ZAE Bayern e.V. *i-MEET* @ FAU EnCN @ FAU

How to stabilize organic solar cells beyond 100.000 hrs of operational stability






C. J. Brabec

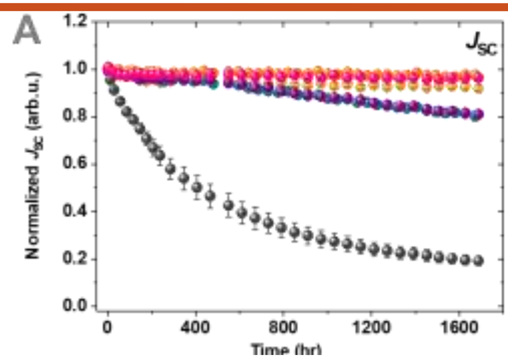
ISOS 2018, Suzhou, 22nd of October

- Tobias Unruh, Joh. Will

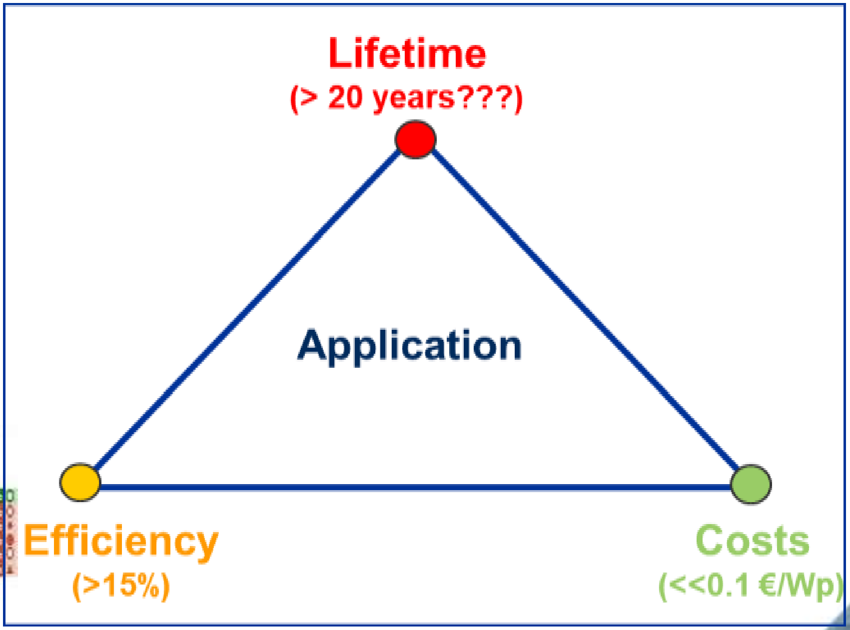
motivation: *importance of* PV „key performance indicators“

