

3G rule for attending in person lectures at KIT:

geimpft – vaccinated

genesen – recovered

getestet – tested



"Solar Energy" WS 2021/2022

Lecture 9: Organic and Perovskite Thin-film Solar Cells

Tenure-Track-Prof. Dr. Ulrich W. Paetzold

Institute of Microstructure Technology (IMT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen Light Technology Institute (LTI), Engesserstrasse 13, Building 30.34, 76131 Karlsruhe

KIT Focus Optics & Photonics



KIT – Universität des Landes Baden-Württemberg und nationales Forschungszentrum in der Helmholtz-Gemeinschaft

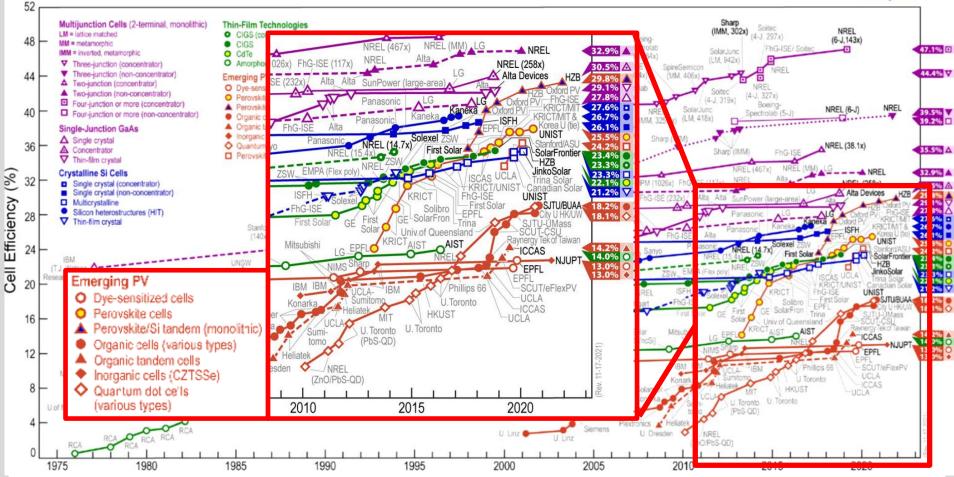
Parts of the material used here have been kindly provided by Prof. T. Kirchartz, and Dr. D. Cheyns.

Why organic or perovskite PV?



CNREI

Best Research-Cell Efficiencies



Source: https://www.nrel.gov/pv/cell-efficiency.html



PART 1 - ORGANIC PHOTOVOLTAICS

Part 1: Organic Photovoltaics



- Material properties
- Inorganic vs. organic semiconductor
- Working principle organic solar cells
- Fabrication of organic solar cells / device architecture
- Major Challenges of the technology
- Applications

What is organic about OPV



How the plants works...? Can we mimic the nature?!!

... greenhouses ?

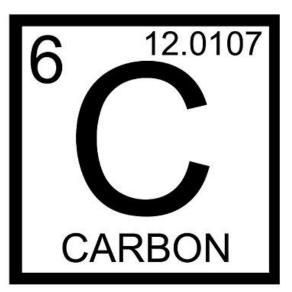


... artificial leaves?



Belectric

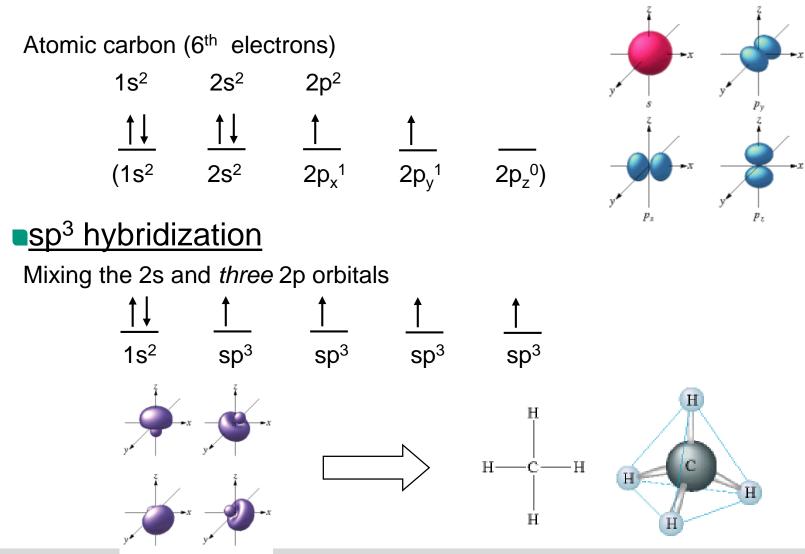
... maybe ... but the point is that we use organic materials, in its various forms that contain carbon atoms!



Sources: belectric Courtesy to Barry Rand & David Cheyns

Carbon Hybridization

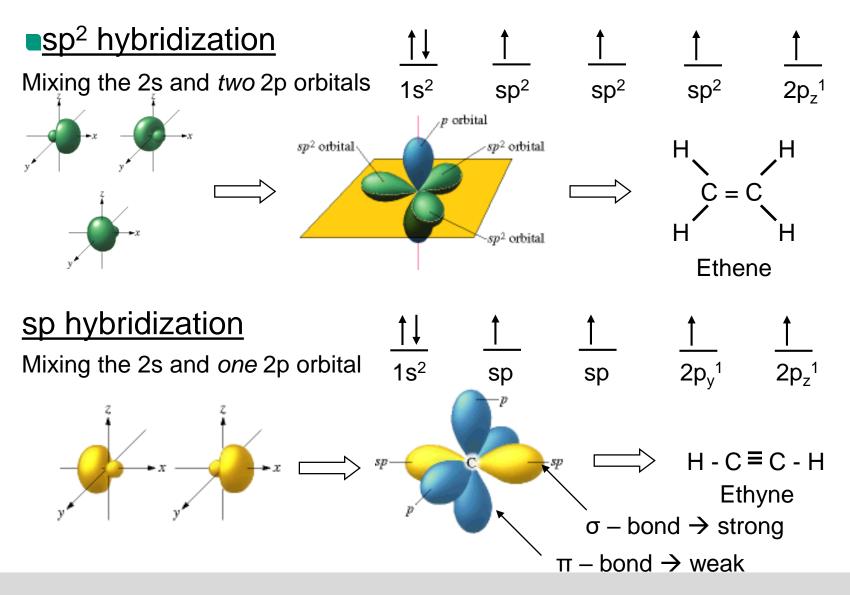




Methane

Carbon Hybridization

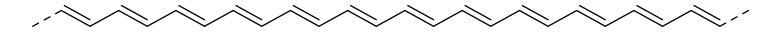




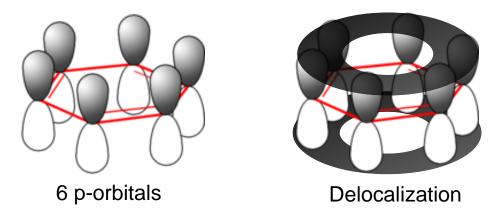
Conjugated Polymers



An organic compound with alternating single and multiple (e.g. double) bonds More specifically: each atom in a chain must posses a *p-orbital*



Example: benzene – connecting a conjugated polymer of sp hybridized C atoms in a ring



- 1. Increase stability/Lower overall energy of the molecule due to delocalized states
- 2. General delocalization of the electrons across all adjacent parallel aligned p-orbitals

-> electrons can move "freely" which gives rise to conductivity

Conjugated Polymers



Nobel Prize in Chemistry 2000

Awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers"





Conjugated Polymers



An organic compound with alternating single and multiple (e.g. double) bonds More specifically: each atom in a chain must posses a *p-orbital*

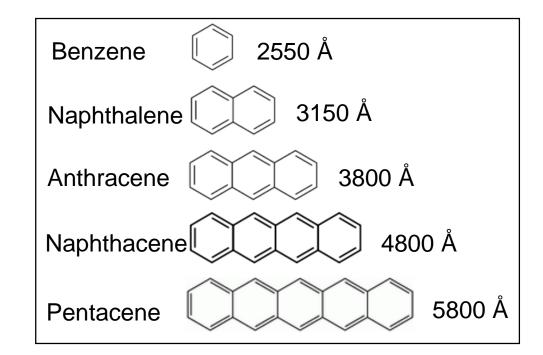
Polyacenes as 2D examples

Color:

With every double bond added, the system absorbs photons of longer wavelength

Stability

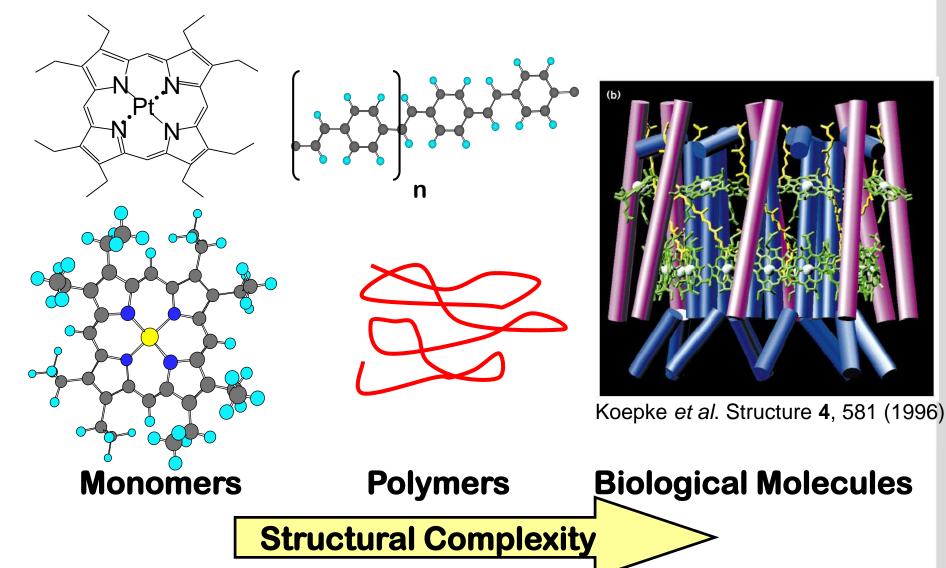
General formula: $C_{4n+2}H_{2n+4}$ where *n* is the number of rings Stability decreases as *n* increases



