Organic and Hybrid Concepts for Photovoltaic Energy Conversion

Vladimir Dyakonov

Julius-Maximilian-University of Würzburg, Germany

Bavarian Center of Applied Energy Research (ZAE Bayern)

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MOTIVATION #1:
CLIMAT PROTECTION OR SHORTAGE OF RESOURCES?

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"We would then have some right to indulge in the pleasant belief that our descendants, albeit after many generations, might live under a milder sky ...."

Svante August Arrhenius (1859-1927)
was professor in Würzburg in 1886

MOTIVATION #2:
COMPETITIVENESS OF ECONOMY?

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„But even if you doubt the evidence, providing incentives for energy efficiency and clean energy are the right thing to do for our future - because the nation that leads the clean energy economy will be the nation that leads the global economy.

B. Obama on Energy,
The Washington Post, January 27, 2010

POLITICAL DECISION – "ENERGIEWENDE"

Energiewende means a radical change in the energy politics:

- **a shift** from nuclear and fossil fuels **to renewables (RE)**
- a change from offer-based to **demand-based** energy politics

and

- a transition from centralized to **distributed** energy generation

Effective on 06.06.2011

TARGETS OF GERMANY

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Target of the year	2020	2030	2040	2050
Change in GHG emission (compared to 1990)	-40%	-55%	-70%	-80 – 95%
Change of primary energy consumption (compared to 2008)	-20%	Steigerung Energie-produktivität um 2,1%/a		-50%
Change of electricity consumption (compared to 2008)	-10%			-25%
Change in final energy consumption in transport sectror (cf 2005)	-10%			-40%
Share of RE in the final energy consumption	18%	30%	45%	60%
Share of RE in the electricity consumption	35%	50%	65%	80%

GERMANY: WHERE ARE WE NOW?

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CONTRIBUTION OF RENEWABLES TO FINAL ENERGY CONSUMPTION

Share of RE in the final energy consumption	[%]	12,6
Share of RE in the total electricity consumption		22,9
an der gesamten Wärmebereitstellung		10,4
am gesamten Kraftstoffverbrauch[1)]		5,5
am gesamten Primärenergieverbrauch[2)]		11,7

GERMANY: PV INSTALLED CAPACITY & YIELD

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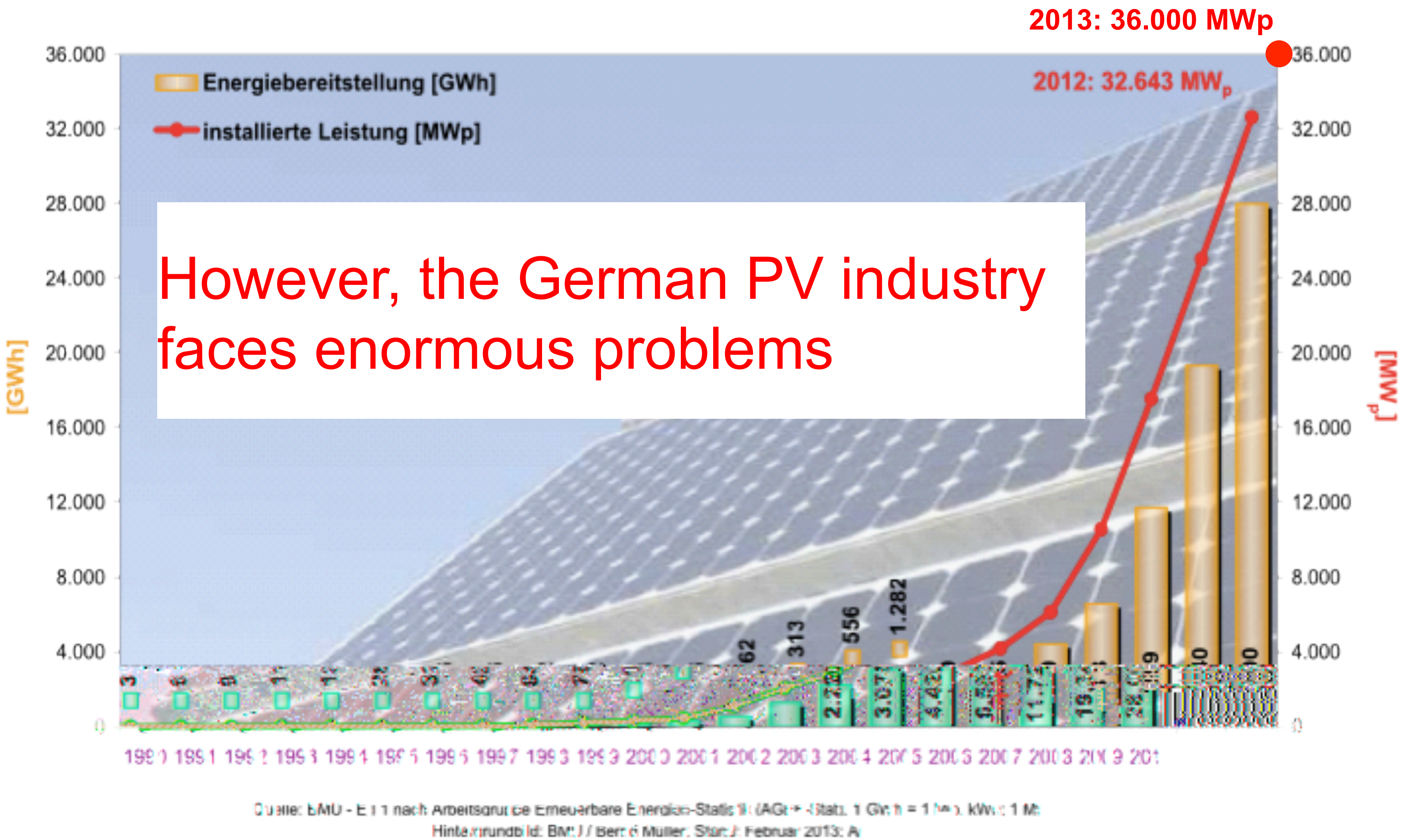

However, the German PV industry faces enormous problems

Newly installed PV-Capacity 2013 3.3 GWp (7.6 GWp in 2012)

SOUTH AFRICA: BIG INTEREST IN PV WAS EXPRESSED during the opening ceremony on July 7, 2014

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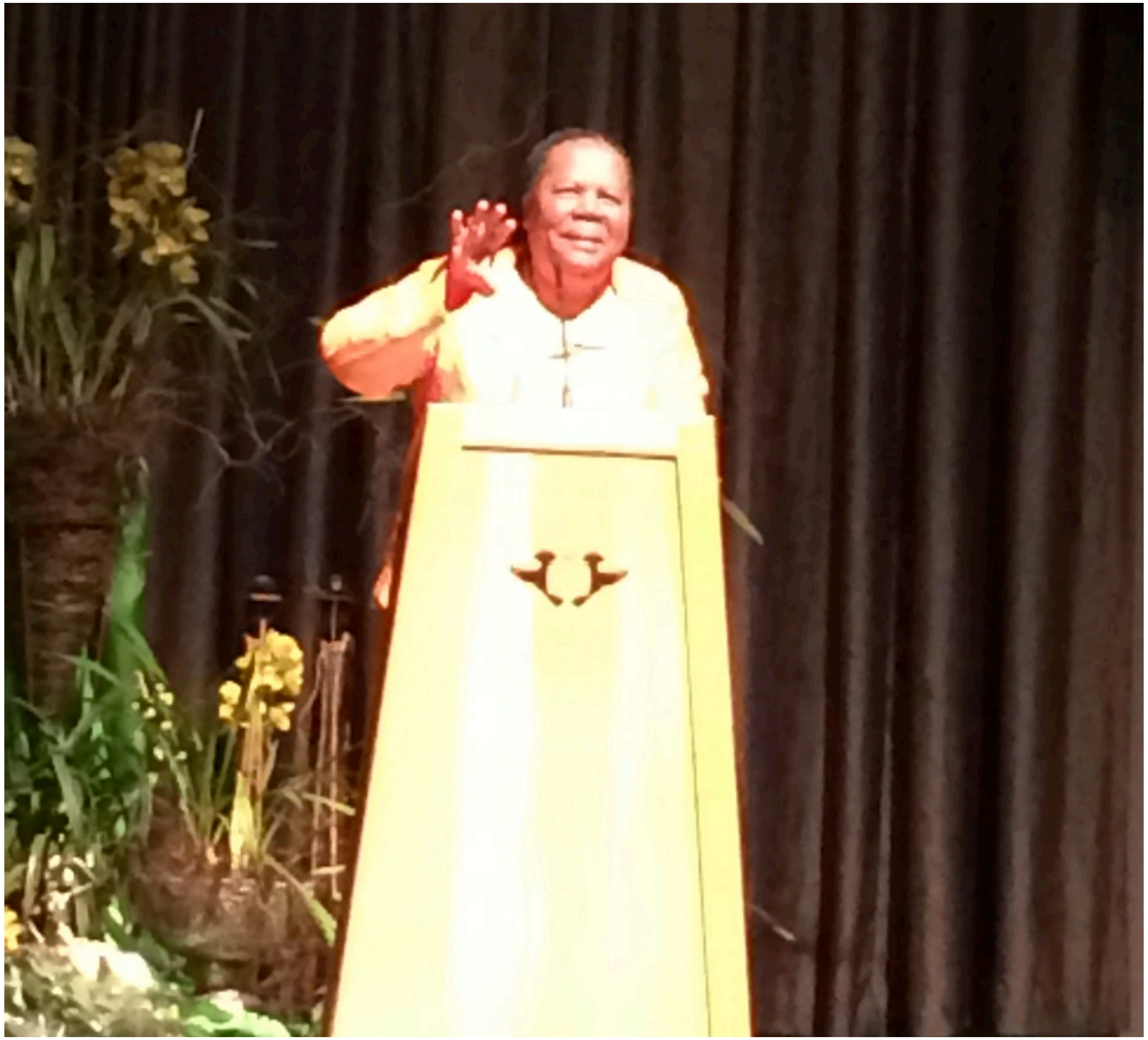
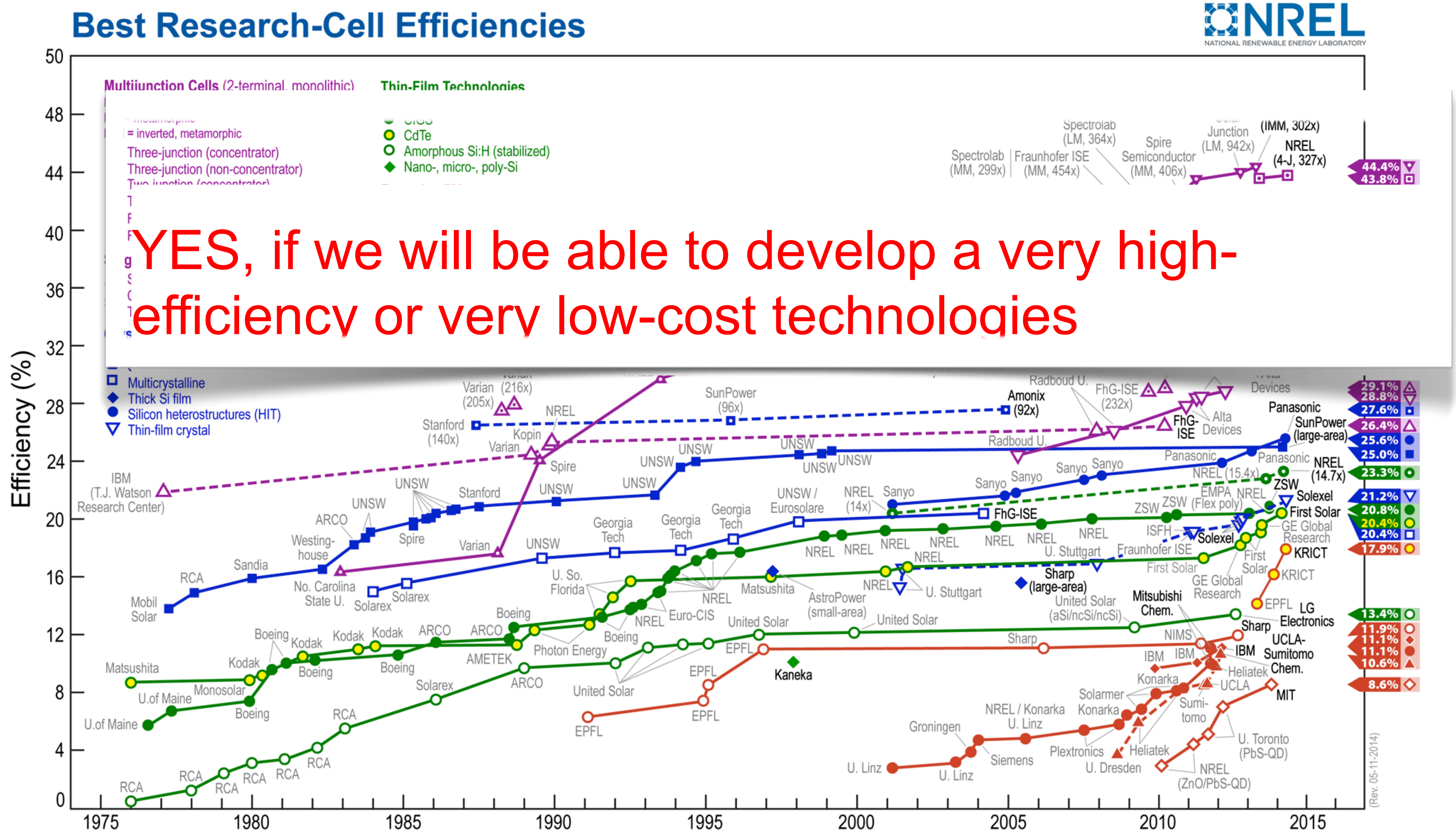


PLEASE, MAKE IT BETTER!

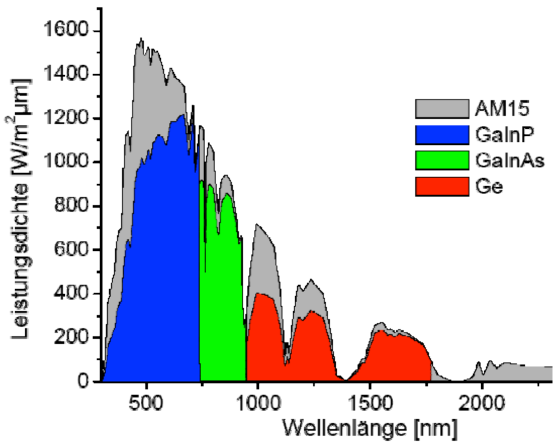
UNIVERSITÄT WÜRZBURG
PHYSIKALISCHES INSTITUT epVI

Do We Need Next Generation PV?

