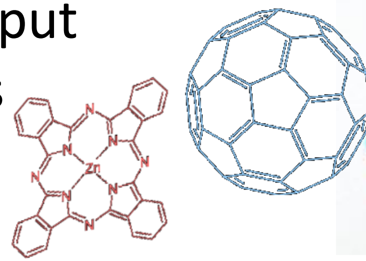
… have a huge potential

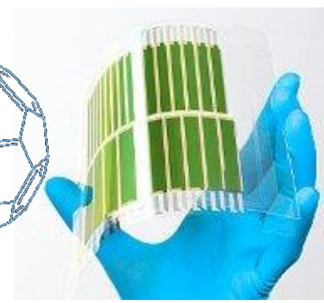
- low cost roll to roll and solution processability
- large area and ultra-thin devices
- variety of different hydrocarbons

konarka.com

… are well suited for solar cells

- low energy input
- different dyes
- abundant

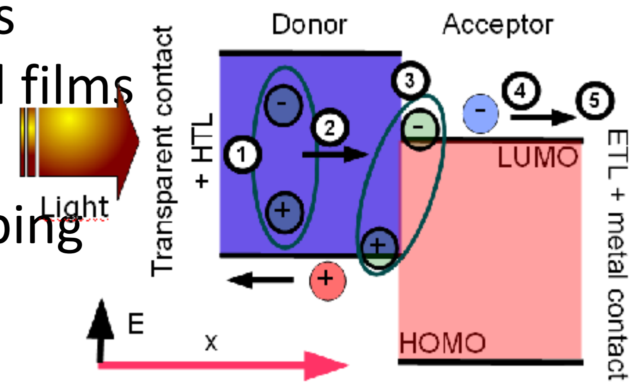




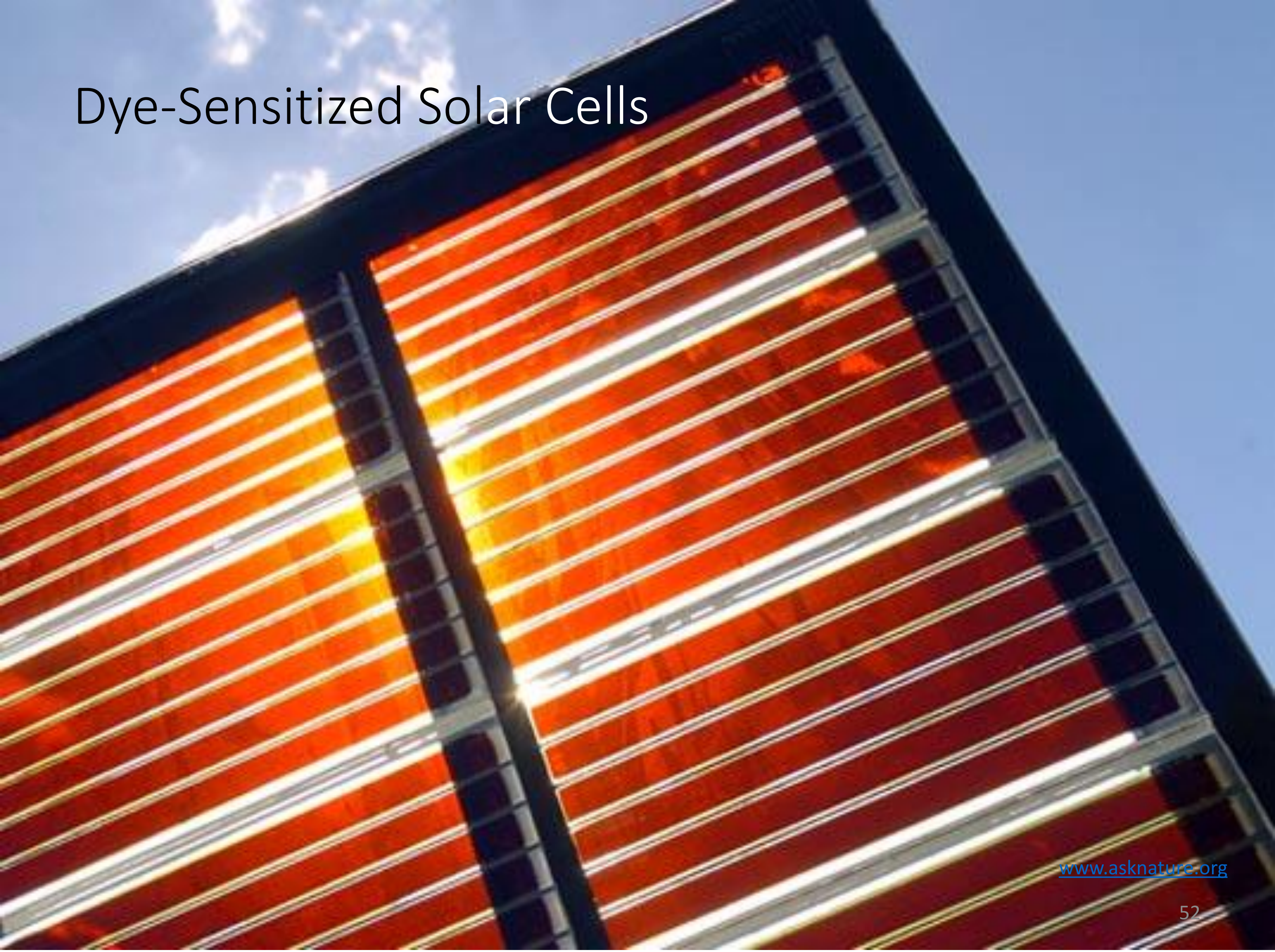
heliatek.com

… are different

- film consists of weakly bound molecules
- mostly amorphous and even intermixed films
- optical excitation is localized
- charge transport occurs mainly via hopping
- optical and electrical gap decoupled