Motivation
Technology
Outlook
Conclusion

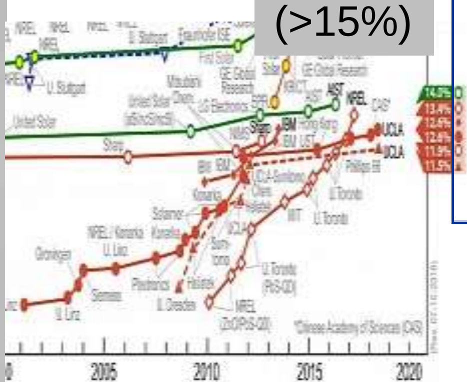
➢ **The magic triangle!**



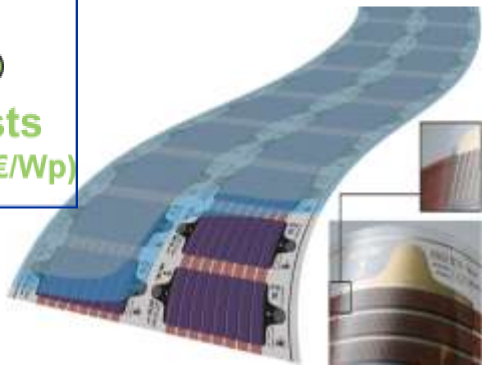
X. Du et al, Joule, 2018



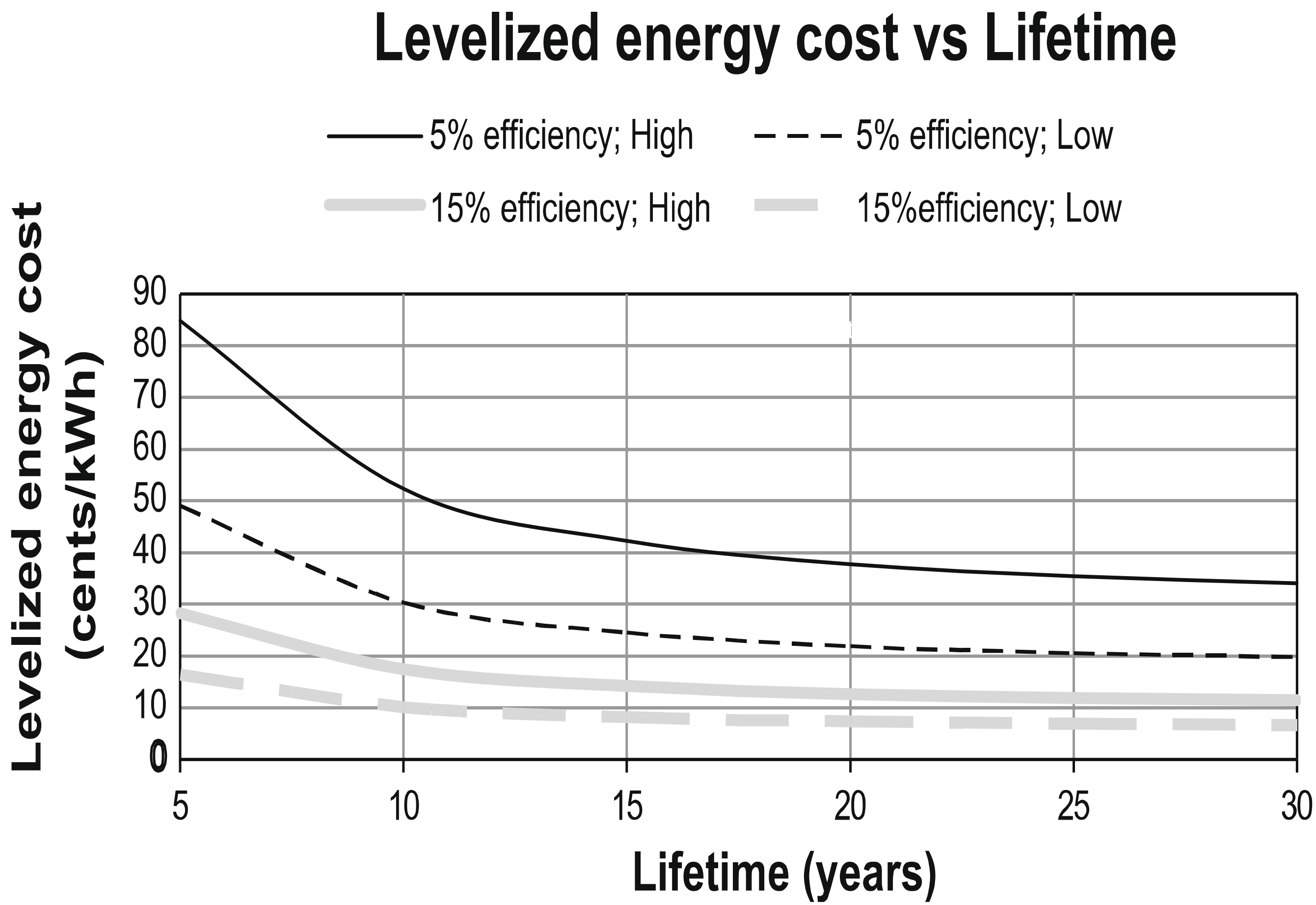
source: NREL chart



Andersen et al., EES 2014



- **Lifetime impacts costs, quite similar to efficiency!**



Espinosa et al., Energy Environ. Sci., 2014, 7, 855
Kalowekamo et al., Solar Energy 83 (2009) 1224

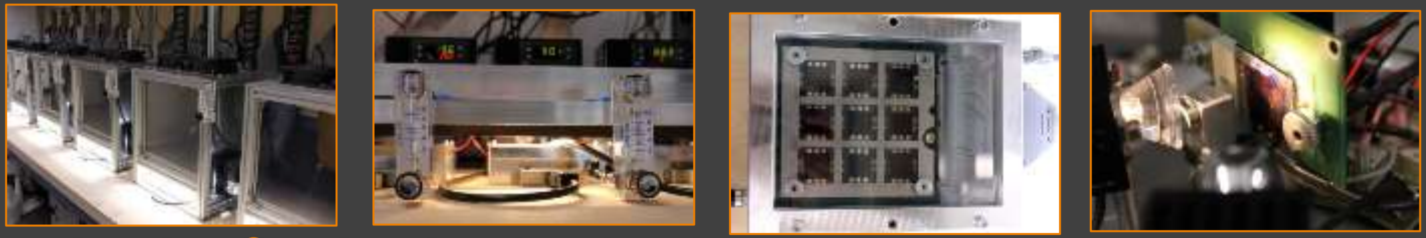
①	Introduction:	1st chapter	Measuring Degradation
②	Overview:	Next chapter	**Fundamental** Aspects
③	Technology:	Next chapter	Microstructure Degradation
④	Technology:	Next chapter	Chemical Degradation
⑤	Technology:	Next chapter	Interface Degradation
⑥	Technology:	Next chapter	Spectrally Induced Degradation
⑦	Outlook:		Accelerated Degradtion - towards 100.000 hrs operation

technology: *High Throughput Testing of Devices*

- Motivation
- Technology-High Throughput
- Outlook
- Conclusion

➢ Statistical Lifetime Testing @ i-MEET

Photo , Thermal & Environmental Degradation



Metal halide Lamps | Dark thermal Testing | <1ppm O_2 | Characterization

- 1200 solar cells in parallel
- Jsc, Voc & mpp monitoring
- In-situ characterization

- T control from 0 C to 100 C
- 0.1 – 2 suns, variable spectra
- Atmospheric control (N_2, O_2, H_2O, sulfur, ..)

technology: *High Throughput Testing of Devices*

➢ Accelerated Lifetime Testing @ i-MEET

Xtreme Accelerated (X-ALT) Photodegradation

3 Degradation setups | High irradiance up to 700 se | N_2 | Active cell temperature control

- 1 – 96 Solar Cells in parallel
- 0.1 – 700 suns
- In-situ jV characterization

- T control from 0 C to 1000 C
- Variable spectra
- Atmospheric control (N_2, O_2, H_2O, sulfur, ..)

technology: *High Throughput Testing of Devices*

Motivation

Technology-
High
Throughput

Outlook

Conclusion

➢ **Statistical (> 1000 devices in parallel) Lifetime Testing in Detail**

Temperature ovens

(Current degradation of layers)

Cooled LED Setup

Metal halide setup

White-light LED setup and in-situ environ. & temp. degradatio

ZAE BAYERN

ENERGIE CAMPUS NÜRNBERG

technology: *High Throughput Testing of Devices*

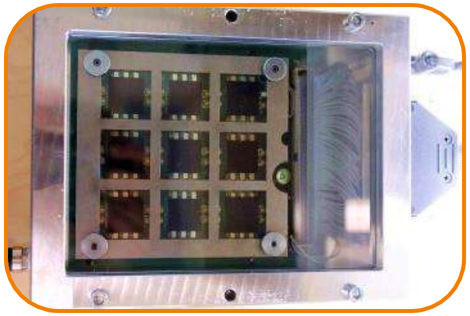
- Why **Statistical** Lifetime Testing – why does it take 100s of samples?