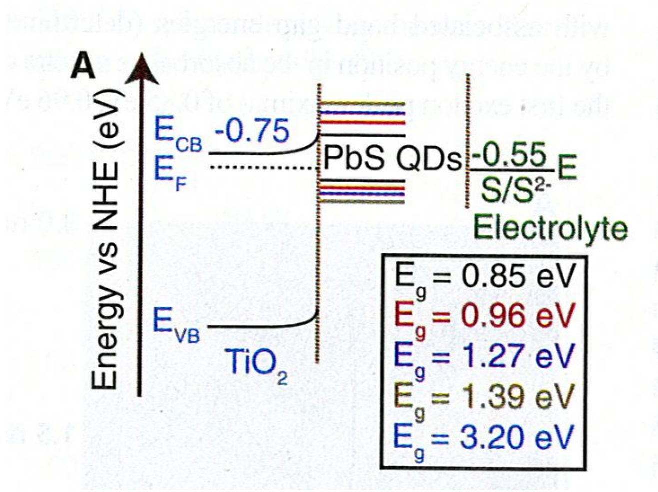


YES, if we will be able to develop a very high-efficiency or very low-cost technologies

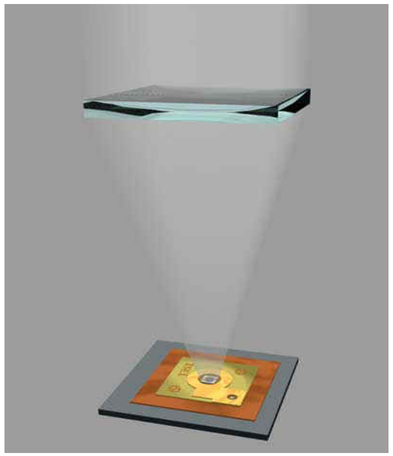
High-eff. option: Photon Management



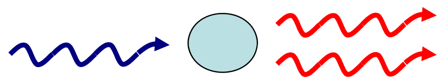
tandem solar cells



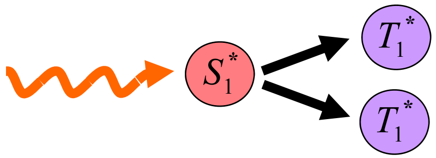
Multiple Exciton Generation



CPV



down converter

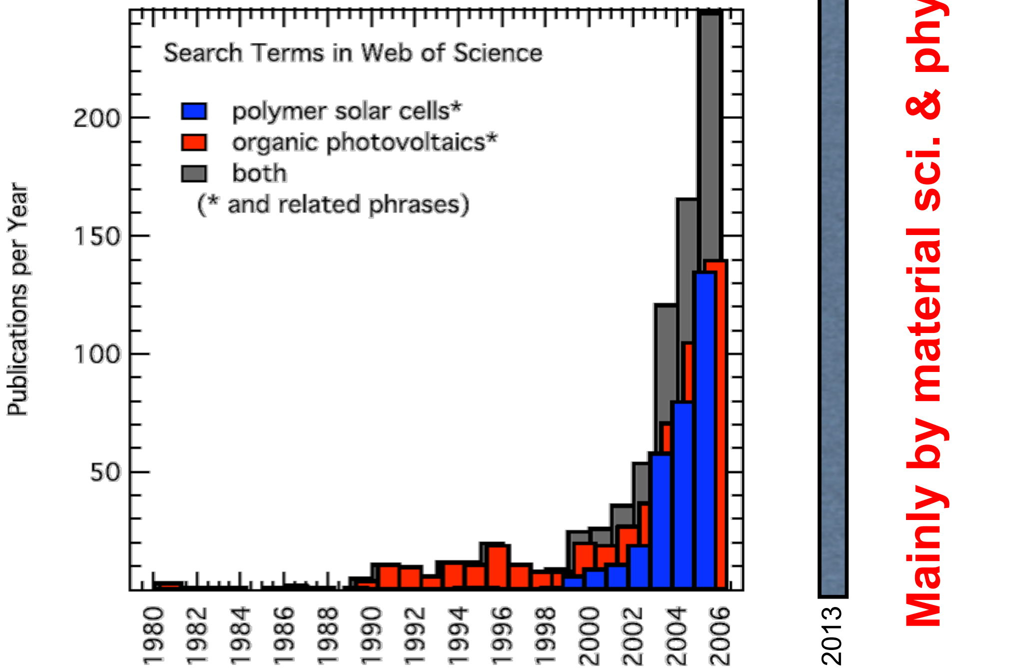


exciton fission

Organic PV as a low-cost Option

- 1986: 1st organic solar cell. C. Tang et al. (ca. 1%)

C. Tang, Kodak-Eastman, Rochester, USA



Mainly by material sci. & physicists

- 2002: 1st efficient single junction polymer cell, S. Shaheen et al. (2.5 %)
- 2007: 1st efficient polymer tandem cell, A. Heeger et al. (6.5 %)
- 2012: record single junction soluble small molecule cell, Mitsubishi Chem. (10.7 %)
- 2013: record tandem small molecule cell, heliatek GmbH (12 %)

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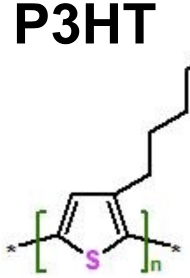
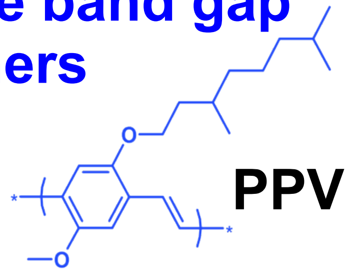
OPV Materials

Conjugated Polymers and Molecules: E_g: 1-3 eV

"Classic" wide band gap Polymers

P3HT



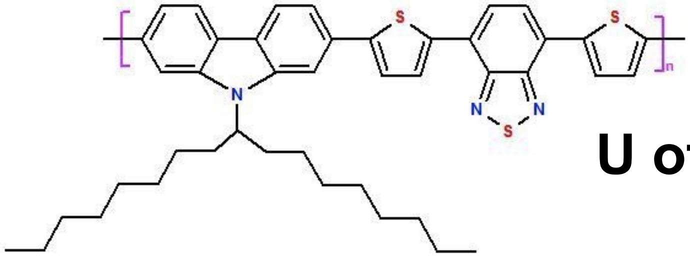


PPV

Burroughes, J. H. et al. *Nature* (**1990**)
Chen & Rieke *JACS* (**1992**)

Low band gap Copolymers

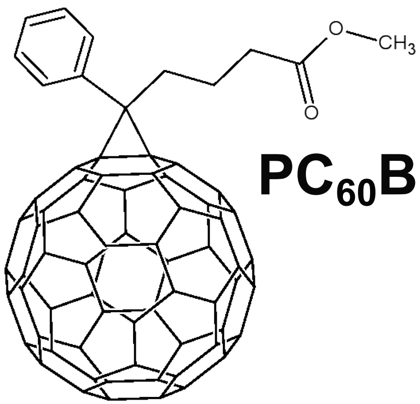
PCDTBT



U of Laval

Blouin, et al. *Advanced Materials* (**2007**)
Blouin et al. *JACS* (**2008**)

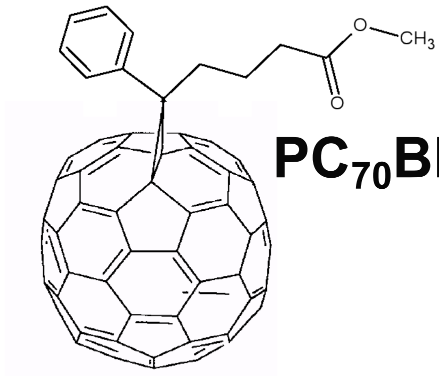
"Classic" Fullerene



$PC_{60}BM$

Hummelen et al. *J. Org. Chem.* (**1995**)

"Absorbing" Fullerene

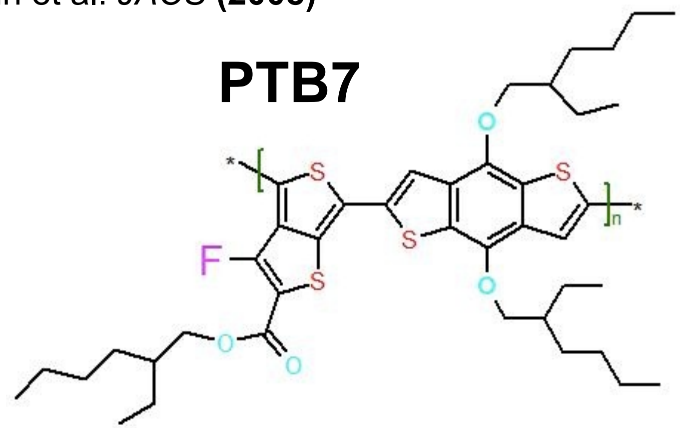


$PC_{70}BM$

Wienk et al. *Angew. Chem. Int. Ed.* (**2003**)

"Exotic" Fullerene $Lu_3N@C_{80}$

PTB7

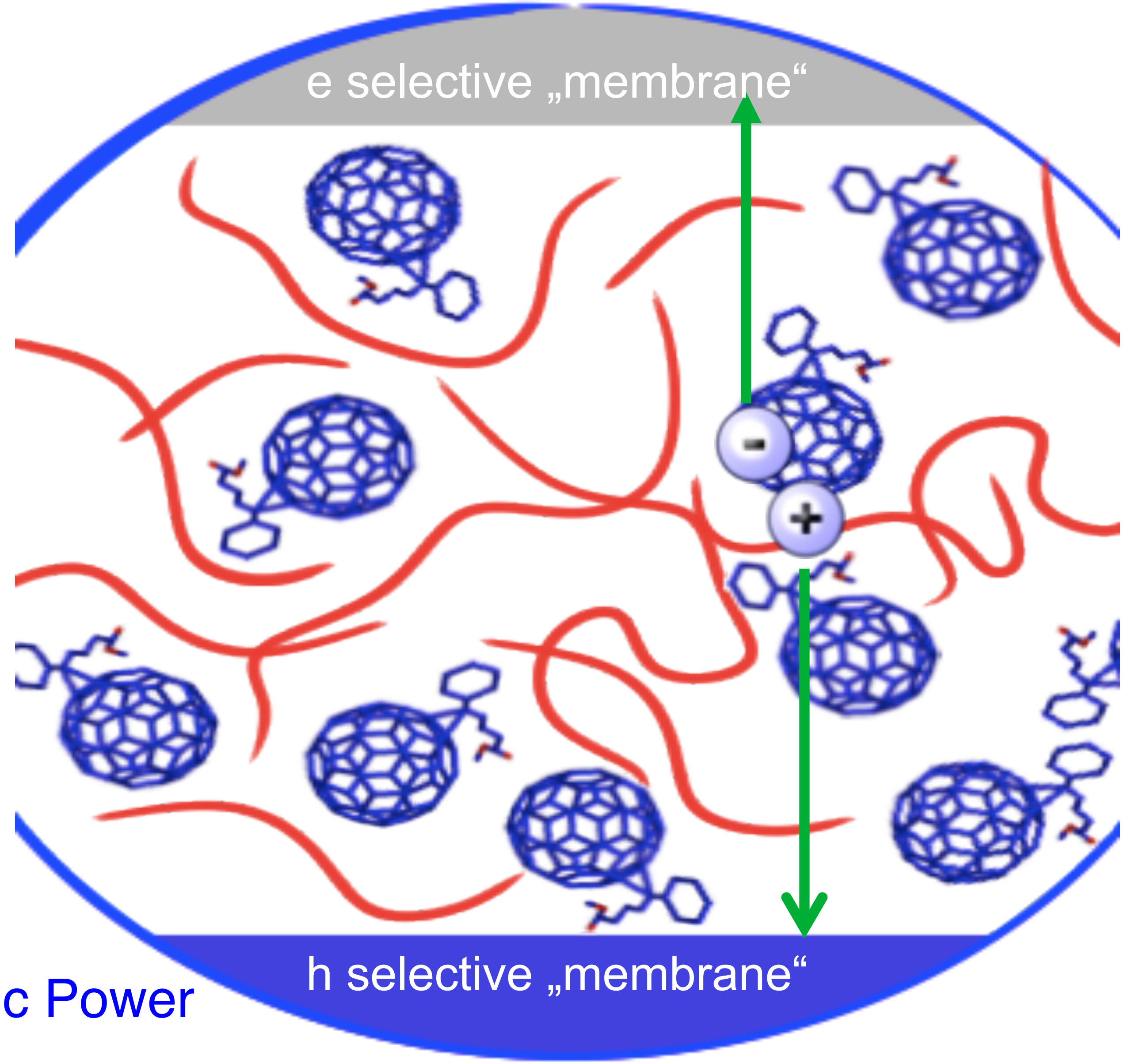


U of Chicago

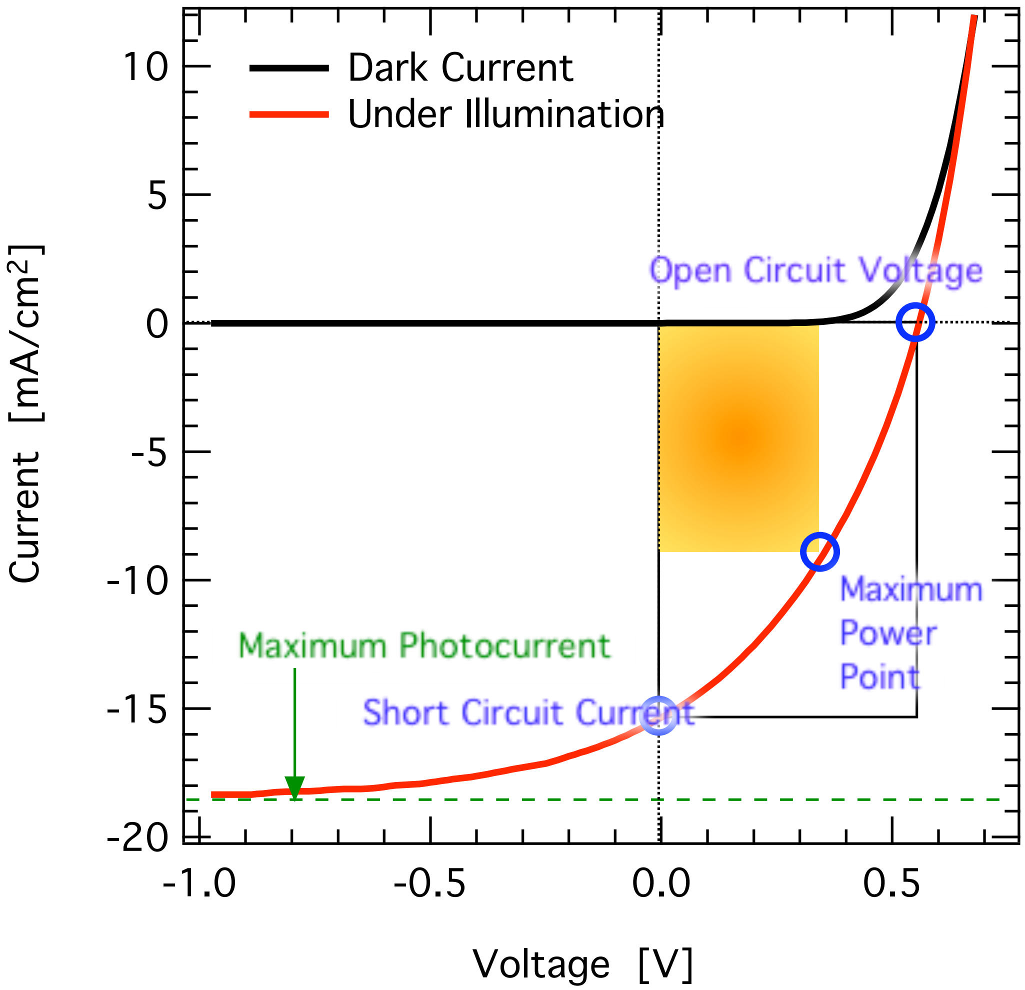
Liang et al. *JACS* (**2009**)
Liang, et al. *Advanced Materials* (**2010**)