Conjugation in cyclic structures results in aromaticity

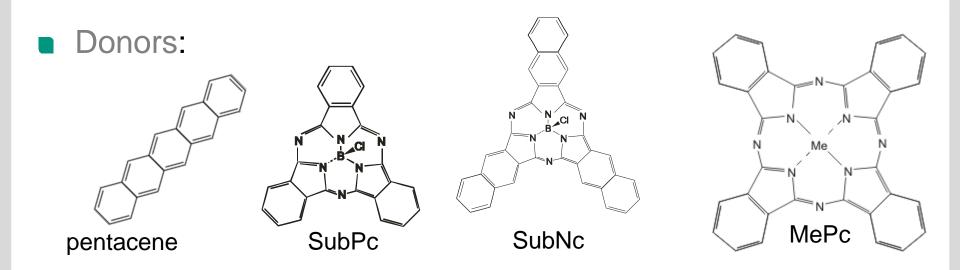
Types of organic materials



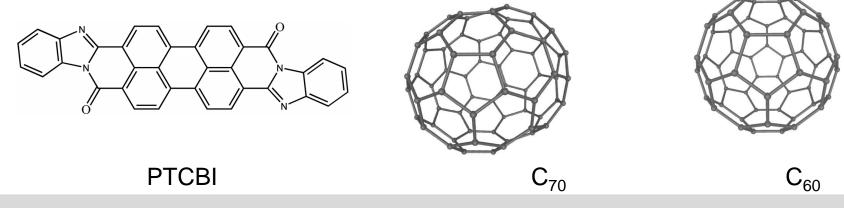


Typical small molecules



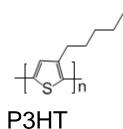


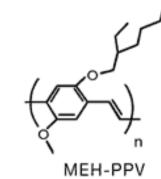
• Acceptors: perylene derivatives, fullerenes

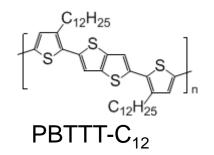


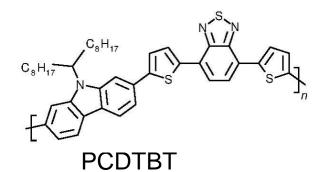
Typical polymers

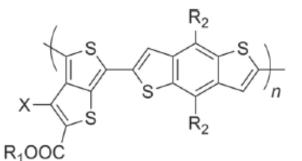












PTB1: X = H, R_1 = dodecyl, R_2 = octyloxy **PTB3**: X = H, R_1 = 2-ethylhexyl, R_2 = octyl **PTB4**: X = F, R_1 = octyl, R_2 = 2-ethylhexyloxy **PTB7**: X = F, R_1 = 2-ethylhexyl, R_2 = 2-ethylhexyloxy **PTB9**: X = H, R_1 = 2-ethylhexyl, R_2 = 2-ethylhexyloxy

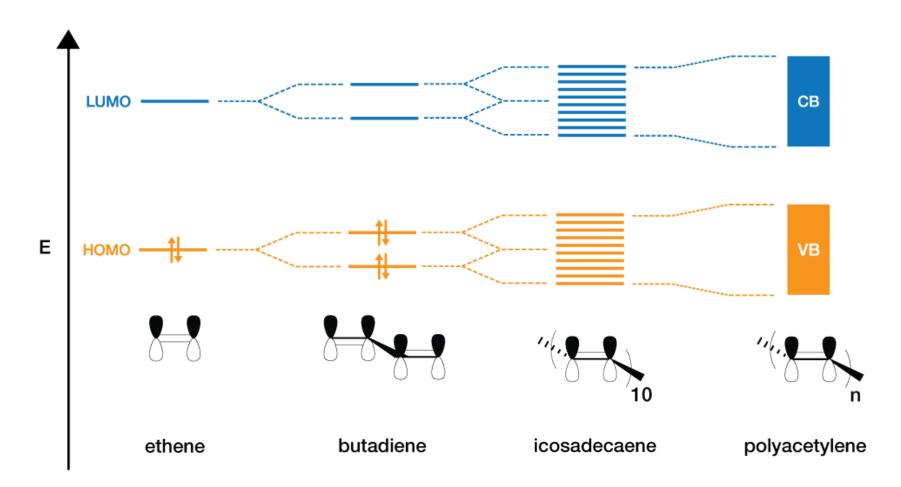
Part 1: Organic Photovoltaics



- Material properties
- Inorganic vs. organic semiconductor
- Working principle organic solar cells
- Fabrication of organic solar cells / device architecture
- Major Challenges of the technology
- Applications

Organic Semiconductors

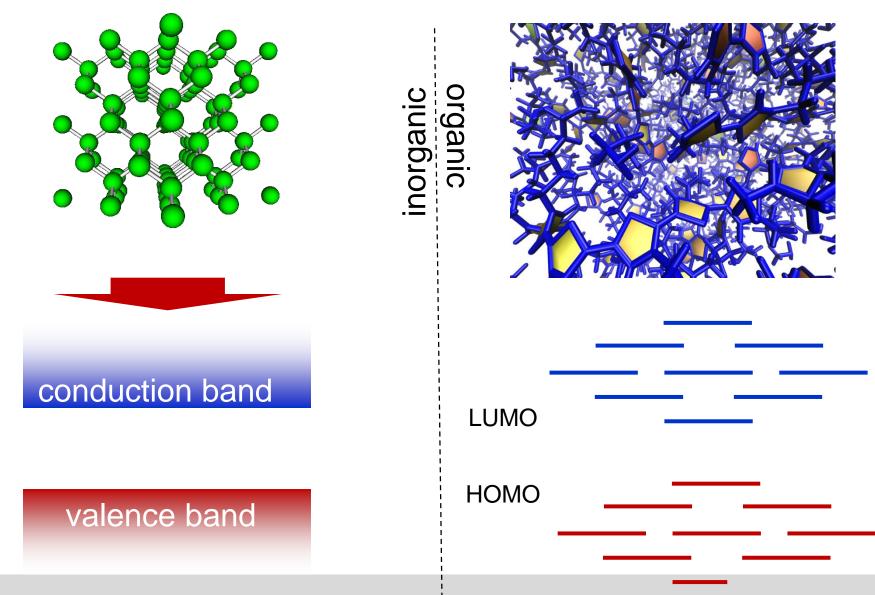




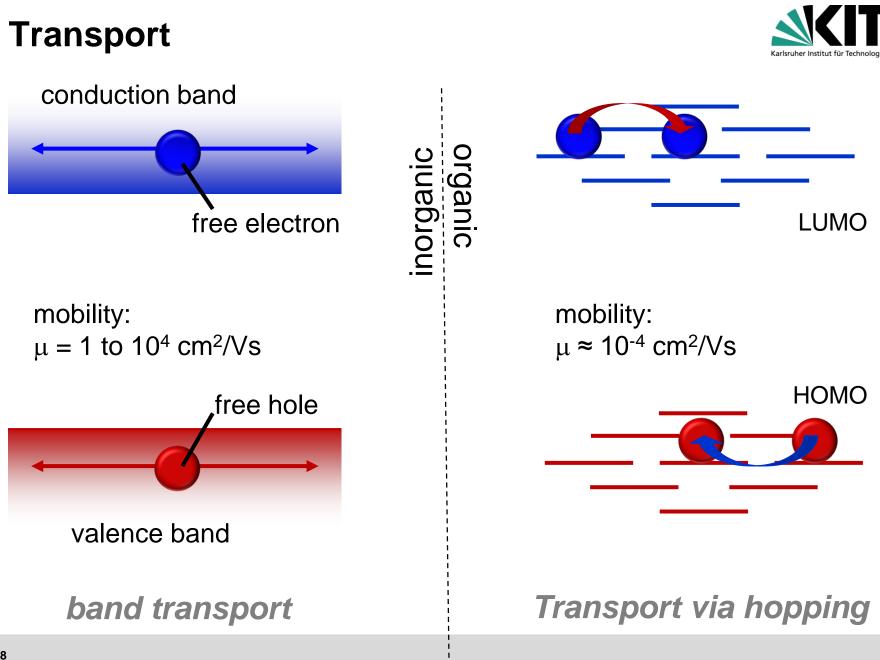
However, real bands are rare to observe because of disorder in relevant polymers.

Inorganic vs. organic semiconductor



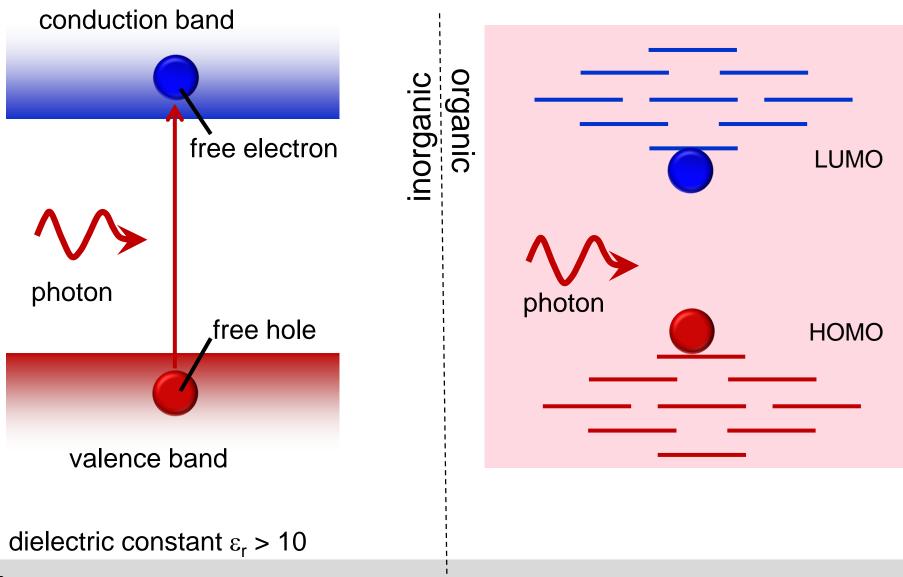


http://www.iue.tuwien.ac.at/phd/hoessinger/node26.html

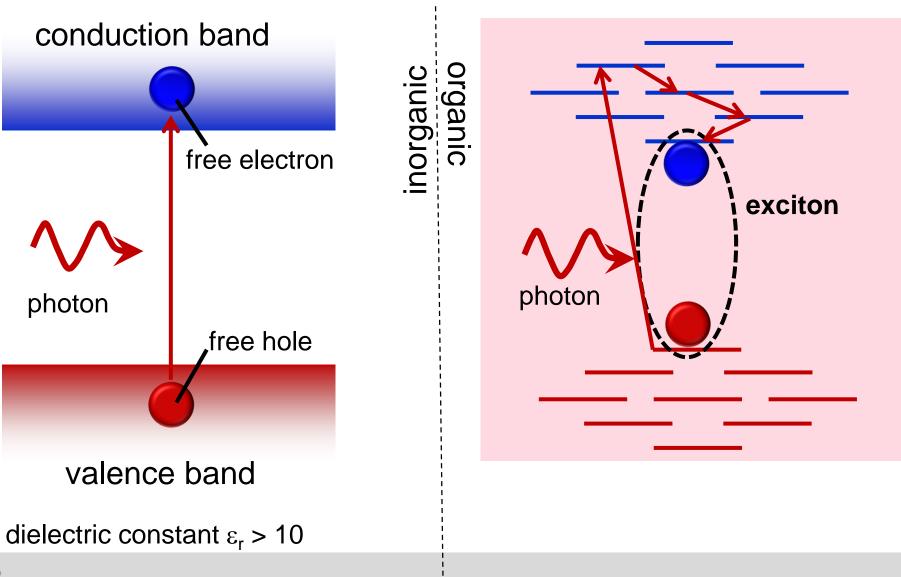


Source: Courtesy of Thomas Kirchartz, Forschungszentrum Juelich











conduction band

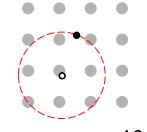
Types of excitons

- Absorption results in exciton creation
 - Bound electron-hole pair
 - Chargeless quasiparticle