Motivation

Technology- High Throughput

Outlook

Conclusion

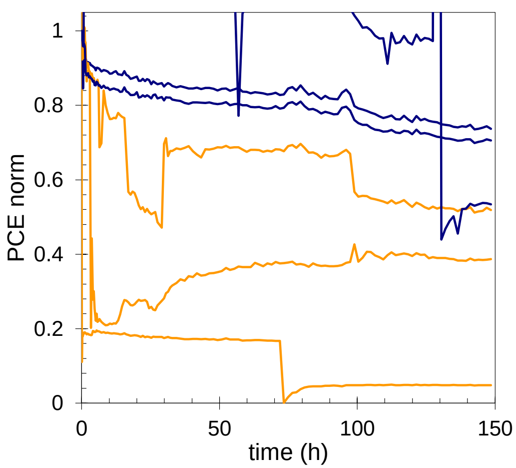


9 substrates per chamber

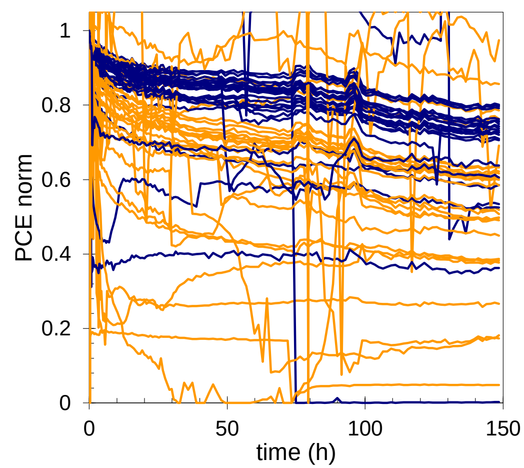
12 LED chambers

12 metal halide chambers

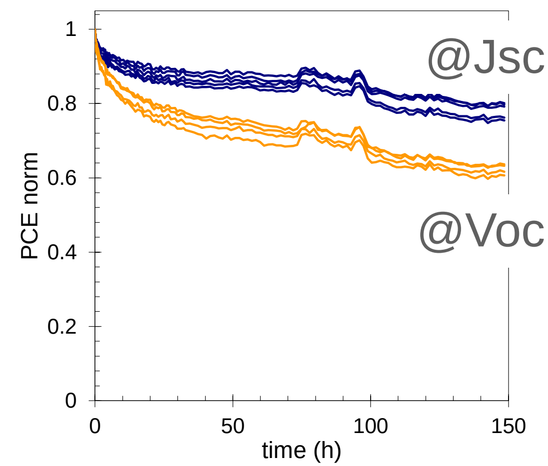
1 substrate, 6 devices



9 substrates, 54 devices



selected devices show trend



Motivation

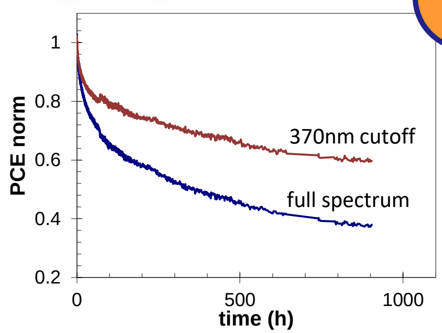
Technology

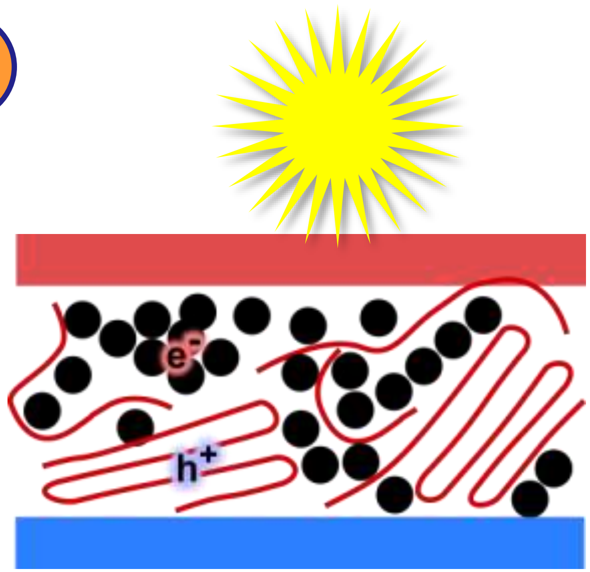
Outlook

Conclusion

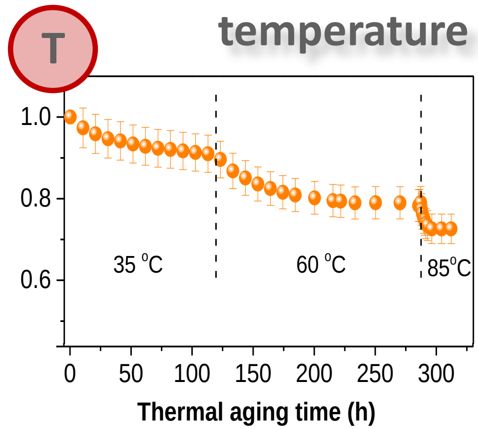
➢ Why precisely **controlling** external conditions

