Organische Photovoltaik – Nanotechnologie auf dem Weg zu Anwendungen

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AKE

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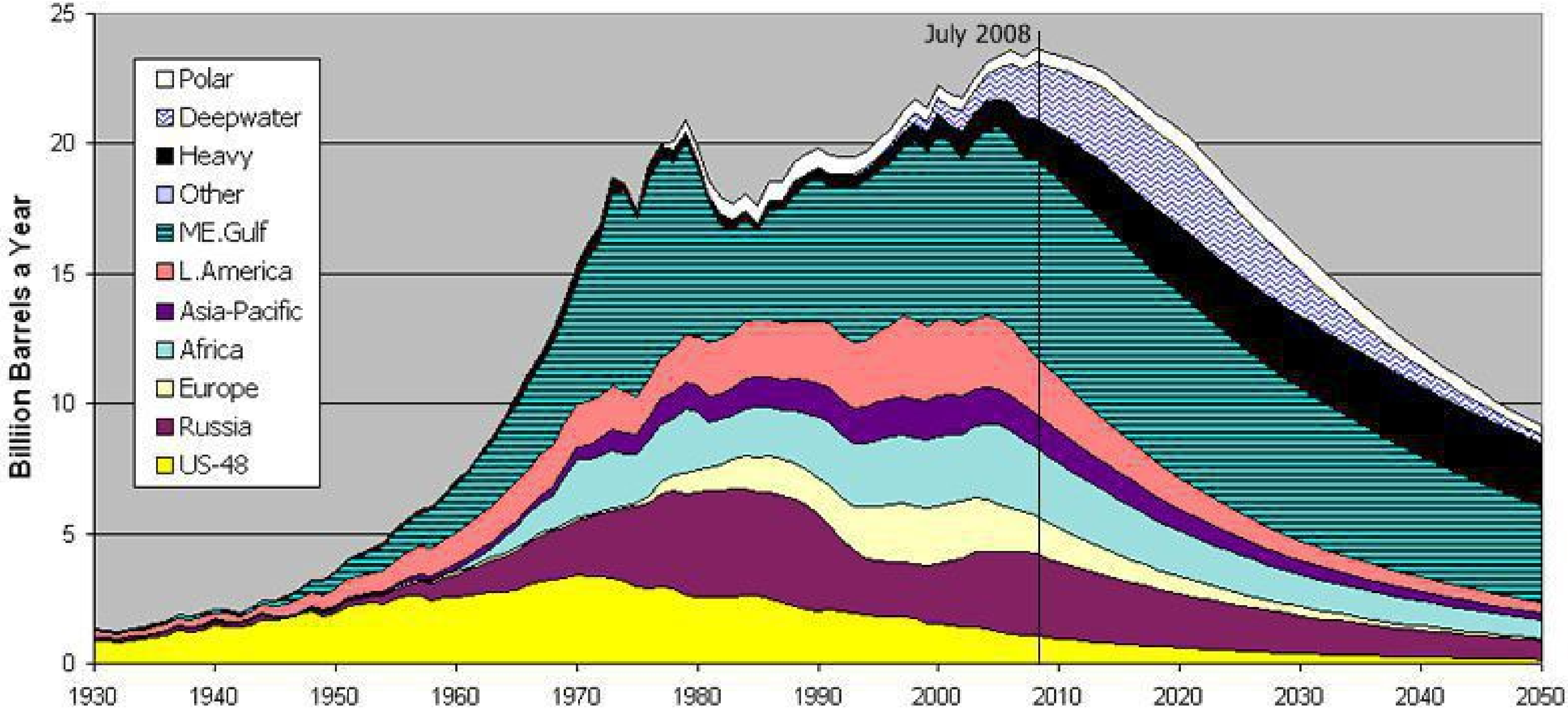
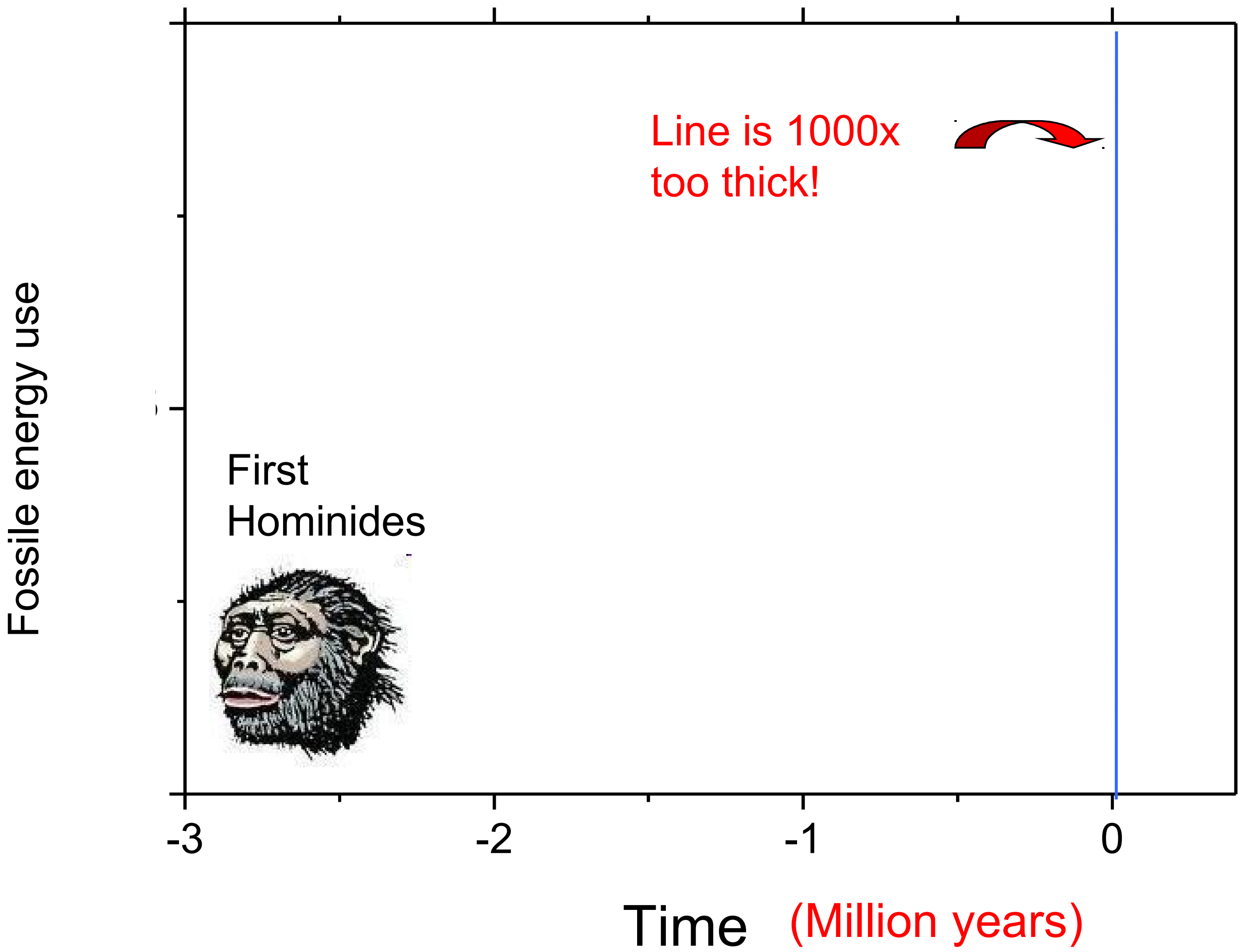
The peak oil discussion....

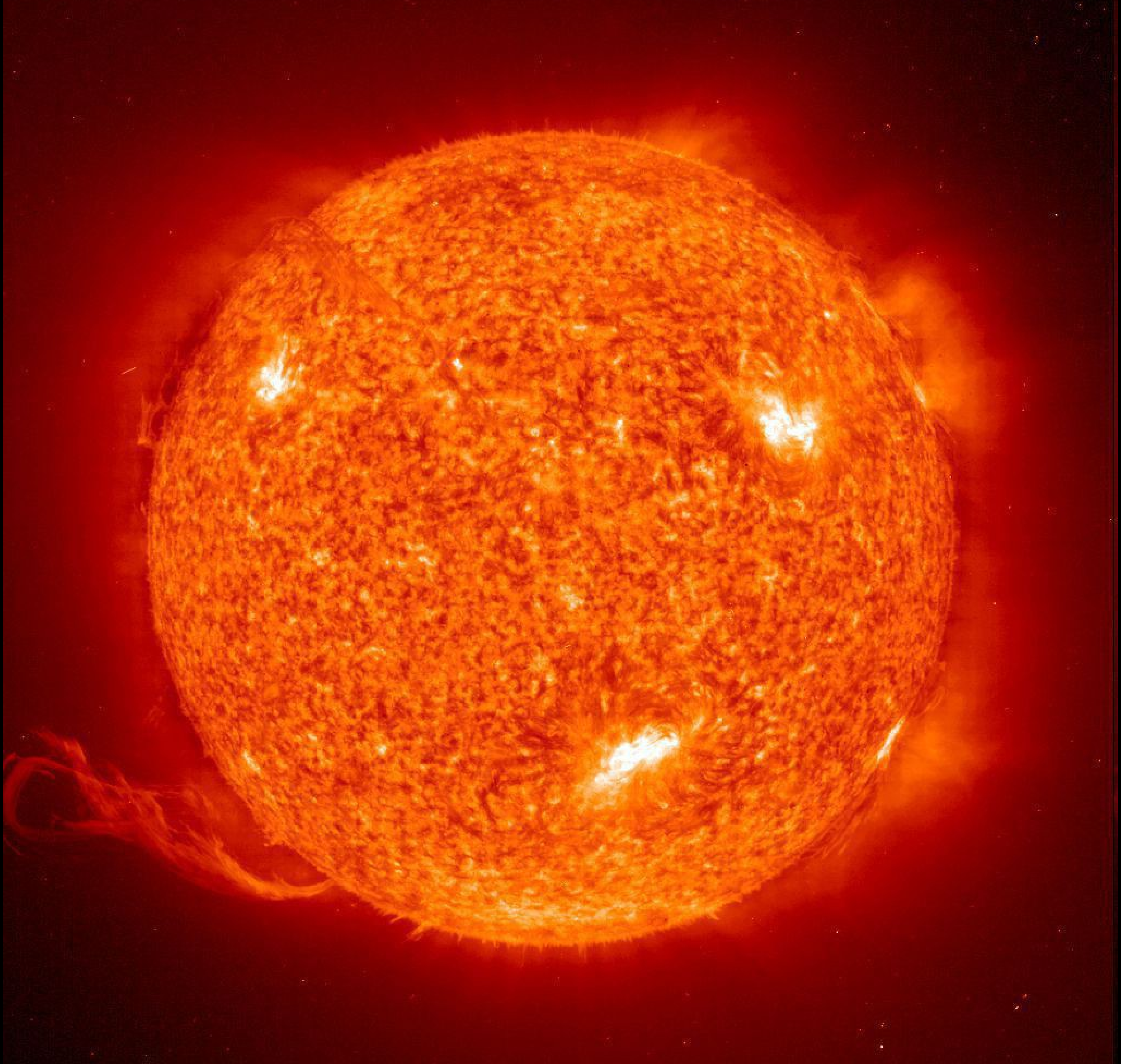
World Oil Production



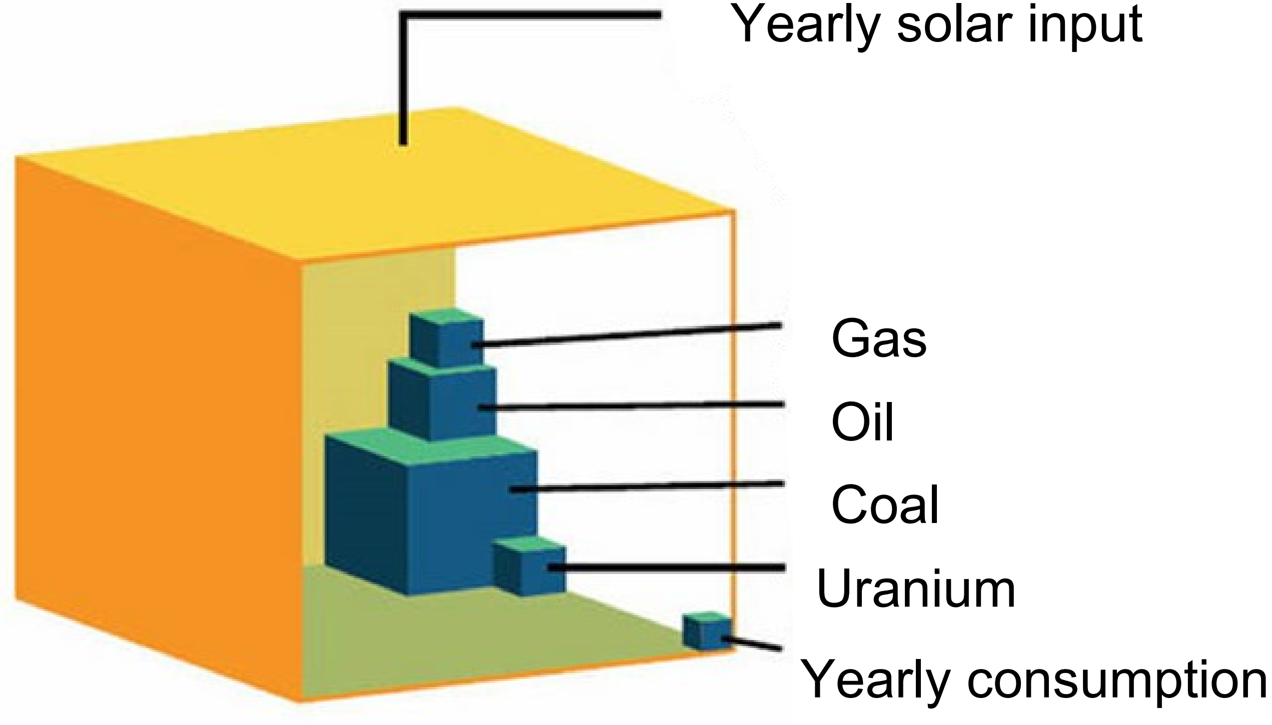
IAE

On a more meaningful time scale...



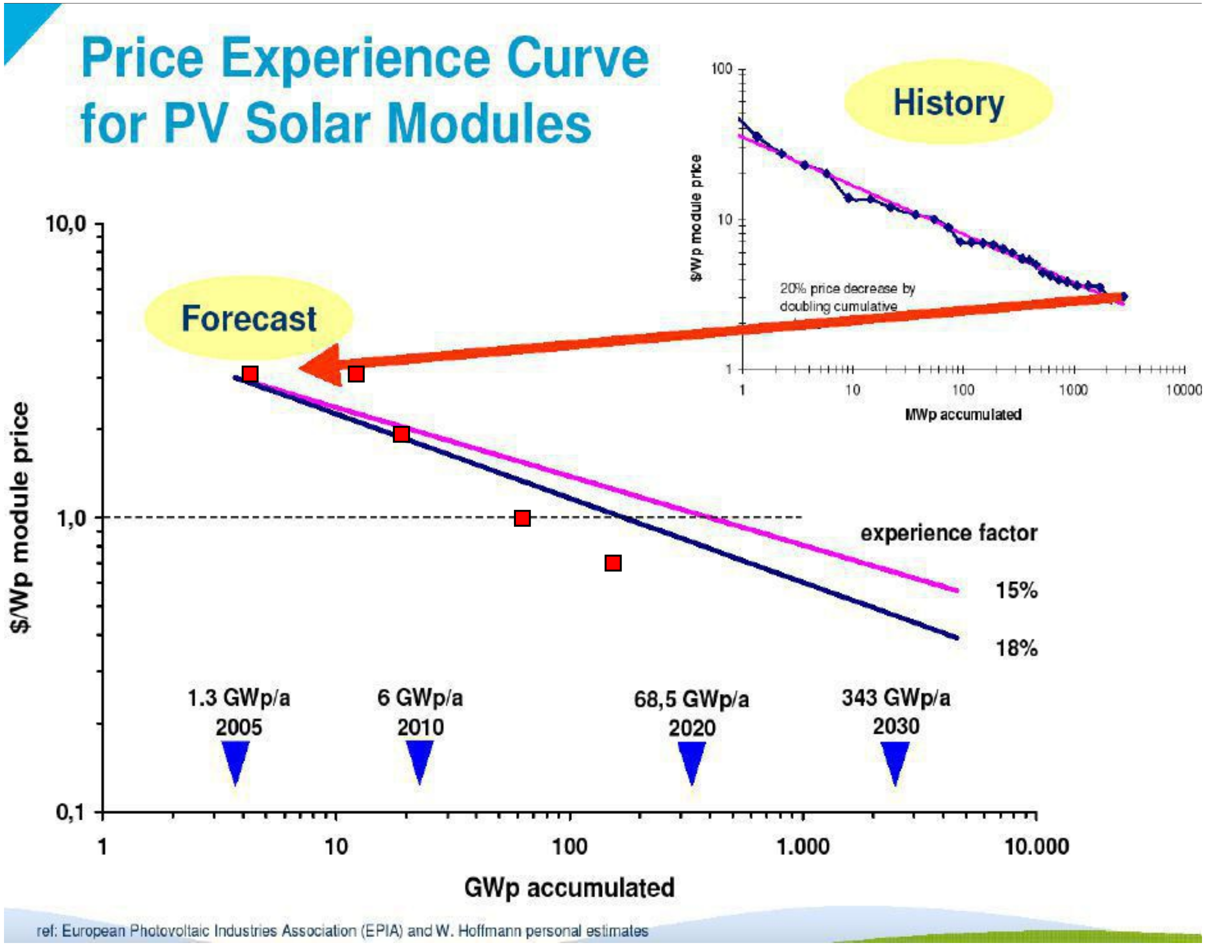


There is plenty of sunlight...



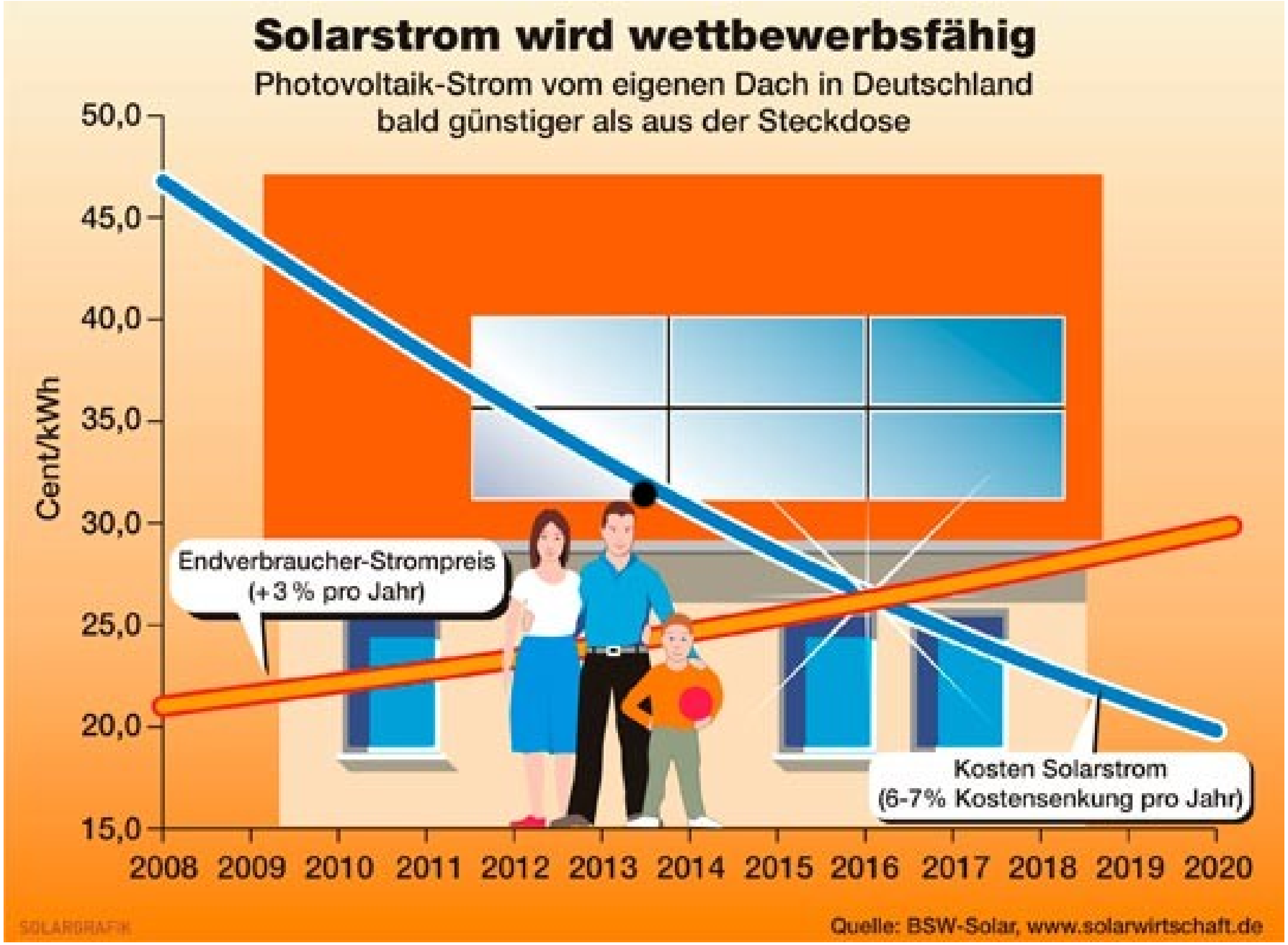
Source: Eco Solar

Photovoltaics learning curve



- 15-18% reduction of price per doubling
- Fluctuations due to subvention cycles
- Currently: sales below cost down to 50 Cent/Wp