Relevant processes in organic solar cells

- Light absorption
- Singlet exciton
- Charge transfer
- Photocurrent x Photovoltage => electric Power



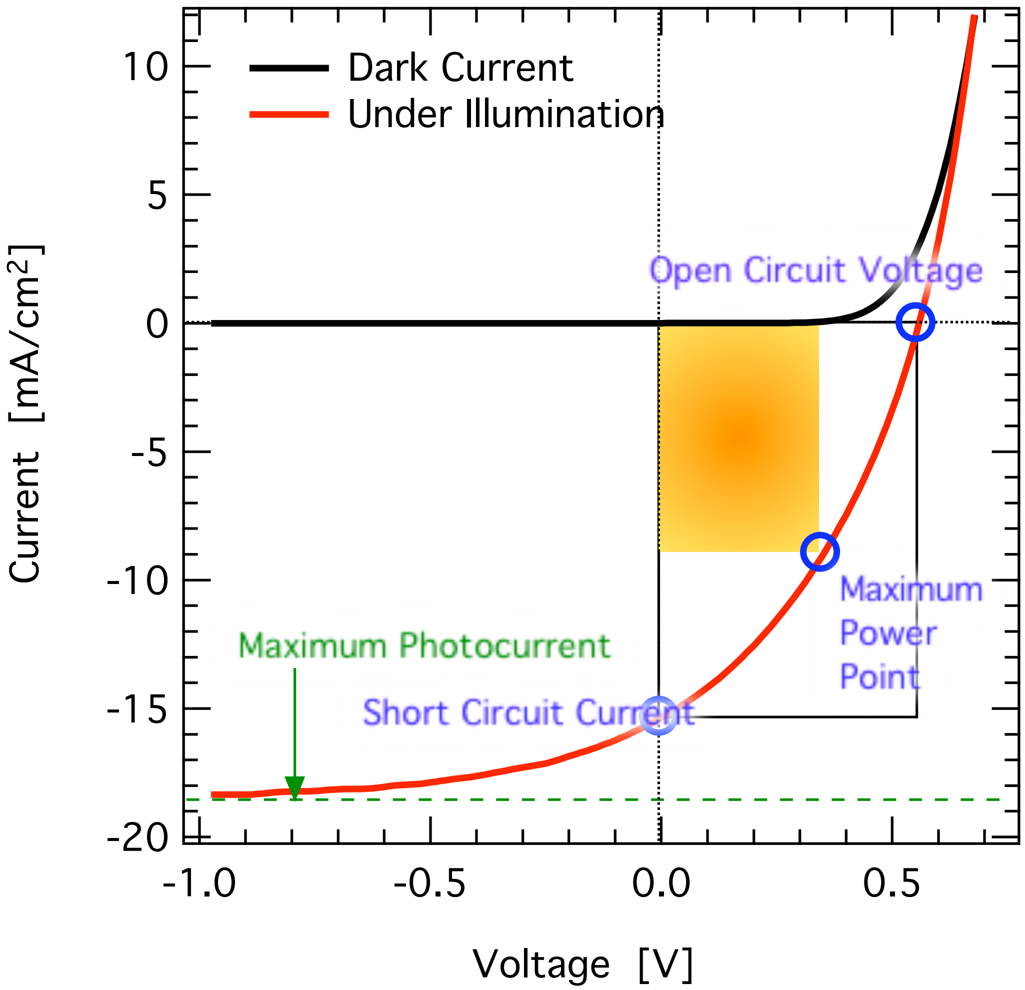
Key parameters of ANY solar cell



$$\eta = \frac{V_{OC} I_{SC} FF}{P_{Light}}$$

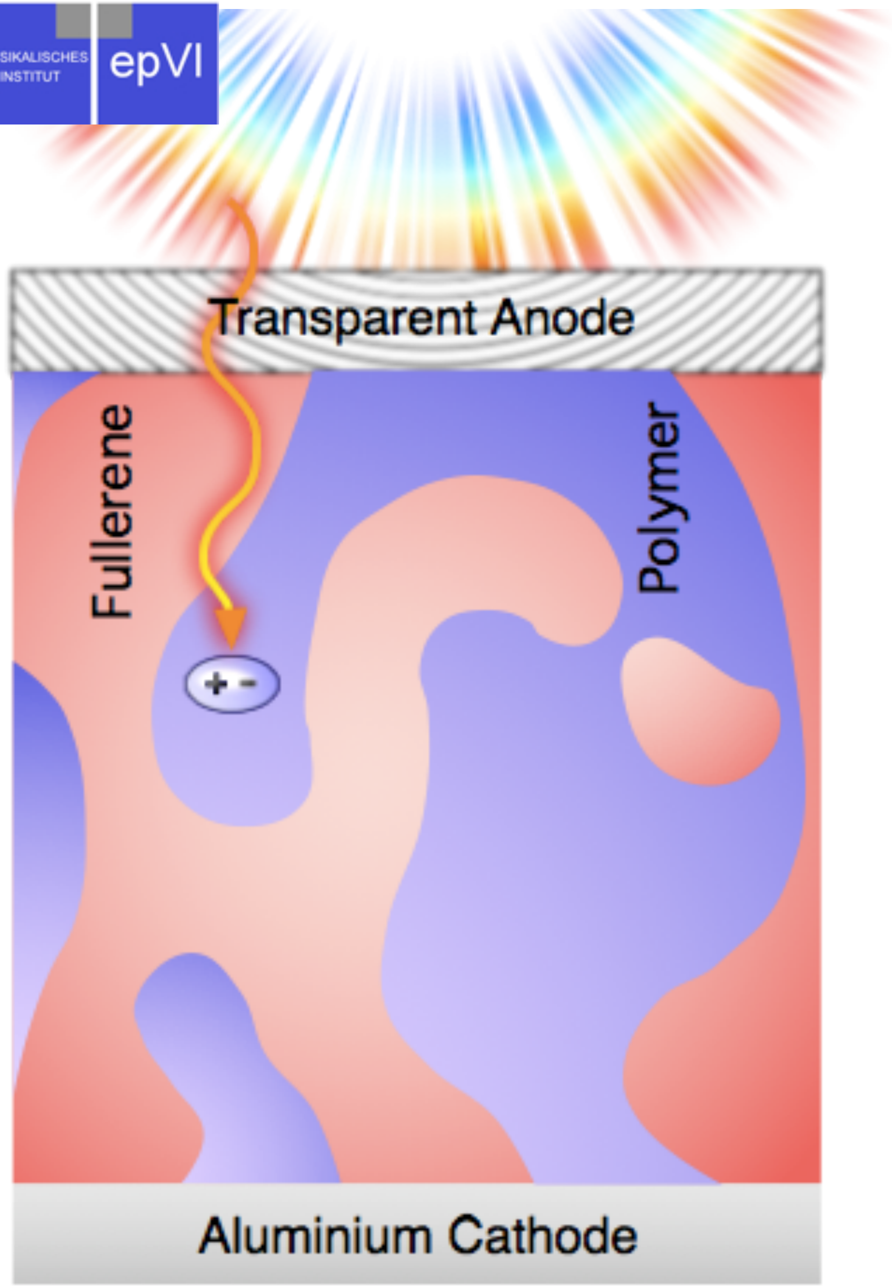
$$J_{Light}(V) = J_{Dark}(V) - constant$$

Key parameters of ANY solar cell



$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_0}\right)$$

Processes in organic solar cells stepwise

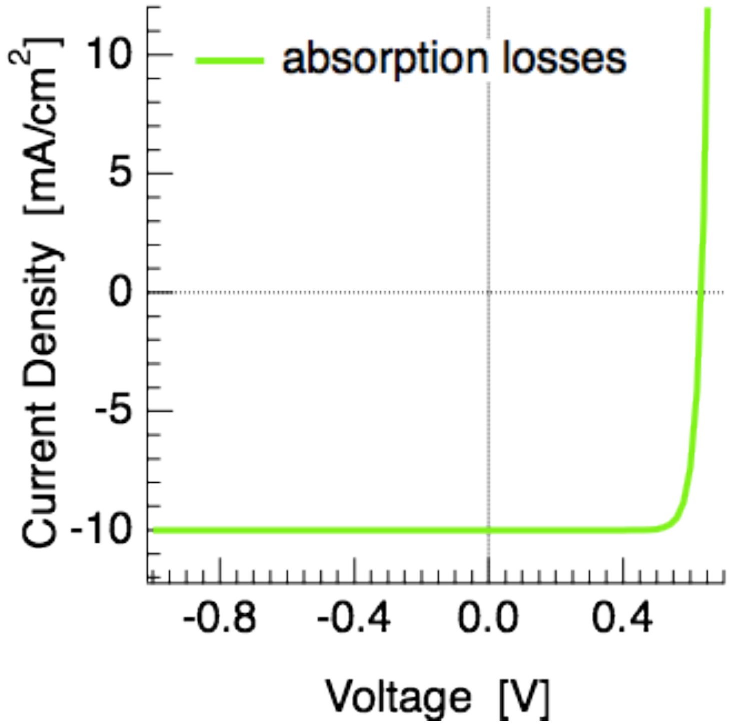


Rep. Prog. Phys. 73, 096401 (2010)

Step 1: Light Absorption

➟ Exciton Generation in Polymer

- very high absorption coefficient, device thickness on ~100nm scale

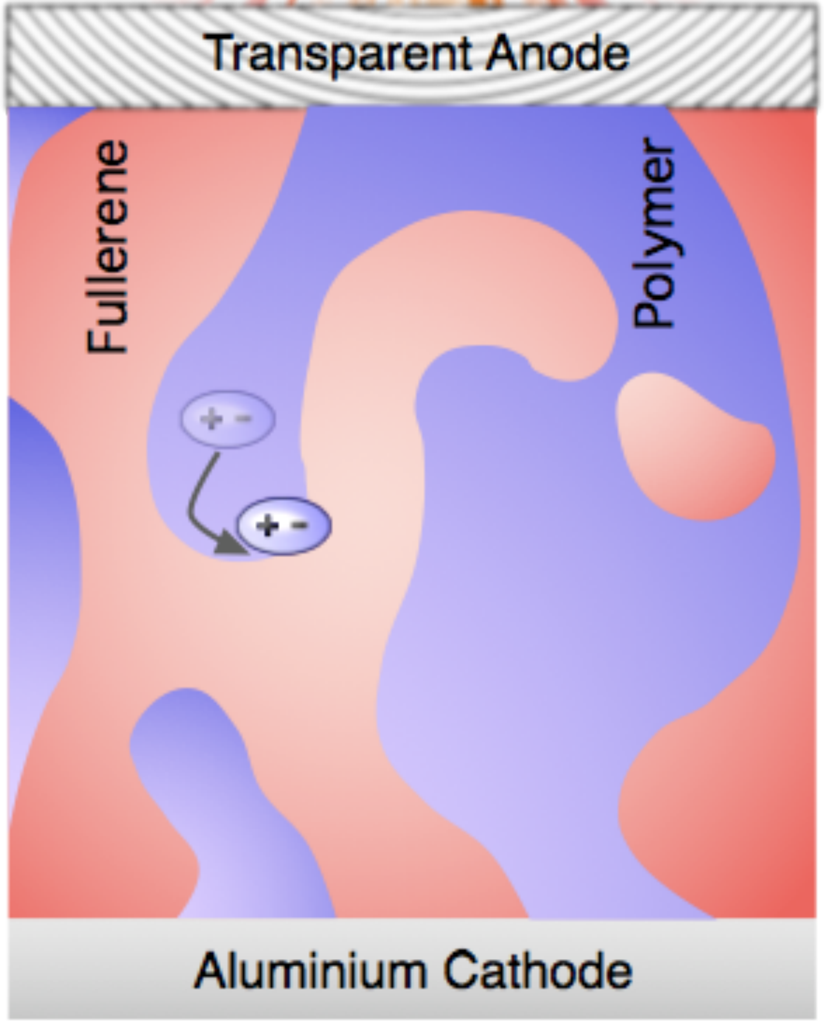


Processes in organic solar cells stepwise

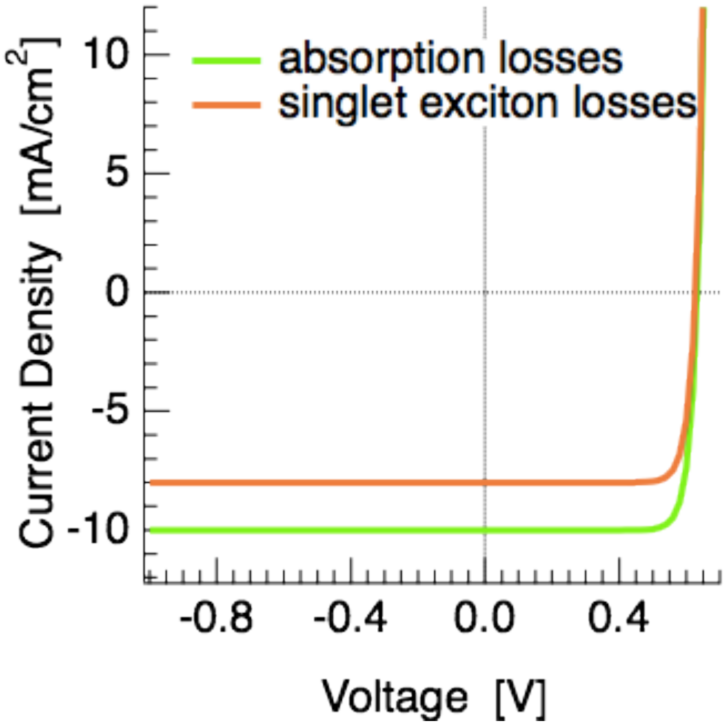
Step 2: Exciton Diffusion

➟ to Acceptor Interface

- short exciton diffusion length of only a few nanometres, otherwise singlet exitons are lost