Frenkel exciton

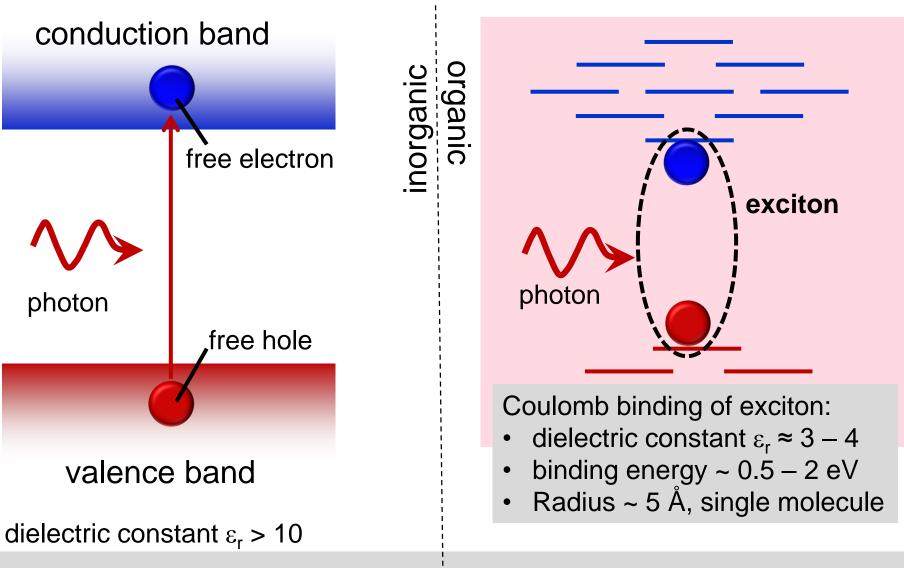
- Obeys boson statistics
- Exciton radius depends sensitively on dielectric environment → screening

Wannier-Mott exciton

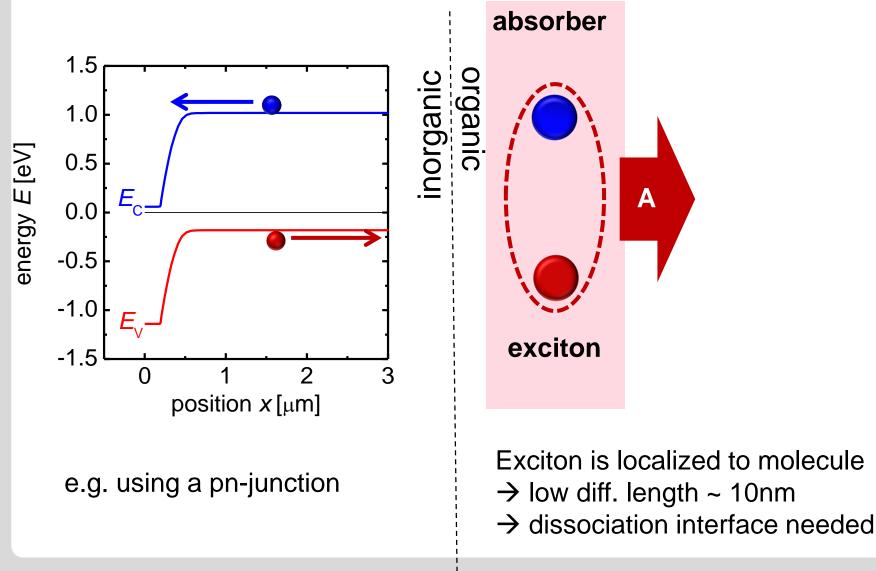


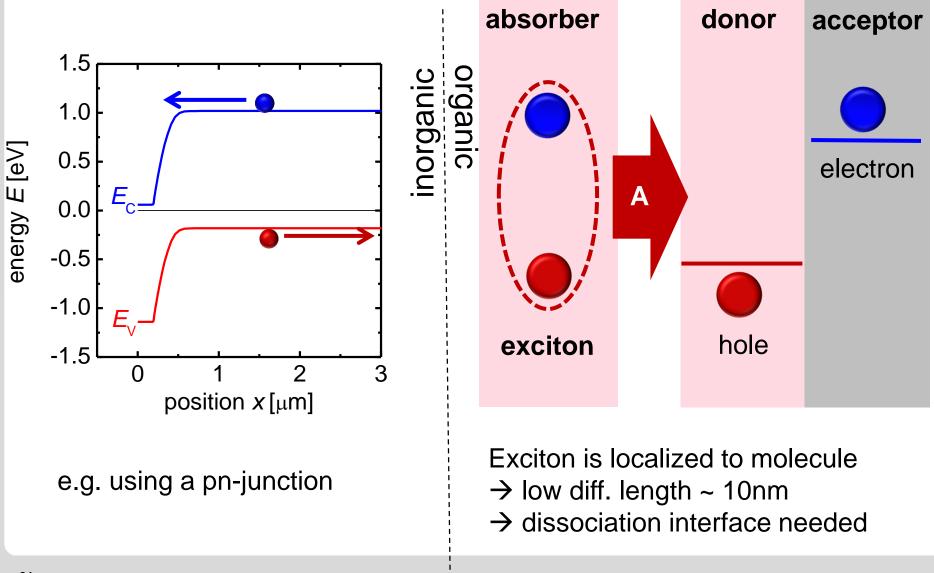
binding energy ~ 10 meV Radius ~ 100 Å Highly delocalized

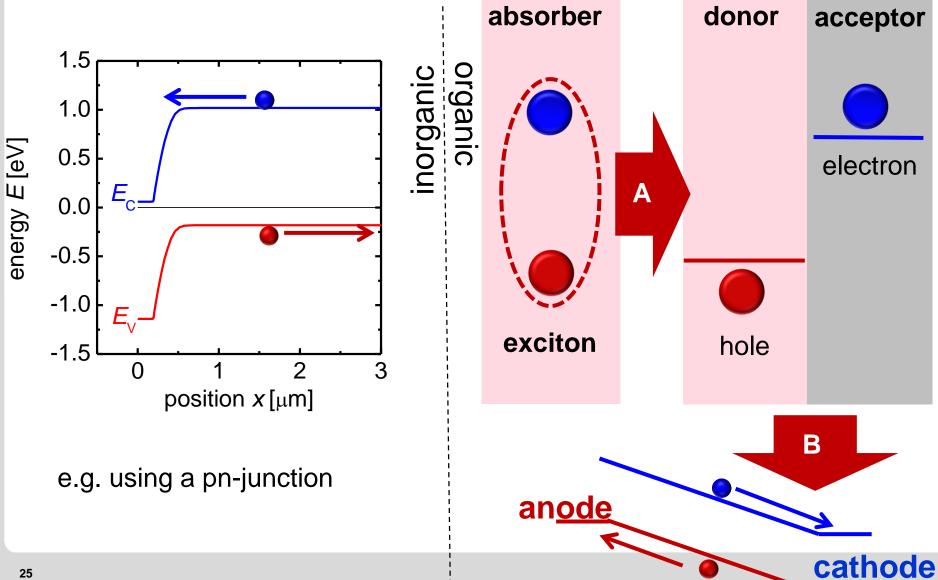










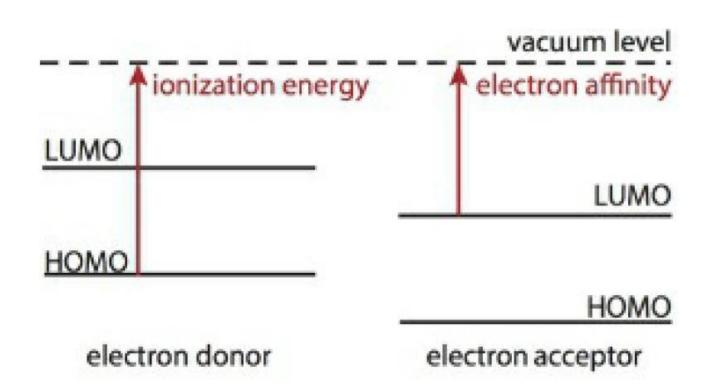


Karlsruher Institut

Charge separation

Illustration of energy levels



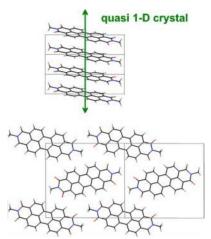


Organic vs. inorganic semiconductors



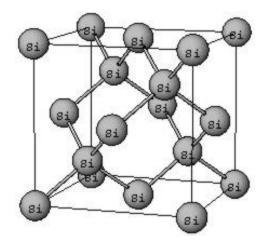
<u>Organic</u>

- Van der Waals interactions between polymers ($E_{VdW} = 10^{-3} 10^{-2} \text{ eV}$)
- Charge carrier and exciton localization
- High Eg → low mobility µ ≈ 1 cm²/V s and mean free path / ≈ a₀ at room T
- Dissociation interface needed for solar cell devices (donor/acceptor blend)
- Soft, flexible



<u>Inorganic</u>

- Covalent-type interactions $(E_{cov} = 2 4 \text{ eV})$
- Charge carrier delocalization
- Higher μ and $l \approx 100 1000 a_0$
- Hard, brittle



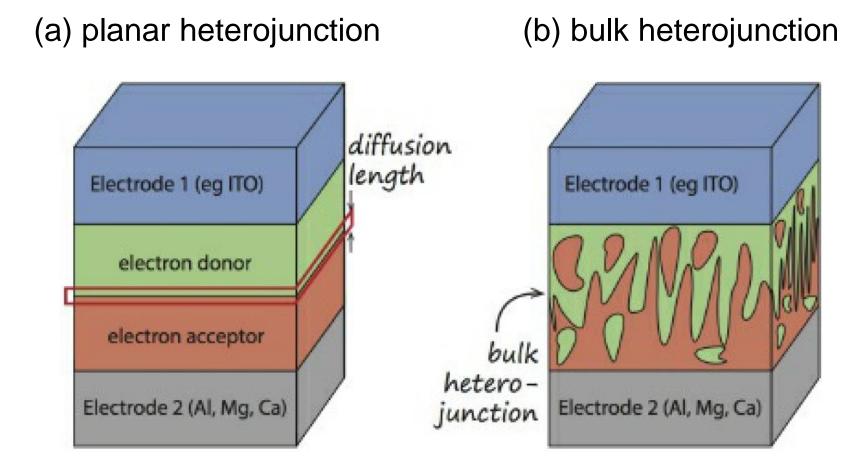
Part 1: Organic Photovoltaics



- Material properties
- Inorganic vs. organic semiconductor
- Working principle organic solar cells
- Fabrication of organic solar cells / device architecture
- Applications

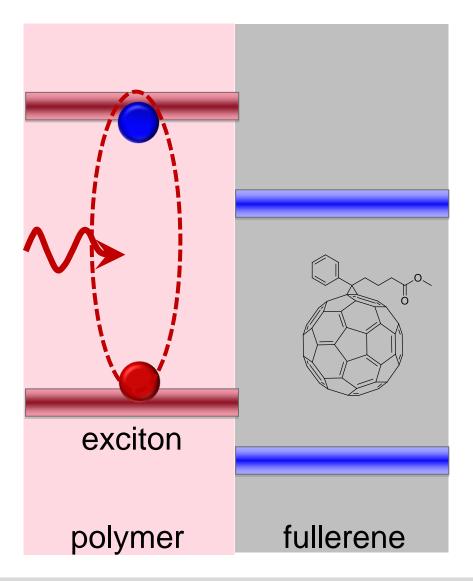
How do organic solar cells work?