Grid Parity – the holy grail of photovoltaics



Energy pricing – a hot topic

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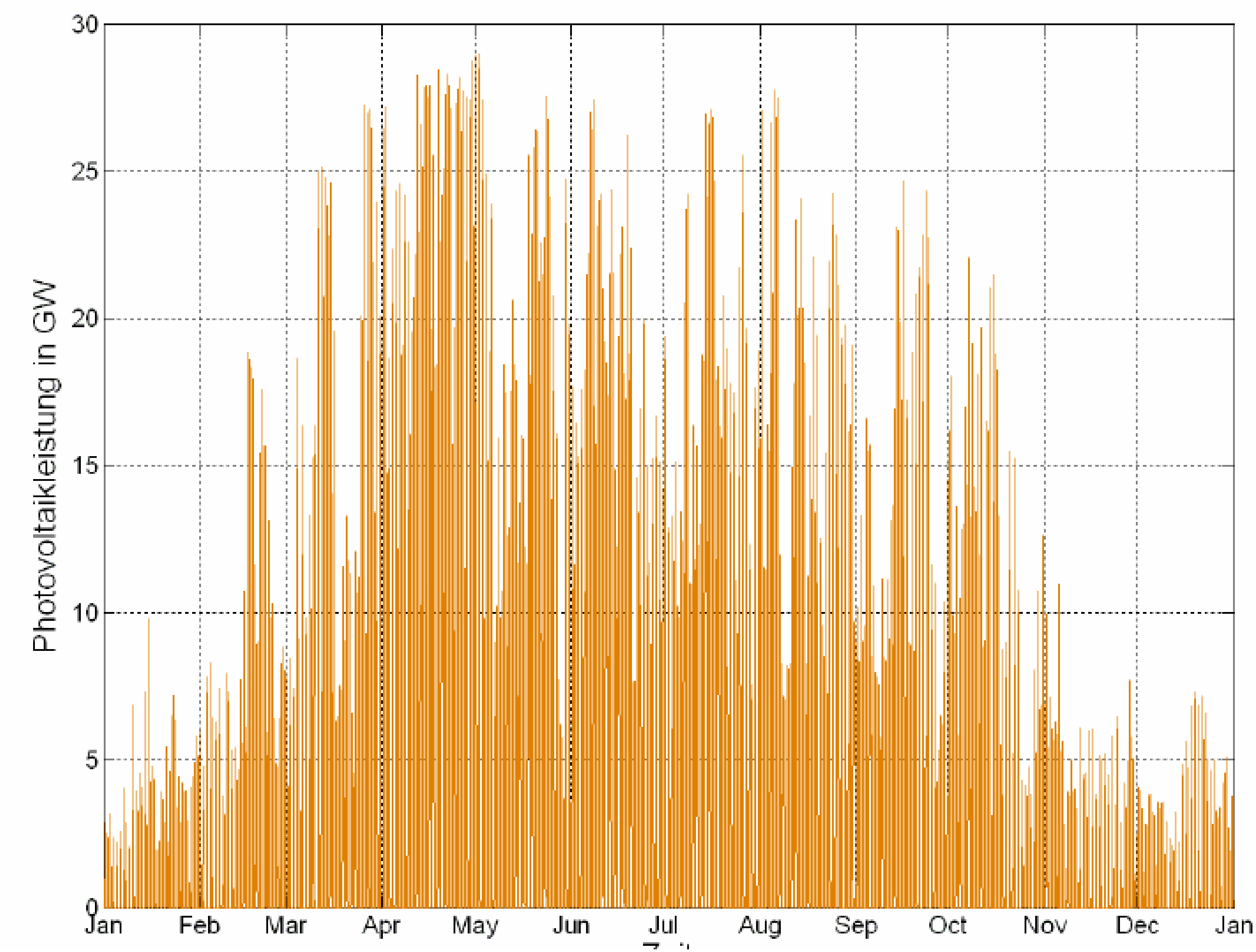
Home › Geld › Wirtschaft › Strompreis-Hammer! Öko-Umlage 50% rauf

ÖKOSTROM-UMLAGE STEIGT UM 50 PROZENT

Strompreis-Hammer!

Familie muss mit 50 Euro mehr im Jahr rechnen

Solar power over the year



Fraunhofer IWES

Storage: expensive, lack of capacity

Bulk Storage System Characteristics

Technology Option/ Characteristics	Zn / Halogen	Na-ion	Sodium Metal Halide	CAES Above Ground	NAS	Adv. Lead Acid	Zn/Br Redox	Vanadium Redox	Fe/Cr Redox	Zn/Air Redox
Unit Capacity MW MWH	83 250	50 250	50 250	50 250	50 300	50 250	50 250	50 250	50 250	50 250
Ac-Ac Efficiency,% (heat rate)* Energy Ratio**	75-80	85-90	87 -------- 1.3MW	-------- (4000) 1.0	75-80	85-90	60-65	75-78	70-75	70-75
Foot print Ft2/kW	2.0	1.9 - 5.1	~0.6	1.6	2.0	1.9 - 5.1	0.9	2.0	4.44	1.3
Total Capital Costs ($/kW)[1]	2021-2470	2367-2894	~2823-3665	1762-1958	2764-3378	1753 - 4897	1506-1841	3361-4107	1,284-1569	1285-1570
Technical Maturity and readiness	R&D	R&D	Demo	Demo	Commercial	Commercial-Demo	Demo	Demo	R&D	R&D
LCOE - $/MWh	447-547	338-413	374-553	260-278	321-392	274-630	257-314	457-559	220-269	187-229

1. For Systems with just one supplier an adjusted Capital Cost range of +/- 10% is illustrated. For Systems with multiple suppliers their total cost range is illustrated.

EPRI ELECTRIC POWER RESEARCH INSTITUTE

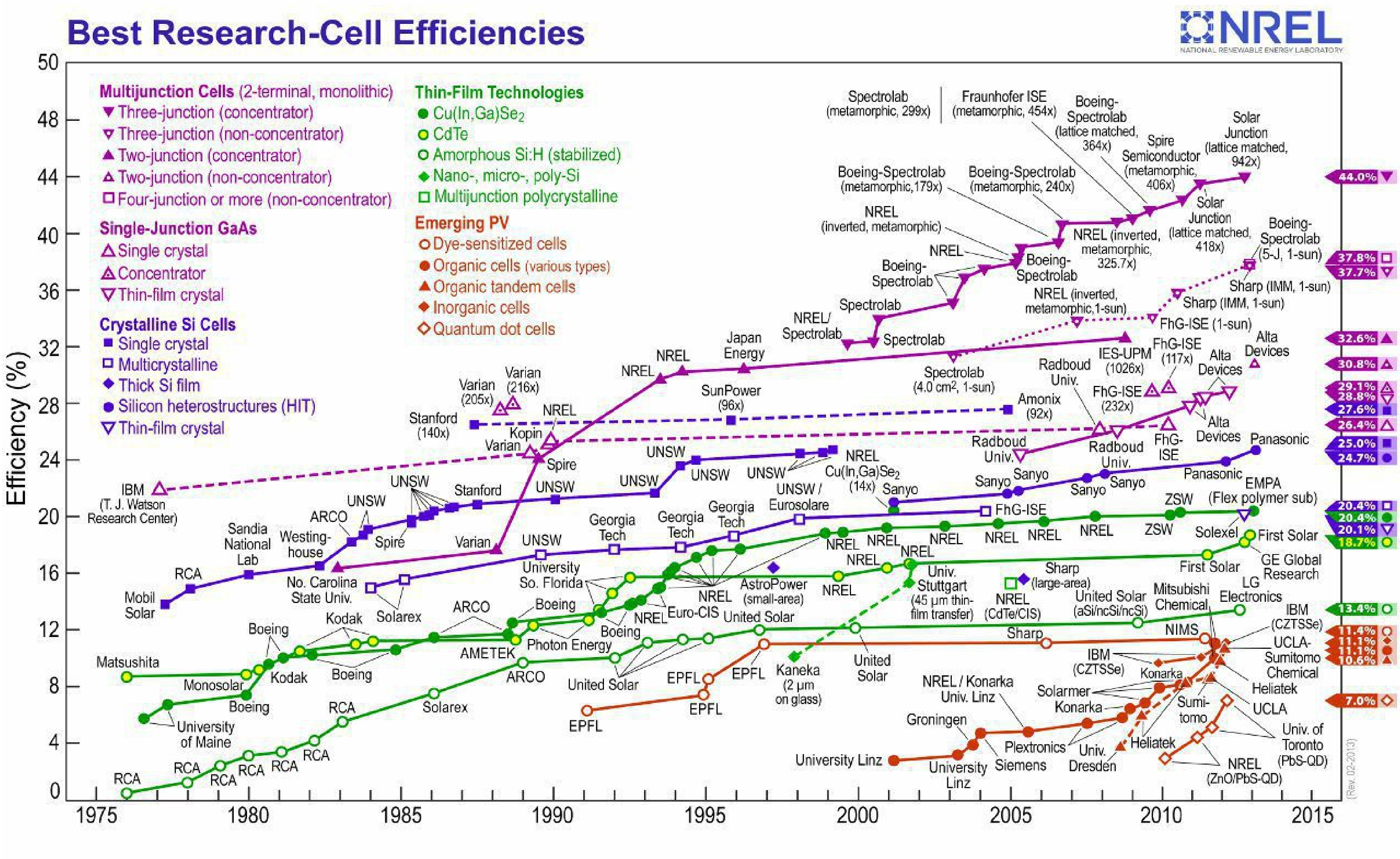
The real challenge for PV

- Real challenge for PV:
- Not grid parity, but PV+storage=“battery parity“
- Requires PV generation below 10 Cent/kWh @ Germany
- Requires module prices ≈ 20 Cent / Wp

Outline

- Comparison of present PV technologies
- Basics of organics
  - Challenges:
    - Exciton Separation
    - Nanomorphology
    - Efficiency
- Long-term stability
- Manufacturing & applications

NREL record chart



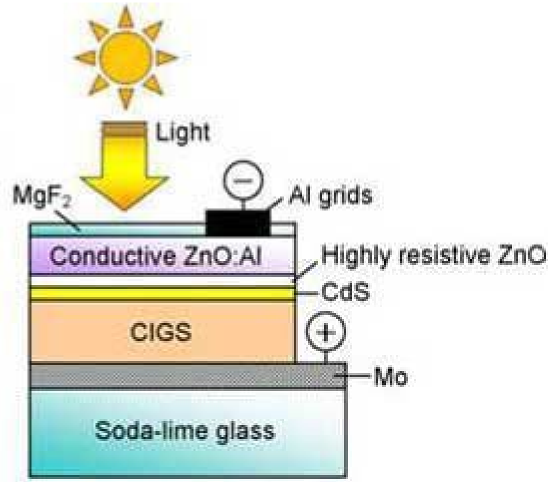
Silicon solar cells

- Abundant material
- Huge synergies with microelectronics
- Efficiency:
  - ca. 25% lab
  - 15-20% module
- ca. 200g material/m^2
- See talk 9:30 Hermle&Glunz

Thin film Photovoltaics

- Three important systems:
    - Amorphous silicon
    - CdTe
    - CuInS/Se

- Problem with rare elements except for a-Si
- Approx. 10g material/m²



Source: yet2.com, Solarion

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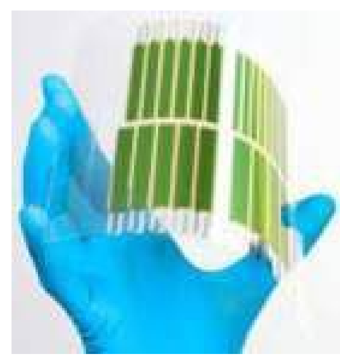
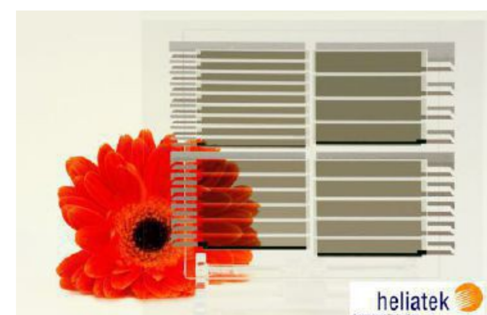
Organic Photovoltaics

- Flexible plastic substrates and thin organic layers
- Low material consumption: approx. $1g/m^2$
- Potentially transparent, color adjustable
- Compatible with low-cost large-area production technologies





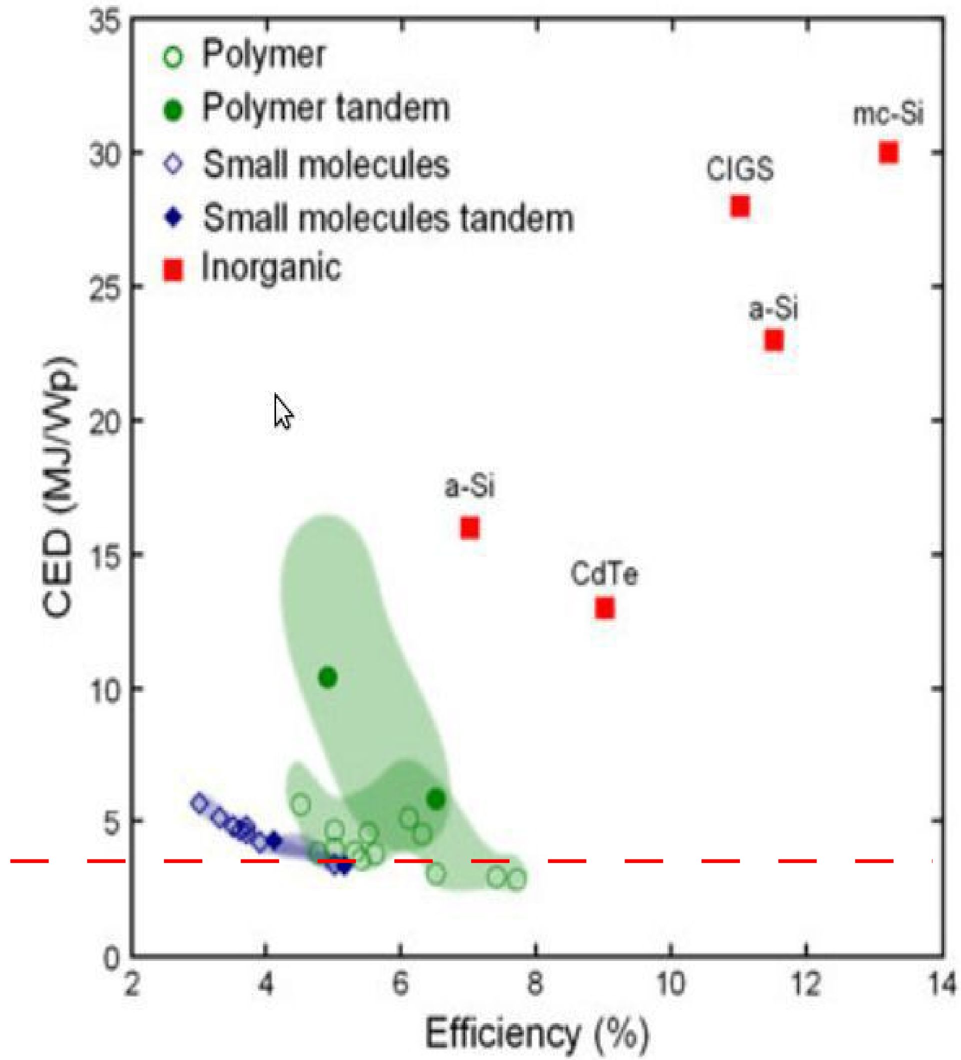
Images: Konarka, Neuber, Heliatek, IAPP

Energy payback comparison

p-Si ■

- Energy payback time:
- Organics clearly ahead
- Payback times <1 year possible
- Go for high-efficiency organic!

Typical yearly yield Germany



A. Anctil et al., Progr. in Photovoltaics 2012

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Outline

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- Comparison of present PV technologies
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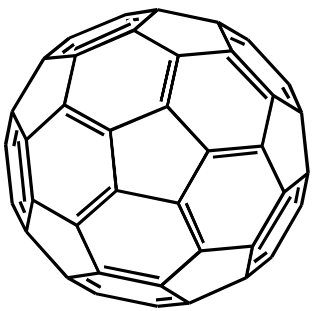
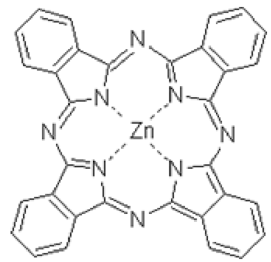
    - Efficiency
- Long-term stability
- Manufacturing & applications

Organic Semiconductors



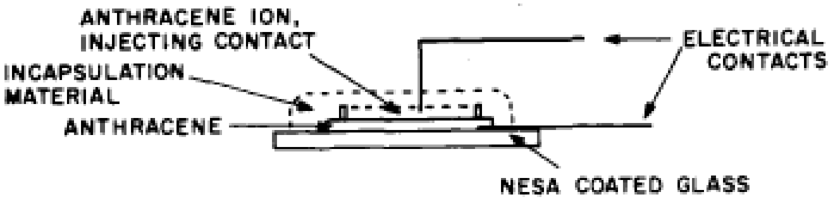


C_{60}

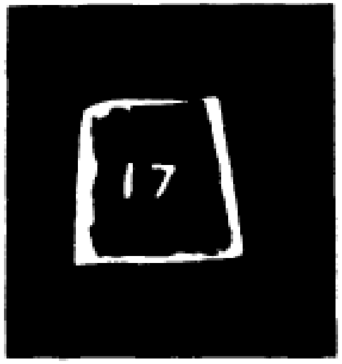
ZnPc

Single crystal electroluminescence

- Williams&Schadt 1969
- 100µm Anthracene crystal, 100V voltage



(a)



(b)

Fig. 1. (a) Schematic diagram of the construction of a typical diode. (b) Photograph showing the electroluminescence from a typical diode in use. The diode has typical dimensions of ~1 cm² surface area.

Progression of Organic Products

4th wave: Organic electronics

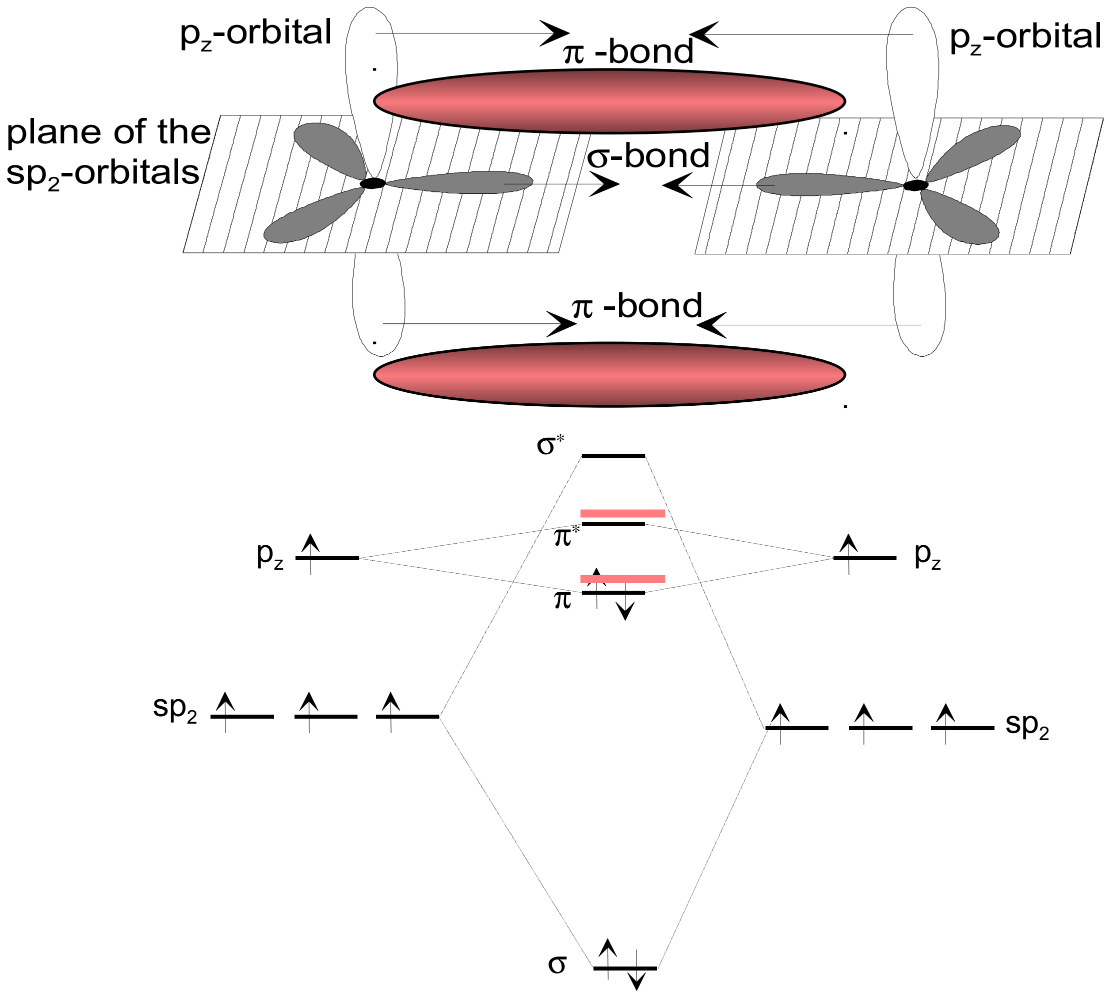
3rd wave: Solar cells

2nd wave: OLED lighting

1st wave: OLED Displays

Time

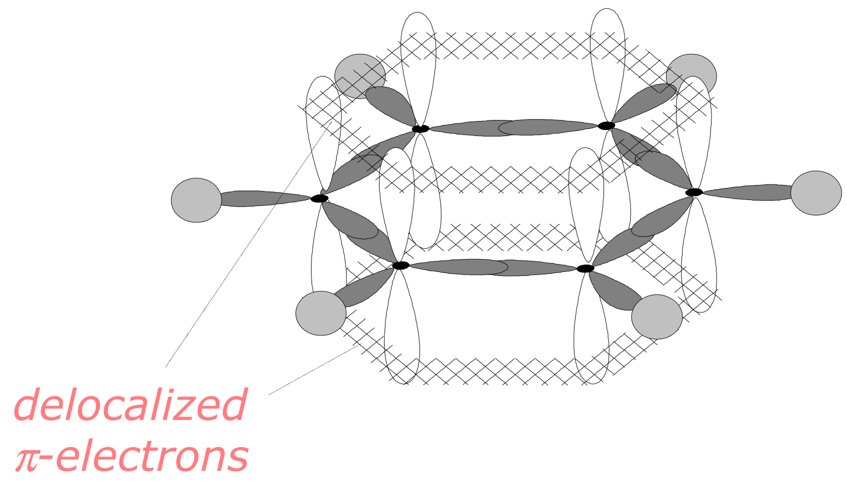
Sp_2-hybridised Carbon:

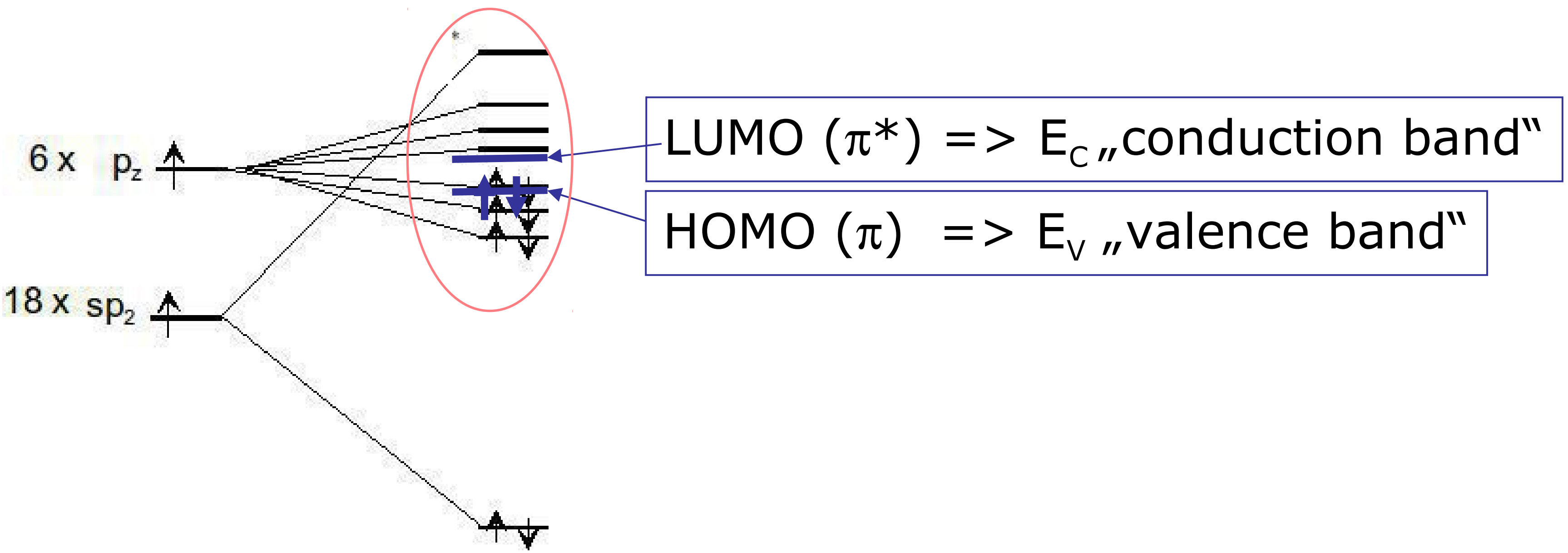


Molecules with conjugated π-electron system

π-electron systems delocalize!

- VdW crystals
- small π–π-overlap, narrow bands
- saturated electron system

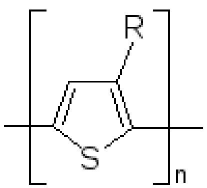


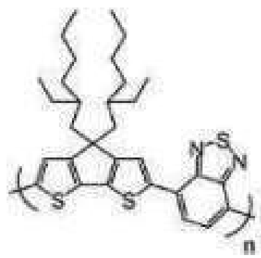


Classification of Organic Solar Cells

Solution-Processing

Polymers&small molecules

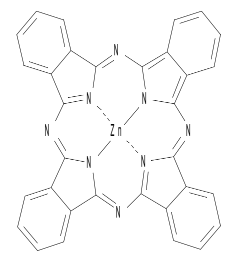


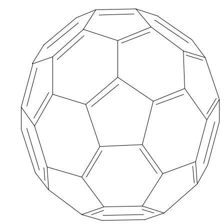


- Layers made by e.g. printing
- High production speeds possible
- Room temperature process

Vacuum-Sublimation

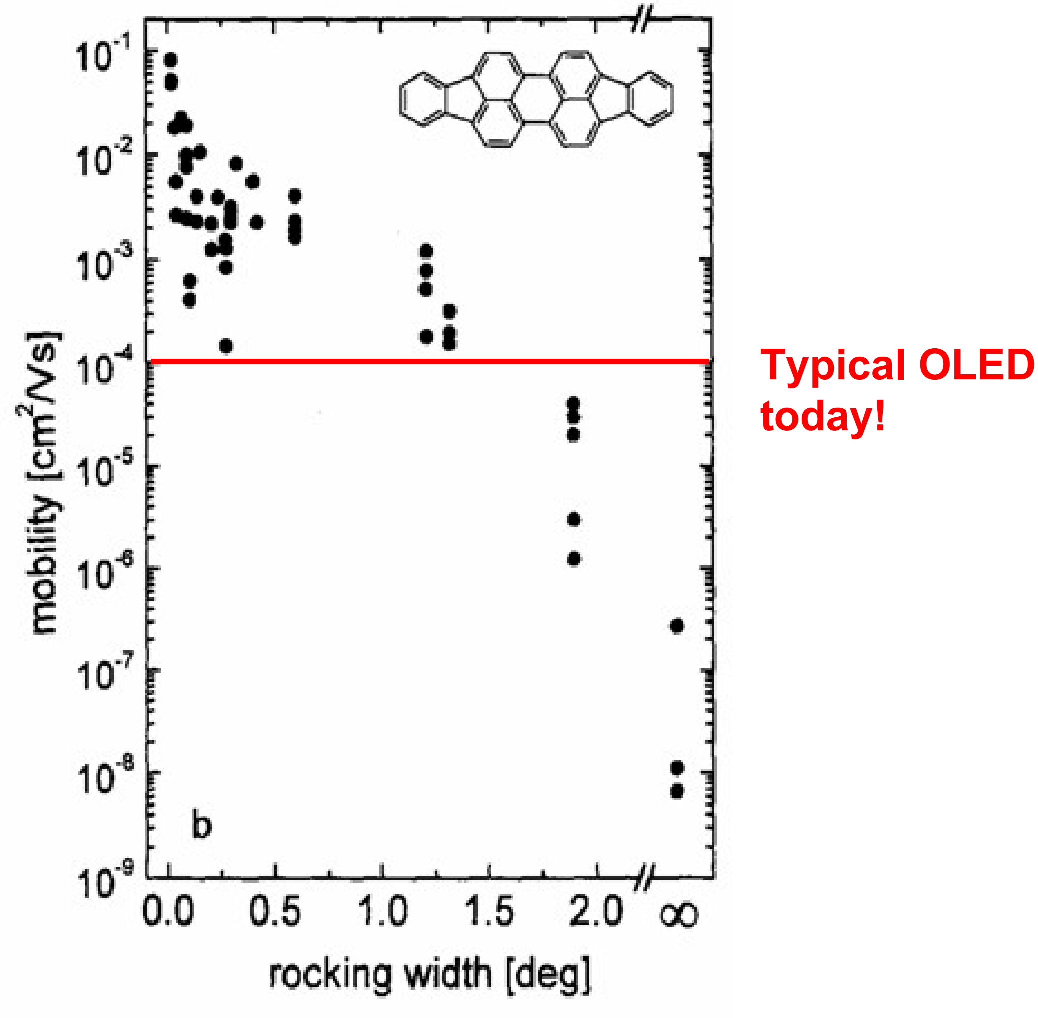
Only small molecules





- Layers made by sublimation of material in vacuum
- Easy access to multi-layer systems
- High material purity

Mobility as a function of disorder

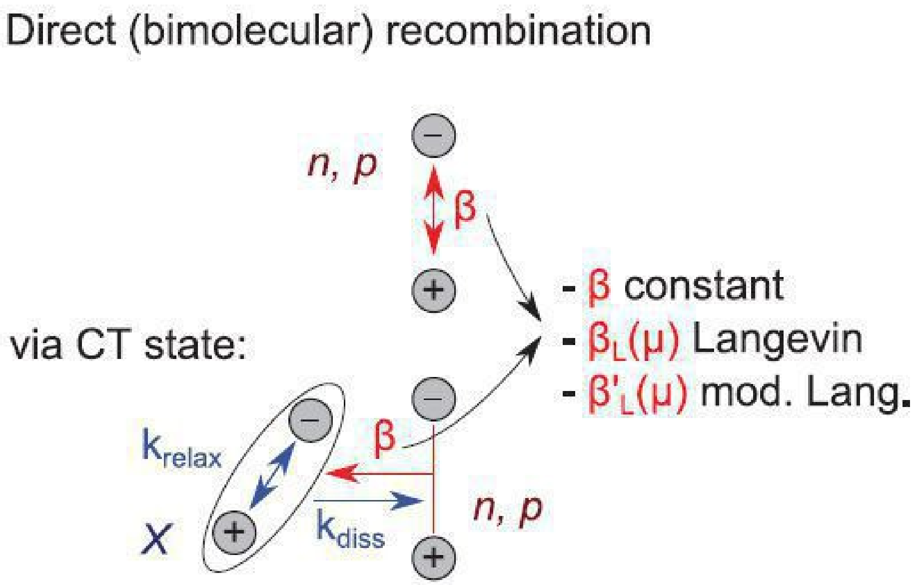


N. Karl et al. 2001

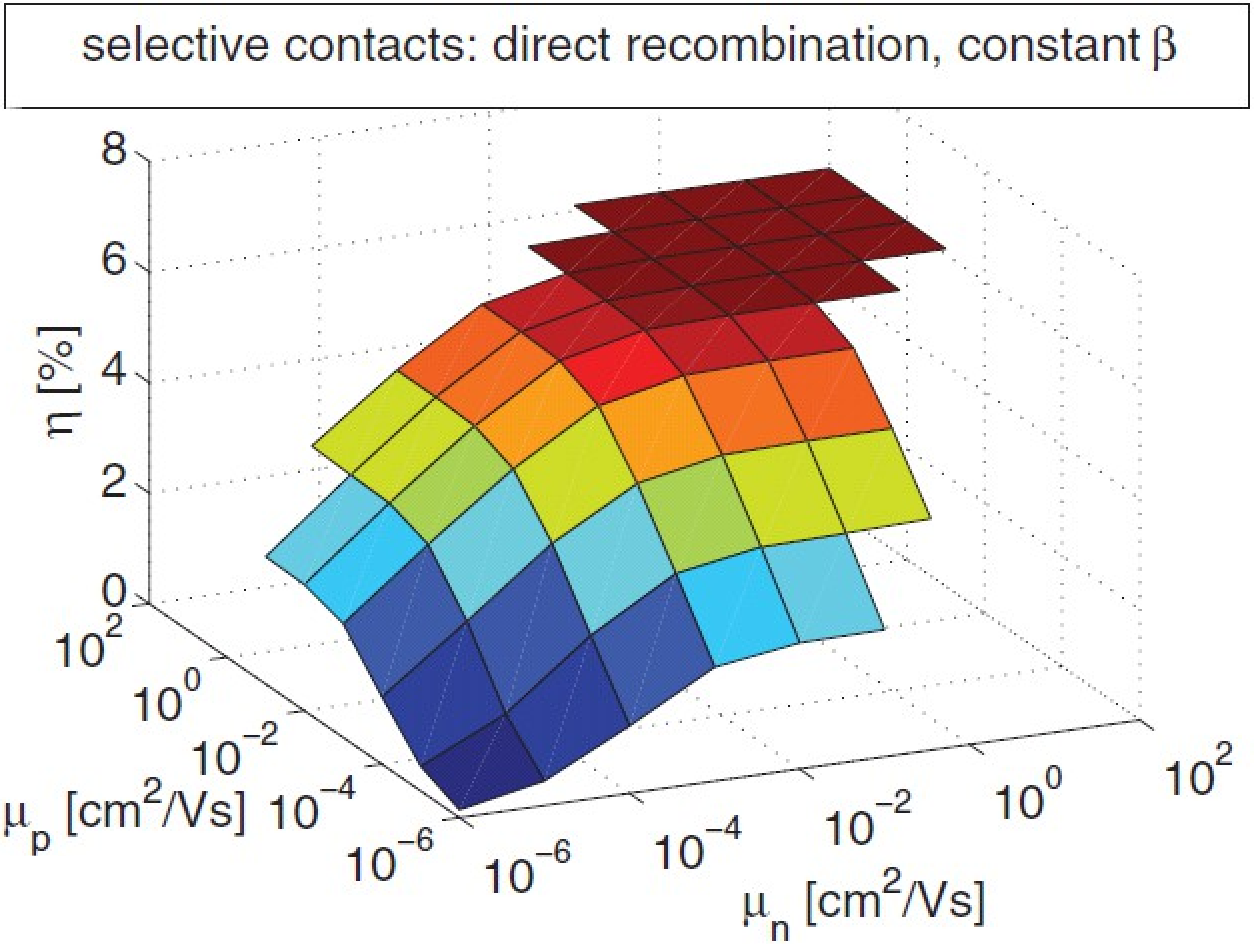
- Rocking width correlates with mobility
- Even small disorder reduces μ strongly
- Conductivities are accordingly low

What mobilities are needed?

- Drift-diffusion model set up by Wolfgang Tress
- Bulk Heterojunction between two contacts
- Different recombination models studied



Efficiency vs n- and p-mobilities



Mobilities of 10^{-3} cm²/Vs are sufficient!

W. Tress et al., Phys. Rev. **B** 85, 155201 (2012)

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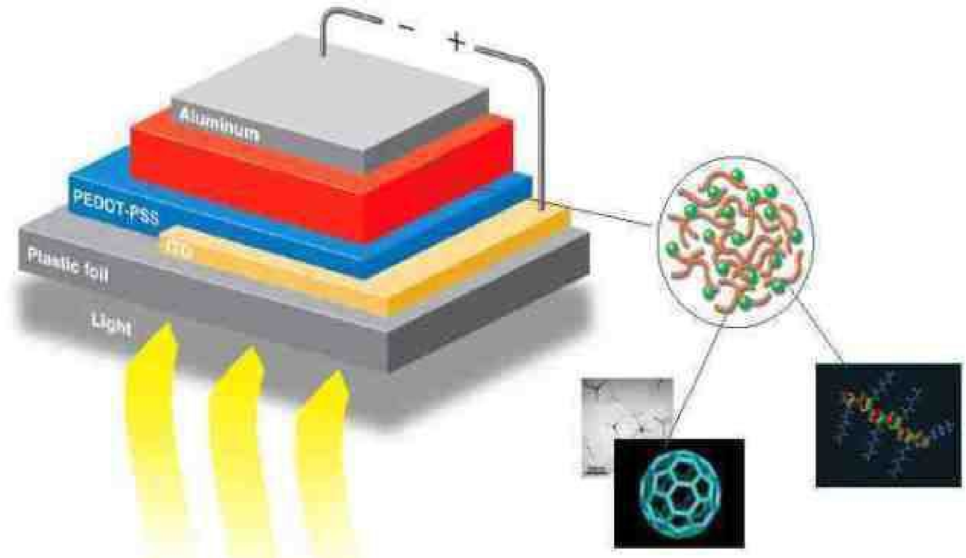
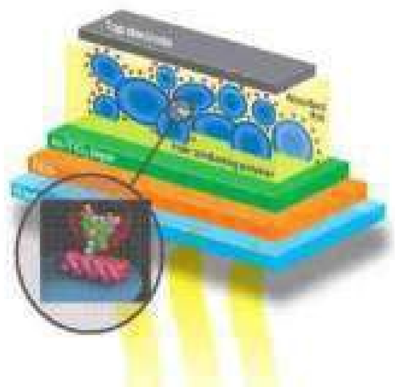
Classes of Organic PV

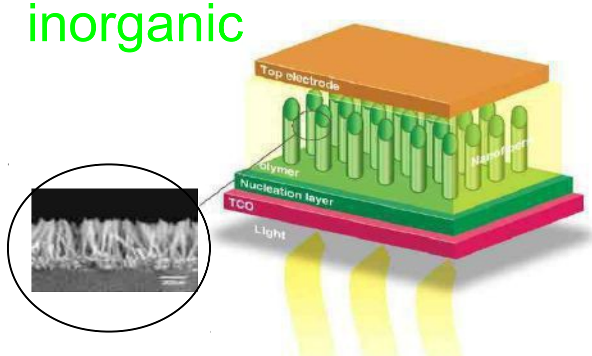
Polymer/small-molecule heterojunction



Dye-sensitized solar cell

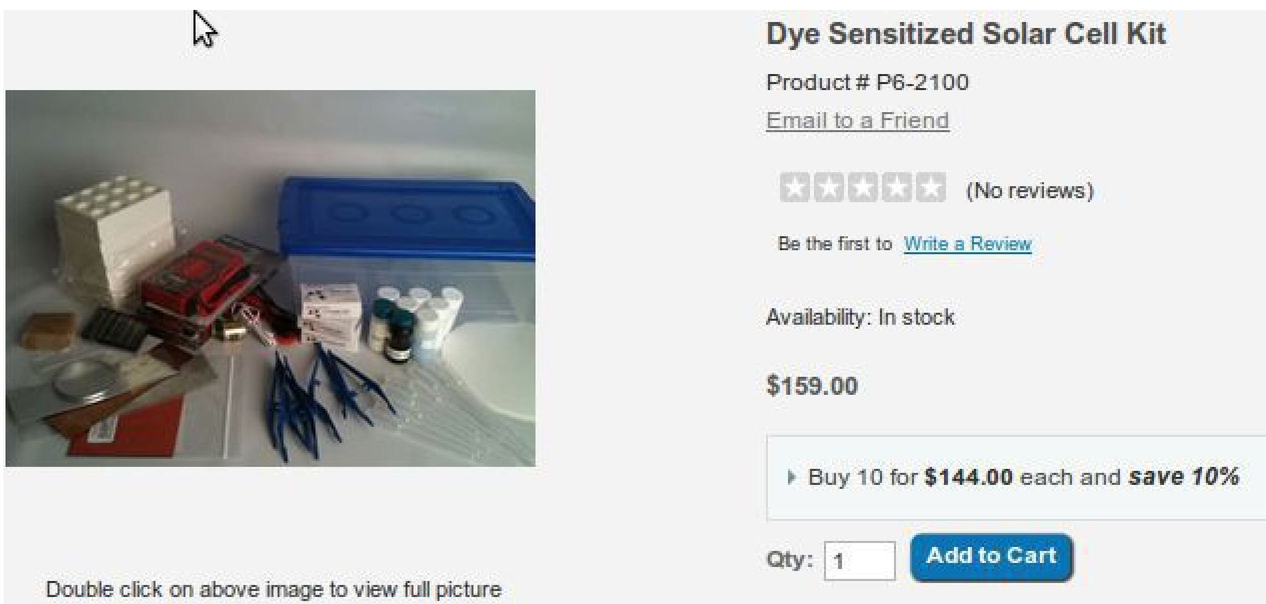


Hybrid organic-inorganic



Dye-sensitized cells (Grätzel cells)

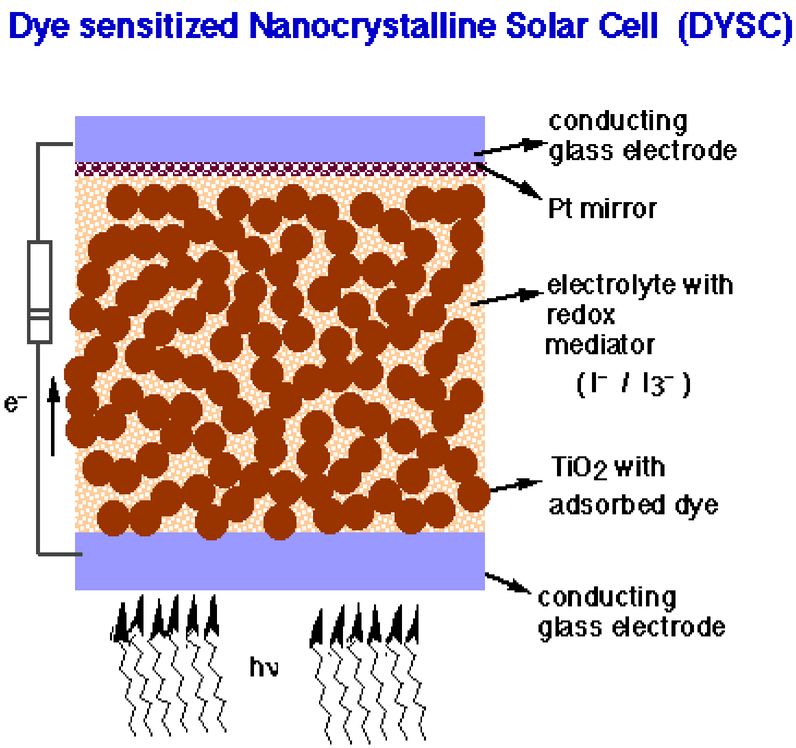
- Photovoltaics following nature: Can be demonstrated with fruit juice and correction fluid
- More than 12% efficiency
- Problem: Liquid electrolyte