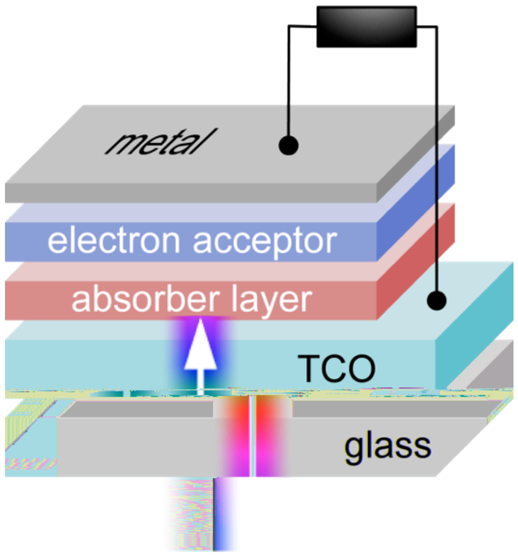


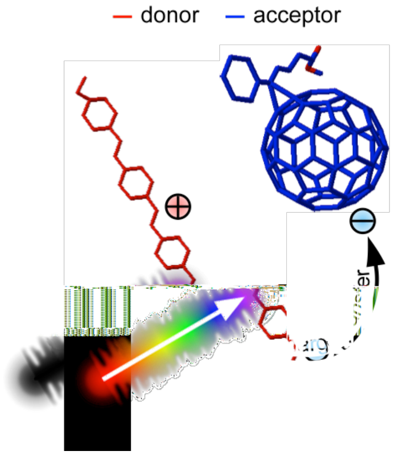
Rep. Prog. Phys. 73, 096401 (2010)

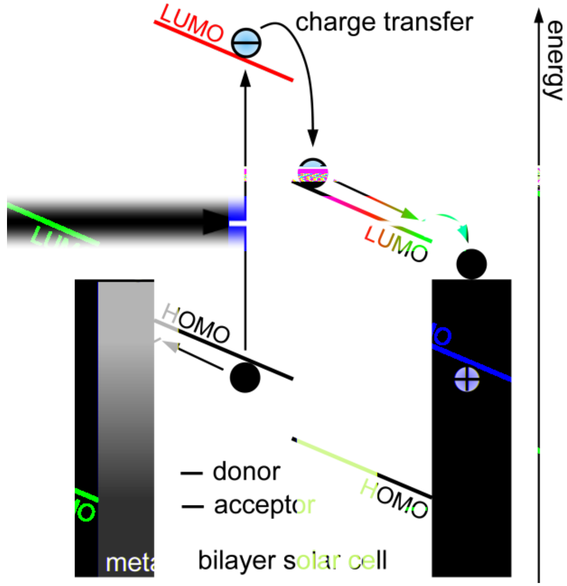


Planar of Bulk Heterojunctions

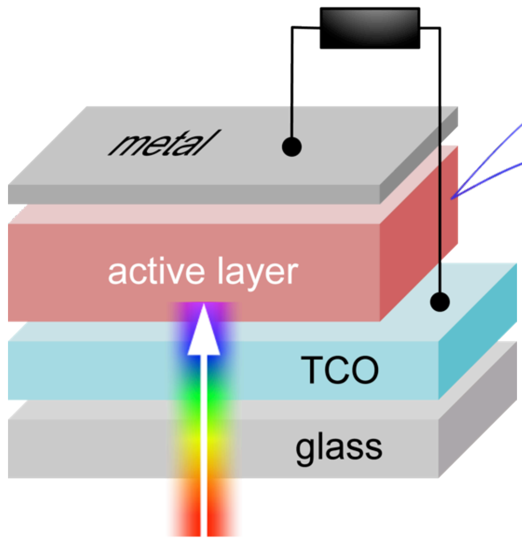
Planar hetero junction **(PHJ)**

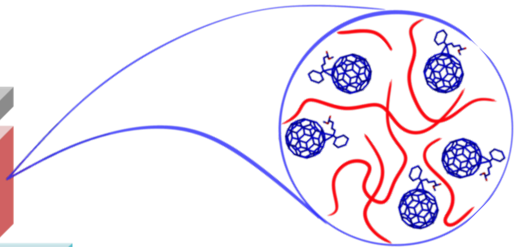


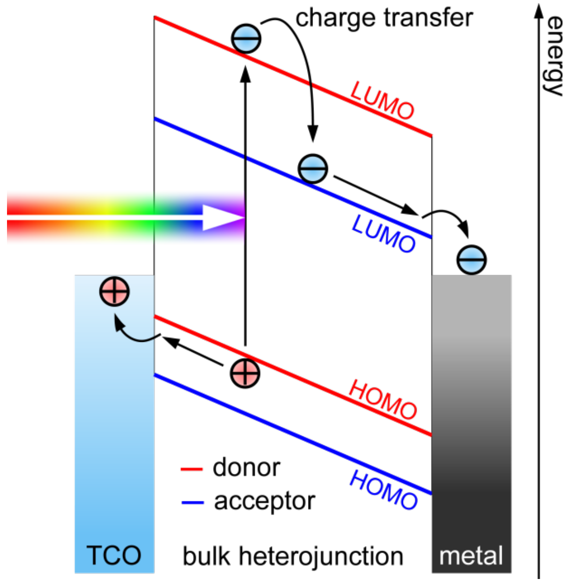




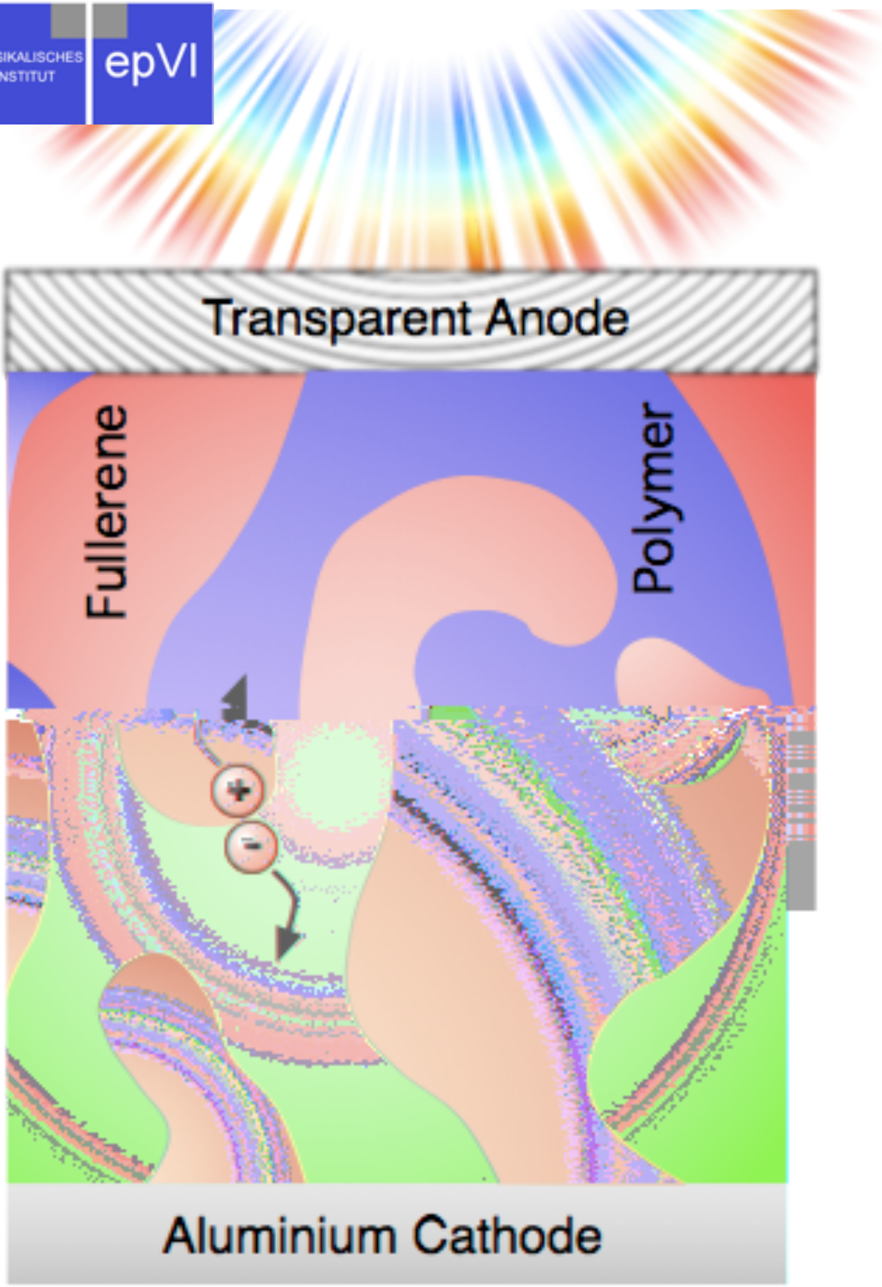
Bulk hetero junction **(BHJ)**







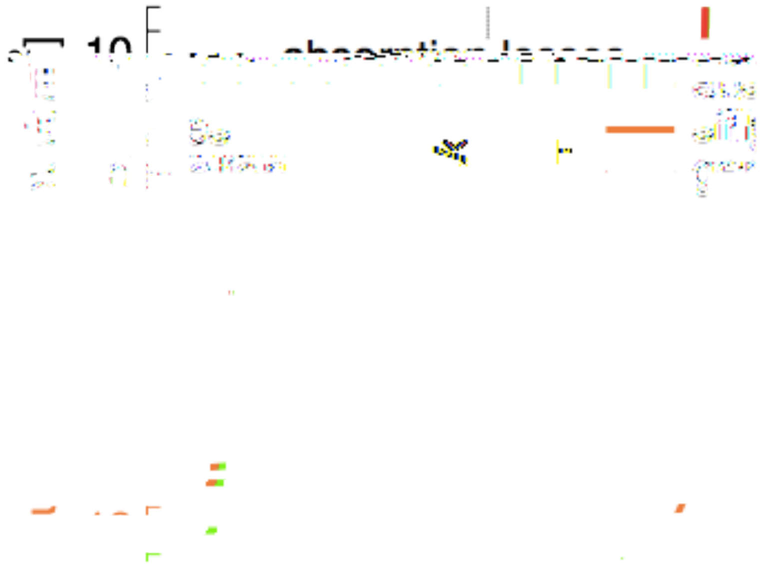
Processes in organic solar cells stepwise



Step 4: Polaron Pair Dissociation

➟ Free Electron–Hole Pairs!

- these electron–hole pairs are still bound due to low screening length



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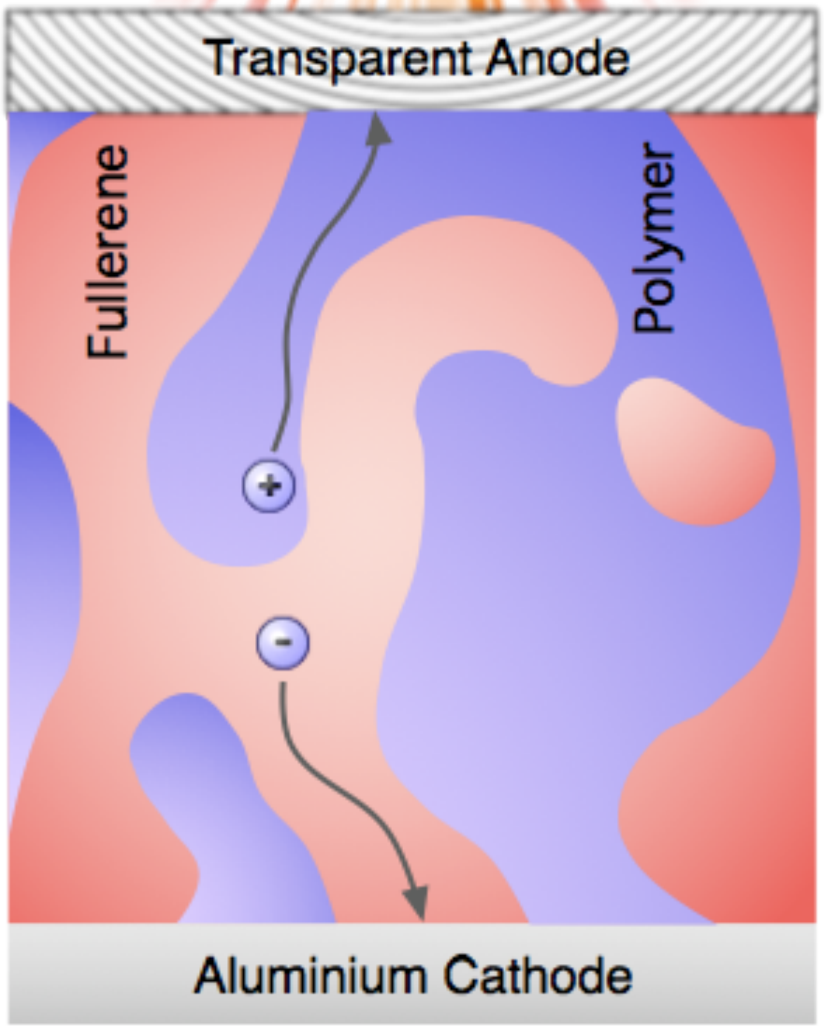
Processes in organic solar cells stepwise

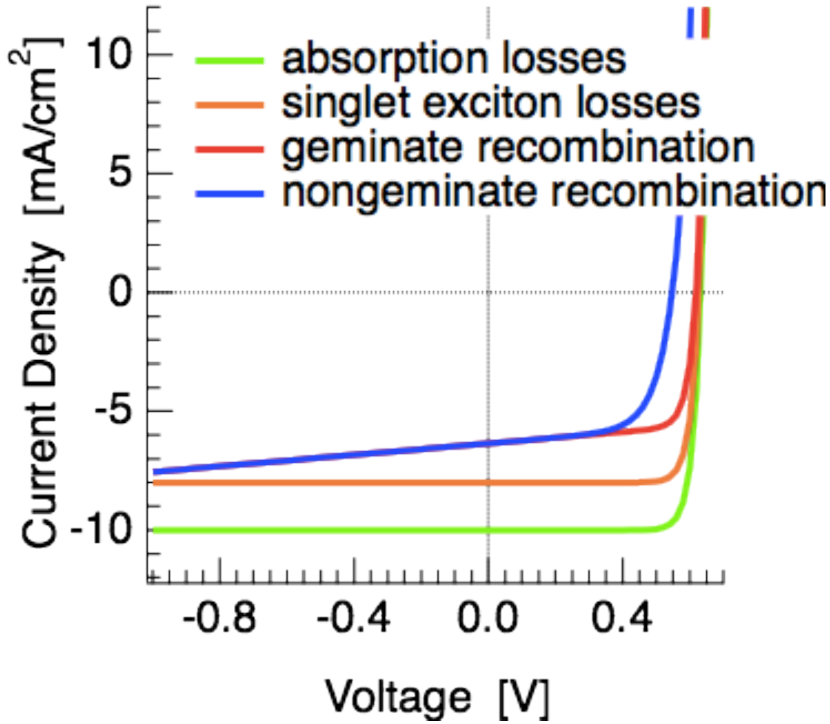


Rep. Prog. Phys. 73, 096401 (2010)