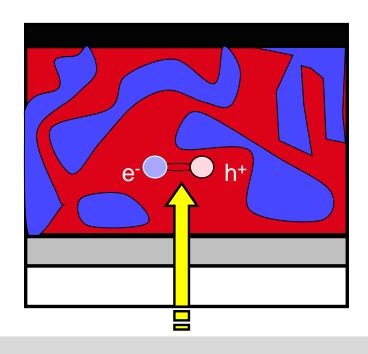


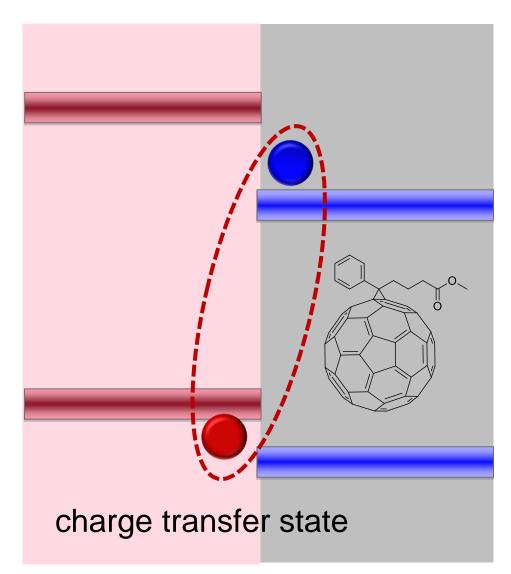
Source: textbook





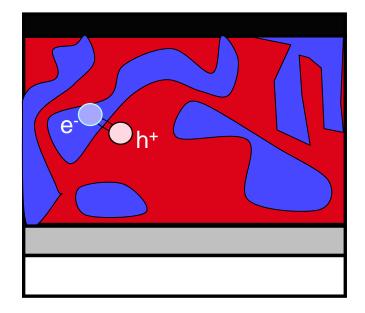
- Photon absorption
- Exciton generation
- Exciton diffusion

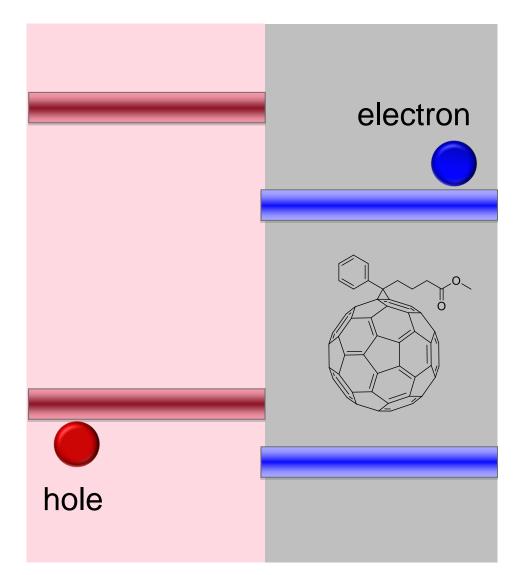






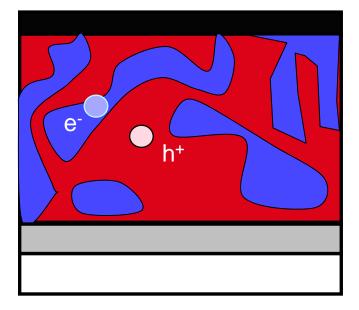
• Charge transfer



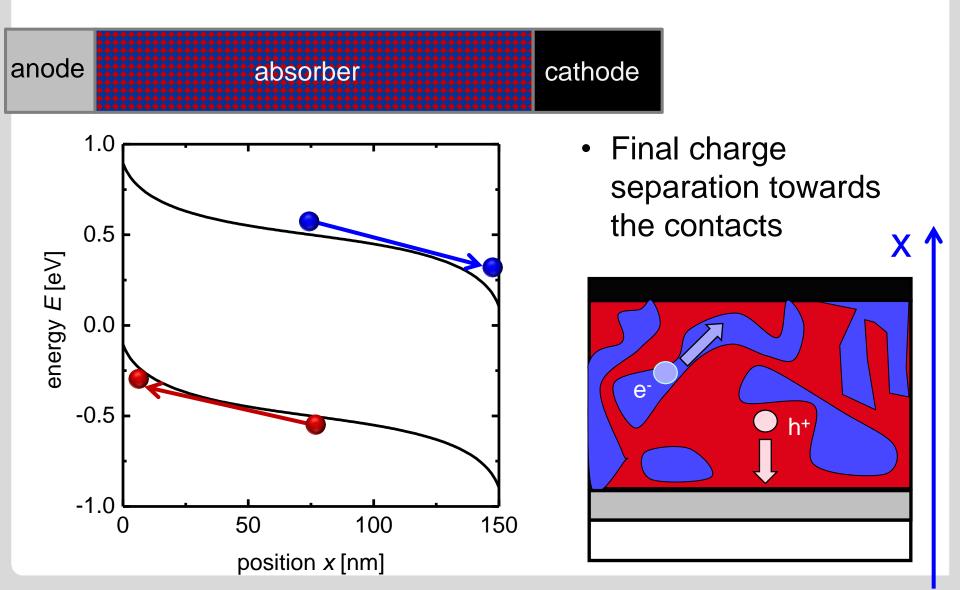




• Initial charge separation







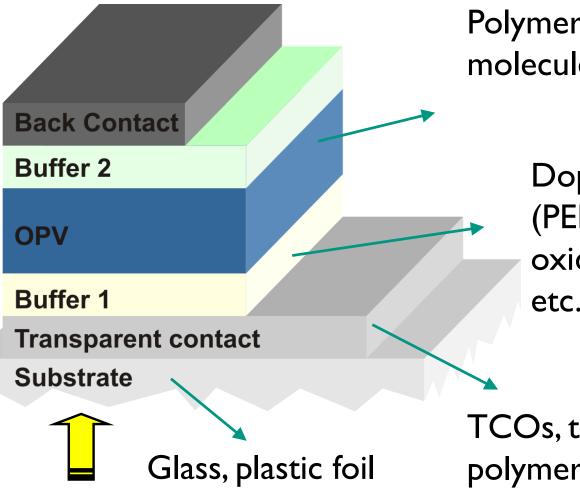
Part 1: Organic Photovoltaics



- Material properties
- Inorganic vs. organic semiconductor
- Working principle organic solar cells
- Fabrication of organic solar cells
- Applications

Anatomy of a typical OPV cell





Polymer-based or small molecule-based

Doped organic films (PEDOT:PSS), metal oxides (TiO_x, ZnO, MoO_x, etc.)

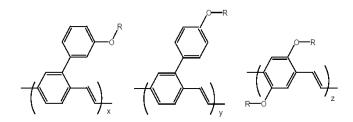
TCOs, thin metals, carbon, polymers, Ag nanowires

Materials for Organic Electronics



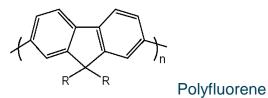
Two approaches lead to similar electronic properties