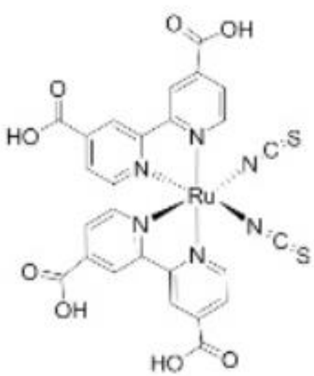
Dye-Sensitized Solar Cells



www.asknature.org

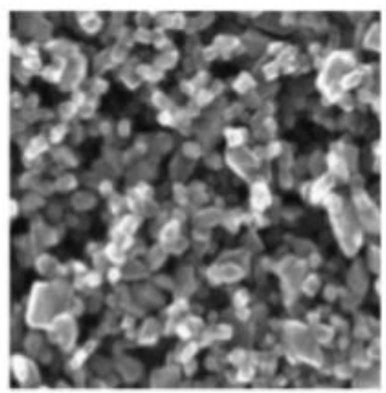
Dye-Sensitized Solar Cell: Ingredients

Sensitizing Dye



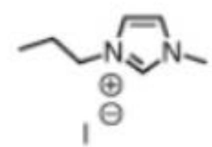
Chemical Structure of N3 Dye

Titania Nanoparticles