light spectrum

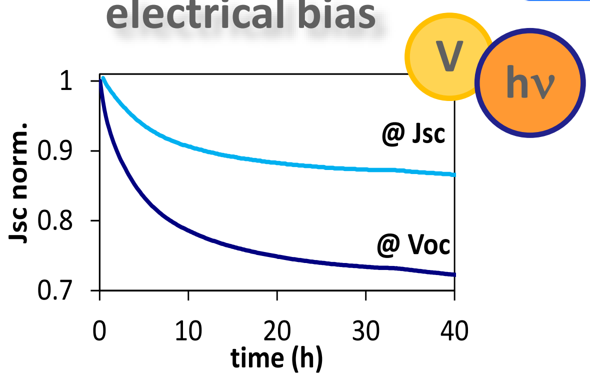




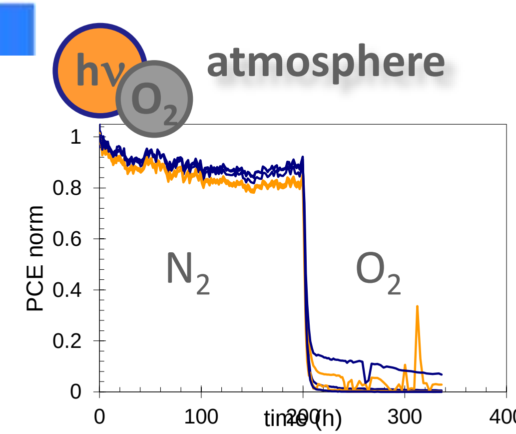
temperature



electrical bias



atmosphere



technology: *High Throughput Testing of Devices*

Motivation

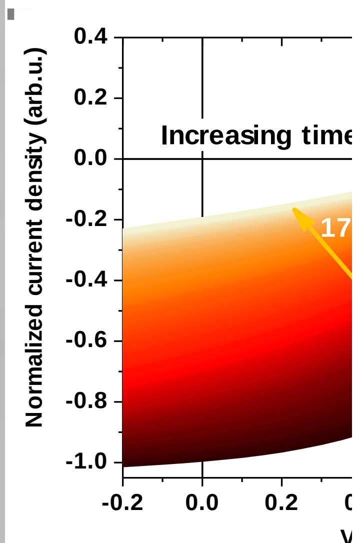
Technology-High Throughput

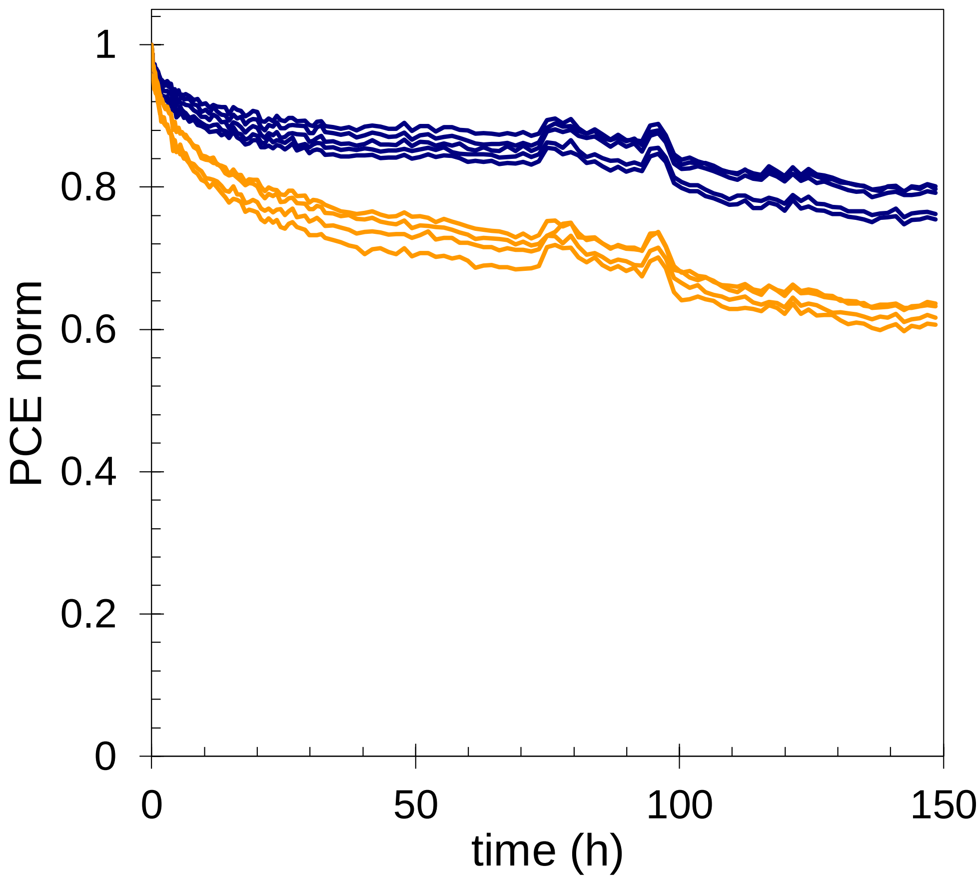
Outlook

Conclusion

➢ When can you **trust** such degradation data to **identify mechanisms**?

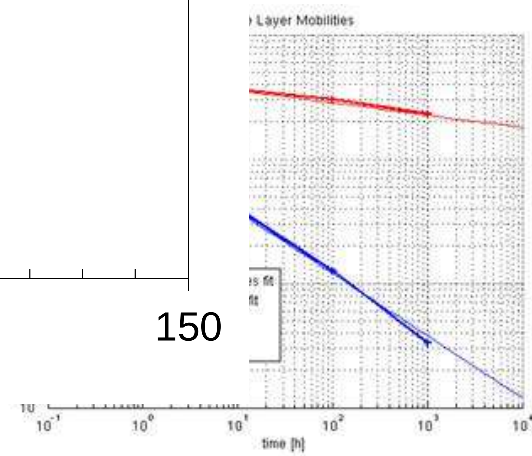
(1) measure





material

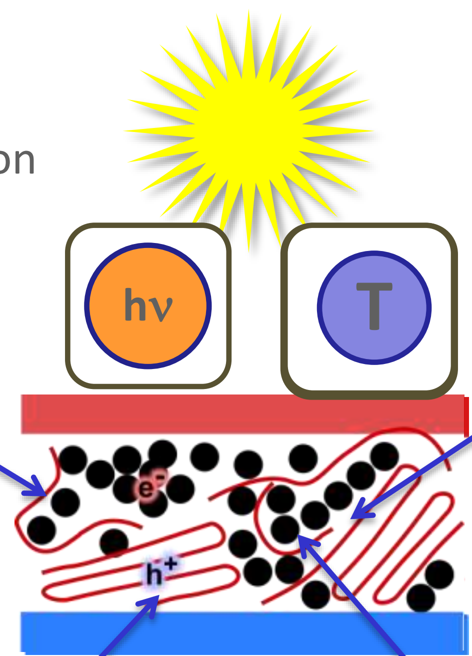
ters vs. time



technology: *Photodegradation Mechanisms*

➢ **What are the failure mechanisms of solar cells under operation?**

Spectral degradation
- breaking of conjugation
- interface degradation
- light soaking
- dimerization