Conjugated polymers



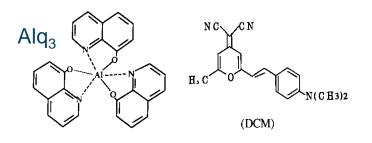
 $R = (CH_2)_3CH(Me)(CH_2)_2CHMe_2$

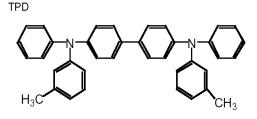
PPV co-polymers

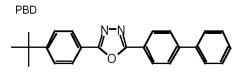


Cannot be evaporated

Small evaporated molecules

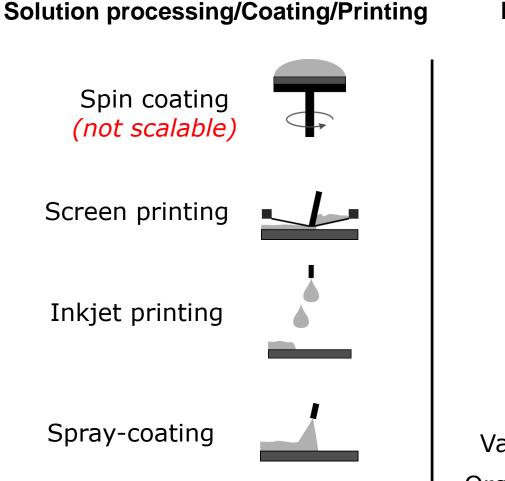




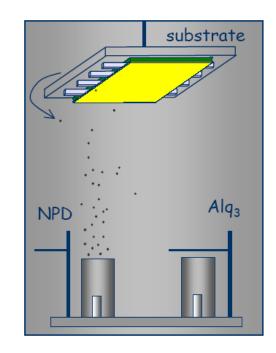


Can be evaporated



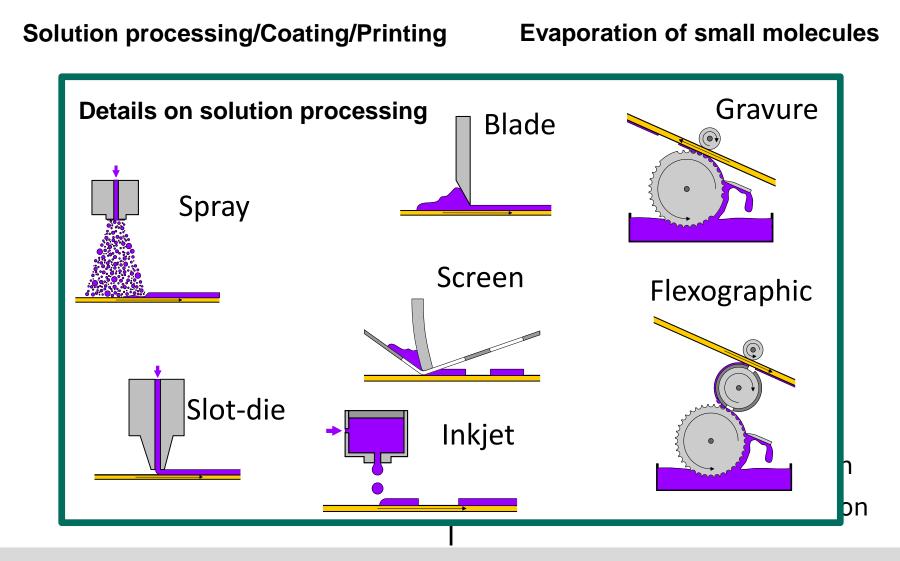


Evaporation of small molecules



Vacuum Thermal Evaporation Organic Vapor Phase Deposition







Solution processing/Coating/Printing

Evaporation of small molecules

Competence Center Printing & Device Physics @ InnovationLab in Heidelberg

Mission Lab-to-Fab	Partners	BASF SE, Merck KGaA, KIT, TU Darmstadt	
1 - Proof of concept	2 - Prototype	3 - Scale Up	
Proof of concept	Large-Area-Prot	otyping R2R R&D platform	
 Fluid < 10 ml 	 Fluid < 100 ml 	 Fluid < 1 l 	
 Low material usage 	 Lab-scale 	 R&D pilot line for 	
 Direct feedback for 	 Up to letter-size 	ze production research	
material design and	substrates	 Web width: 330 mm 	
formulation development	 Targeted later 	al • Web speed: up to	
	resolution: <	10 µm 100 m/min	



bn

Evaporation of small molecules

Solution processing/Coating/Printing

11m long in-line evaporation equipment at Fraunhofer IPMS Dresden

Organic Photovoltaics



- Material properties
- Inorganic vs. organic semiconductor
- Working principle organic solar cells
- Fabrication of organic solar cells

Applications

OPV in everyday applications



Efficient operation at low light intensity





OPV in everyday applications



Flexibility, aesthetic, light-weight and free-from



Semitransparent solar cells





Organic Photovoltaics



from a product perspective

Pro	Con
Light-weight	Rather low efficiency (< 18%), especially too low for multijunction solar cells
Flexible and free-form	Long-term stability ?
Semitransparent	Material costs ?
Solution processable	However, best efficiency is reached with evaporation, which is more costly
Can be non-toxic	

→ At the current stage OPV is not competitive on the large volume for the standard solar modules PV market for residential rooftops and solar plants. However, special applications where flexible and semitransparent solar cells are needed could be a niche for OPV (e.g. indoor (low-light) or Building Integrated PV). Nowadays, Organic Electronics is more suitable for OLEDs and cheap sensors!

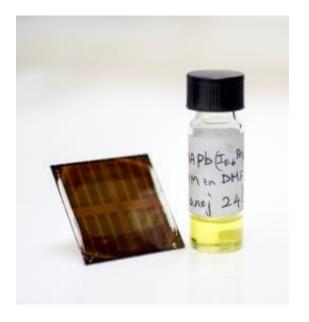


PART 1 - PEROVSKITE PHOTOVOLTAICS

Perovskite Photovoltaics



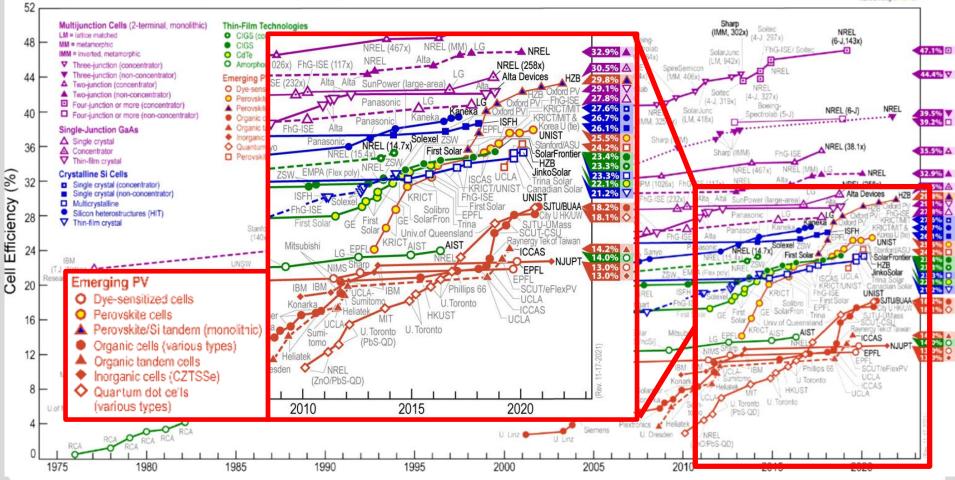
- Why perovskite materials?
- Fabrication of perovskite solar cells
- Challenges of perovskite PV
- Perovskite PV Research at KIT



Why perovskite PV?



Best Research-Cell Efficiencies



Why perovskite PV?



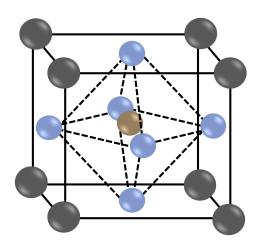


Source: https://www.nrel.gov/pv/cell-efficiency.html

What is a perovskite?



Generic formula: ABX₃





(In)organic cation (e.g. CH₃NH₃,)



Inorganic cation (e.g. Pb)



Anion (e.g. I)

Found in 1830 by Mr. Perovski in the Ural mountains

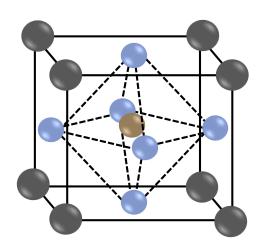


Calcium Titanium Oxide/Calcium Titanate: $CaTiO_3$

Perovskite - a class of crystals



Generic formula: ABX₃



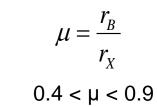
Coarse guidelines for crystal formation

1. Goldschmidt's tolerance factor

$$t = \frac{\left(r_A + r_x\right)}{\sqrt{2}\left(r_B + r_x\right)}$$

 $0.8 \leq t \leq 1.1$

2. Ratio of ionic radii





Inorganic cation (e.g. Pb)

(e.g. CH_3NH_3)

(In)organic cation



Anion (e.g. l)

Source: textbook

Perovskite - a class of crystals



Prominent inorganic examples:

	t	μ
CaTiO3	0.97	0.43
SrTiO3	1.00	0.43
BaTiO3	1.06	0.43

Ba=1.61 Å;	Dielectric	CaTiO3
Ca=1.34 Å;	Ferroelectric	BaTiO3
Sr= 1,44 Å; Ti=0.605 Å; O=1.4 Å;	Piezoelectric	Pb(Ti,Zr)O3
	Superconducting	SrTiO3
	Semiconducting	SrTiO3

Only recently for Optoelectronics/PV: Semiconducting and strongly absorbing MAPbI3

Coarse guidelines for crystal formation

1. Goldschmidt's tolerance factor

$$t = \frac{\left(r_A + r_x\right)}{\sqrt{2}\left(r_B + r_x\right)}$$

$$0.8 \leq t \leq 1.1$$

2. Ratio of ionic radii

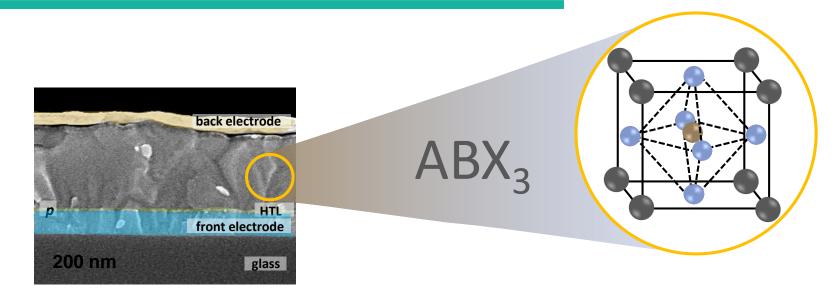
$$\mu = \frac{r_B}{r_X}$$

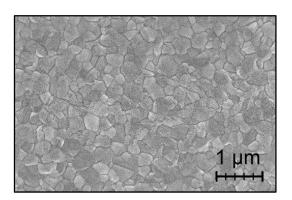
$$0.4 < \mu < 0.9$$

First reported for PV in 2009 (3.9%), however research only booming since 2012.., now up to 25.2%!!

Metal Halide Perovskite Thin Films









(In)organic cation (e.g. CH₃NH₃⁻, Cs⁻)



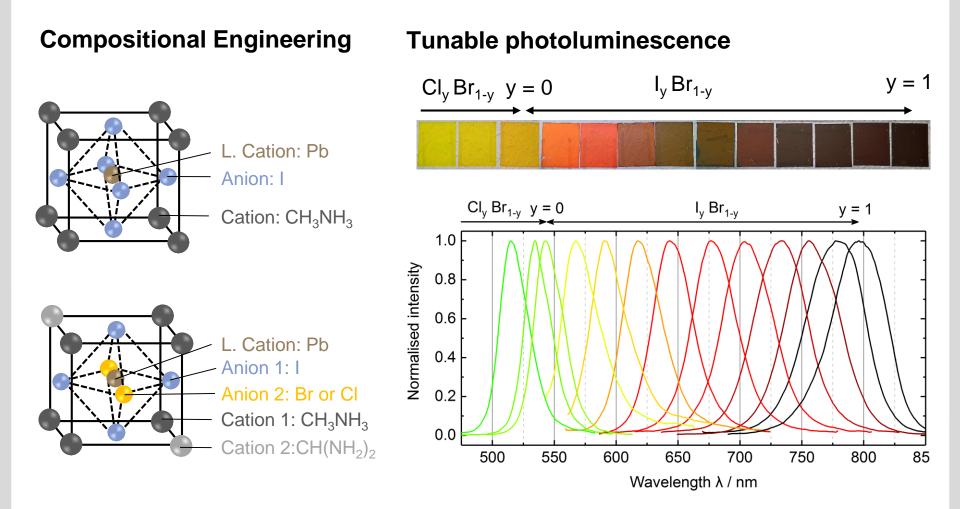
Inorganic cation (e.g. Pb^{-,} Sn⁻)



Anion (e.g. l^{+,} Br⁺)

Tunable Bandgap of Multi-Cation Perovskite





Brenner et. al, Optical Mat. Express. Vol. 7, 11, 4082-4094 (2017).