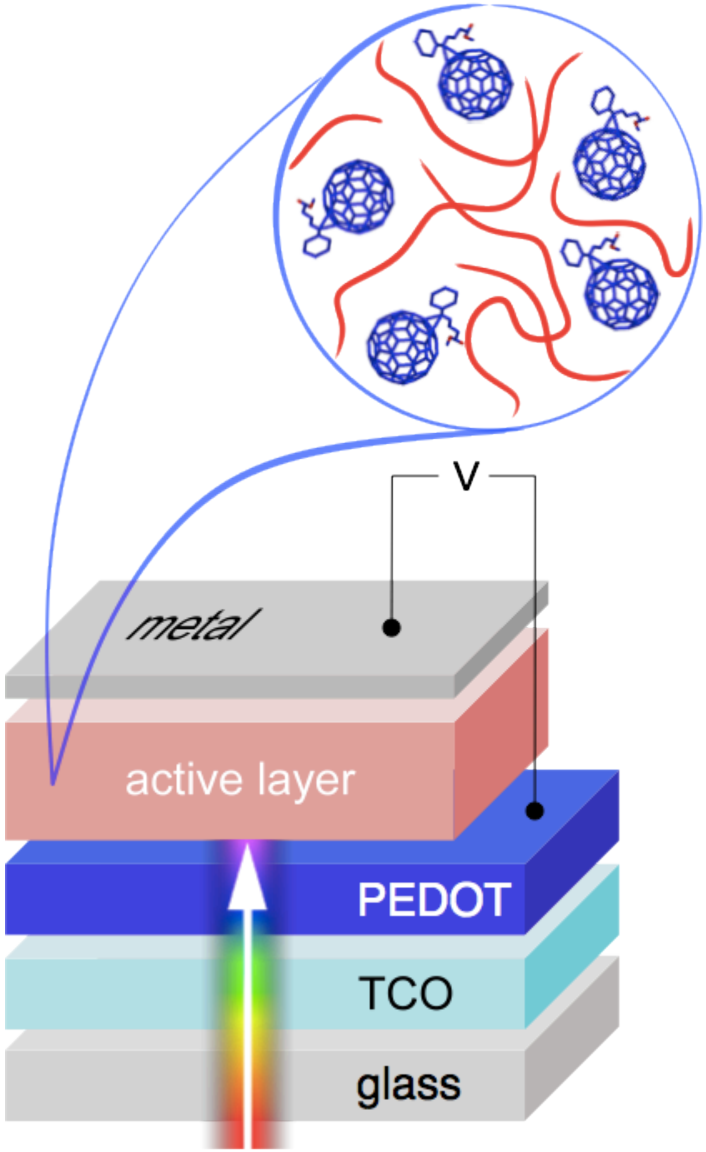
Step 5: Charge Transport

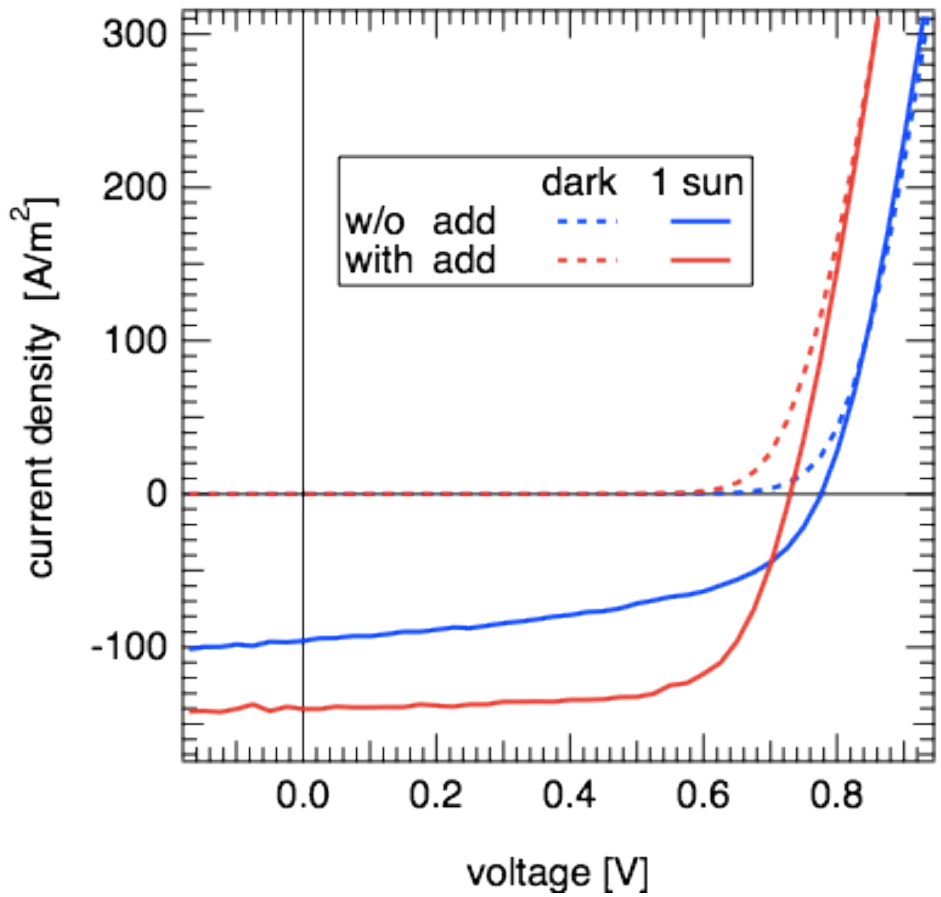
➟ Photocurrent!

- very slow charge transport, low carrier mobility, inefficient extraction
- recombination



Current–Voltage characteristics of PTB7:$PC_{70}BM$

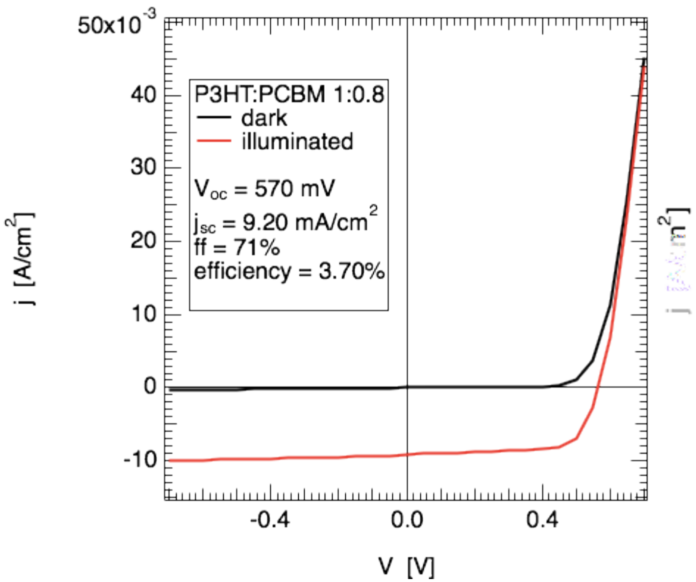


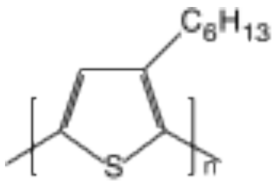


	PCE [%]	FF [%]
w/o add	3.8	51
with add	7.1	69

Typical OPV efficiencies of various Polymers

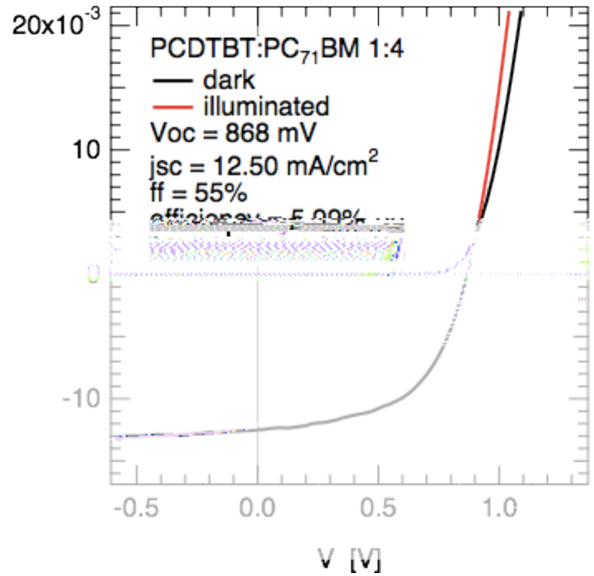
Eff.=4%

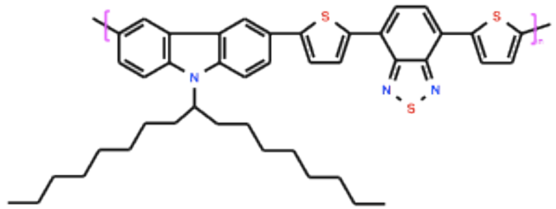




regio-regular poly(3-hexylthiophene)

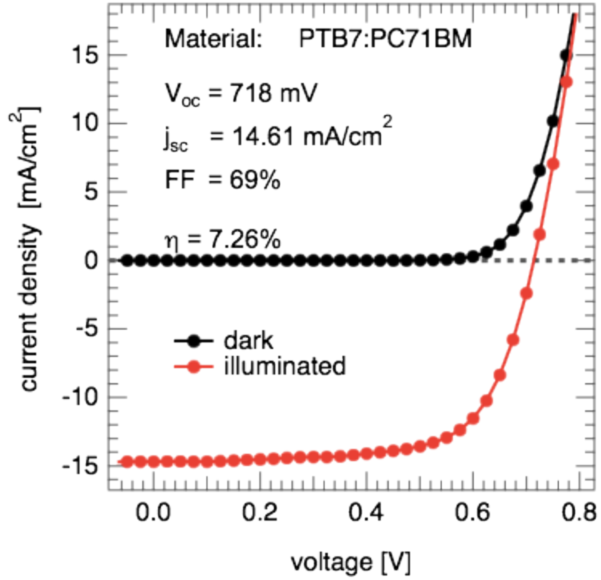
Eff.=6%

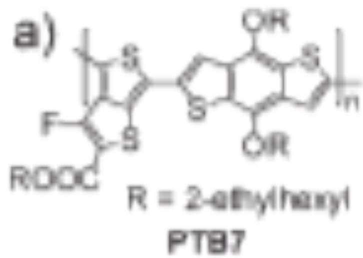




Poly[[9-(1-octylnonyl)-9H-carbazole- 2,7-diyl]-2,5-thiophenediyl- 2,1,3-benzothiadiazole-4,7 diyl-2,5 thiophenediyl]

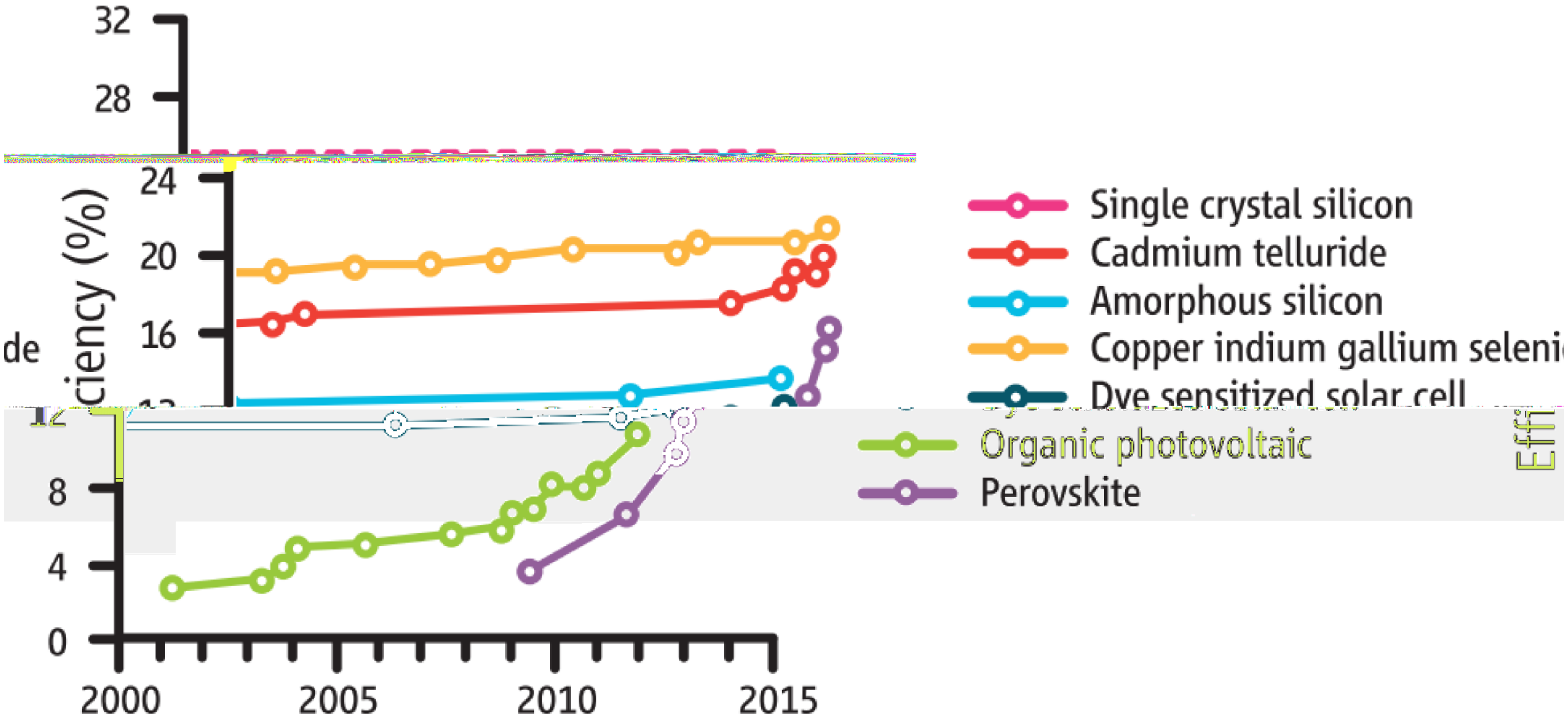
Eff.>7%





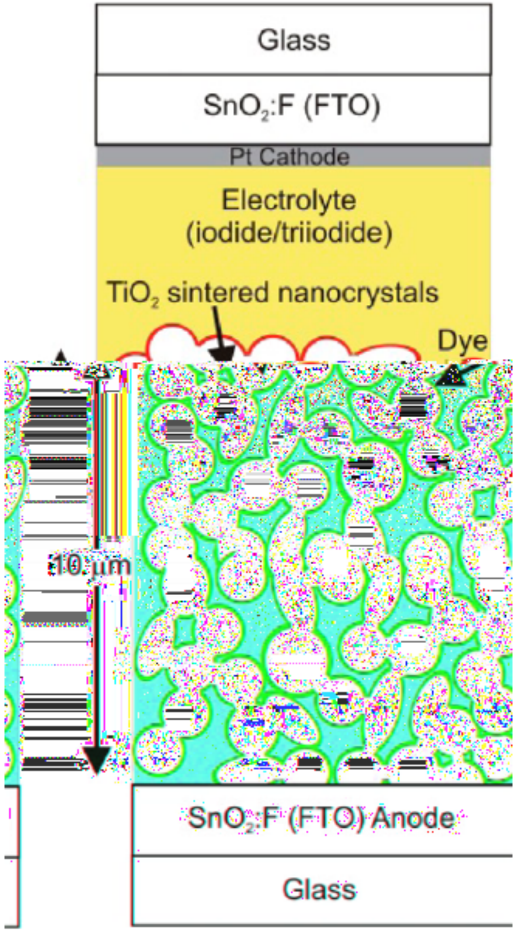
thieno [3,4-b] thiophenebenzo dithiophene

But there are even better news …



Robert F. Service, "Turning Up the Light", *Science*, 15 November 2013, Vol. 342 no. 6160 pp. 794-797

Hybrid PV- a brief history



1991

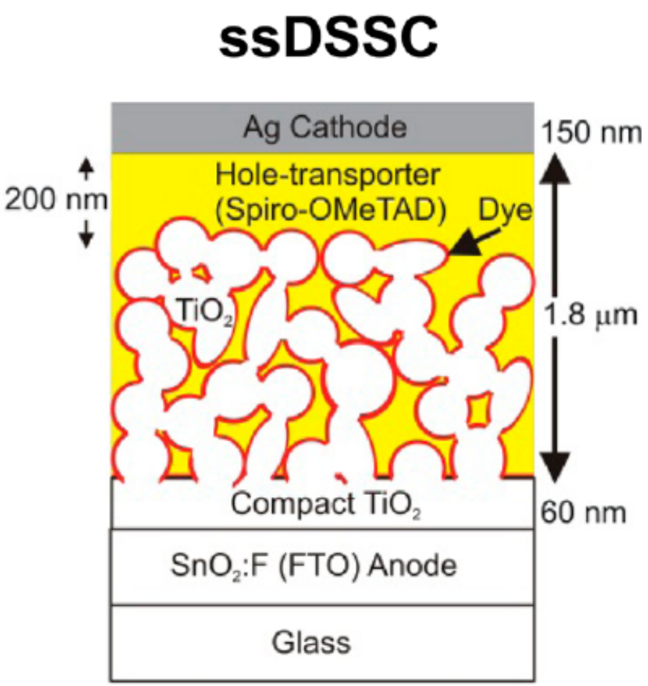
<u>Dye Sensitized Solar Cell</u> [1] consists of:

- Dye (light absorber),
- mesoporous TiO_2 (Electron transport, sufficient internal surface area)
- Electrolyte (hole transport)

[1]O'Regan; Grätzel, et al., "A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO2 Films.", *Nature,* 1991, 353, 737–740.