Chemical degradation
- breaking of conjugation
- sidechain splitting
- Impurity doping

Interface degradation
- chemical reactions
- delamination
- metal diffusion
- corrosion

Microstructure degradation
- burn-in
- demixing
- re-crystallization
- molecular diffusion

① Introduction: 1st chapter Measuring Degradation

② Overview: Next chapter Fundamental Aspects

③ Technology: Next chapter **Microstructure** Degradation

④ Technology: Next chapter Chemical Degradation

⑤ Technology: Next chapter Interface Degradation

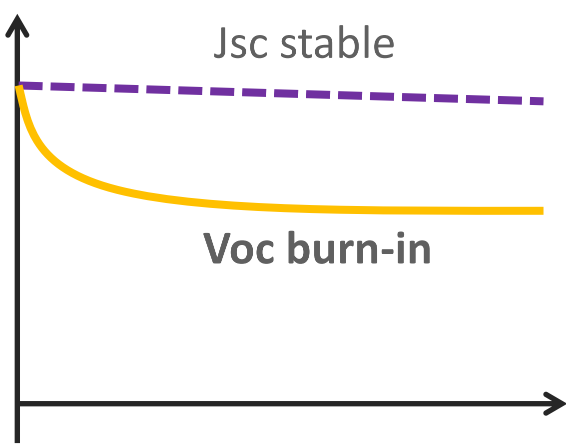
⑥ Technology: Next chapter Spectrally Induced Degradation

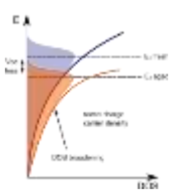
⑦ Outlook: Accelerated Degradtion - towards 100.000 hrs operation

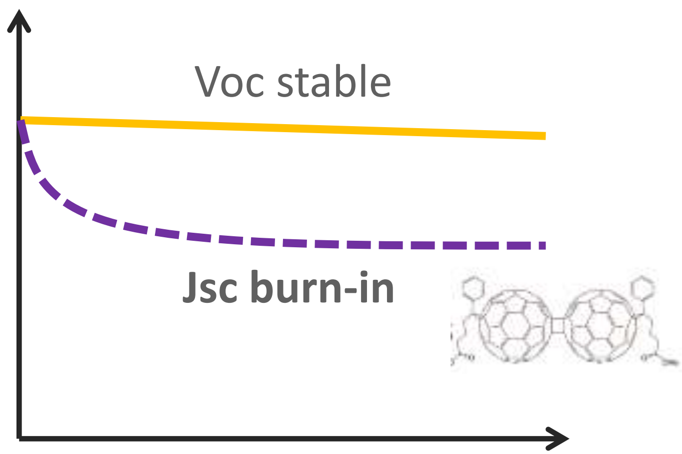
- **„Burn-In“ – currently a dominant degradation mechanism**

amorphous Polymers
-> good intermixing
-> insensitive to dimerization
-> sensitive to **energetic disorder**

crystalline Polymers
-> pure domains reduce recombination
-> insensitive to energetic disorder
-> tend to **fullerene dimerization**





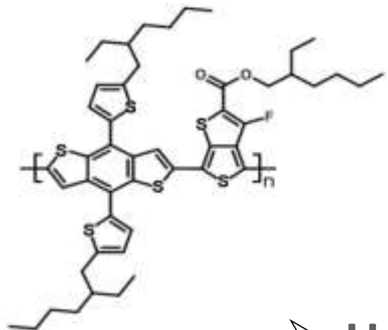


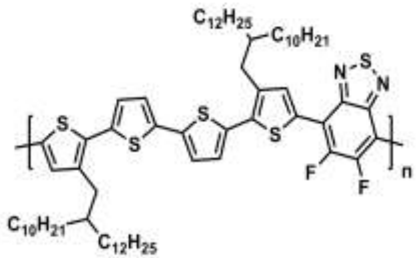
in 2016 : we found that many high performance systems are demixing during operation – phase separation!

technology: *materials, formulation & microstructure*

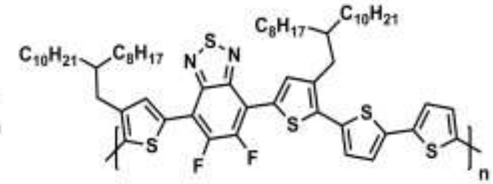
- Motivation
- Technology
- Outlook
- Conclusion

➢ Some of the +10 % materials can show **instabilities!**



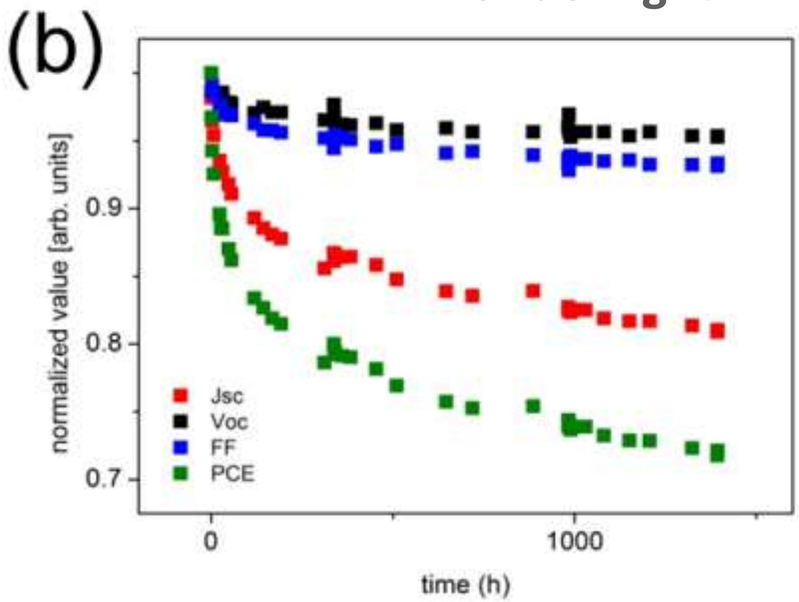


FBT-Th_4(1,4)