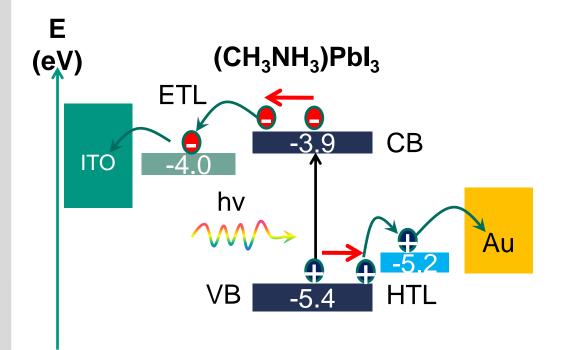
Perovskite Photovoltaics



- Why perovskite materials?
- Working principle of perovskite solar cells
- Fabrication of perovskite solar cells
- Challenges and promises of perovskite PV
- Perovskite PV Research at KIT

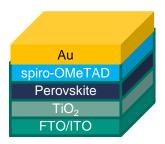
Working Principle





Important intrinsic material requirements for PV

- 1. high absorption coefficient (α)
- 2. large diffusion length (I_{diff})



<u>Steps:</u>

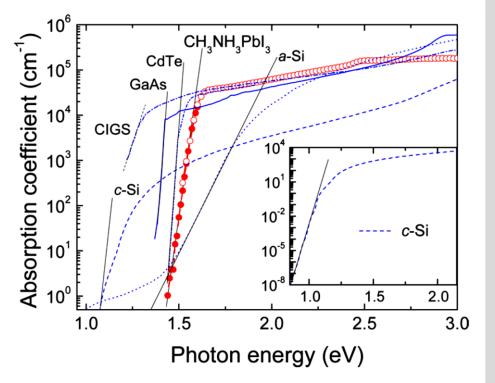
- 1. Light absorption
- 2. Excitation of free charge carriers (exciton binding energy $< k_BT$)
- Diffusion to the charge selective transport layers (HTL and ETL)
- 4. Transport to the contacts

Promises of Perovskite Photovoltaics



High absorption coefficient

- High absorption coefficient
 → abs. length 1/α < 0.3 μm
- Direct band gap at ~1.6 eV
- Small Urbach tail (slope below Eg)
 → low degree of disorder
- Even polycrystalline perovskite layers behave like monocrystalline materials!

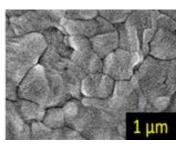


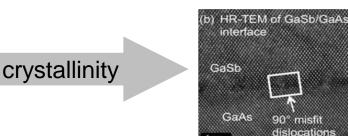
Excellent Optoelectronic Properties



Low non-radiative recombination losses yield high open-circuit voltage.

	Perovskite [1]	CIGS [2]	Si [3]	GaAs [4]
Max. V _{oc}	1.21 V / 1.31V	0.757 V	0.73 V	1.12V
E _G	1.62eV / 1.72eV	1.15eV	1.07eV	1.39eV
eV _{oc} /E _G	74-76%	~65%	~68%	82%





Polycrystalline perovskite thin films yield almost as high eV_{oc} / E_{G} as epitacially grown GaAs thin films.

[1] S. Gharibzadeh et al., Adv. Energy Mater. 9(21), 1803699 (2019)

[2] V. Bermudez et al. 3, 466–475 (2018)

[3] K. Yoshikawa et al., *Nat. Energy*, 2, 17032 (2017).
[4] M. A. Green, *Prog. Photovoltaics* 20, 472 (2012)

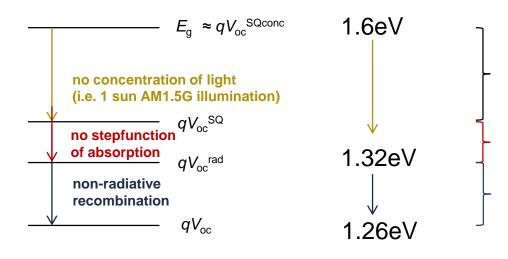
Promises of Perovskite Photovoltaics



High voltage

٠

Perovskites are typically polycrytalline layers but **almost as good** as the best known epitaxially grown semiconductors (GaAs)



~ 250 meV (depends slightly on band gap)

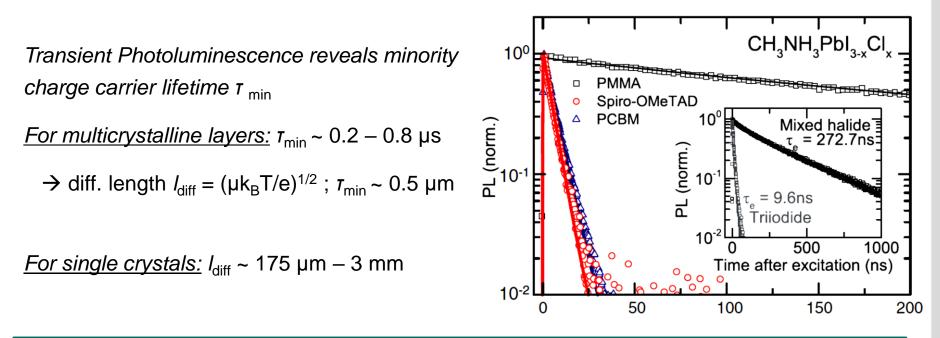
Negligible for direct semiconductors with small Urbach tail (few meV for perovskites)

The interesting part: Depends on e.g. trap density. **Minimizing non-radiative recombination is crucial!**

Promises of Perovskite Photovoltaics



High absorption coefficient + long diffusion length



high current generation

 $I_{\rm diff} > 1/\alpha \implies$

60

We can use layer thickness where all light with $E > E_g$ is absorbed and all charge carriers can be collected.

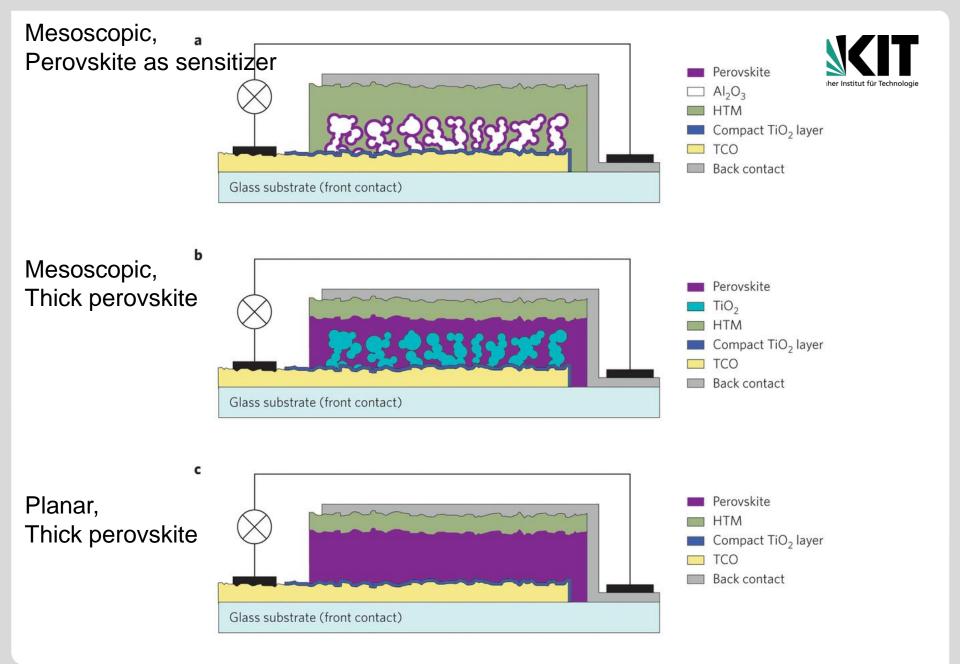
[1] S. Gharibzadeh et al., Adv. Energy Mater. 9(21), 1803699 (2019)
[2] V. Bermudez et al. 3, 466–475 (2018)

[3] K. Yoshikawa et al., *Nat. Energy*, 2, 17032 (2017).
[4] M. A. Green, *Prog. Photovoltaics* 20, 472 (2012)

Perovskite Photovoltaics

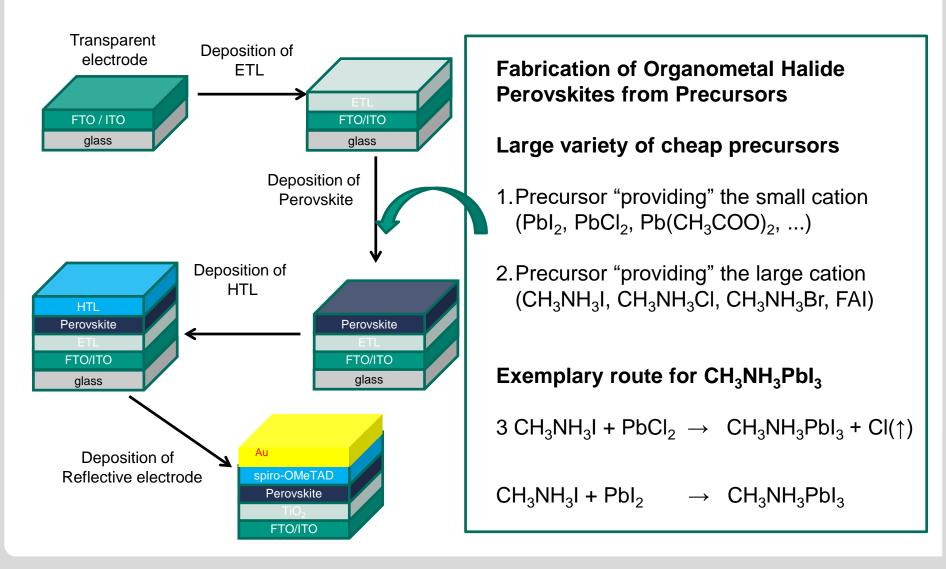


- Why perovskite materials?
- Working principle of perovskite solar cells
- Fabrication of perovskite solar cells
- Challenges and promises of perovskite PV
- Perovskite PV Research at KIT