Hybrid PV- a brief history

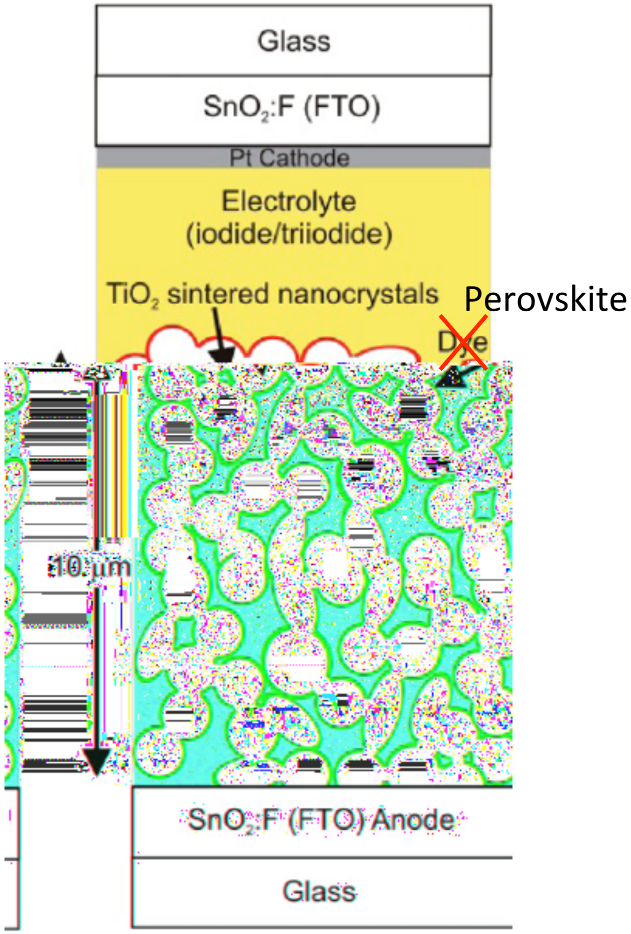
1998



solid state Dye Sensitized Solar Cell [2] :
Replace electrolyte with solid state hole transporting material (Spiro-OMeTAD)

[2]Bach et al., „Solid-State Dye-Sensitized Mesoporous TiO2 Solar Cells with High Photon-to-Electron Conversion Efficiencies." *Nature*, 1998, 395, 583.

Hybrid PV- a brief history



2009

First approach with perovskites 2009 [3]:
Replace Dye with perovskite as absorbing material

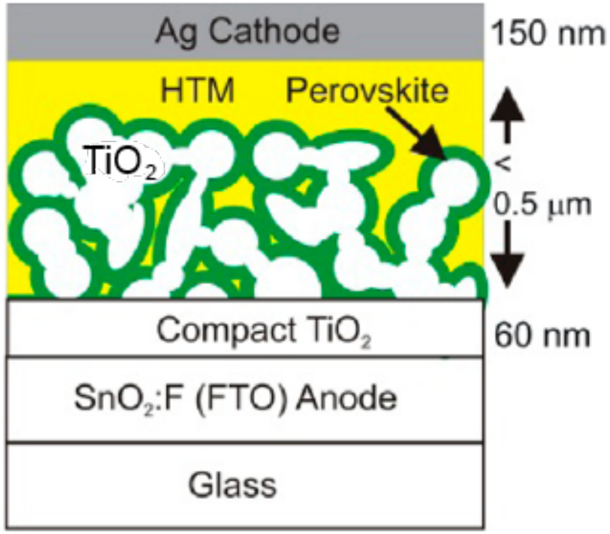
- 3.81 % Efficiency
- but unstable

[3] Miyasaka et al., „Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells“, *JACS*, 2009, 131, 6050-6051

Hybrid PV- a brief history

2012

Perovskite Sensitized Solar Cell



Perovskite Meso-Superstructered Solar Sell [4][5]

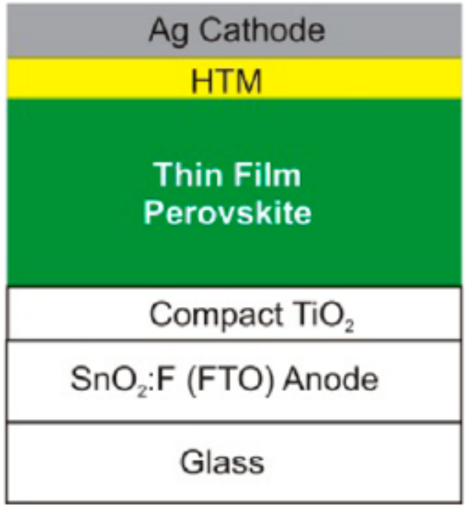
Replace

- electrolyte with solid state hole transporting material
- Dye with perovskite as absorbing material leads to Efficiency between 8 [5] and 9.7 % [4]
- stronger absorbing over a wider range -> thinner films

[4] Kim, Grätzel et al., "Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%." *Sci. Rep.*, 21 August 2012, 2, 591.
[5]Lee, Snaith et al., "Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites.", *Science*, 2 November 2012, 338, 643–647.

Hybrid PV- a brief history

“*p-i-n*” thin-film perovskite

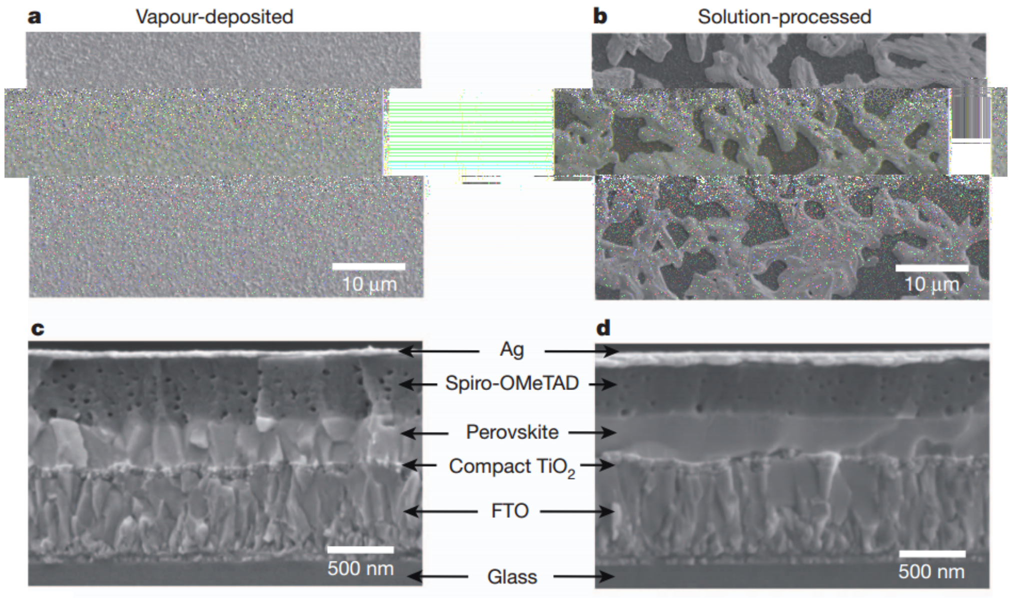


<u>„p-i-n“ thin-film perovskite</u>

p: Spiro-OMeTAD (hole selective contact)

i: perovskite $CH_3NH_3PbI_{3-x}Cl_x$ (absorber)

n: TiO_2 (electron selective contact)



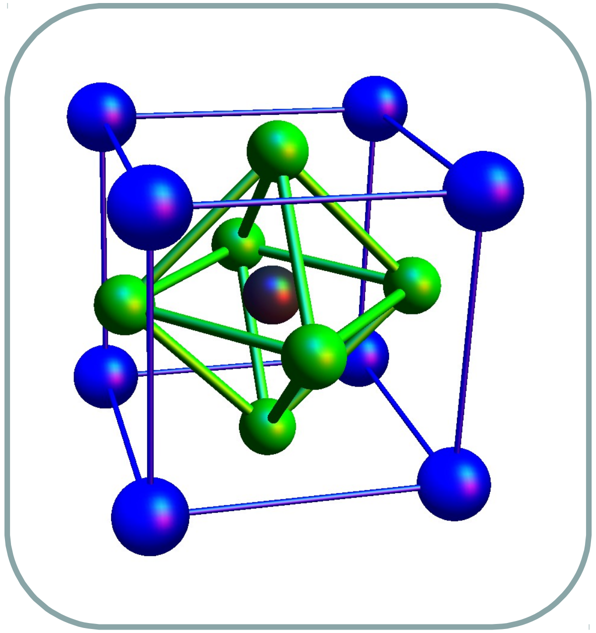
Efficiency: 15.4% [7] 5% [6], 8.6% [7]

[6]Ball, Snaith et al., “Low-temperature processed meso-superstructured to thin-film perovskite solar cells“, *Energy Environ. Sci.*, 28 March 2013,6, 1739-1743

[7]Liu, Snaith et al., “Efficient planar heterojunction perovskite solar cells by vapour deposition.“, *Nature*, 19 September 2013, 501, 395–398

Perovskites- What is this?

All materials of the form ABC_3



%&'	(&&)*+',-+&'. '/012)	%&'.),*+/3.4 5607
[A] $CH_3NH_3^+$	8#	89:;;
[B] Pb^{2+}	<	9:;
[C] Cl^- / I^-	#	8<9;.."...##:;

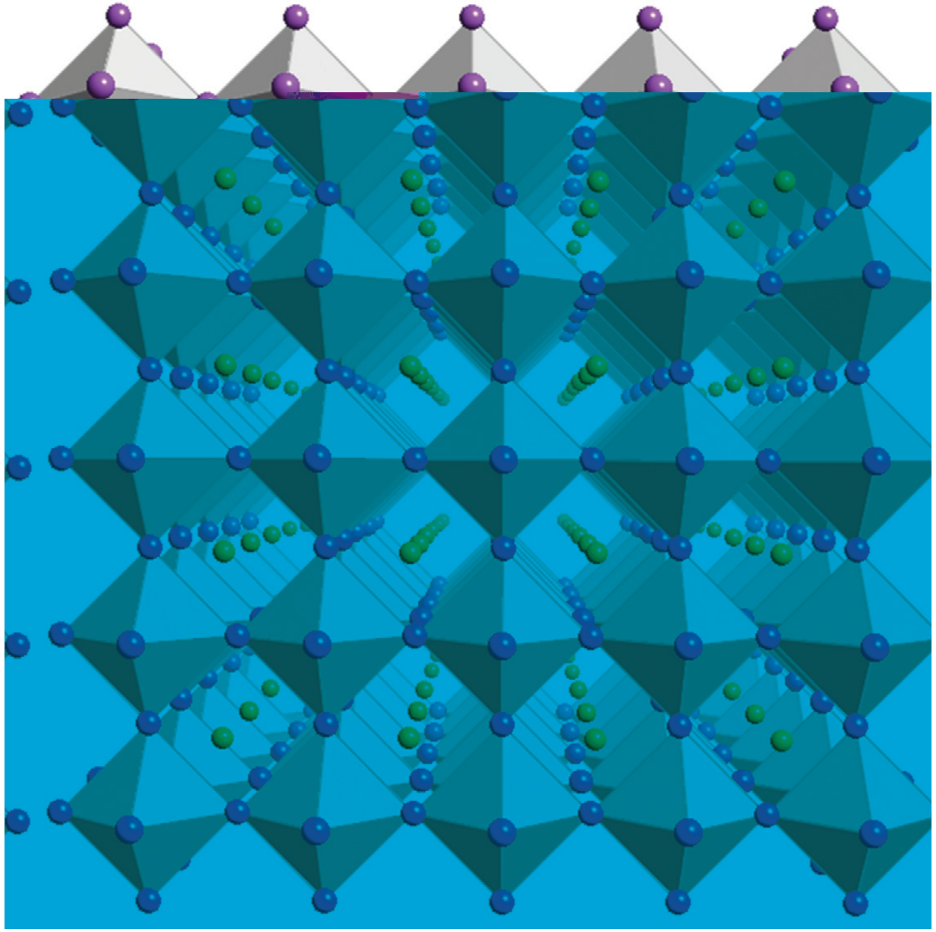
$$t=\frac{R_A+R_B}{\sqrt{2}\left(R_B+R_C\right)}\approx 0.9^{;;;}$$

R2)&N3Z+-2.>-)/?-/)2.+U.:B$.[.-.[.8B:

;=.>&/)?2@.AB.C/D22E.,'*.A2+-2)B.F'&)G,'+3?D2.(D20+2B.*2.H)/E-2)I.#.2*+-+&'.J8KK!=
;;=.F66)&M+0,-2*.N+,.O+'*+'G.P2'G-D
;;;=>&/)?2@.4B.Q,3&'B.R/S32*.P,32).T26&3+-+&'.&U.VD+'.W+S03B.X&D'.Y+S2E.,'*.>&'3.%'?B.J#::<=