20 nm Titania nanoparticles

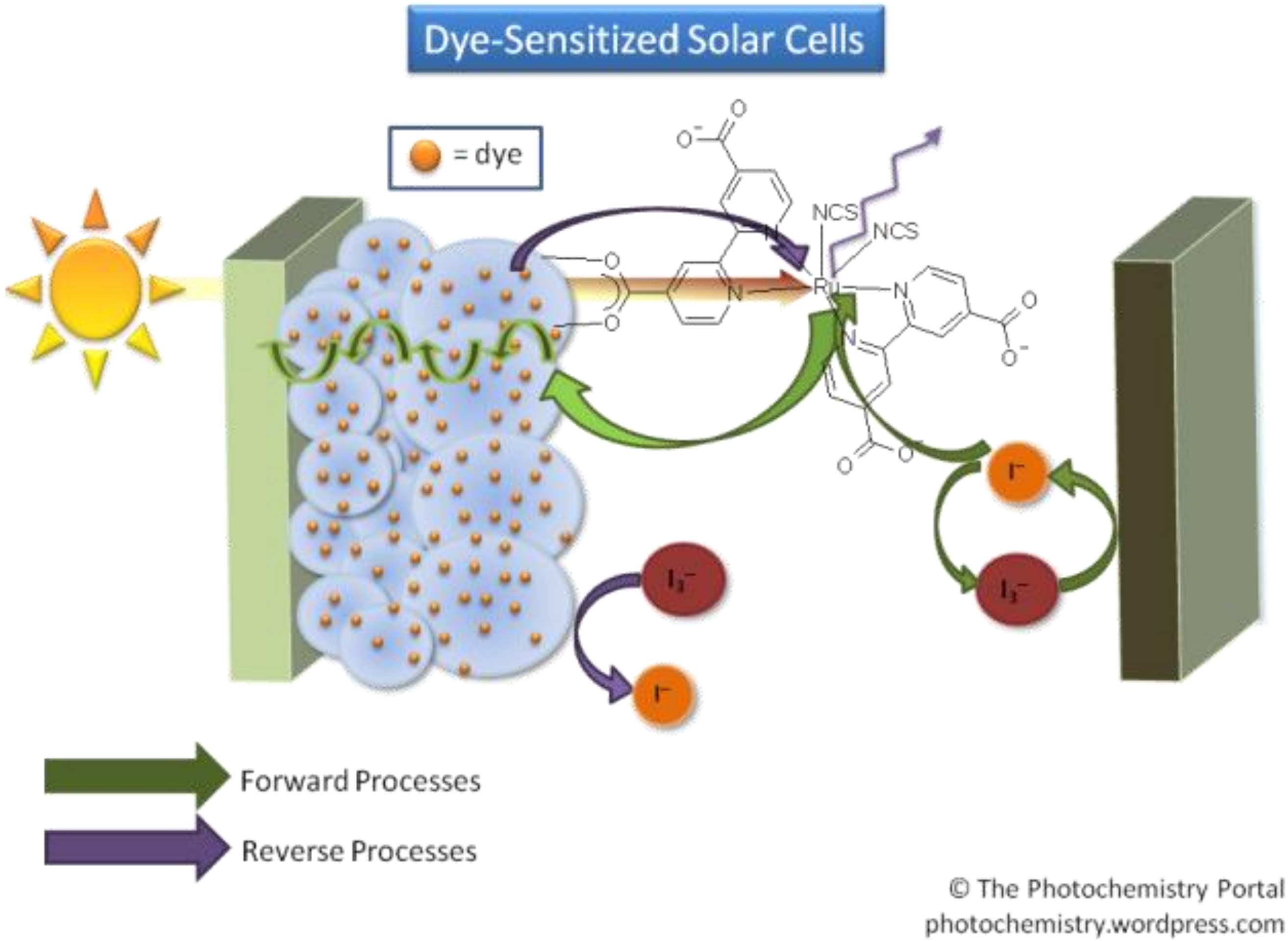
Electrolyte



Iodide/Tri-iodide
Redox Couple

Hardin, Slideshare

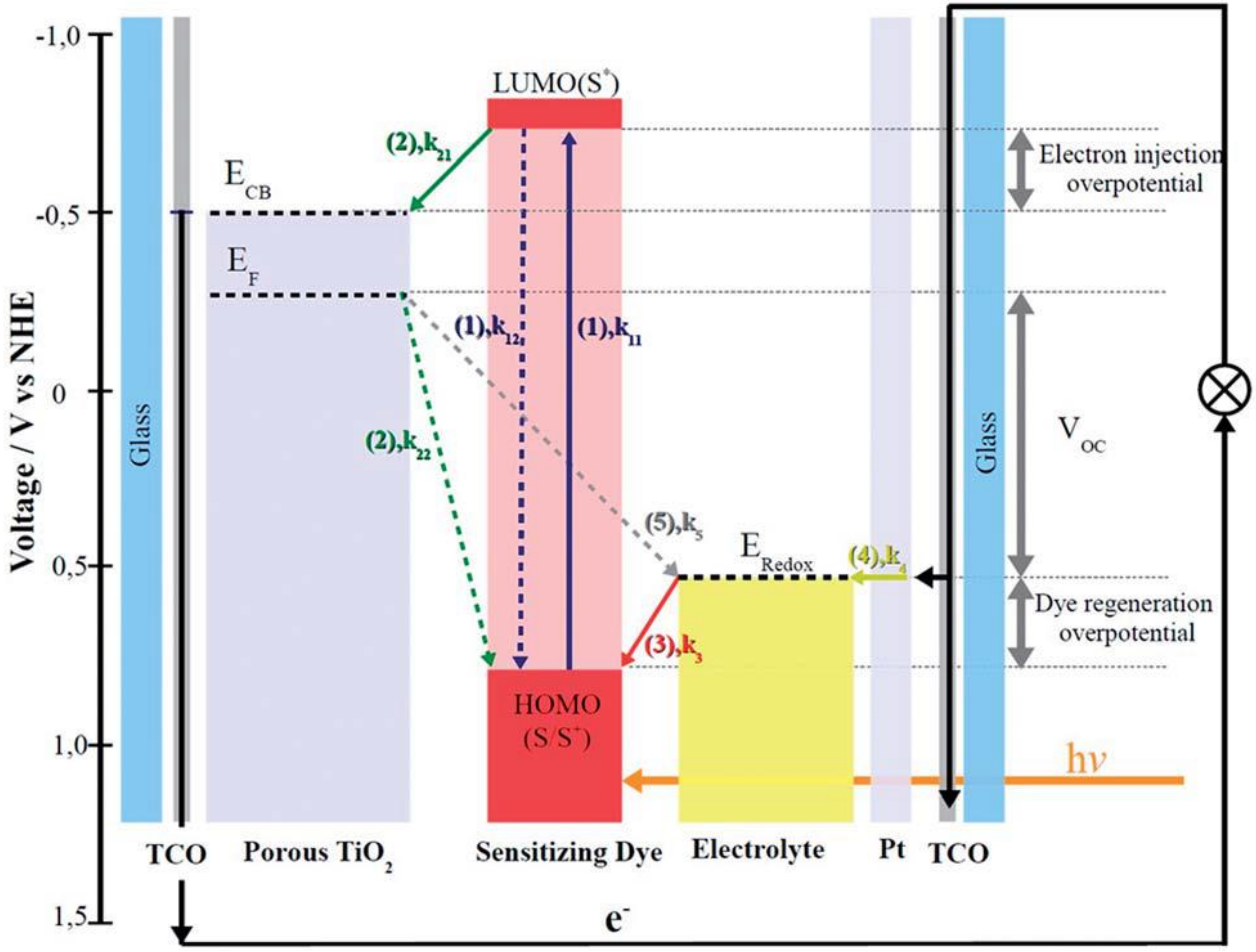
Dye-Sensitized Solar Cell: Schematics



- Absorption on monolayer of dye, decoupled from transport
- Nanostructure → surface area