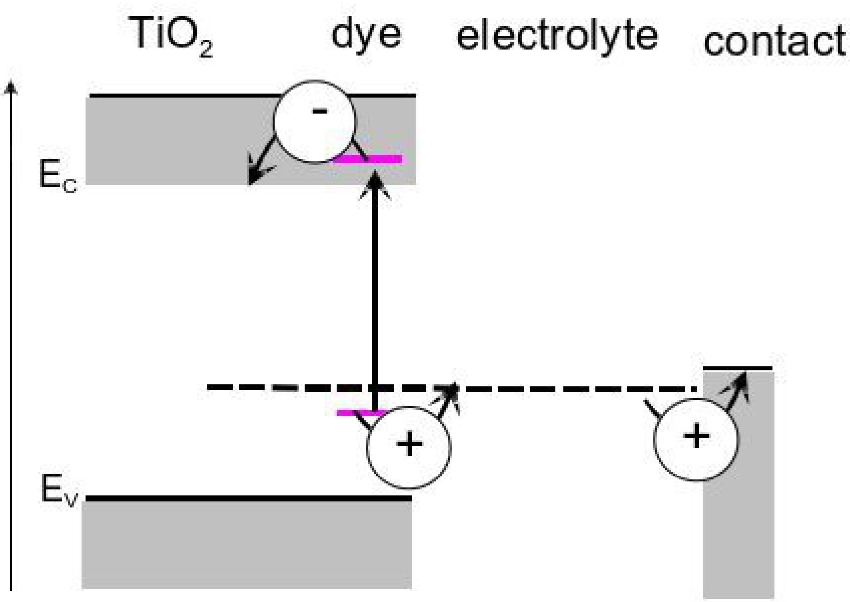


Dye-sensitized Solar cell

Structure

Energy scheme





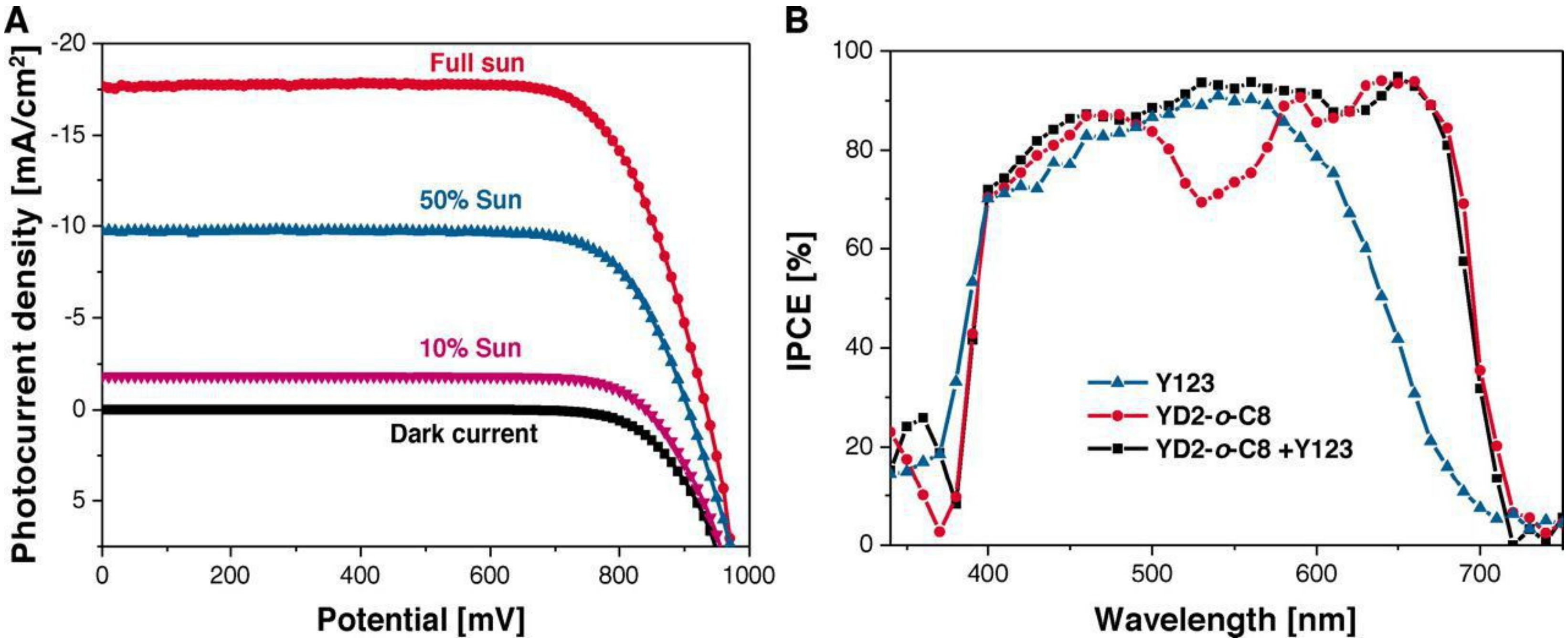
TiO_2 grains of 10 to 30nm size

Efficiencies >12% demonstrated

Grätzel cell

IV-curve | **quantum efficiency**

A. Yella et al., Science **334,** 629 (2011)



- Efficiency potential: ≈ 15%
- Key problem: Aggressive electrolyte (encapsulation)
- Solid-State hole transport is challenging

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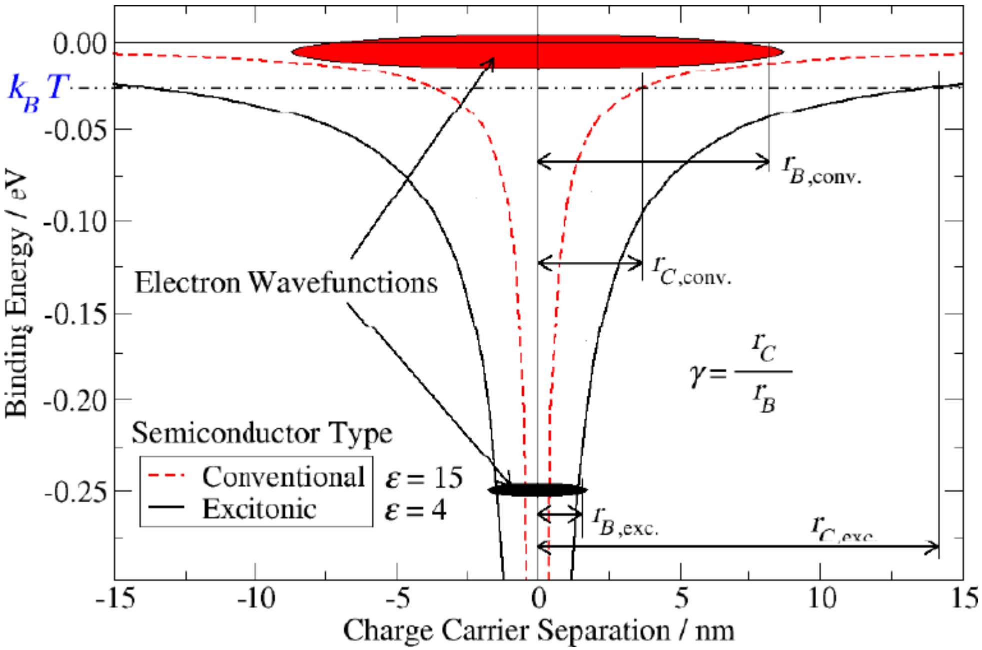
Challenges of organic photovoltaics

- Challenges of organic vs. inorganic PV:
- Exciton Separation
  - Binding Energy >> kT
- Diffusion Length:
  - Typically shorter than absorption length
- Stability:
  - Does this organic stuff has any stability?

The exciton separation problem



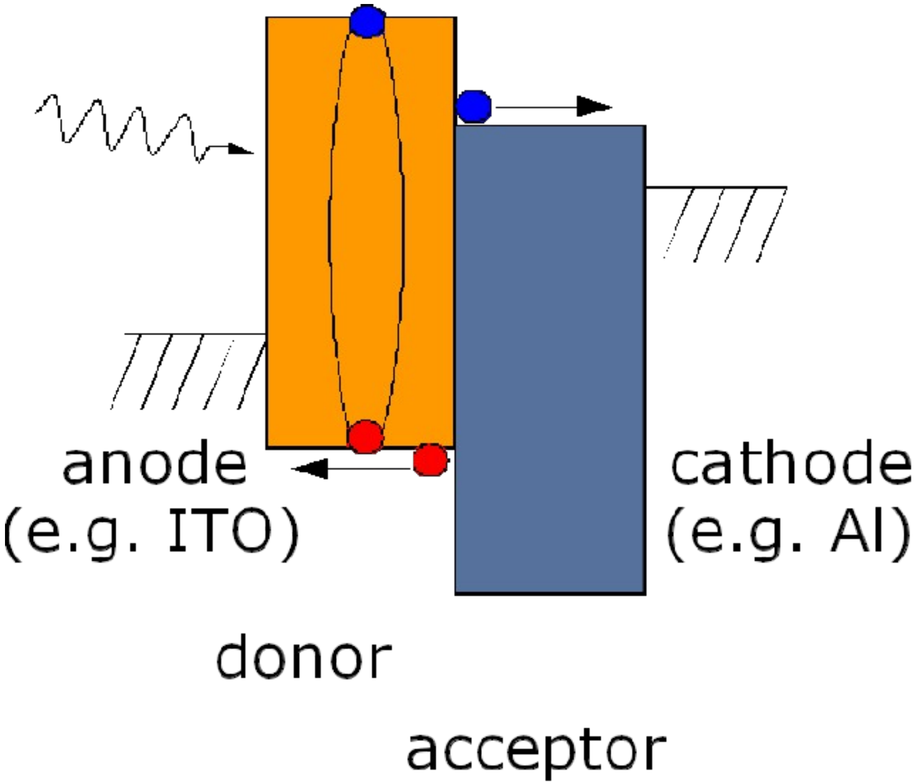
- Absorption leads to tightly bound (0.2 … 0.5 eV) excitons
- Separation in electric field inefficient
- Usual solar cell structure does not work

S. E. Gledhill et al. J. Mat Res. 20, 3167 (2005)

P. Würfel, CHIMIA 61, 770 (2007)

Exciton separation at a heterojunction

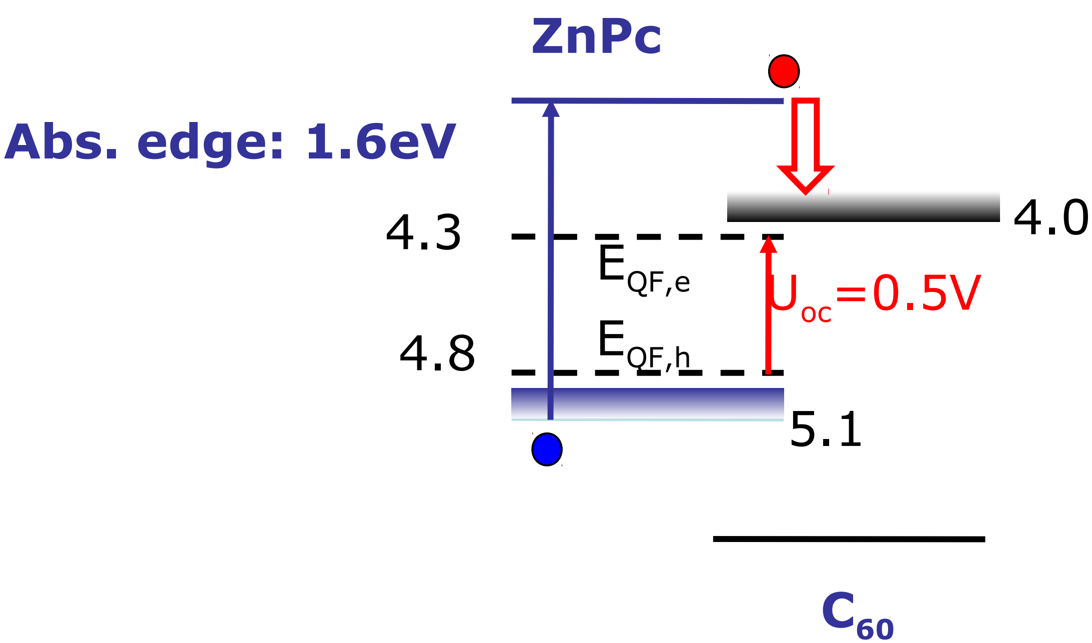
Flat heterojunction (FHJ)



C. W. Tang, Appl. Phys. Lett. 48, 183 (1986)

Energy loss at heterojunction

Example system: ZnPc/C_{60}



Open circuit voltage: ≈0.5V
⇒Large loss of energy

Minimum energy loss upon charge separation: 0.2….0.7 eV?

The exciton diffusion length problem

- Exciton diffusion lengths seem to be small: ≈ 10 nm
- Limited by extrinsic or intrinsic processes?
- Much higher values have been reported for materials with higher order: up to micrometers...

Exciton diffusion lengths: other data

TABLE I. Calculated quenching layer Förster radii (R_Q) and diffusion lengths (L_D) for singlet (S) and triplet (T) excitons of crystalline (C.) and amorphous (Amorph.) films.

Material	Exciton	Crystallinity (Orientation)	Quenching/Blocking Layers	R_Q with C_{60} (nm)	L_D (nm)
NPD	S	Amorph.	C_{60}/BCP	2.4	5.1 (±1.0)[a]
CBP	S	Amorph.	C_{60} (or NTCDA)/Bare	2.7	16.8 (±0.8)[a]
SubPc	S	Amorph.	C_{60}/Bare	1.1	8.0 (±0.3)
PTCDA	S	C.-55 nm (flat)	C_{60} (or NPD)/NTCDA	0.9	10.4 (±1.0)
DIP	S	C.->150 nm (upright)	C_{60}/Bare	1.2	16.5 (±0.4)
DIP	S	C.-30 nm (flat)	C_{60}/Bare	1.2	21.8 (±0.6)
PtOEP	T-Mon.	C.->150 nm (upright)	C_{60}/BCP	0.6	18.0 (±0.6)
PtOEP	T-Dim.	C.->150 nm (upright)	C_{60}/BCP	0.6	13.1 (±0.5)

[a]Corrected for energy transfer to the quenching layer.

R.R. Lunt et al., J. Appl. Phys. **105**, 053711 (2010)

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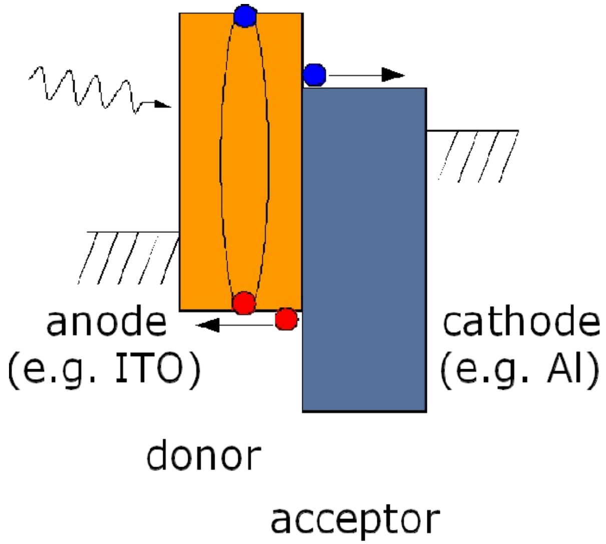
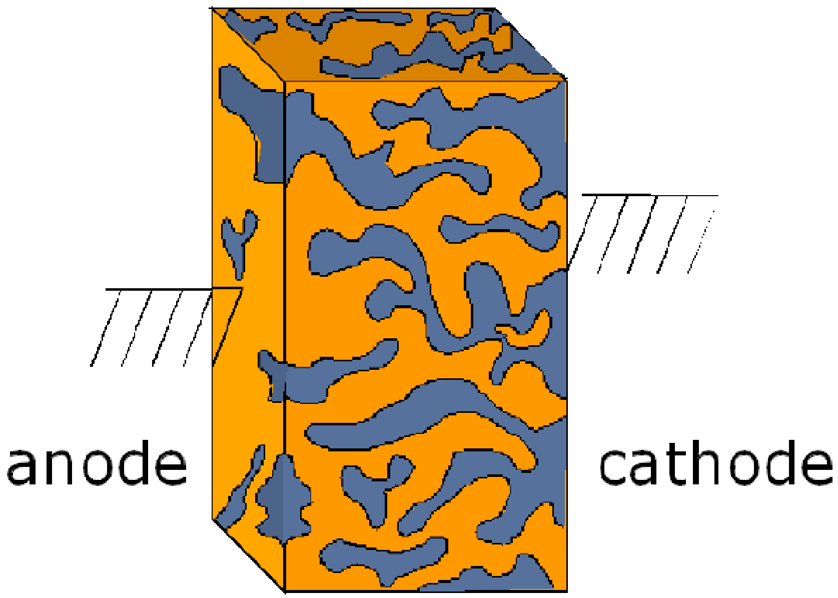
Exciton separation at a heterojunction

Flat heterojunction (FHJ)



bulk heterojunction (BHJ)

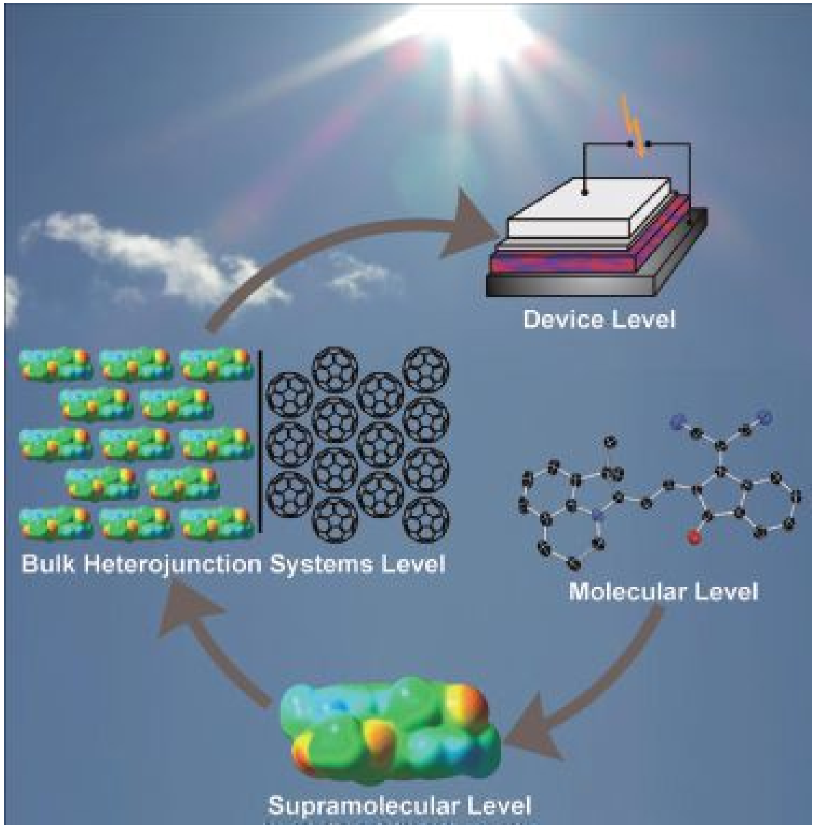


Acceptor and donor domains on 10nm scale

C. W. Tang, Appl. Phys. Lett. 48, 183 (1986)
M. Hiramoto et al., Appl. Phys. Lett. 58, 1062 (1991)
J. J. Hall et al., Nature 376, 498 (1995)
G. Yu et al. Science 270, 1789 (1995)

Which molecule and morphology?

- Multi-scale approach needed for materials development
- Connection between molecular structure and device performance very complex

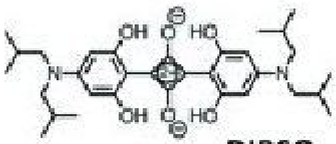


New Small Molecule Absorber Materials

- Benzoporphyrins: Y. Matsuo et al., J. Am. Chem. Soc. **131**, 16048 (2009)

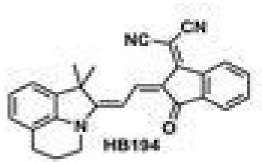
BP

- Squaraines: F. Silvestri et al, J. Am. Chem. Soc. **130**, 17640 (2008); G. Wei et al., ACS Nano **4**, 1927 (2010)



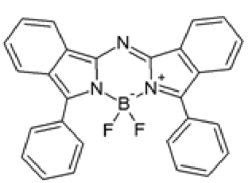
DIBSQ

- Merocyanines: N. Kronenberg et al., J. Photon. Energy **1**, 011101 (2010)

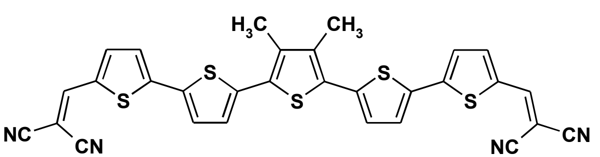


HB194

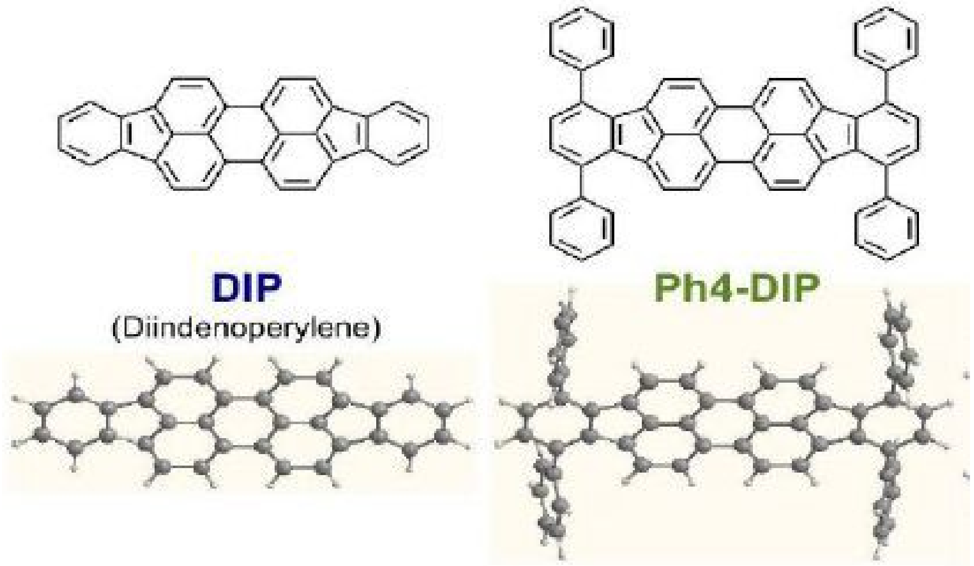
- Bodipys: T. Rousseau et al., Chem. Comm. 1673 (2009), R. Gresser et al., Tetrahedron **67**, 7148 (2011)



- Thiophenes: K. Schulze et al., Adv. Mat. **18**, 2872 (2006); E. Ripaud et al., Adv. En. Mat. **1,** 540 (2011), Y. Sun et al., Nature Mat. **11**, 44 (2012)



Case study: Perylene derivatives



Christoph Schünemann

Chris Elschner

Steric hindrance???