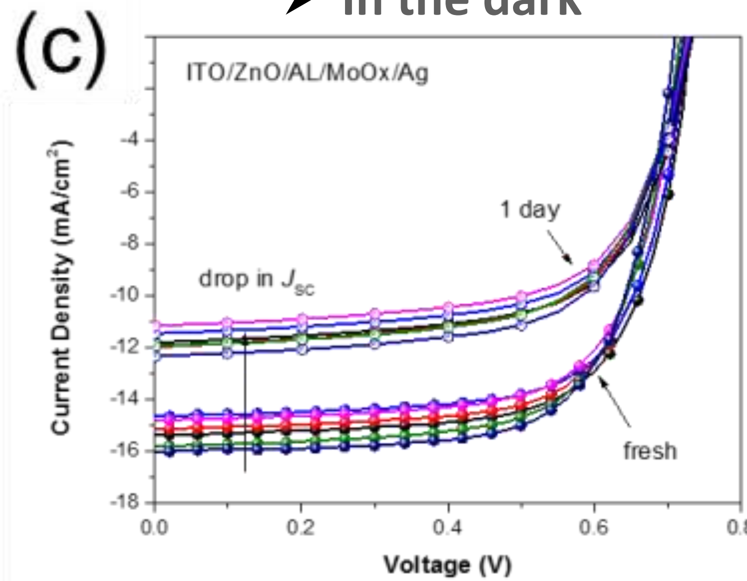


PffBT4T-2OD

➢ Under light



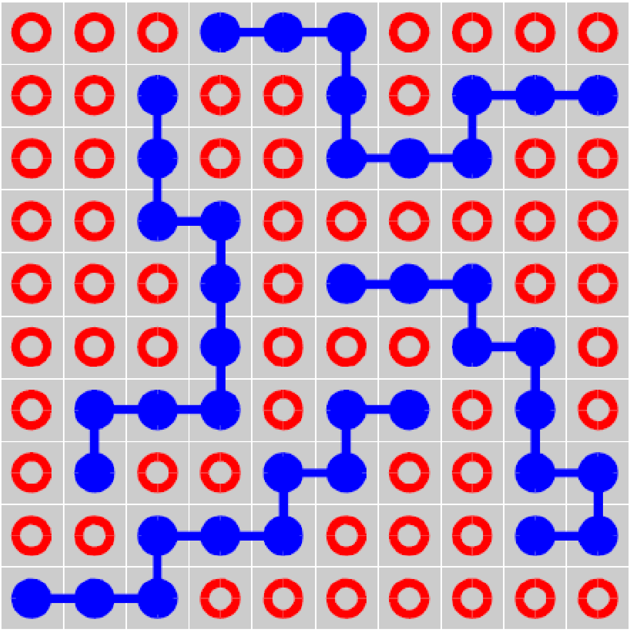
➢ In the dark



Ning Li, … & CJB, *Energy Environ. Sci.*, 2016.
Ning Li, … & CJB, Nature Communication 2017

➢ **Predicting miscibility in TD limit** requires two parameters

- Spinodal demixing – depends on mixing ratio and mol. weight
- Enthalpic demixig - positive χ_{12} causes demixing



$$\Delta G_m = RT\left[\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2\right]$$

Entropic contribution causes mixing

Enthalpic contribution χ_{12} can cause demixing

Determination of χ_{12} is essential!
Experimental? **Theoretical?**

technology: *predicting miscibility*

- **Calculation of χ_{12} and miscbility – towards a novel Figure of Merit (FoM)**