Dye-Sensitized Solar Cell: Energetics

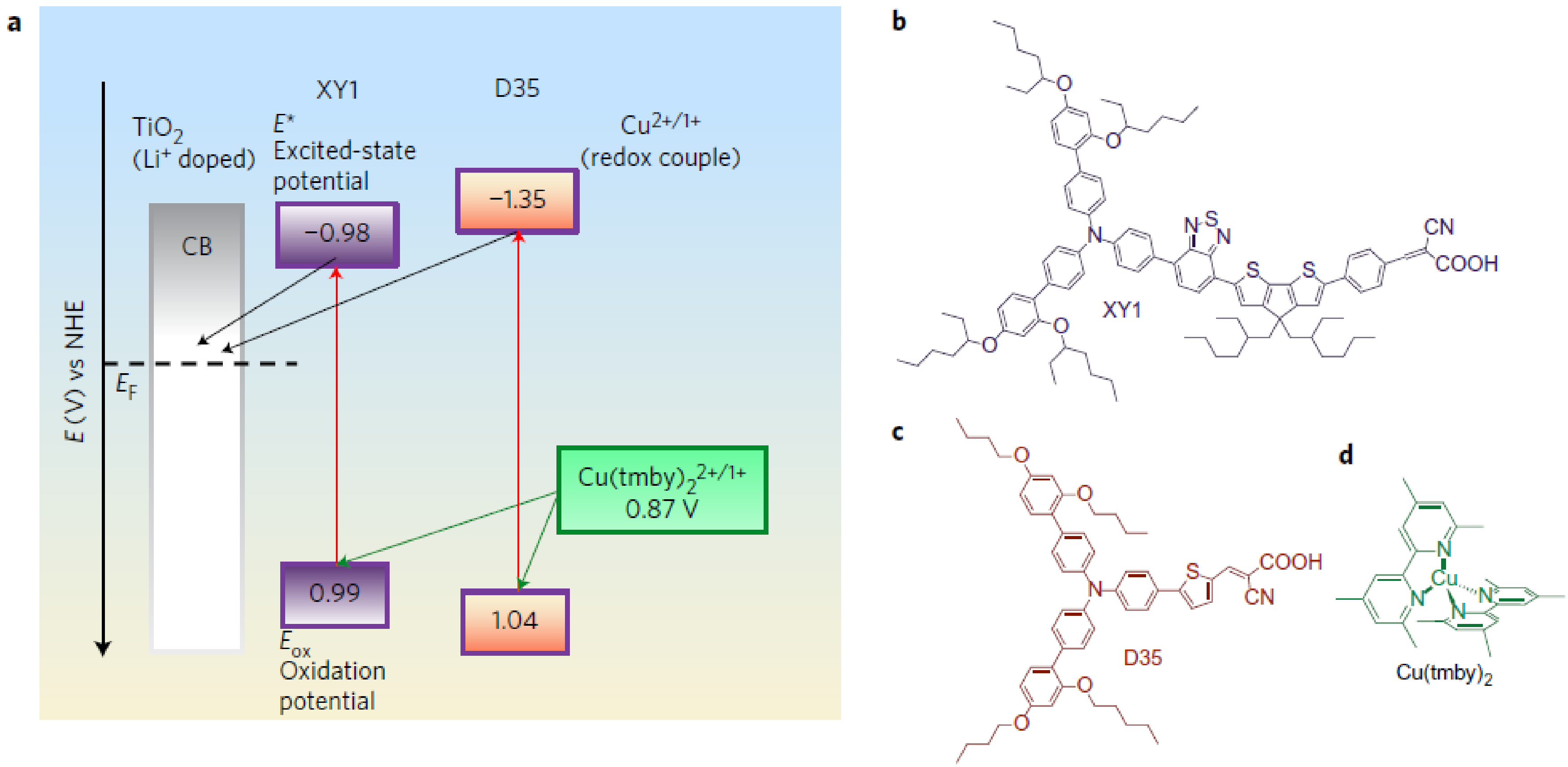
Maçaira, J., Andrade, L. & Mendes, A. Modeling, simulation and design of dye sensitized solar cells. *RSC Adv.* **4,** 2830–2844 (2013).



- Redox potential of electrolyte fixed

Dye-Sensitized SC: Recent Developments

Freitag, M. *et al.* Dye-sensitized solar cells for efficient power generation under ambient lighting. *Nature Photonics* **11,** 372–378 (2017).



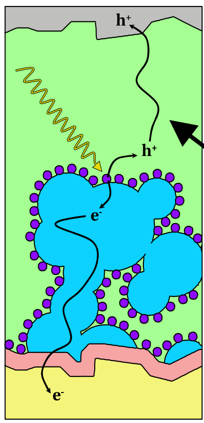
f

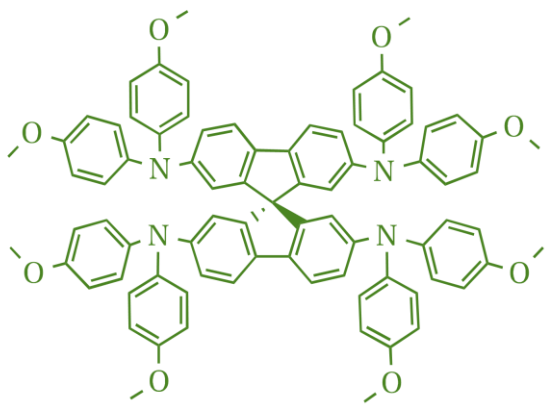
efficiency 11.3%

- Co-sensitized system → higher photocurrent
- $Cu(tmby)_2$ as redox mediator → higher photovoltage

History and State of the Art

- 1980s sensitization of TiO_2
- 1991 Nature paper: η = 7 %
- Solid state DSC





- Now: η = 13 %
- Dye with designated (broad or IR) spectrum
- Electrolyte for high voltage

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

* Present address: Department of Chemistry, University of Washington, Seattle, Washington 98195, USA.
† To whom correspondence should be addressed.

Applications

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- Consumer: Indoor, Internet of Things
- Building integrated
- Challenges: Efficiency, Stability