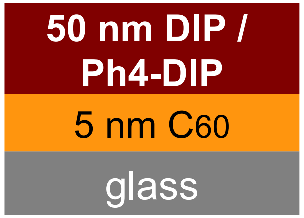
→ effect on molecular **orientation?**

→ effect on **phase separation** in blend layers with C_{60}?

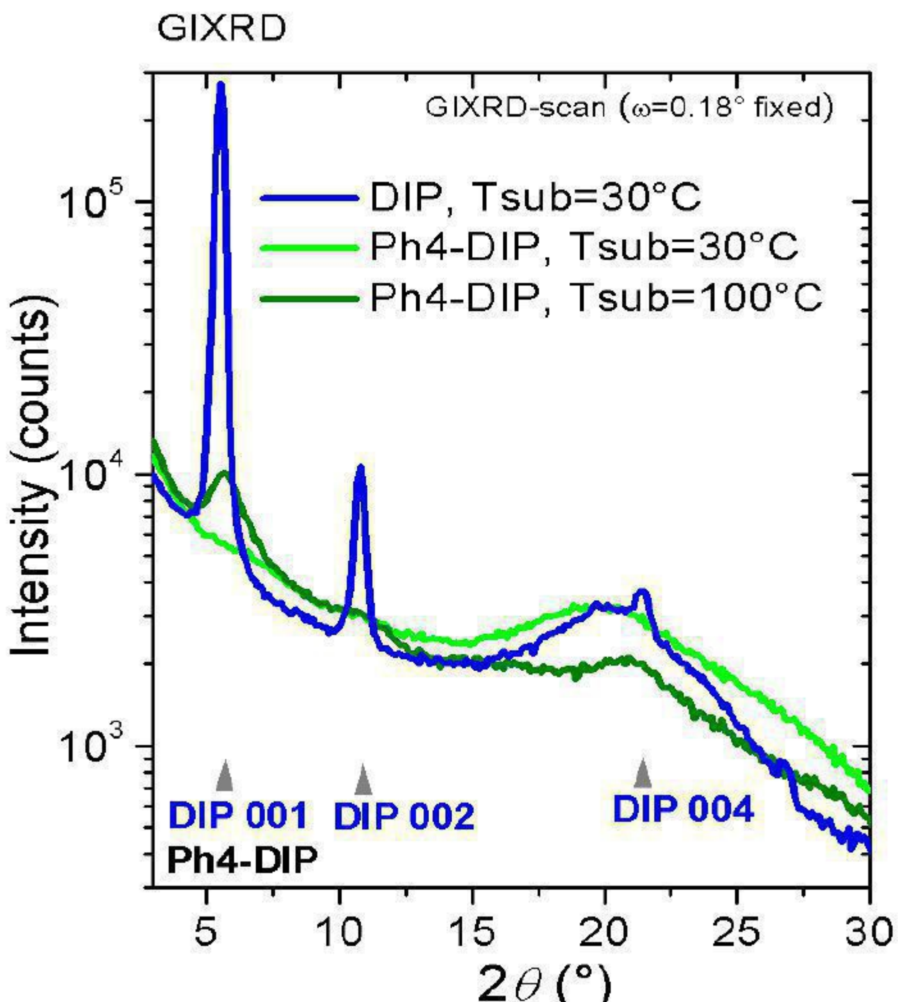
→ differences in planar and bulk heterojunction **solar cells???**

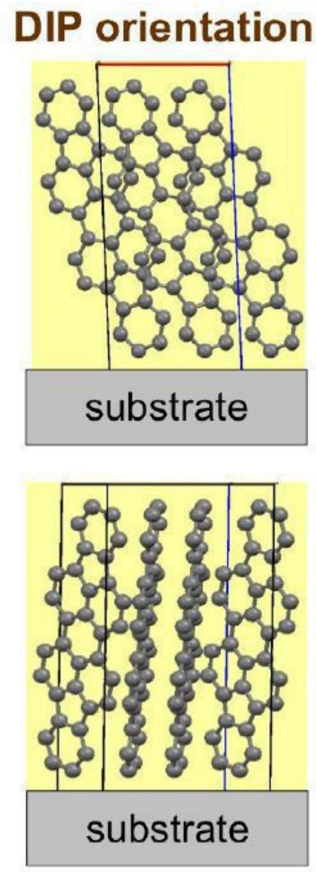
Grazing incidence X-ray diffraction

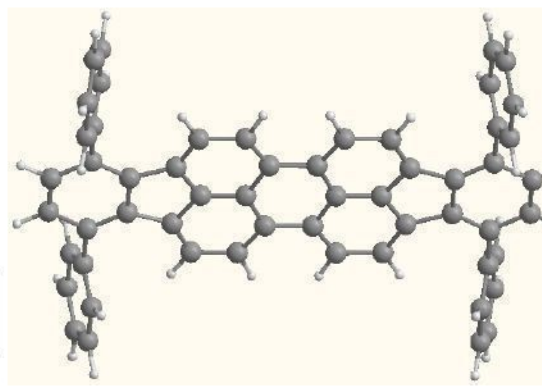
XRD measurements performed by Lutz Wilde, Fraunhofer CNT Dresden



GIXRD of pristine DIP/Ph4-DIP films







→ **Phenyl rings** disturb dense crystalline packing

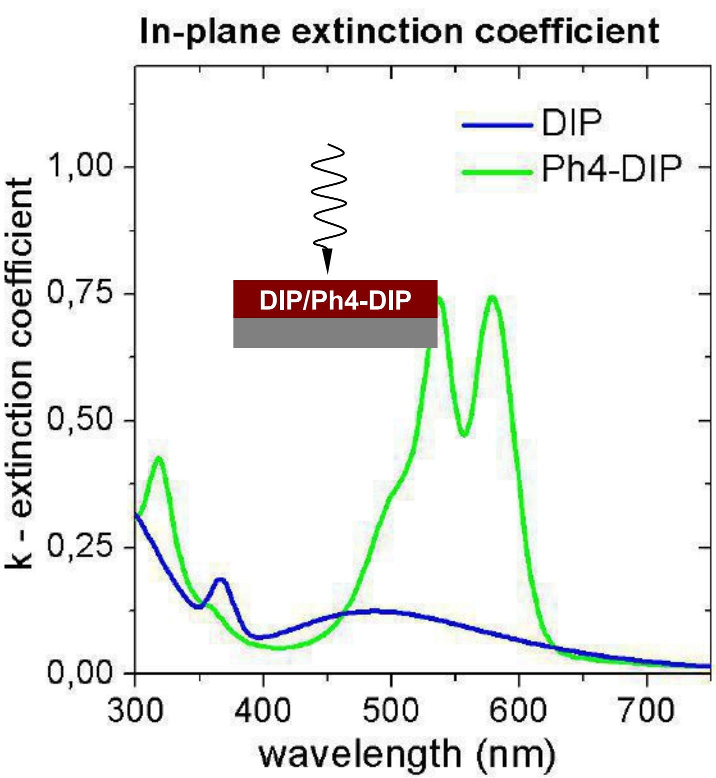
Ellipsometry (VASE)

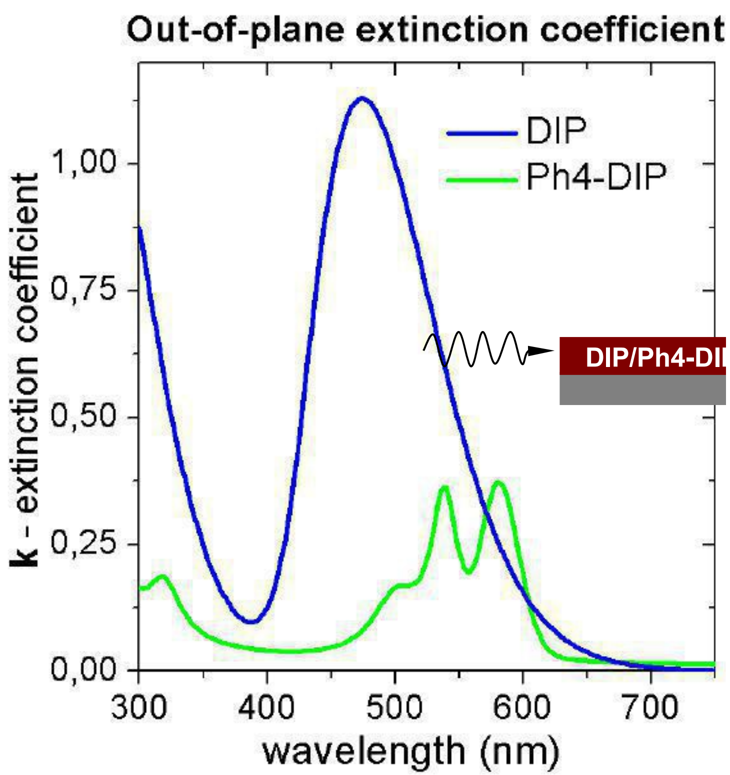
VASE measurements performed by David Wynands and Roland Schulze, IPF Dresden

100 nm DIP / Ph4-DIP
SiO_2 (IES)

Wavelength dependent extinction values by VASE:

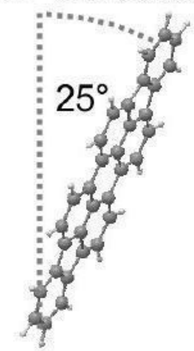
Main direction of transition **dipole moment parallel** to the **long axis**



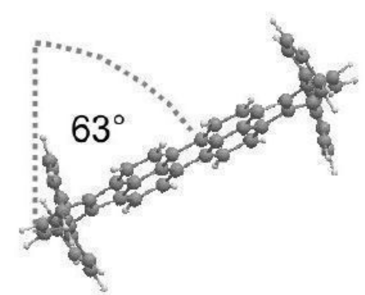


Mean tilt angle of

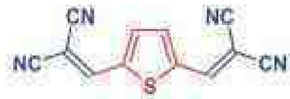
- **DIP molecules**



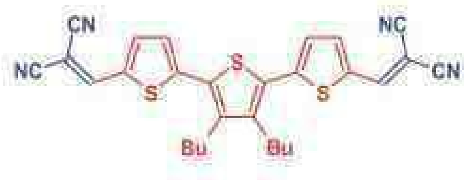
- **Ph4-DIP molecules**



Low gap thiophene oligomers



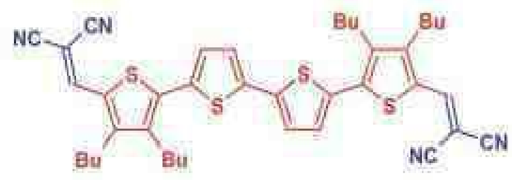
DCV1T



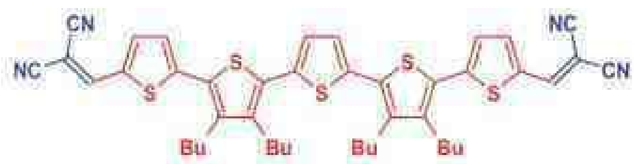
DCV3T

University of Ulm
Department Organic
Chemistry II

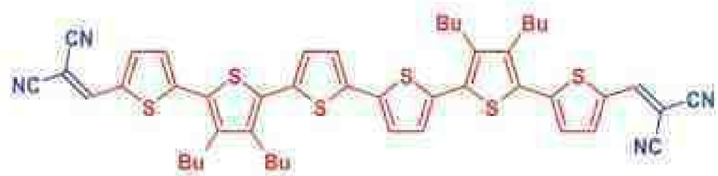
E.Brier,
E. Reinold,
P. Kilickiran,
P. Bäuerle



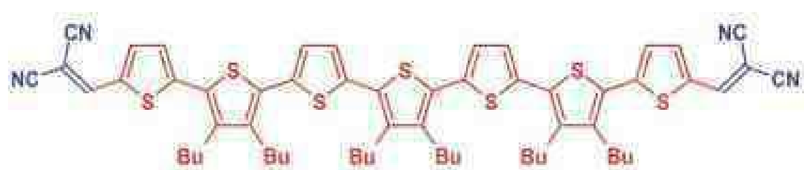
DCV4T



DCV5T

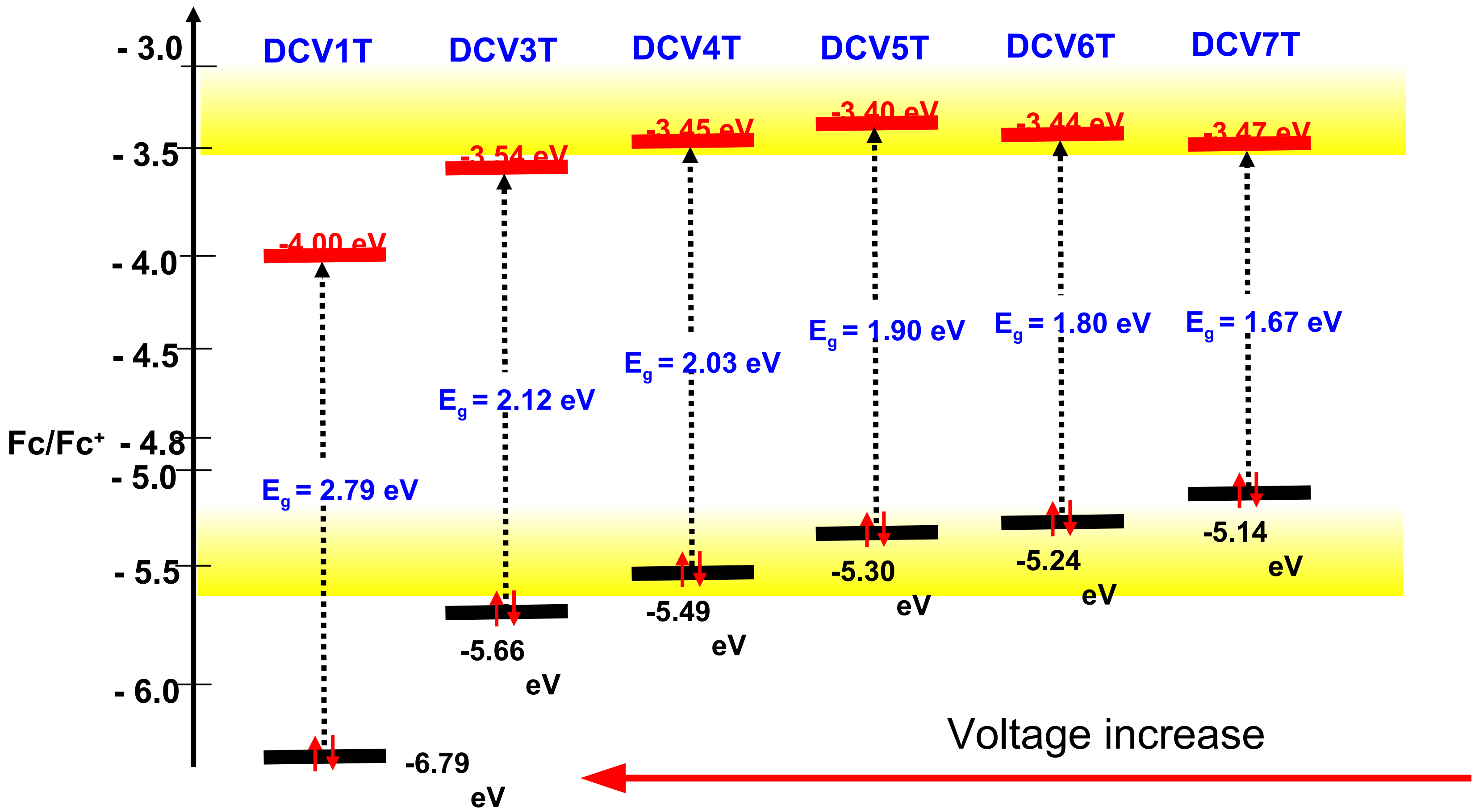


DCV6T



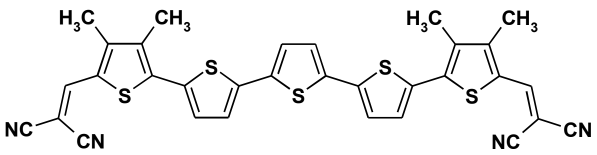
DCV7T

Thiophene oligomers: energy gaps

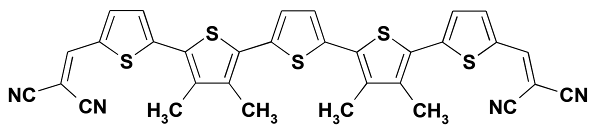


Minimum loss due to exciton separation: roughly 0.3V

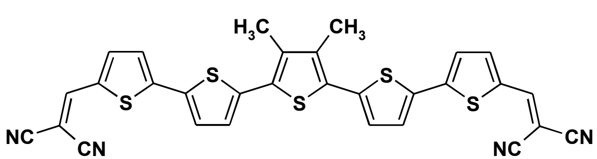
New Thiophenes: DCV5T-Me Series



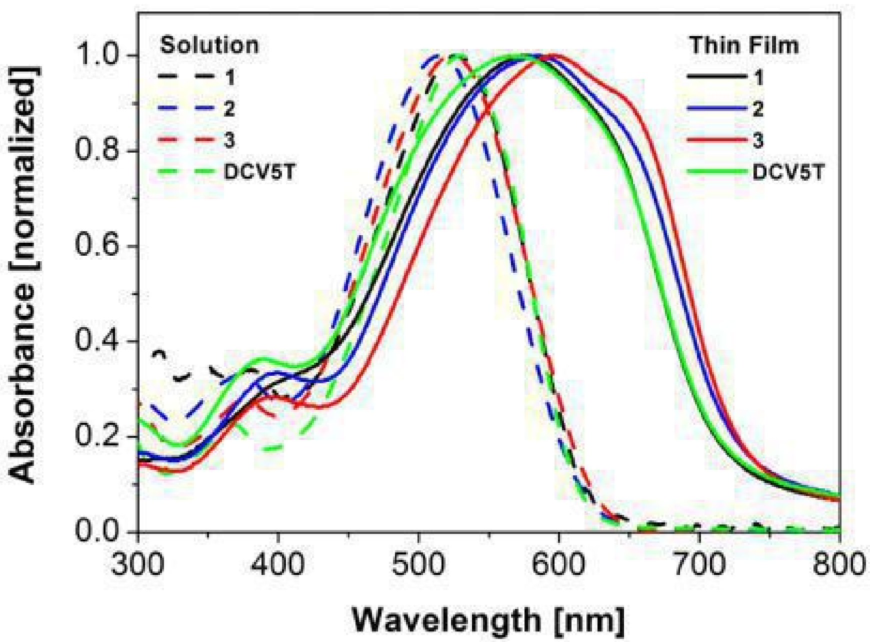
1: DCV5T-Me(1,1,5,5)



2: DCV5T-Me(2,2,4,4)



3: DCV5T-Me(3,3)



7.2% reached: following talk (Christian Körner)

Heliatek

University of Ulm Department Organic Chemistry II

R. Fitzner *et al.*, JACS **134**, 11064 (2012)

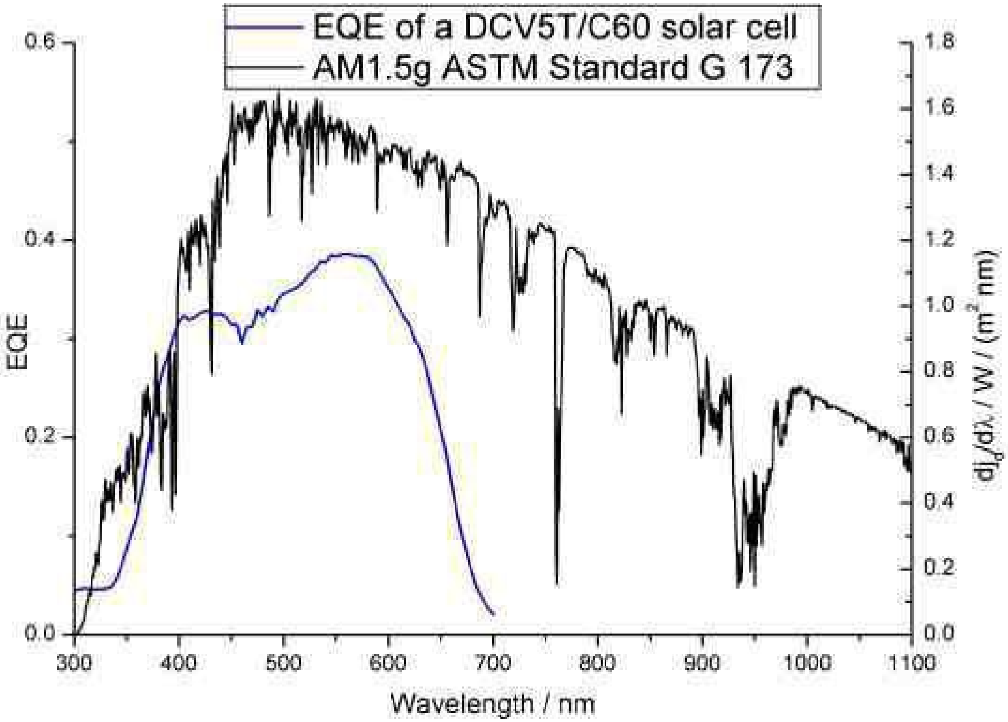
Outline

- Comparison of present PV technologies
- Basics of organics
  - Challenges:
    - Exciton Separation
    - Nanomorphology
    - **Efficiency**
- Long-term stability
- Manufacturing & applications

Covering the full solar spectrum

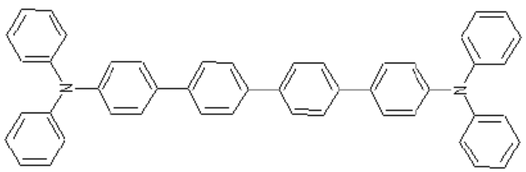
- Much of the solar spectrum is currently not used!