Implementation of ANN & ML

Technology

Outlook

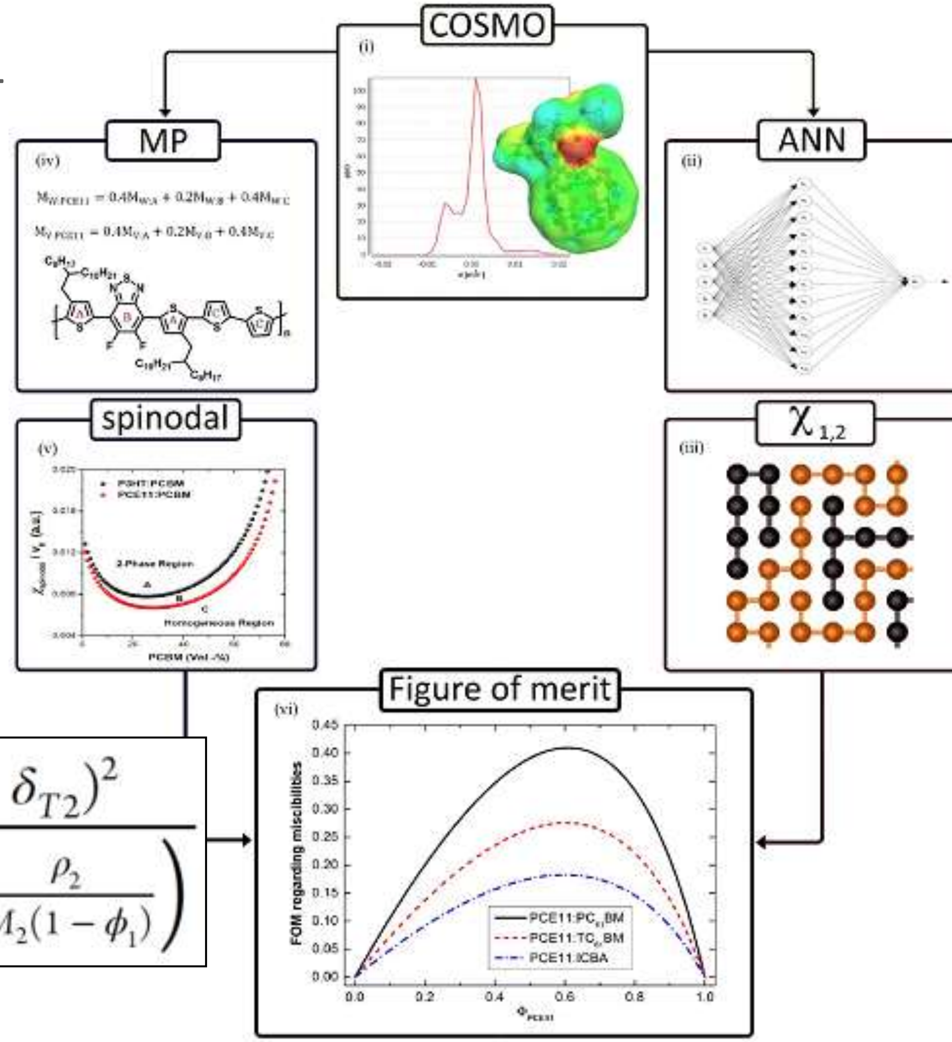
Conclusion

$$(\delta)^2 = (\delta_D)^2 + (\delta_P)^2 + (\delta_H)^2$$

$$\chi_{1,2} = \frac{v_{1,2}}{RT}(\delta_{T1} - \delta_{T2})^2$$

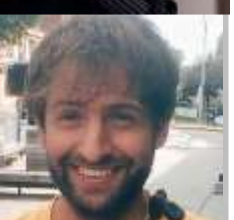
$$\chi_{\text{Spinodal}} = \frac{v_{1,2}}{2}\left(\frac{\rho_1}{M_1\phi_1} + \frac{\rho_2}{M_2(1-\phi_1)}\right)$$

$$\text{FoM} = \frac{\chi_{1,2}}{\chi_{\text{Spinodal}}} = \frac{2}{RT}\frac{(\delta_{T1} - \delta_{T2})^2}{\left(\frac{\rho_1}{M_1\phi_1} + \frac{\rho_2}{M_2(1-\phi_1)}\right)}$$

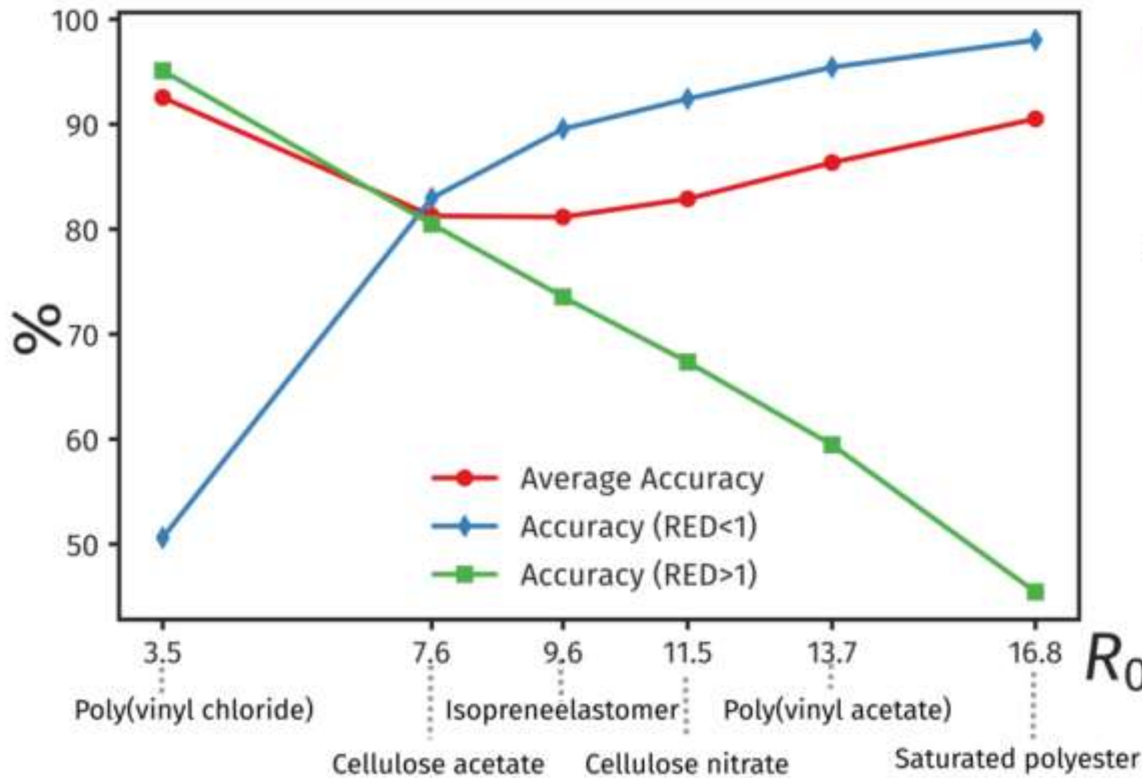


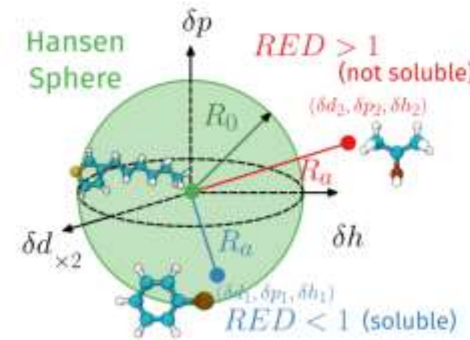
J. Perea … & CJB, Handbook of Conjugated Polymers, 2018
J. Perea … & CJB, Ecnyclopedia of Phy Org Chemistry, Wiley, 2017
J. Perea … & CJB, JPC-B 2016
J. Perea … & CJB, JPC-C 2017