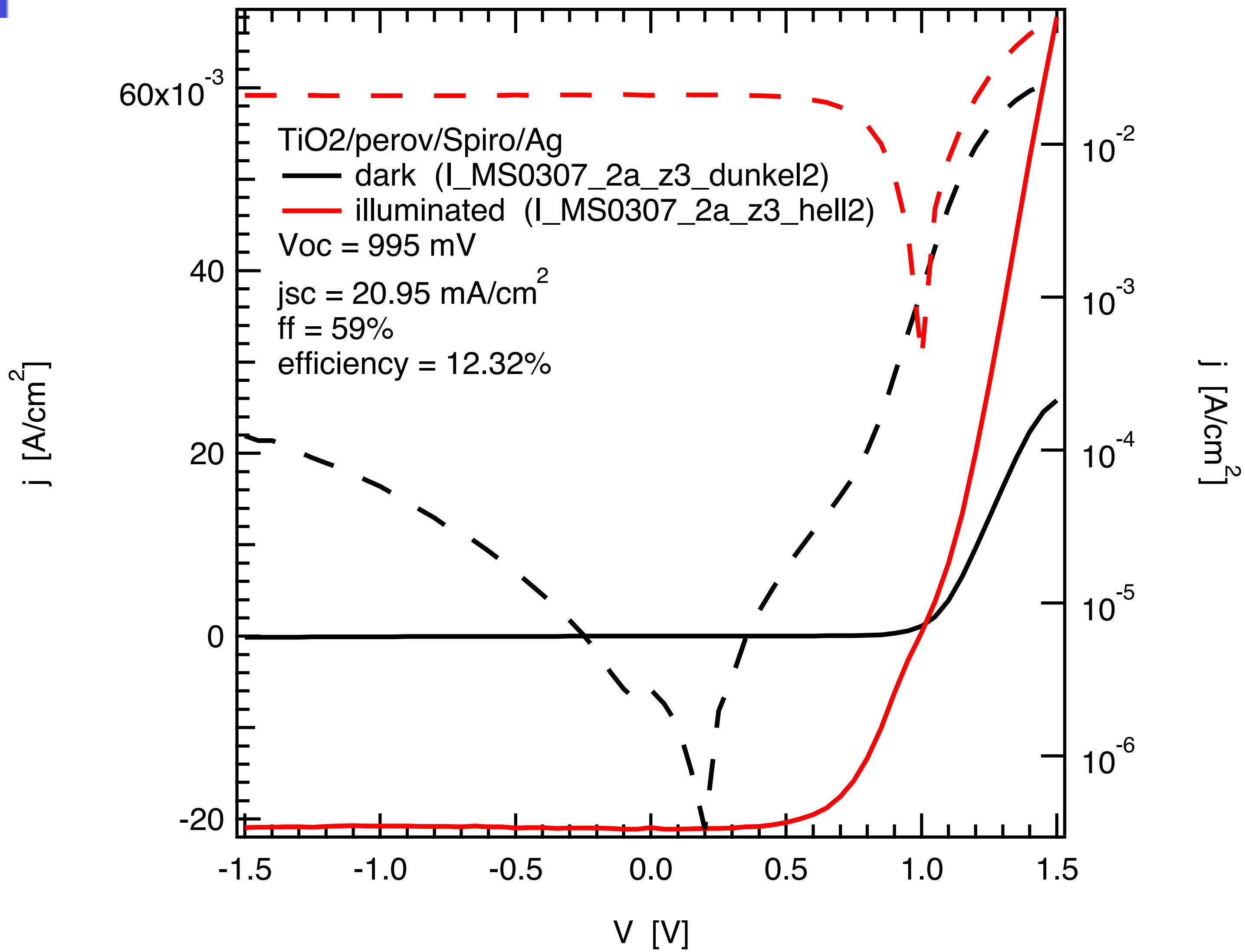
Perovskites- What is this?

Perowskites form crystalline structure



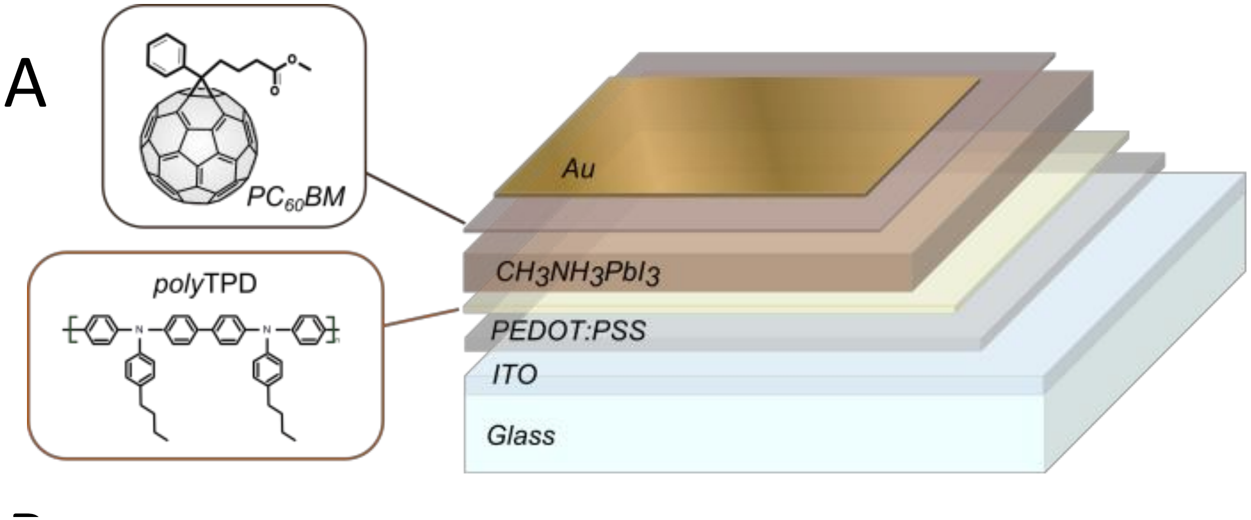
Pb atoms are placed at the centre of the grey octahedrons, lavender spheres represent iodine atoms and green spheres represent the methylammonium cations (after Henk Bolink et al., Nat. Photonics, 2014)

Making Perovskites Solar Cells



U Würzburg

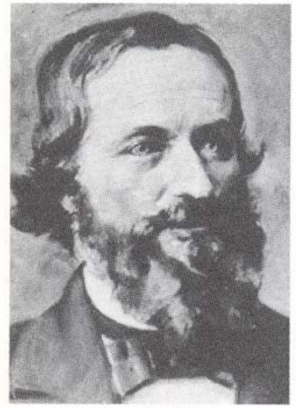
Why Perovskites work better than OPV?



... in part due to their ability to emit the light!

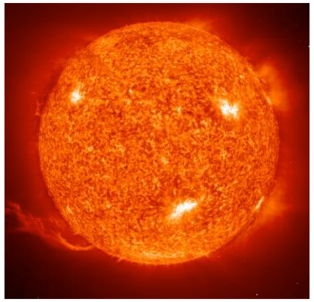
Optical Reciprocity Relation

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} = \frac{E_S}{A_S} = \frac{E_S}{1}:$$

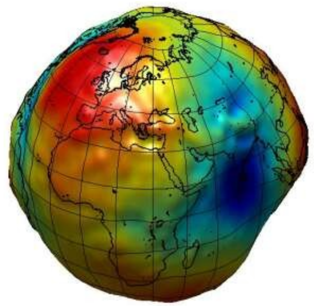


G. R. Kirchhoff

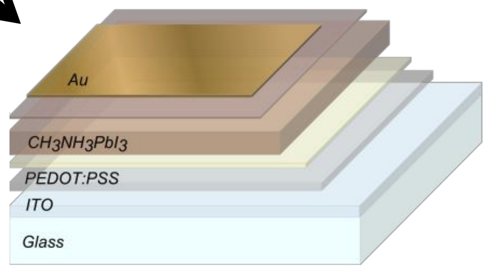
(1824 - 1887)