- Tandem or triple cells
- Extend absorption to IR



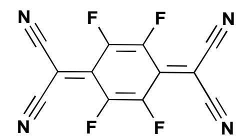
M. Hiramoto et al., Chem. Lett. **1990** (1990) 327; A. Yakimov & S.R. Forrest, Appl. Phys. Lett. **80** (2002) 1667

Organic p-i-n Solar Cells

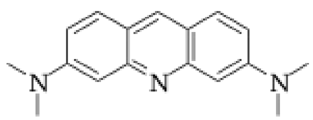


4P-TPD

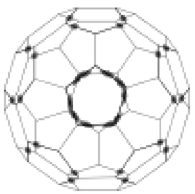
F4-TCNQ

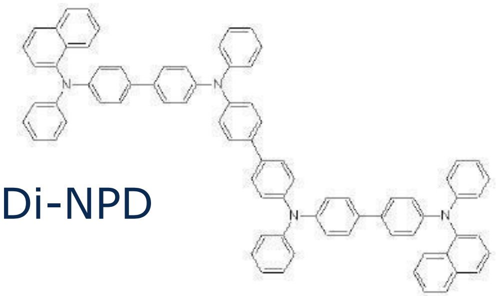


AOB

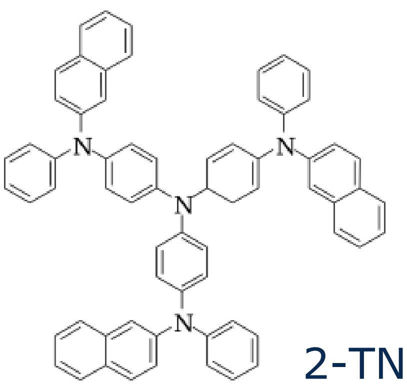


C60

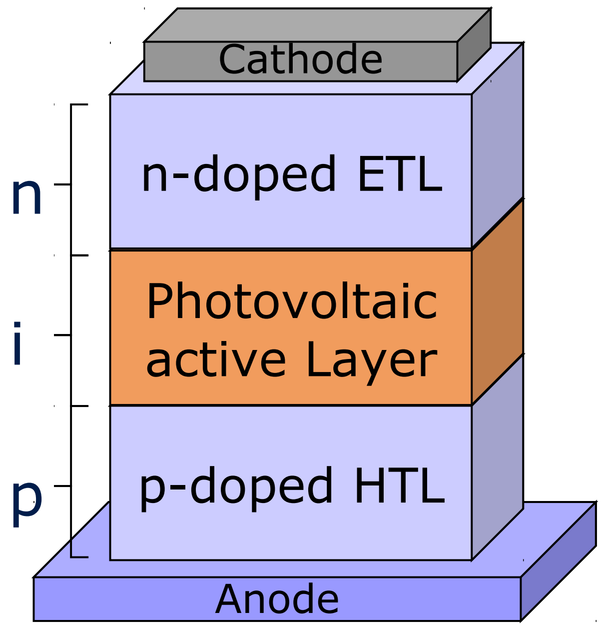


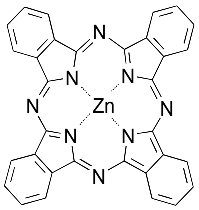


Di-NPD

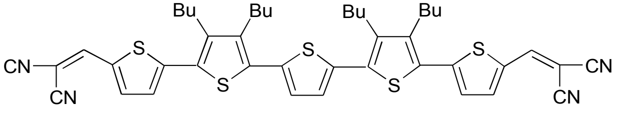


2-TNATA





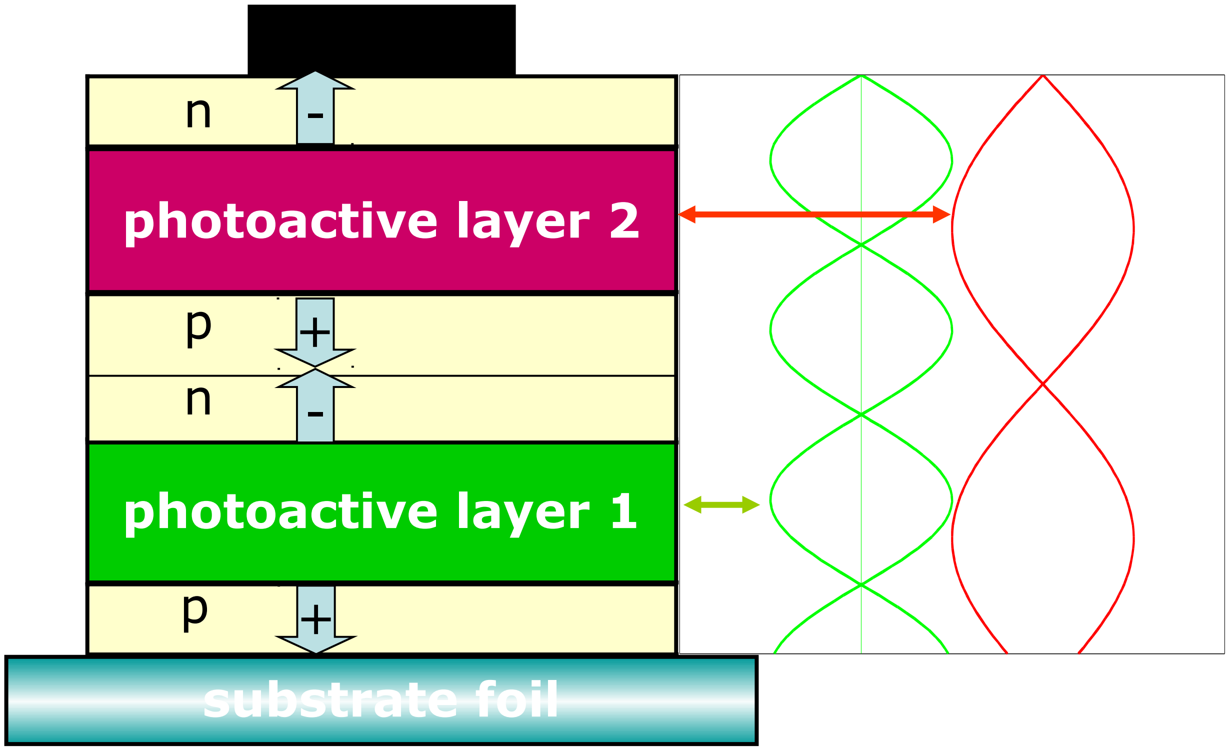
ZnPc



DCV5T-Bu

B. Maennig *et al.*, Appl. Phys. A 79, 1 (2004)
M. Riede *et al.*, Nanotechnology 19, 424001 (2008)

Pin-tandem cells: doped layers are critical for optical optimization



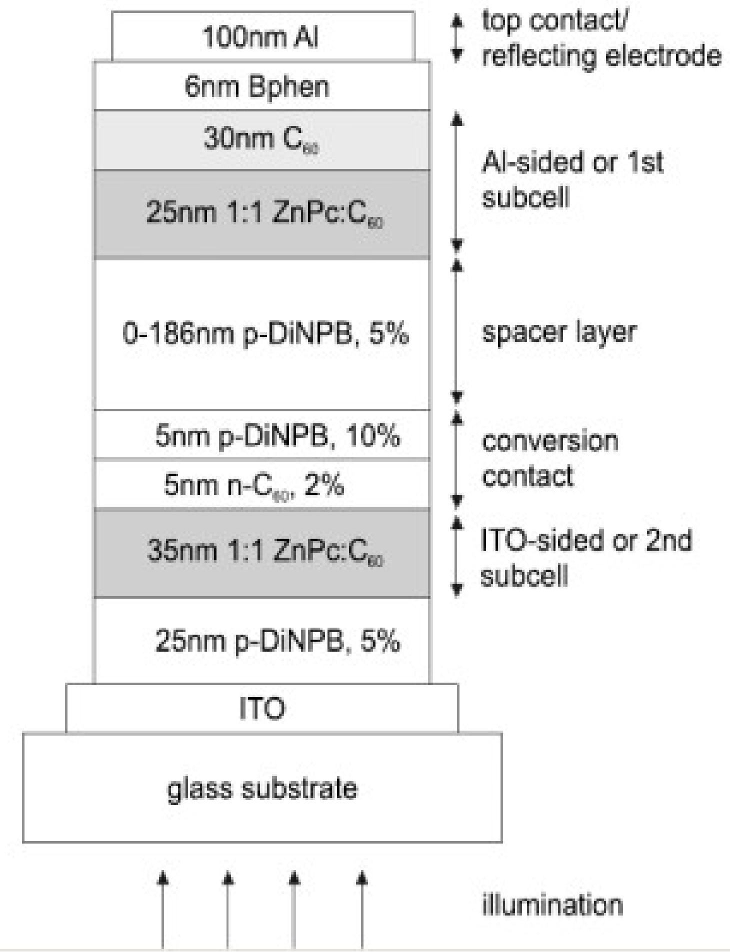
p-i-ntandem cells:

- Pn-junction is ideal recombination contact
- optimizing interference pattern with conductive transparent layers

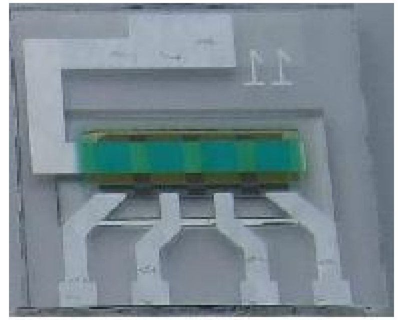
=>optical engineering on nanometer layer thickness scale

J. Drechsel et al., Appl.Phys.Lett. **86**, 244102 (2005)

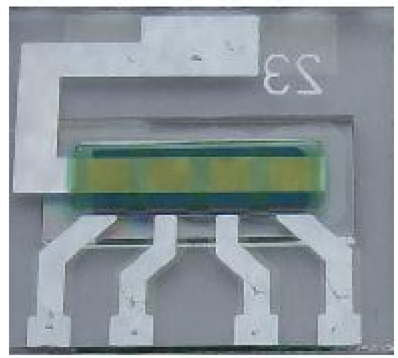
Pin-tandem cells: perfect optical control



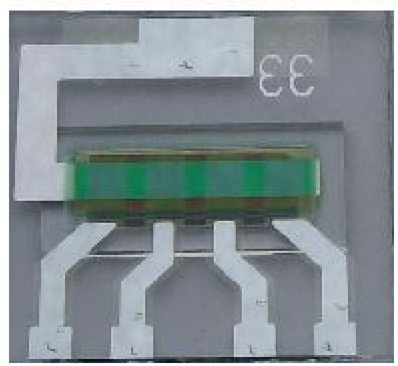
Thickness of spacer layer:



0 nm (1st max)



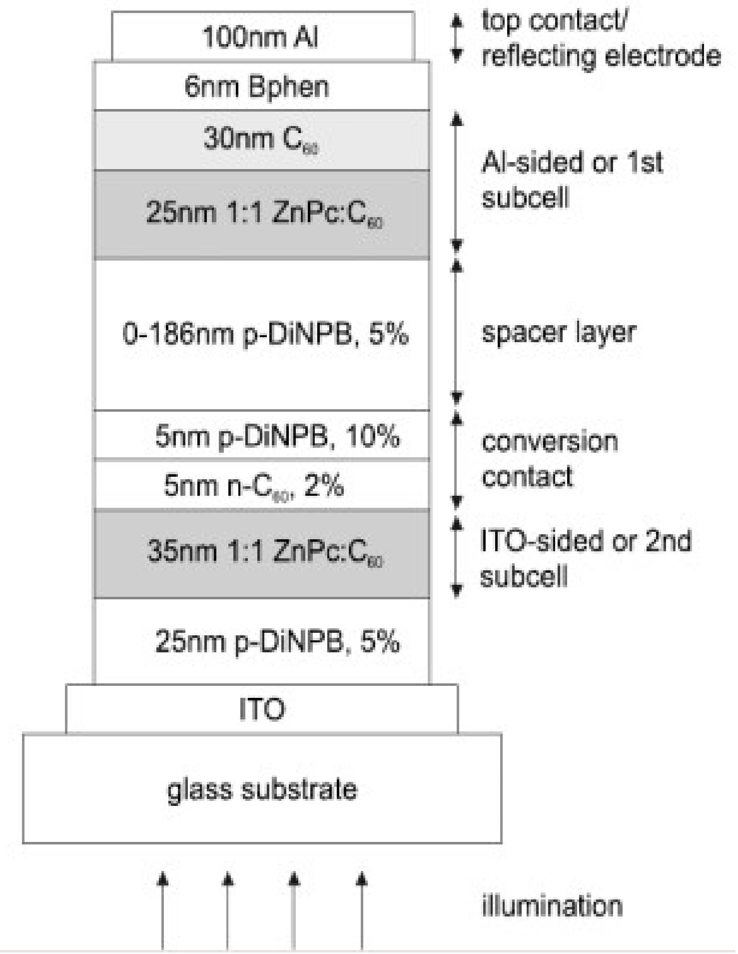
74nm (1st min)

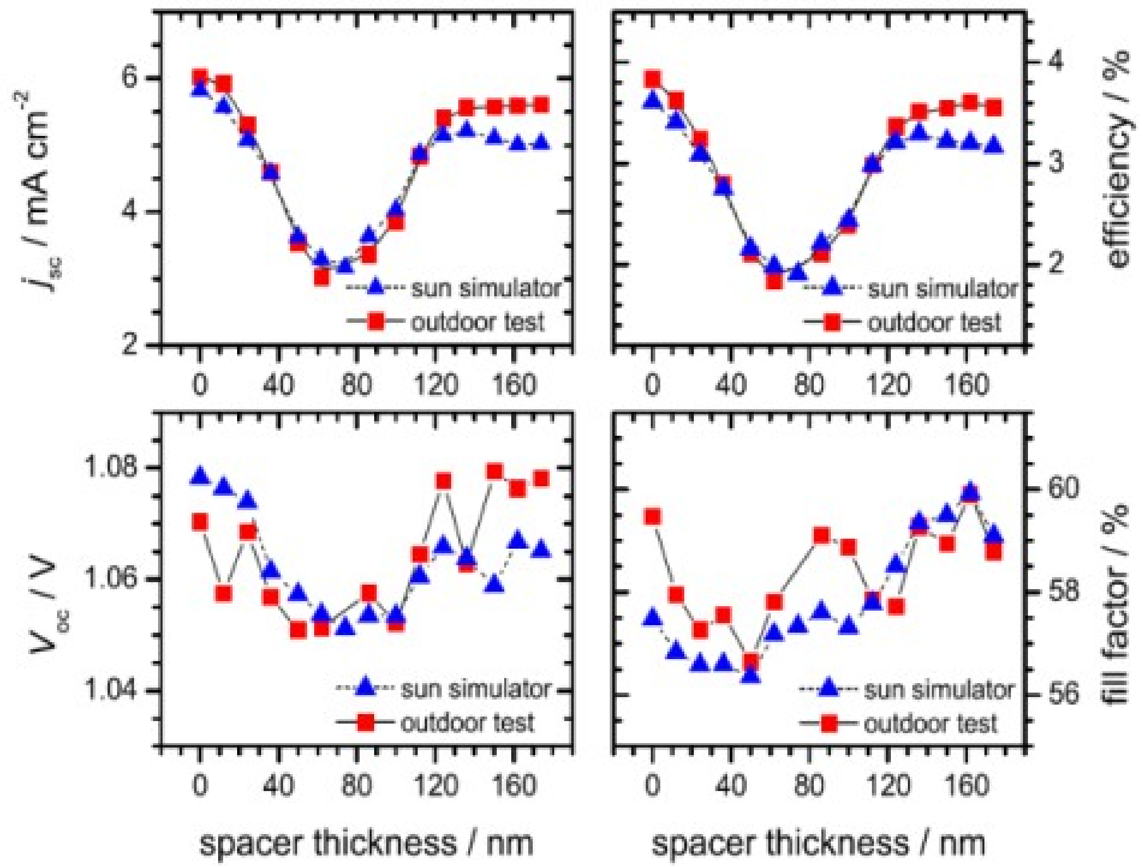


124nm (2nd max)

R. Schüppel et al., J. Appl. Phys. **107**, 044503 (2010)

Pin-tandem cells: perfect optical control



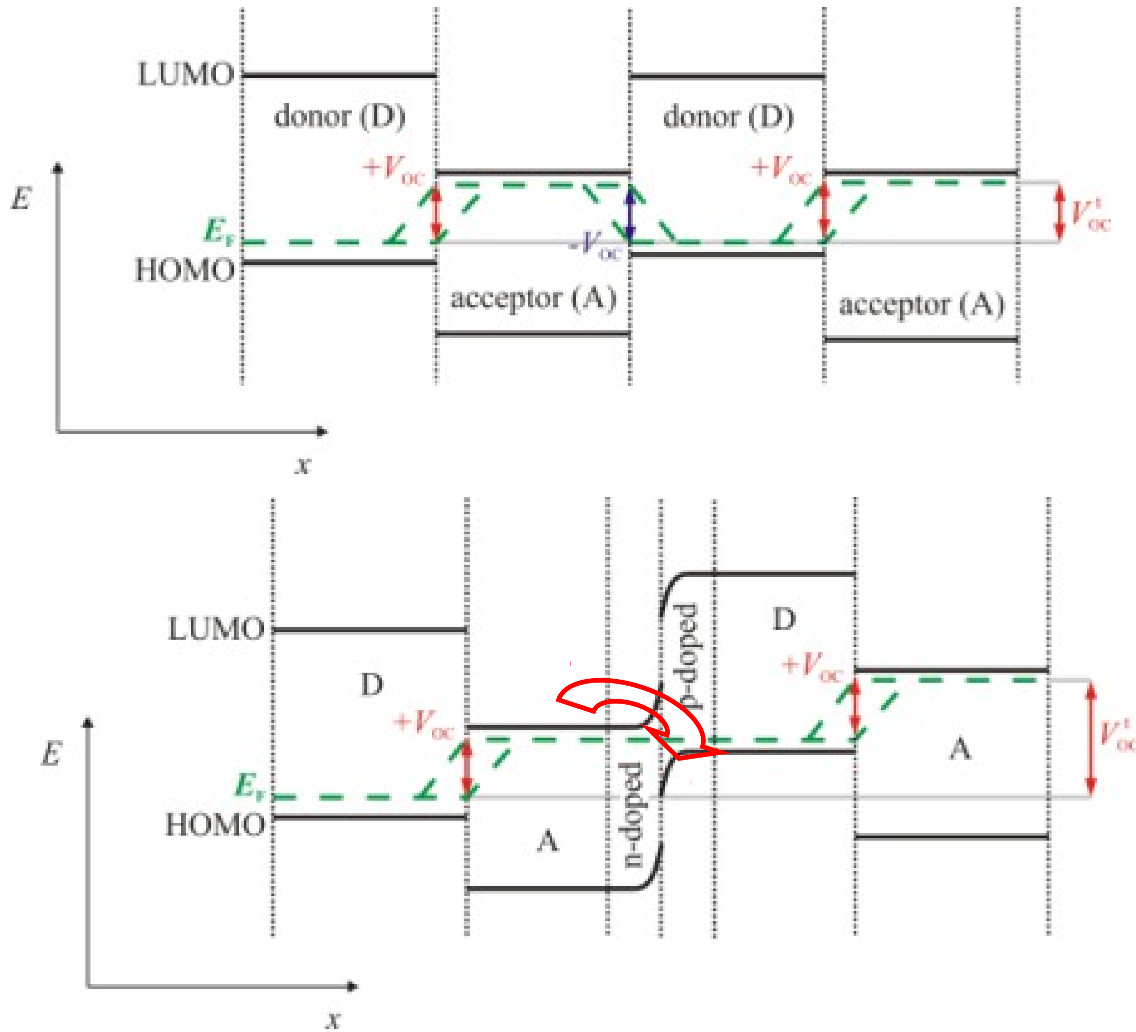


R. Schüppel et al., J. Appl. Phys. **107**, 044503 (2010)

Efficient Recombination Contact

- Stacking two D/A heterojunctions
  → reverse HJ
  → voltage loss

- Our Approach:
  - highly doped layers for energy level alignment at the interface
  - no quasi-Fermi level splitting
  - no loss of V_{oc}