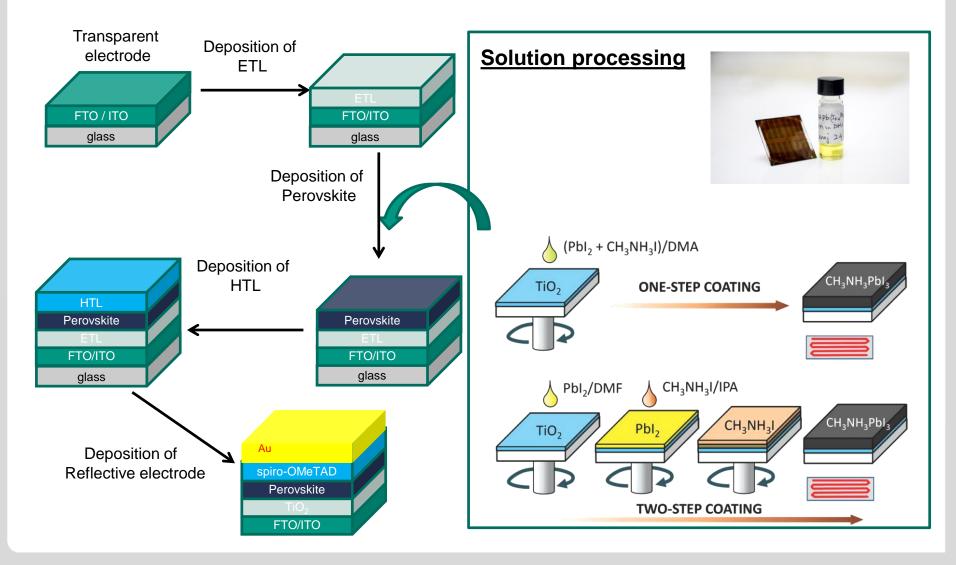
Fabrication of devices





Fabrication of devices

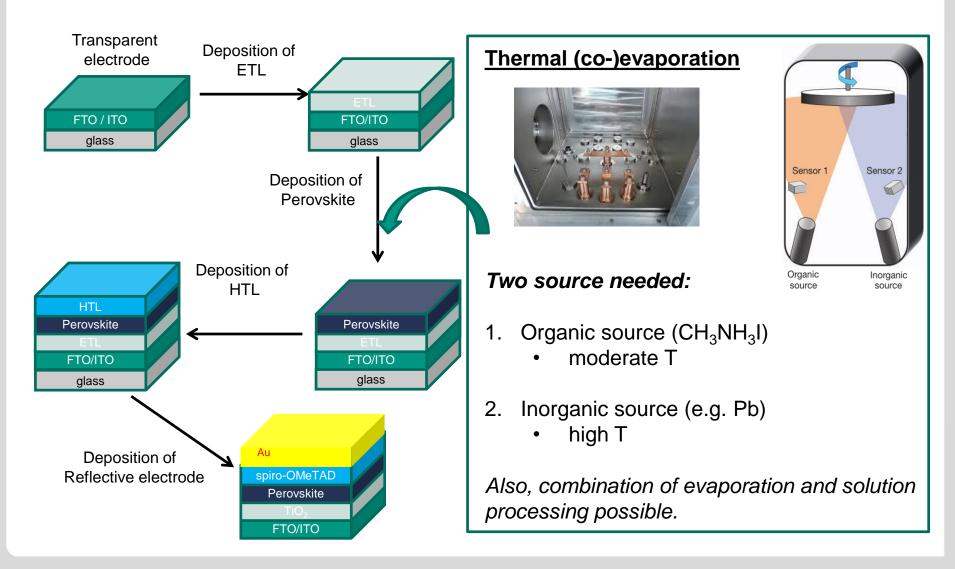




Source: J.-H. Im, H.-S. Kim, N.-G. Park, APL Mater. 2, 081510 (2014).

Fabrication of devices





Perovskite Photovoltaics



- Why perovskite materials?
- Working principle of perovskite solar cells
- Fabrication of perovskite solar cells
- Challenges and promises of perovskite PV
- Perovskite PV Research at KIT

Toxicity of Pb

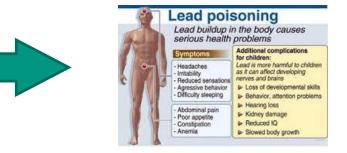
"Lead is a highly poisonous metal (whether inhaled or swallowed), affecting almost every organ and system in the body".

Today, all high efficient perovskite materials for PV contain Pb.

- one m2 of perovskite solar cell contains ~1,4 g of lead.
- a 75 kg person takes up 0.09 mg of lead by food per day.

Replacement for lead would be preferred.

(Restriction of Hazardous Substances Directive 2002/95/EC)



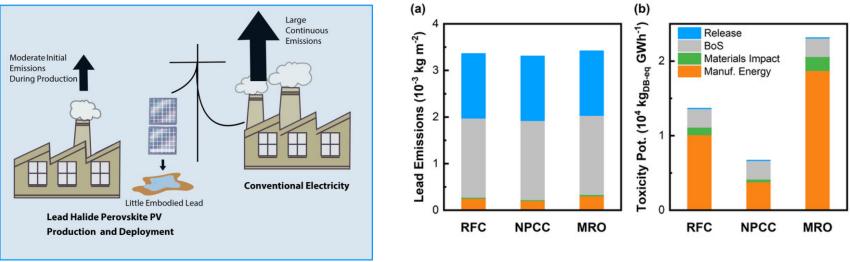






Toxicity of Pb

The discussion is complex: Compared to conventional electricity the emissions are low!



Lead missions associated with different categories of LHP-PV manufacturing and operation.

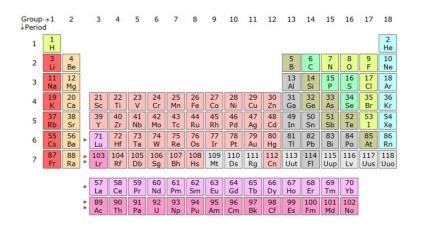
Looking at today energy mix, the majority of the emissions do not originate from the perovskite film, but the energy used during production.



Toxicity of Pb: Research on Pb-free perovskites

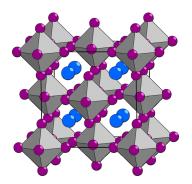
Sn / Ge based perovskites

- Same main group as Pb
- Devices were fabricated with acceptable PCE
- Problem: Oxidization, Sn²⁺ => Sn⁴⁺



Double perovskites

- Very young field (< 3 year)
- Few devices reported only
- $A_2BB'X_6$ with A+, X⁻ and B+x, B'+4-x
- Challenging thin-film deposition
- High stability
- High charge carrier lifetimes



1. Billen, P. et al. Comparative evaluation of lead emissions and toxicity potential in the life cycle of lead halide perovskite photovoltaics. Energy 166, 1089–1096 (2019).



Stability

A perovskite solar module is exposed to harsh outdoor conditions.



- 1. humidity/water
- 2. Light
- 3. Temperature
 - All of them are still critical today !

-Č-

Active layer Interlaver P P ITO 2 3 Glass P I Application Encapsulation glue/adhesive External contacts Busbars Connections

Encapsulation glass

Top contact

Stability Heat Light Water

U-Ö- 🜔

- Yet no complete understanding of degradation processes.
- Next to replacing Pb the stability is the major challenge for this technology.

٠

Promises of Perovskite Photovoltaics



Coloured Perovskite Photovoltaics



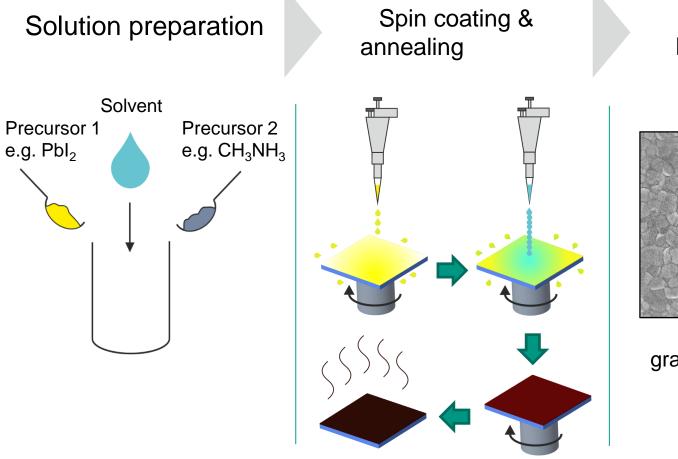




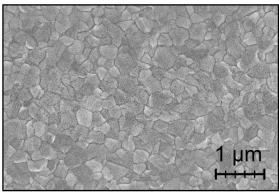
Promises of Perovskite Photovoltaics



Facile Processing of Perovskite Thin Films



Polycrystalline perovskite thin film

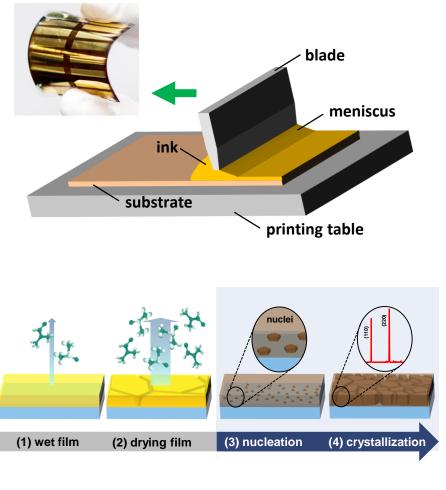


grain size: 100nm - 1µm

Promise: Coated and Printed Perovskite PV

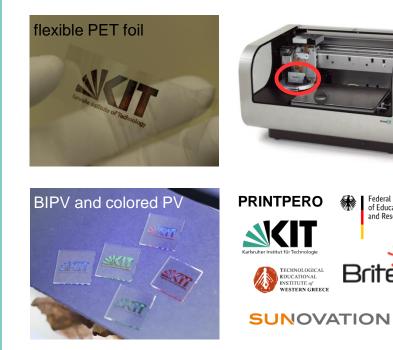


Federal Ministry of Education and Research



I. A. Howard et al. Adv. Mater. 31(15), 1602807 (2019)

Inkjet-printed perovskite optoelectronics



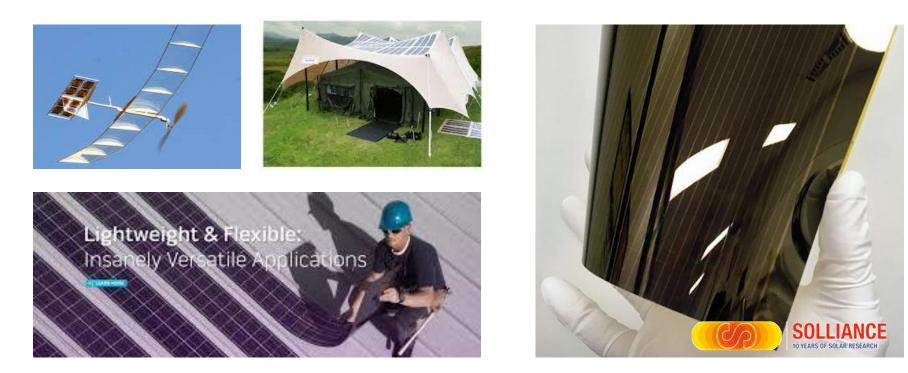
Publications:

H. Eggers et al., Adv. Energy Mater. – in press (2019) F. Mathies et al., ACS Appl. Energy Mat. 1(5), 1833 (2019) S. Schlißke et al., ACS Appl. Energy Mat. 2(1), 764 (2019) F. Mathies et al., J. Phys. Chem. A 4(48), 994209 (2016)

Promises of Perovskite Photovoltaics



Flexible and light weight

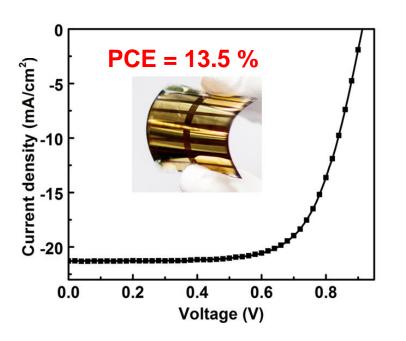


- Significant market for flexible and light weight solar cells
- Any application that does not allow for heavy "glass"

Promises of Perovskite Photovoltaics



Flexible and light weight



After 50 bending cycles up to 90% of the initial performance can be maintained.