Black body
T=5800 K

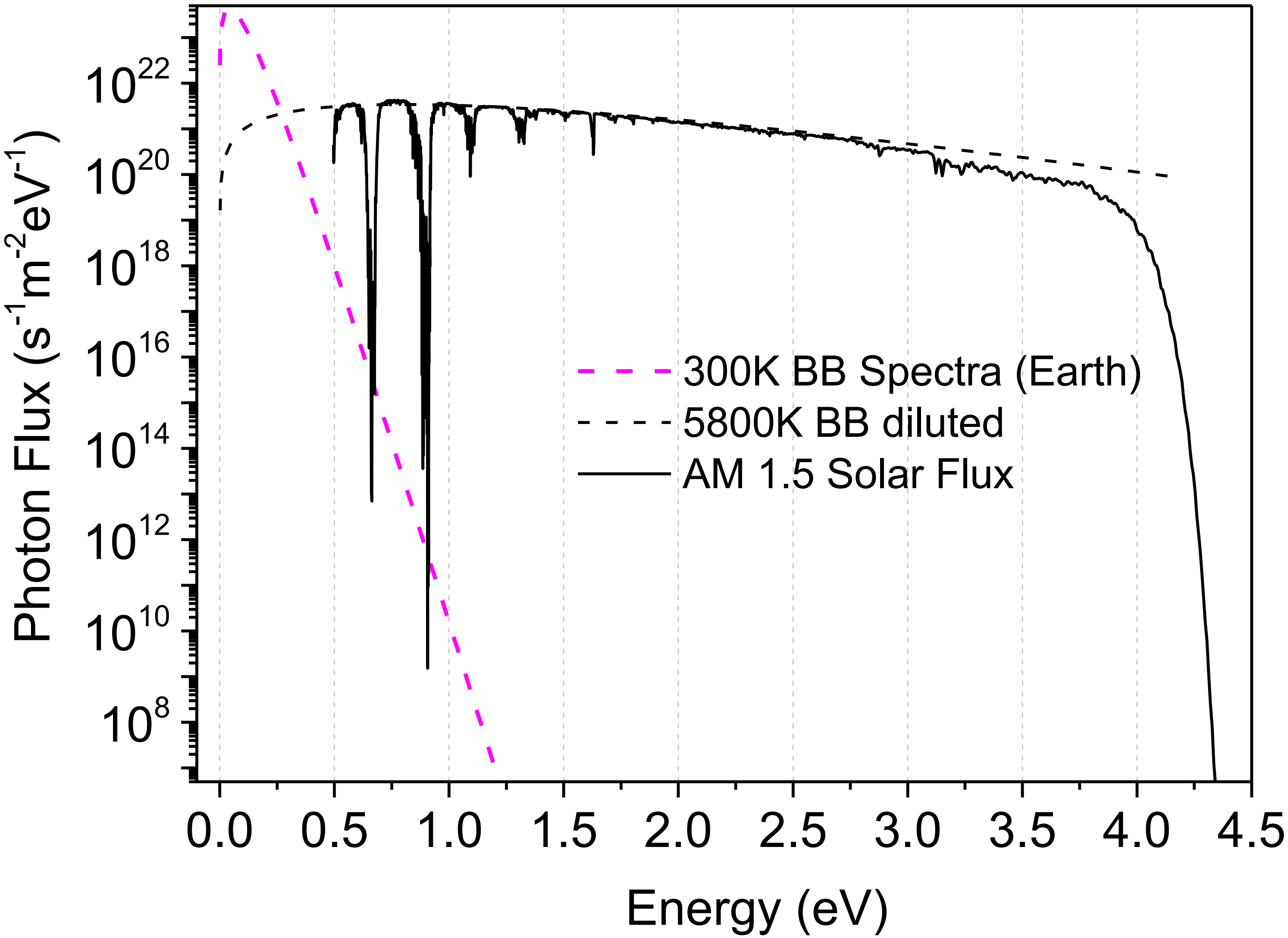


Black body
T=300 K



Grey body

Emission of Two Relevant BBs

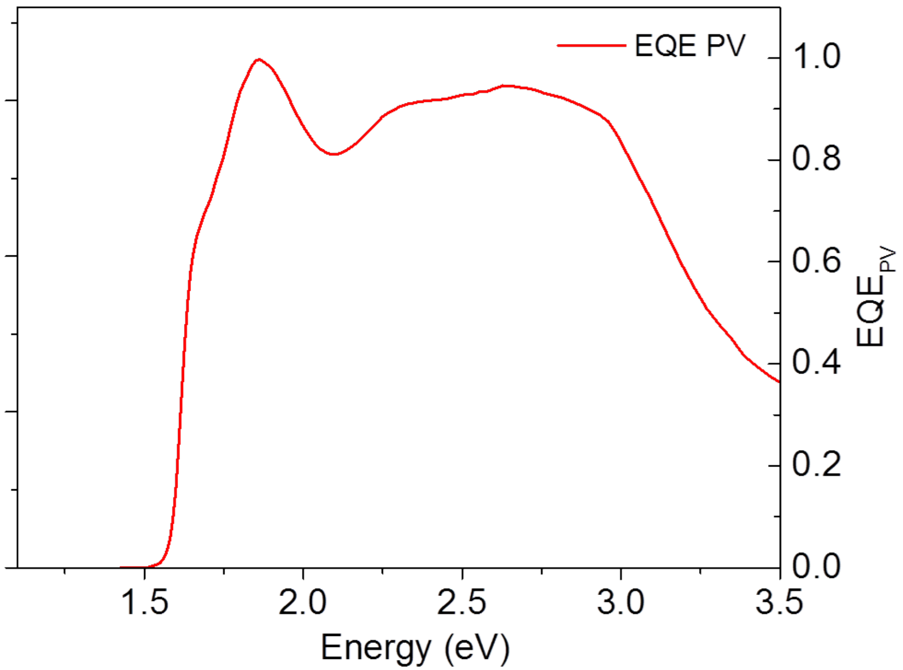


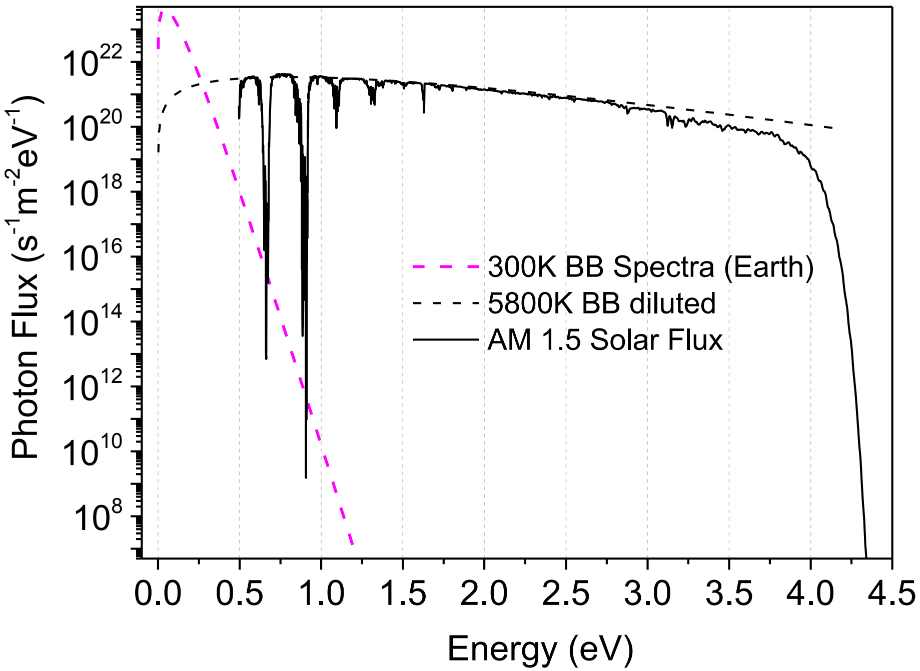
Reciprocity Relation for Solar Cells

$$J_{0,Rad} = q \cdot \int_0^\infty EQE_{PV}(E) \cdot \phi_{BB}(E) dE$$

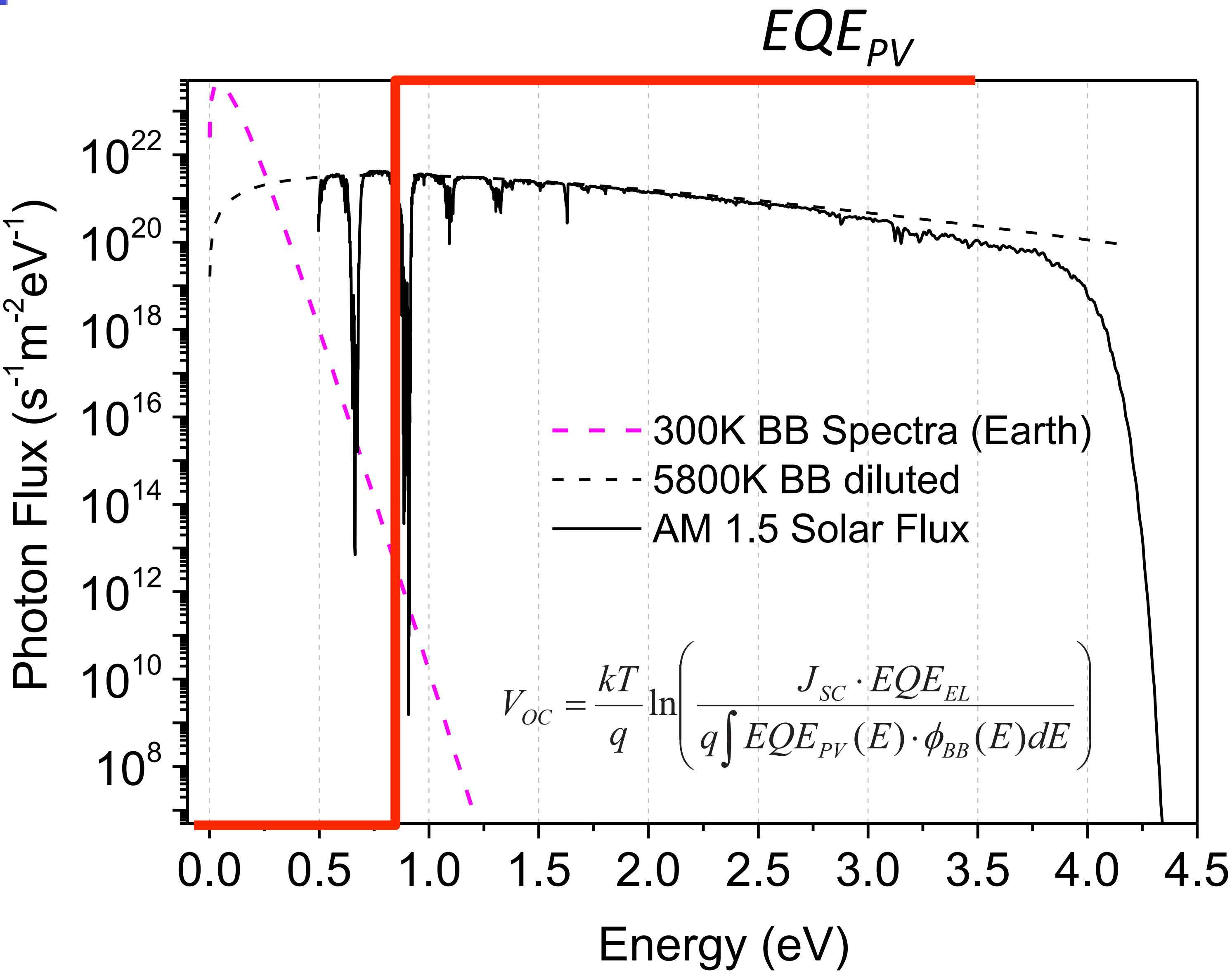
@ EQE_{EL}=1, or
x $(EQE_{EL})^{-1}$

$$J_{sc} = q \int_0^\infty EQE_{PV}(E) \phi_{AM1.5}(E) dE$$



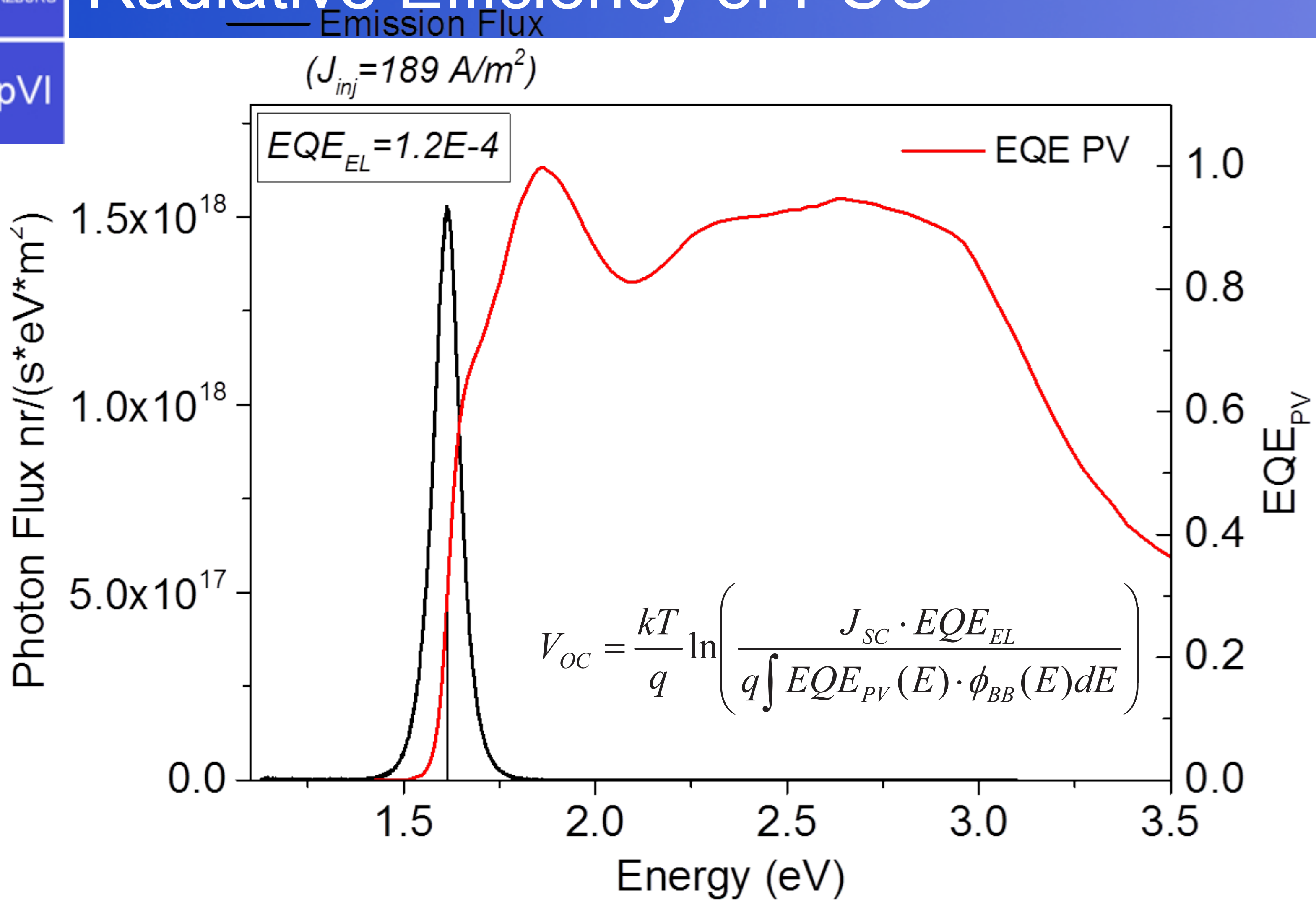


Emission of two relevant BBs



$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_{SC} \cdot EQE_{EL}}{q \int EQE_{PV}(E) \cdot \phi_{BB}(E) dE} \right)$$

Radiative Efficiency of PSC

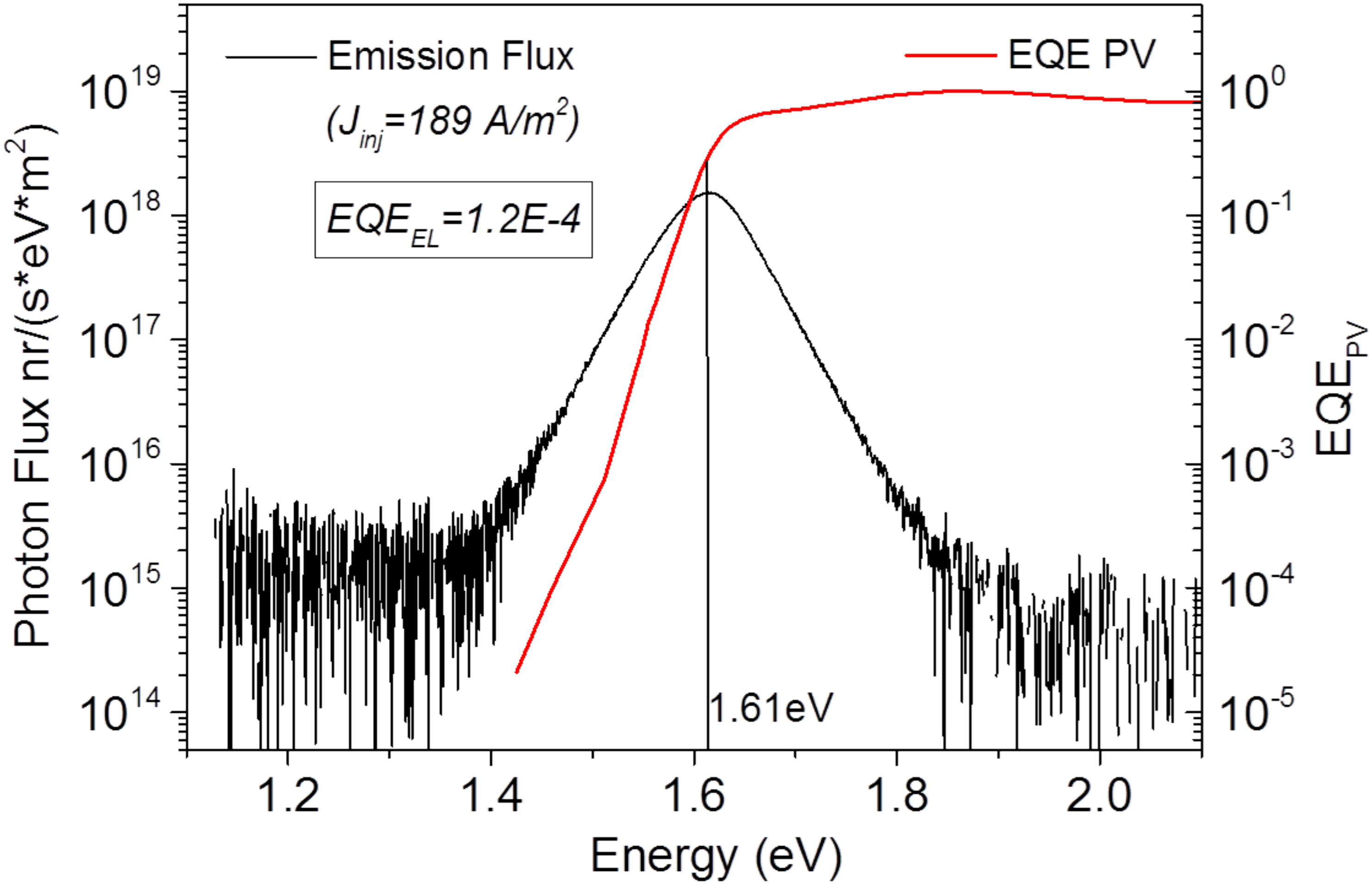


$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_{SC} \cdot EQE_{EL}}{q \int EQE_{PV}(E) \cdot \phi_{BB}(E) dE} \right)$$

- Emission comes from a narrow distribution of states likely located at the band edge @1.61eV
- No (or very small) Stokes shift

K. Tvingstedt et al. *Sci. Reports (2014)*

Radiative Efficiency of PSC



Logscale

Measure the *EL* photon flux by injecting a forward current as close as possible to the short circuit photocurrent, integrate over all E and divide by injected current

K. Tvingstedt et al. *Sci. Reports (2014)*

Radiative Efficiency of Various Materials

Table I. External radiative efficiency (ERE) and other relevant performance parameters at 25 °C for the state-of-the-art devices [3,4] included in the present study.

Device	V_{oc} (mV)	J_{sc} (mA/cm^2)	Efficiency (%)	ERE (%)
Si UNSW	706	42.7	25.0	0.57
Si SPWR	721	40.5	24.2	0.56
GaAs Alta	1107	29.6	27.6	22.5
GaAs ISE	1030	29.8	26.4	1.26
CIGS ZSW	740	35.4	20.3	0.19
CIGS NREL	713	34.8	19.6	0.057
MAPI PEROVSKITE	**1080**	**18.9**	**13.8**	**0.012**
CdTe* ASP	838	21.2	12.5	1.0E−4
a-Si Oerlikon	886	16.8	10.1	5.3E−6
Dye* Sony	719	19.4	9.9	7.2E−6
OPV Konarka	816	14.5	8.3	2.7E−7
OPV Solarmer	759	15.9	8.1	3.8E−7

*Minimodule: results on a 'per cell' basis.

A radiative efficiency of ~1E-4 puts the perovskite solar cell in a good position, when compared to other earlier generation photovoltaic technologies.

Prog. Photovolt: Res. Appl. **20**:472 (2012)
K. Tvingstedt et al. *Sci. Reports (2014)*

More intriguing physics related to PSC

- Ferroelectricity (polarisation)?
- Dielectric constant („giant“)?
- Band gap tuning (MA replaced by FA)
- Excitons of free e-h?
- Charge transport and recombination
- Potential for injection stimulated emission
- Stability, toxicity?
- ....

Conclusions

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„[…] it is now time to investigate the physical properties that make hybrid perovskites so promising for solar-energy conversion."
M. Loi et al., Nature Materials, **2013**, 12, 1087.

Don't treat solar cell research as something unworthy for physicists. Combine efforts!

Thank you!

dyakonov@physik.uni-wuerzburg.de

Chair of Experimental Physics VI, Julius-Maximilian University of Würzburg, Germany