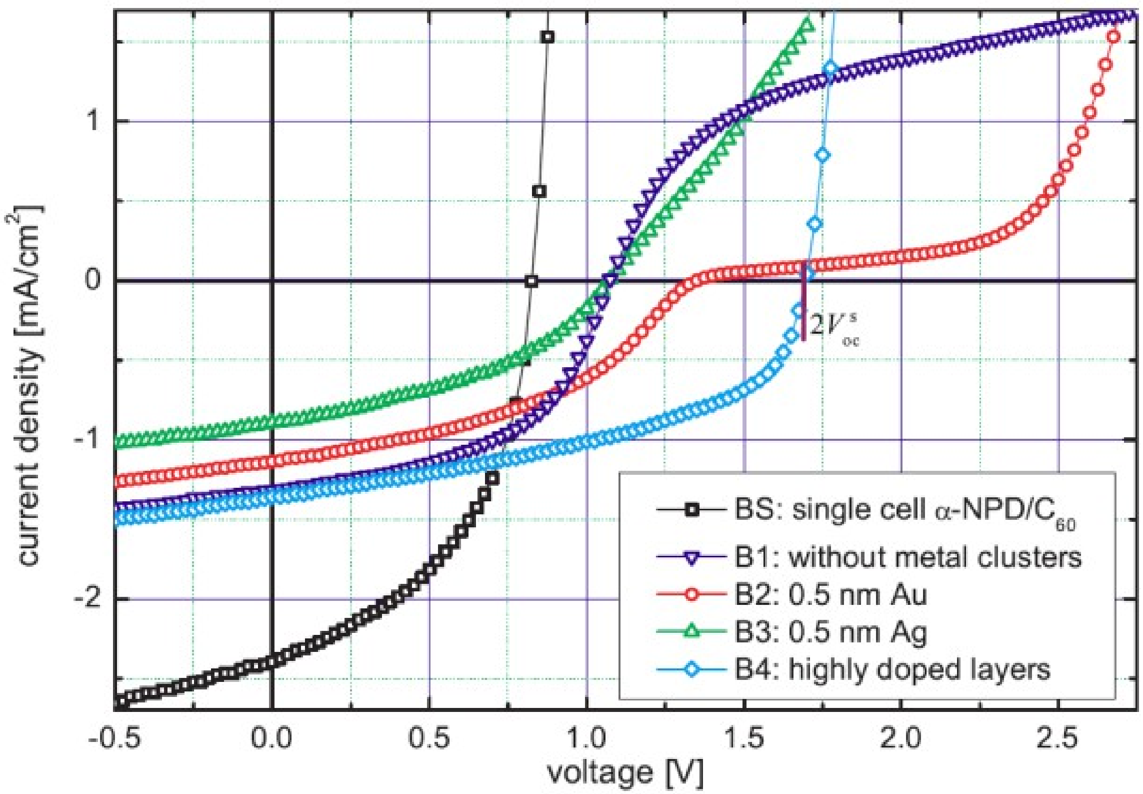
R. Timmreck *et al.*, J. Appl. Phys. 108, 033108 (2010)

TECHNISCHE UNIVERSITÄT DRESDEN

Efficient Recombination Contact

iapp

- Metal clusters have only weak effect on efficient recombination
- Highly doped pn-junction is very efficient, stable and simple recombination contact



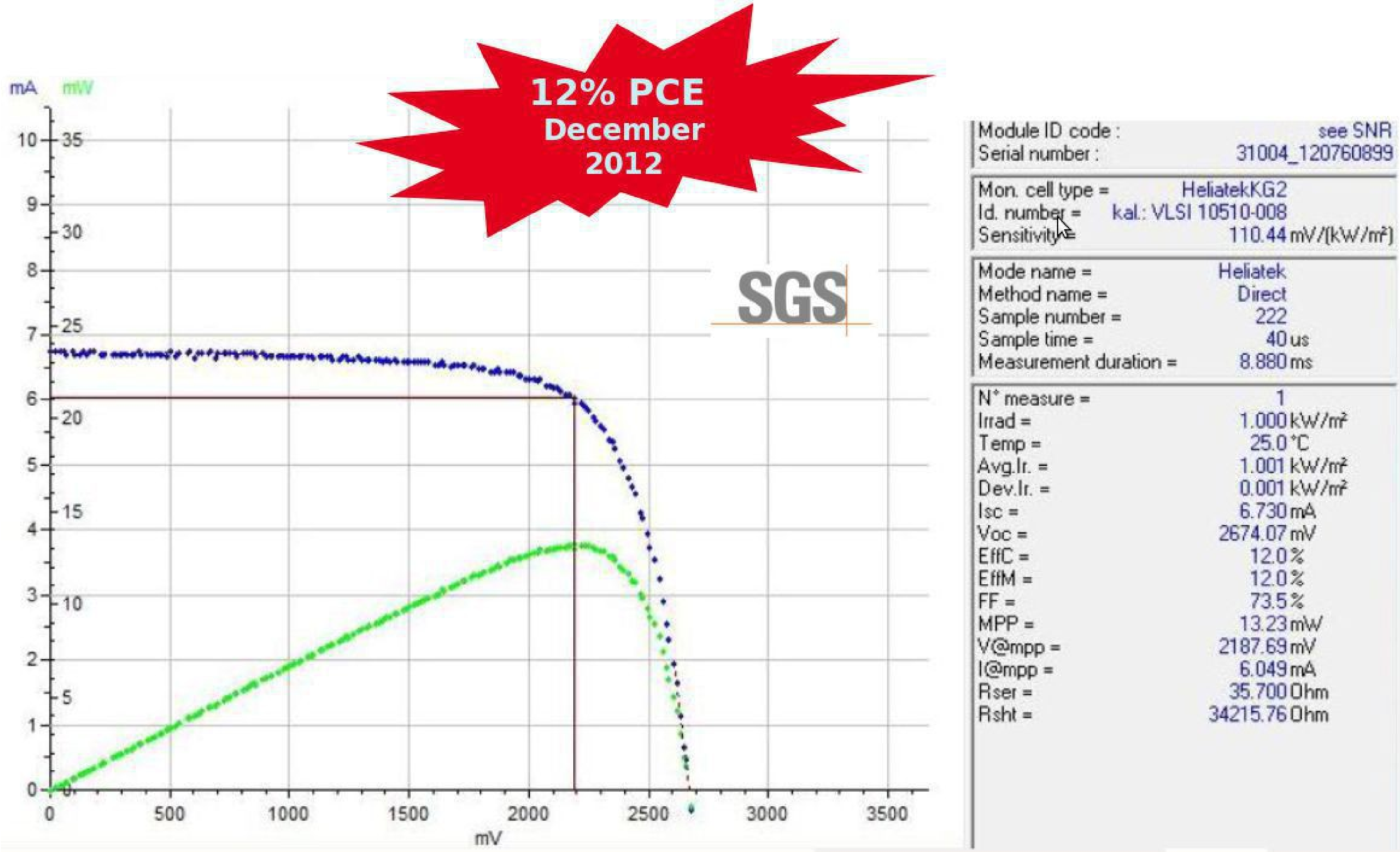
R. Timmreck *et al.*, J. Appl. Phys. 108, 033108 (2010)

Small-Molecule OPV Record > 1cm²

12 % Efficiency – new world Record for OPV

Measured by SGS at standard test conditions (December 2012)

Heliatek®
Say hello to solar. Wherever you are

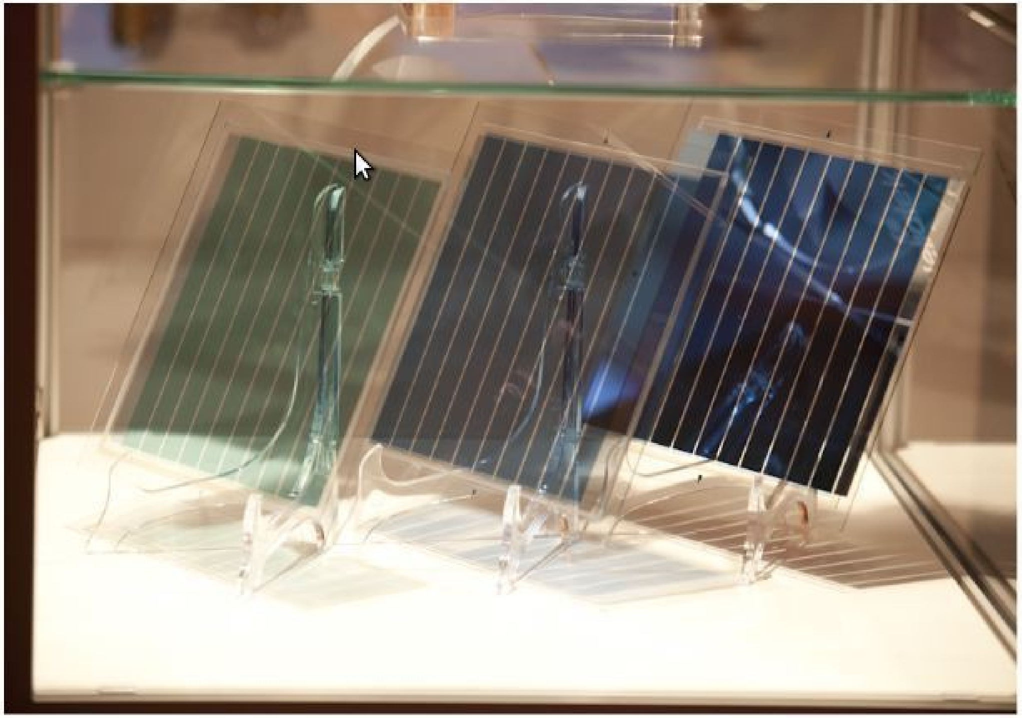


OPV Module record

9% Module Efficiency on Glass

Record efficiencies thanks to minimum upscaling losses

Heliatek® Say hello to solar. Wherever you are



7 Cells in Series	Active Area 122 cm²	Total Area 142 cm²
VOC	11.8 V	11.8 V
VOC per cell	1.67 V	1.67 V
JSC mA/cm²	1.21	1.04
FF	63 %	63 %
Efficiency	**9.0 %**	**7.7 %**

Development of OPV Efficiencies

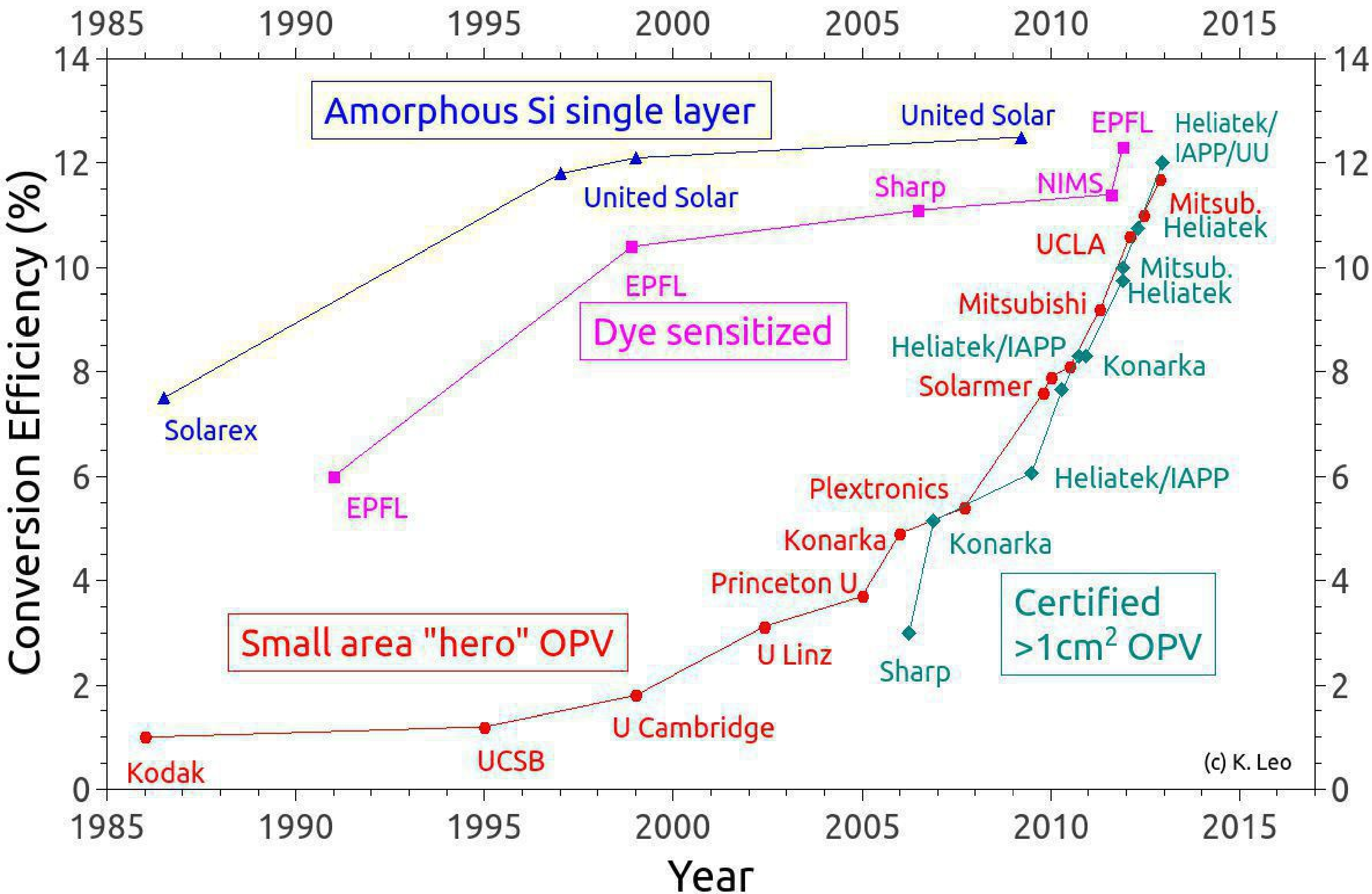


diagram available under www.orgworld.de

Organics is more: The O-Factor

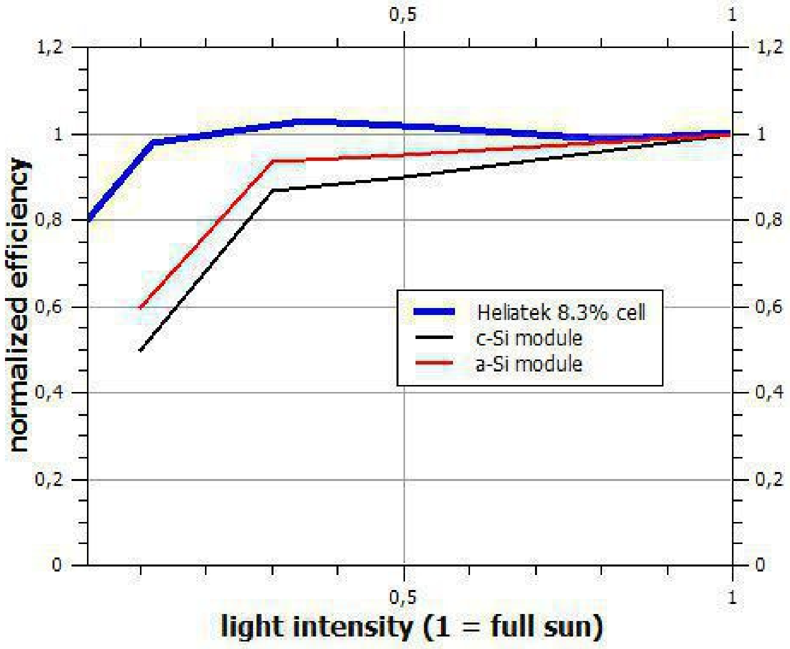
- Standard measurement: 1 sun, 25 ^{0}C, perpendicular incidence

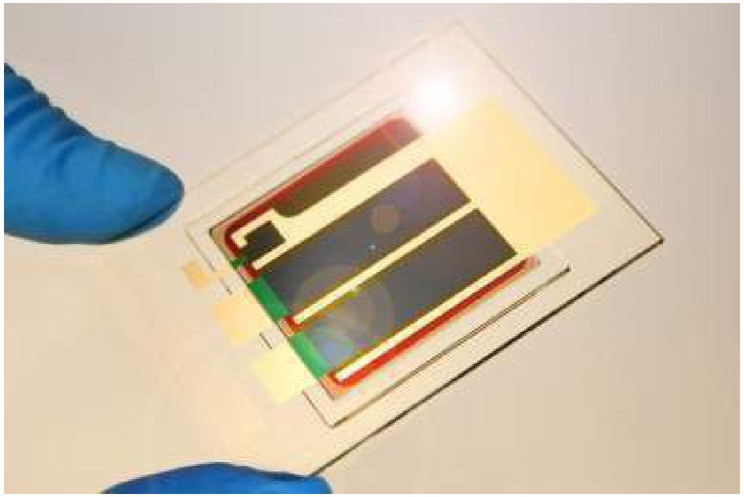
- Reality: 40-60 ^{0}C, often less than 1 sun, diffuse light

- Organics:
  - Positive temperature coefficient
  - Higher efficiency for lower intensity
  - Special diffuse light responsivity

- Sums up in the O-Factor: approx. 30% better!

Intensity Performance





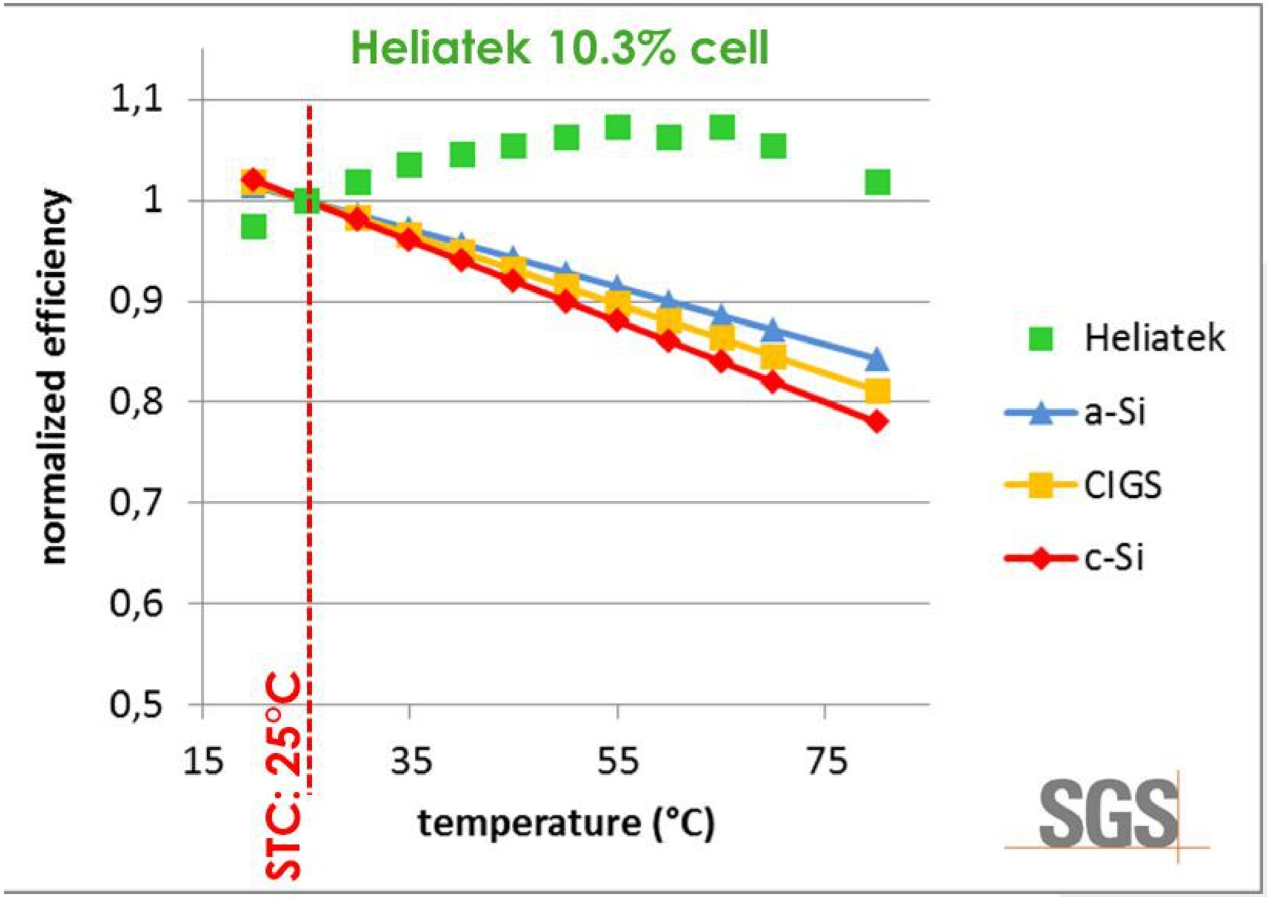
Superior low-light performance:

97 % of full-sun efficiency at 1/10th sun

- Heliatek Absorber
- Certified Efficiency: **8.3 %** (1 cm^2)
- Collaboration of Heliatek und IAPP (TU Dresden)

Temperature performance

Positive temperature coefficient



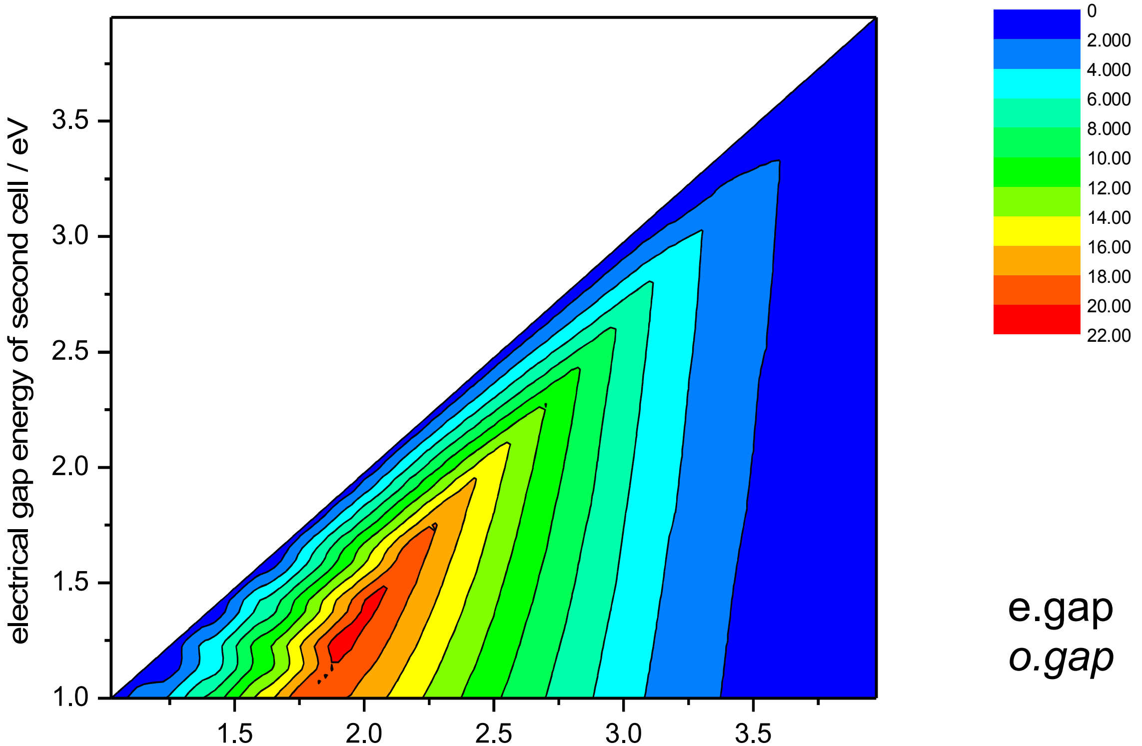
- **Heliatek OPV: Efficiency has broad maximum between 30°C and 60°C**
- c-Si and CIGS:

  15 % lower efficiency at 60 °C
- µc-Si/a-Si:

  10 % lower efficiency at 60 °C

Efficiency Outlook for Tandem Cells

Power conversion efficiency of a tandem cell (in %)



Main assumptions:

- EQE 60%
- FF 60%

	first cell	second cell	
e.gap	1.9eV	1.25eV	~21%
o.gap	*~770nm*	*~1300nm*	
e.gap	2.1eV	1.5eV	~20%
o.gap	*~690nm*	*~1030nm*	
e.gap	2.225eV	1.7eV	~19%
o.gap	*~645nm*	*~890nm*	

T. Mueller et al.

Main challenge: Infrared absorbers with good transport properties!