- All processes must be compatible with the process temperature of the flexible substrate
- Solar cells needs to withstand bending
- Deposition more complex
- Advantage:
 - New applications
 - R2R fabrication

Perovskite Photovoltaics



from a product perspective

Pro	Con
High efficiency (>25%)	Material costs (perovskite is cheap, but what about the other layers?)
Flexible and light-weight	Long-term stability?!
Can be semitransparent → Multijunction PV with >30% efficiency possible!	Pb based perovskites are toxic, Pb-free (e.g Sn based) perovskites still show much lower efficiency
Solution processable (i.e. printable \rightarrow upscaling)	Upscalability and reproducibility still pose big challenge for mass production
Potentially cheap production!	

→ At the current stage, the most straight-forward application of perovskite PV is for multijunction solar cells (e.g. in combination with Si or CIGS), to push the efficiency beyond 30%. But research is still young and new details are discovered on a short timescale, hence other applications are realistic!



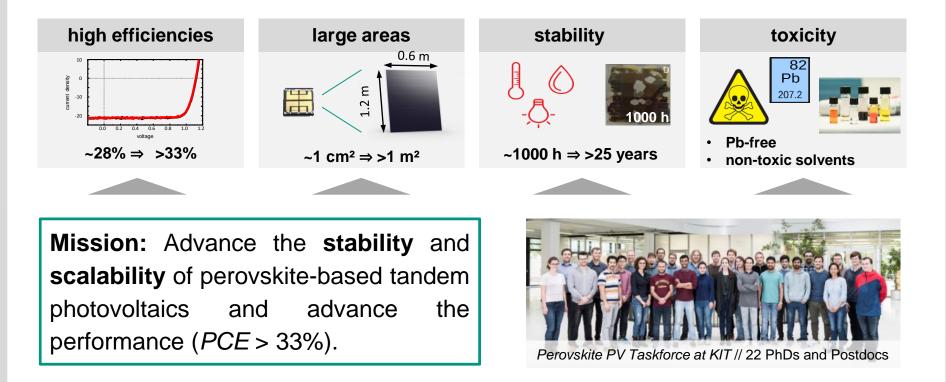




PEROVSKITE PHOTOVOLTAICS @KIT



Taskforce Perovskite Photovoltaics





Where to find us?

Thin-film Lab





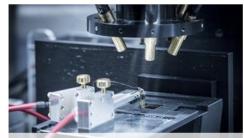
Thin Film Deposition



Perovskite Processing Plattform



Solar Simulator



Characterization in Inert Atmosph.



Where to find us?

UPSCALING LAB

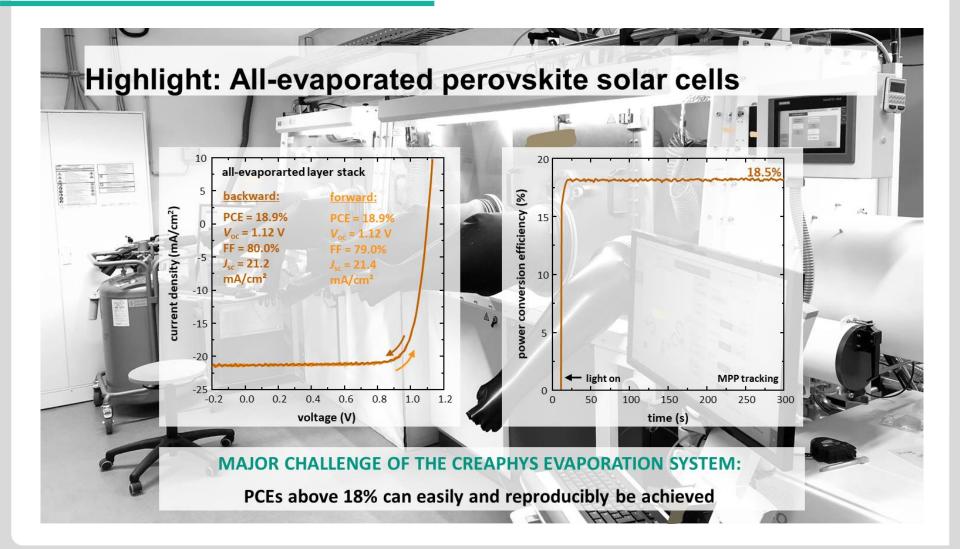




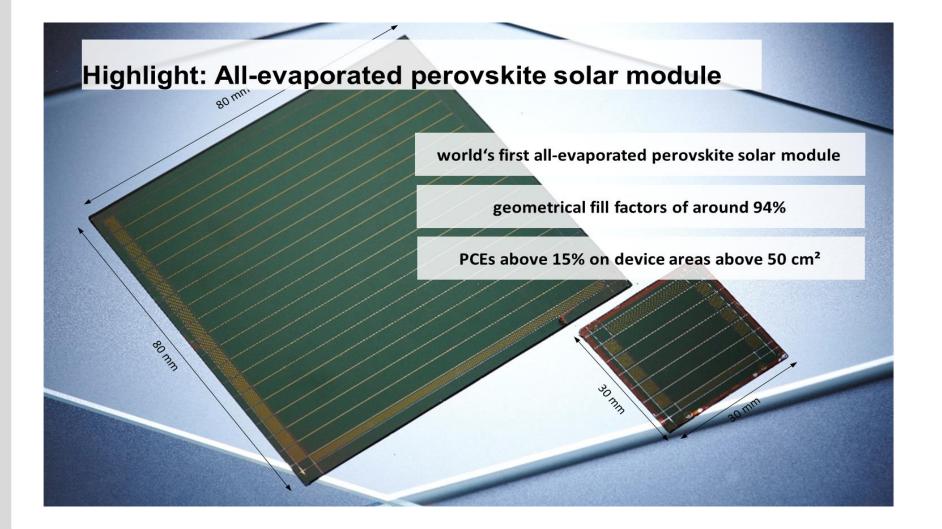


In Situ Characterization Platform





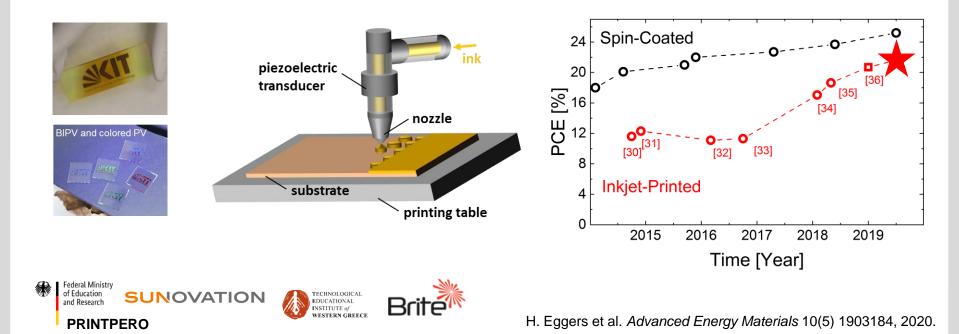






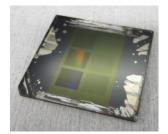
Highlights: Inkjet-Printed Perovskite Solar Cells

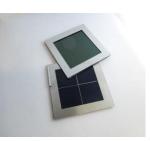
Focus KIT: Scalable deposition techniques (solution processed and evaporated)

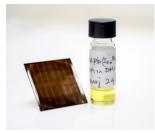


Perovskite Research at KIT

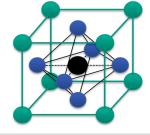








adamzadeh)



Highly dynamic and expanding field at LTI and IMT

20stDocs

Cross <u>stitute</u> "Tasforce Perovskite PV"

with

Possible topics

- Lead-free & perovskites ٠
- Perovskite Lasers (Yang Li) ٠
- EN Masterprojects !!! Contact: ulrich.paetzold@kit.edu Evaporated perovskite PV (Tobias Abzieher, Thom ٠
- Perovskite/Si tandem solar cells (Paul Faßl, Ihteaz Hossain) ٠
- Optics/Photonics in perovskite PV (Fabrizio Gota) .
- Inkjet-printed perovskites (Fabian Schackmar) •
- Laminated perovskite PV (Julie Roger) ٠
- Stability of perovskite materials and devices (Sara Moghadamzadeh, Roja Singh) ٠



Summary

Requirements for any new PV material ...



... wanting to compete with existing technologies:

- It must be competitive in (1) efficiency, (2) stability, and (3) yield.
- It should be **abundant** and **non-toxic**.
- It shall offer **low-cost fabrication**.
- It would be nice to offer **extra features/added values**.

Requirements for any new PV material ...



... wanting to compete with existing technologies:

Requirement	OPV	Perovskite PV
High-efficiency	17.4% (however, strong improvements recently)	>25%
Stability	Still needs to be investigated in more detail for new materials	Promising results in the last 1-2 years, but still the most pressing issue
High Yield	Moderate, good in low-light	Yes
Abundance	Depends on material	Yes
Non-toxic	Yes	No
Low-cost fabrication	Potentially, but depends on used material	Yes, but upscaling is still an issue
Flexible	Yes	To some extent
Tunability of Eg	To some extent	Yes



Questions ?



Self-Test

- What does "organic" mean ?
- What are the main differences between an organic seminconductor and a classical semiconductor ?
- Name some unique features of organic solar cells ?
- What are the main features of perovskite PV to allow high efficiencies?
- What are the main issues with perovskite PV nowadays?
- What are the main requirements for any new PV material?