Outline

- Comparison of present PV technologies
- Basics of organics
  - Challenges:
    - Exciton Separation
    - Nanomorphology
    - Efficiency
- **Long-term stability**
- Manufacturing & applications

Lifetime measurements

- Lifetime is complex parameter depending on cell and encapsulation

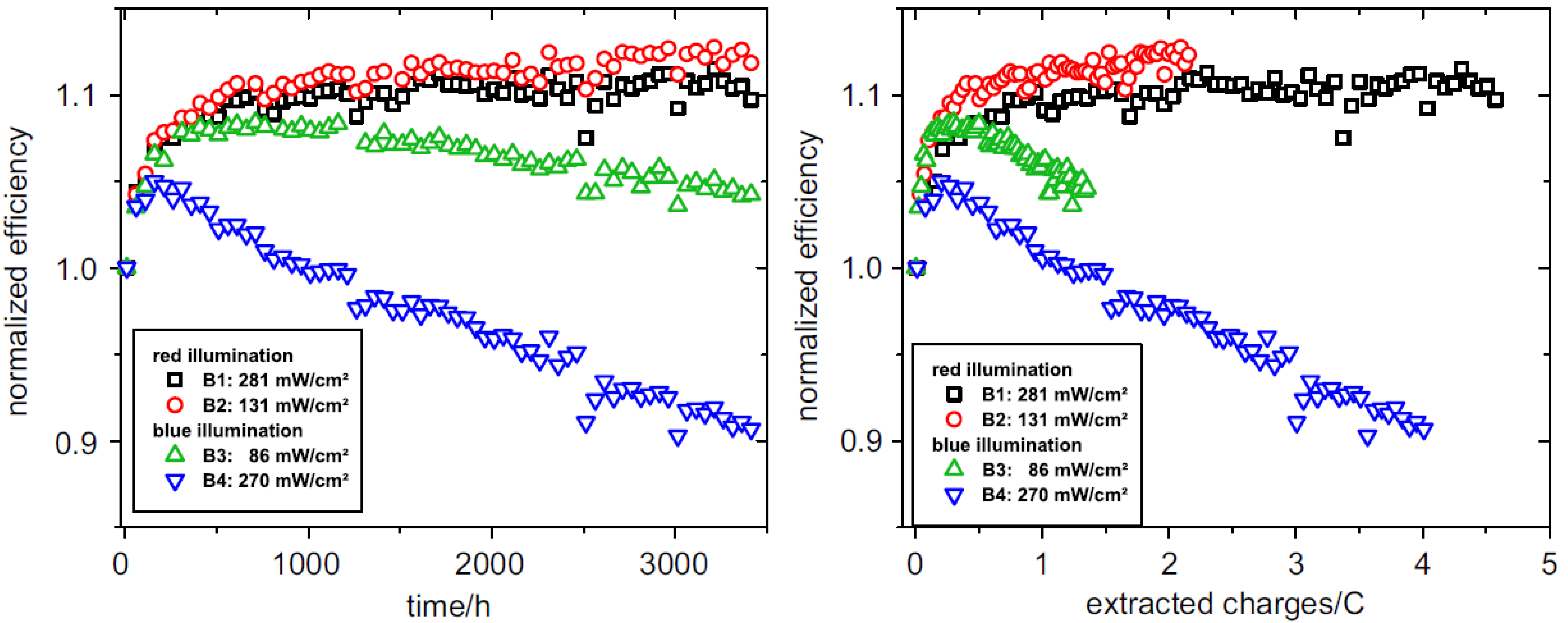
- Extrapolated measurements indicated that cells can be extremely stable

- Detailed studies:
- Water and oxygen induced degradation of small molecule organic solar cells, M. Hermenau, M. Riede, K. Leo, S. Gevorgyan, F. Krebs, and K. Norrman, Solar Energy Materials & Solar Cells **95**, 1268-1277 (2011)

- Total charge amount as indicator for the degradation of small molecule organic solar cells, M. Hermenau, S. Scholz, K. Leo, and M. Riede, Solar Energy Materials & Solar Cells **95**, 1278-1283 (2011)

Dependence of degradation on photocurrent

- Degradation is directly proportional to photocurrent



M. Hermenau et al., Solar EnergyMaterials&SolarCells **95,** 1278 (2011)

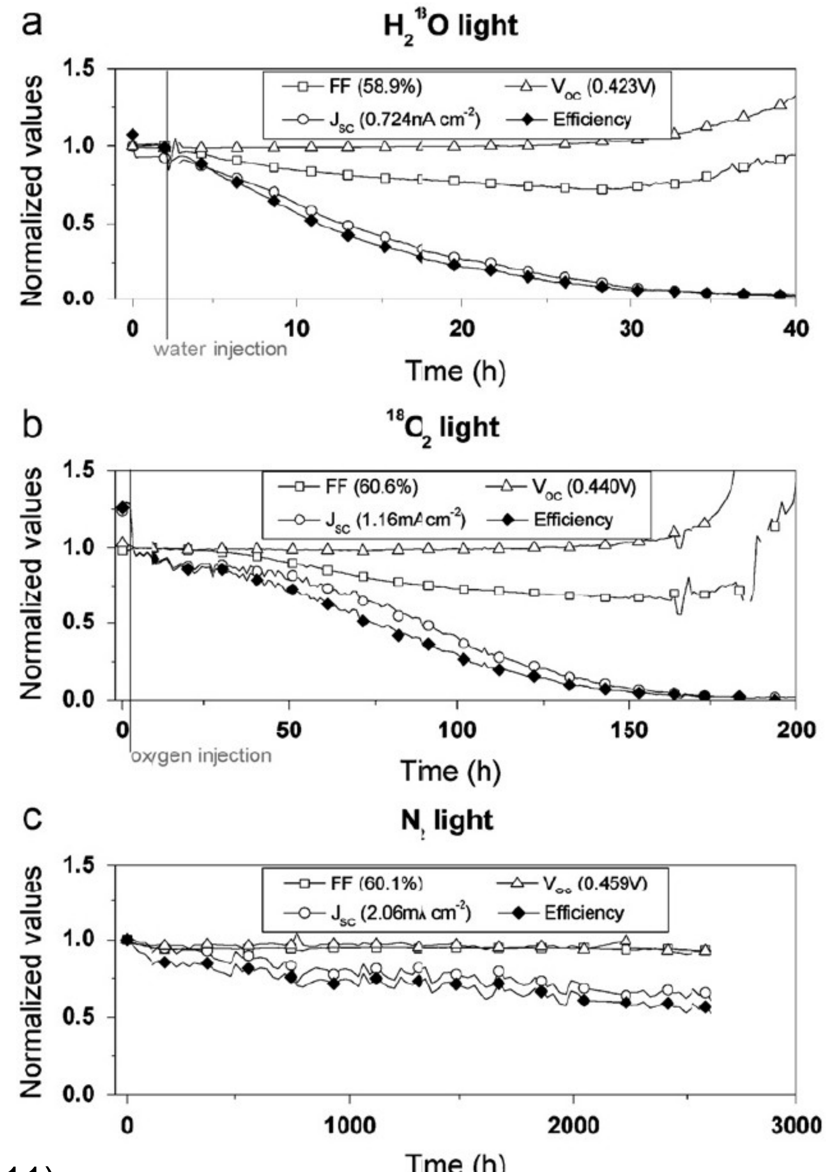
Results of degradation study

- Mainly current and FF degrade; V_{oc} is rather stable

- Water is much more relevant than oxygen

  - Water leads to oxidation of Al electrode

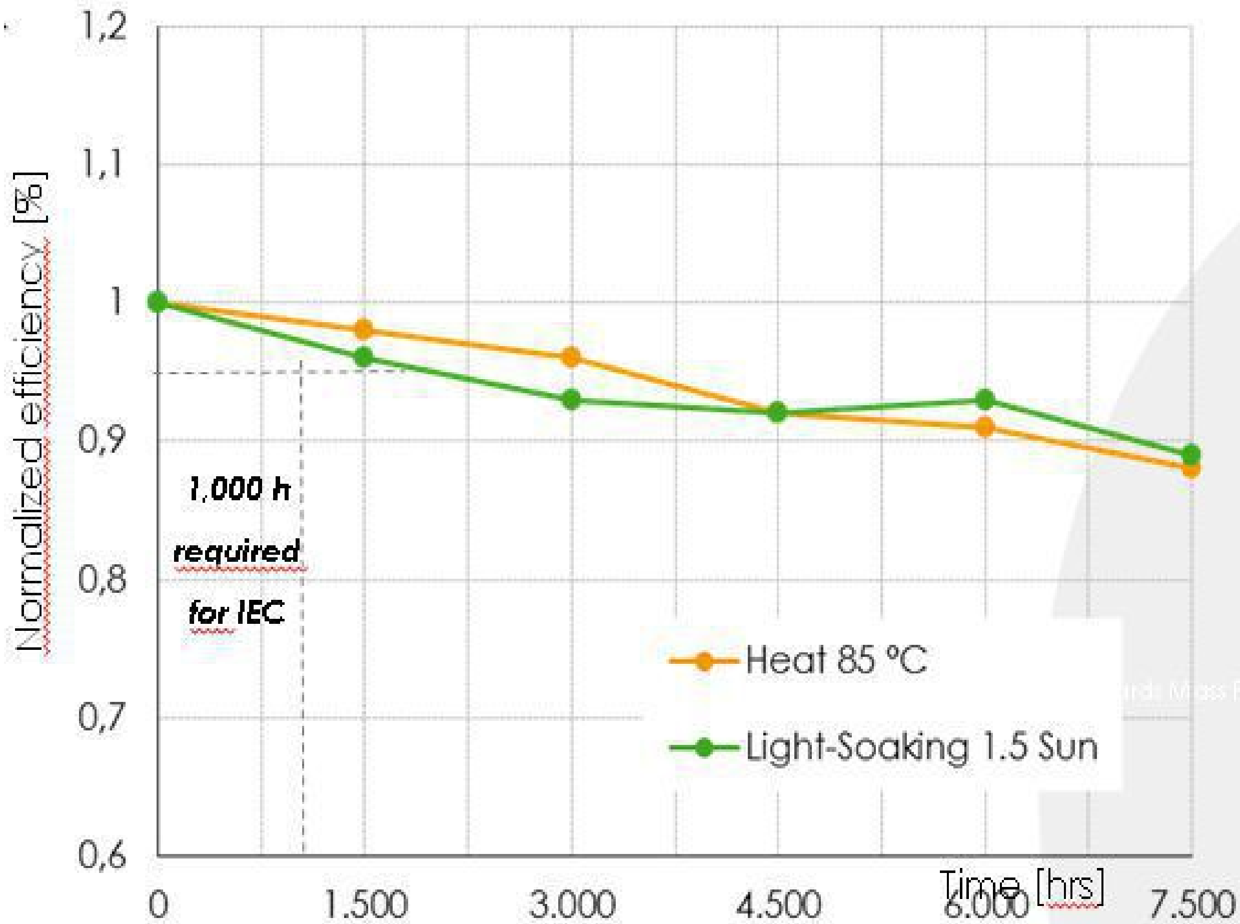
  - Water induced ZnPc degradation



M. Hermenau et al. Solar En. Mat. & Solar Cells **95**, 1268 (2011)

Lifetime of high-efficiency cells

Aging tests performed on 8.3% record cell, glass encapsulated



Still > 95 % efficiency after 1,800 hrs both in light soaking test and at 85 °C

Outline

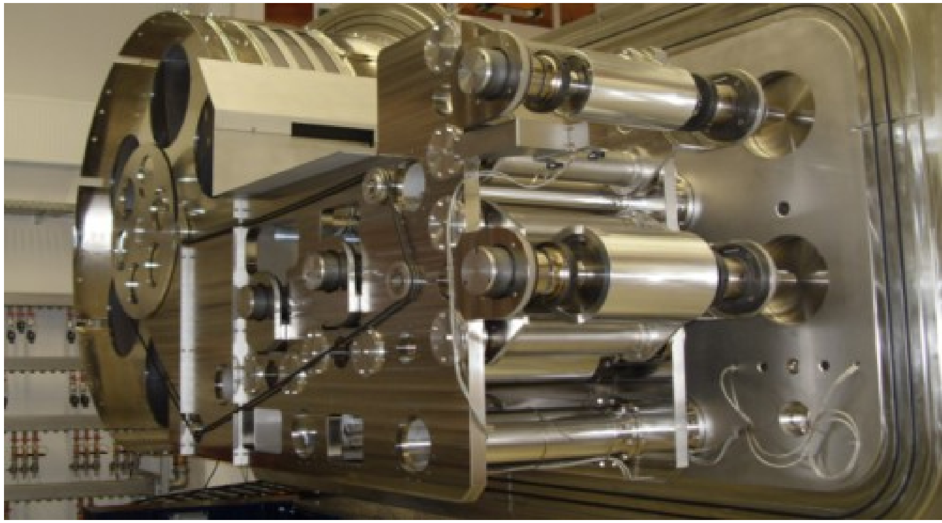
- Comparison of present PV technologies
- Basics of organics
  - Challenges:
    - Exciton Separation
    - Nanomorphology
    - Efficiency
- Long-term stability
- **Manufacturing & applications**

Roll to roll vacuum coater

deposition cylinder

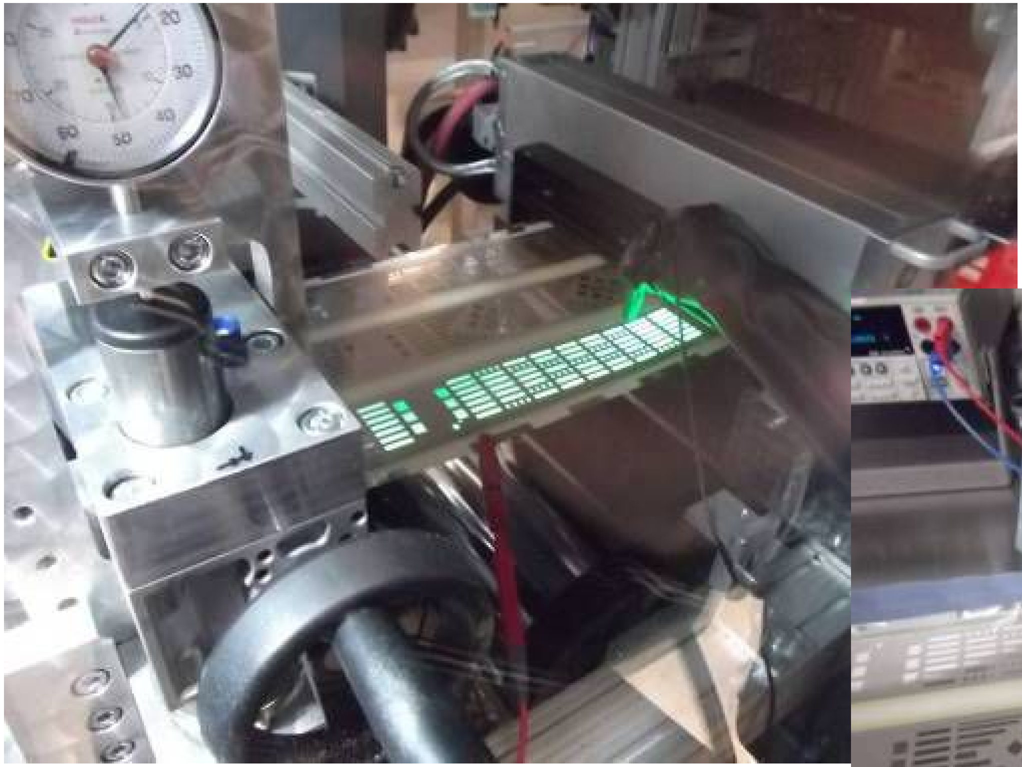
attachement possibility
for a glove box

winding units

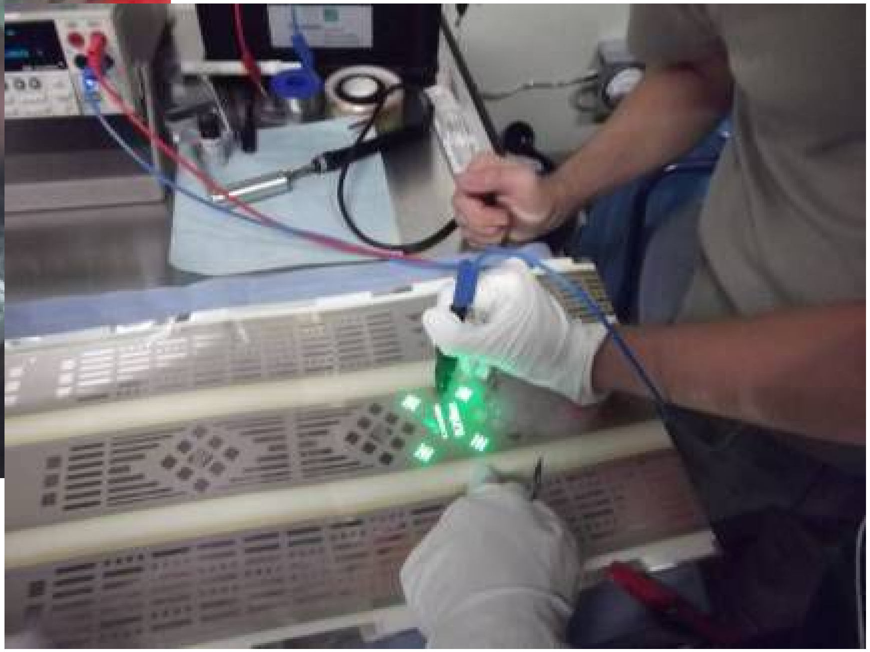


VON ARDENNE

OLED OPERATION TESTS UNDER INERT CONDITIONS AND AFTER LAMINATION



Electrical tests in the inert box



Electrical tests after the encapsulation

Heliatek Roll coater

First applications

- Building integrated PV (BIPV)
- Automotive
- Outdoor
- Sun shades
- Key advantages:
  - Thin, lightweight
  - Transparent
  - Attractive color

Source: Heliatek

Conclusions

- Organic Solar Cells have developed from lab curiosity to a serious technology
- First serious applications in automotive and building integration
- Module efficiencies beyond 15% seem possible
- Low-cost manufacturing is possible in mid-term future

Acknowledgment

- S. Reineke, S. Hofmann, S. Pfützner, H. Ziehlke, C. Körner, T. Menke, T. Müller, L. Burtone, D. Ray, C. Elschner, J. Meiss, M. Furno, C. Sachse, L. Müller-Meskamp, M.K. Riede, B. Lüssem, J. Widmer, M. Hummert, M. Gather (IAPP), T. Fritz
- K. Fehse C. May, C. Kirchhof, M. Toerker, M. Hoffmann, S. Mogck, C. Lehmann, T. Wanski (FhG-IPMS)
- J. Blochwitz-Nimoth, J. Birnstock, T. Canzler, S. Murano, M. Vehse, M. Hofmann, Q. Huang, G. He, G. Sorin (Novaled)
- M. Pfeiffer, B. Männig, G. Schwartz, K. Walzer (Heliatek)
- J. Amelung, M. Eritt (Ledon)
- D. Gronarz (OES)

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- K. Schmidt-Zojer (Graz), J.-L. Bredas (Atlanta)
- R. Coehoorn, P. Bobbert (Eindhoven)
- T. Fritz (Jena)
- M. Felicetti, O. Gelsen (Sensient)
- A. Hinsch, A. Gombert (ISE)
- D. Wöhrle (Bremen), J. Salbeck (Kassel), H. Hartmann (Merseburg/Dresden)
- C.J. Bloom, M. K. Elliott (CSU)
- P. Erk (BASF) and others from OPEG
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