technology: *Prediction of HSP, miscibility & stability of blends*



- **Calculation time was significantly shortened with the help of Machine Learning (Gaussian Prediction – gpHSP method)**
- **< 1 second calculation time when using partial information (FP) instead of QC calculations**





technology: *Prediction of HSP, miscibility & stability of blends*

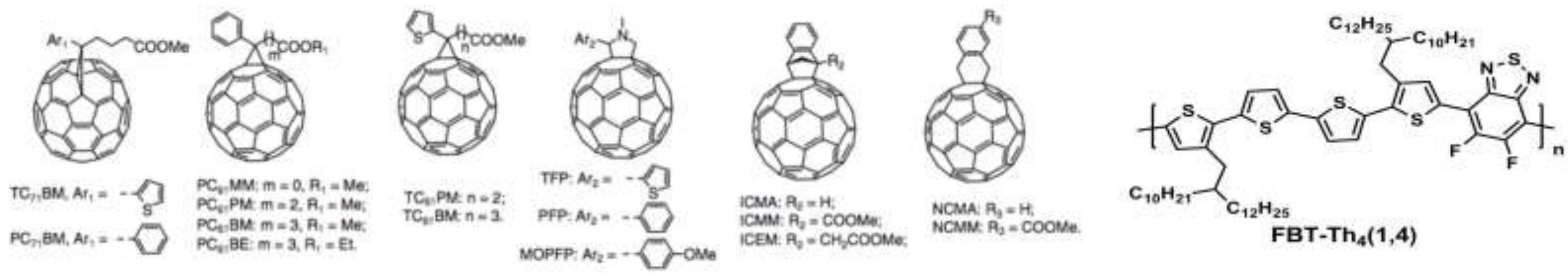
Motivation

Technology-
High
Throughput

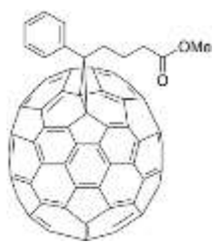
Outlook

Conclusion

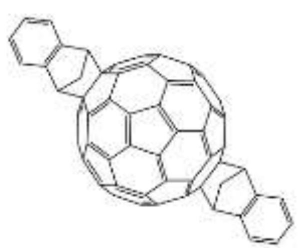
- **Microstructure FoM – allows to predict burn-in and stability**

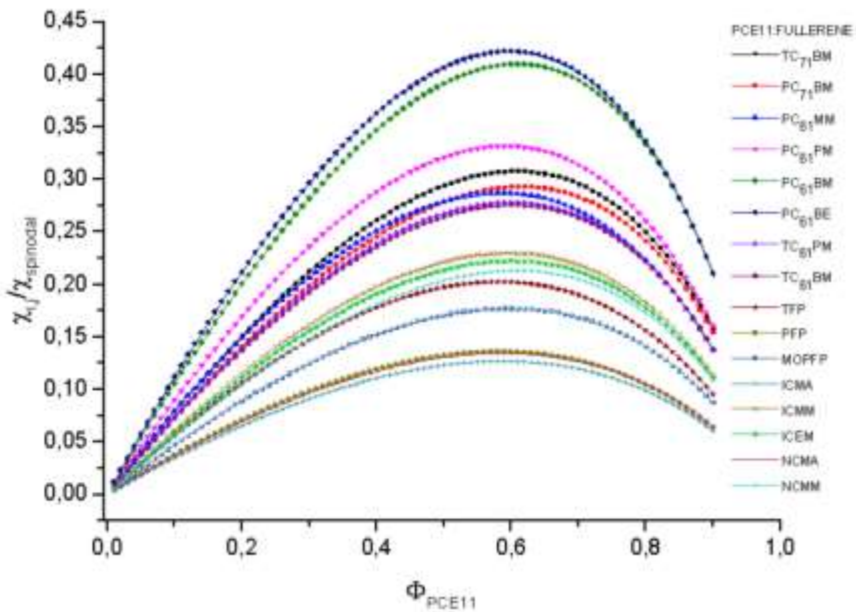


$PC_{71}BM$

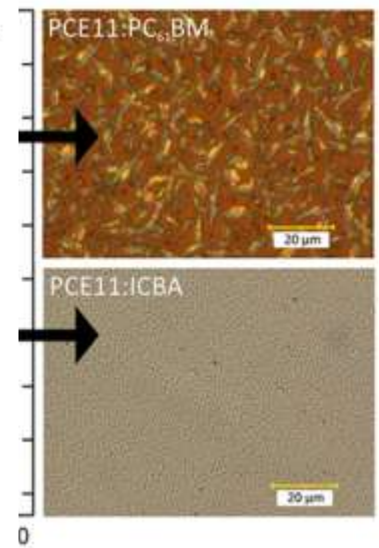


ICBA





After 72 h at 80° C

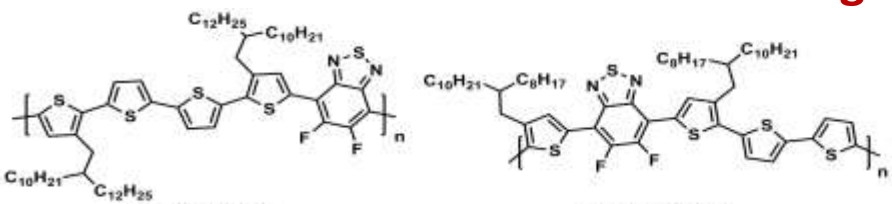


J. Perera … & CJB, JPC-C 2017

J. Perea …. & CJB, JPC-B 2016

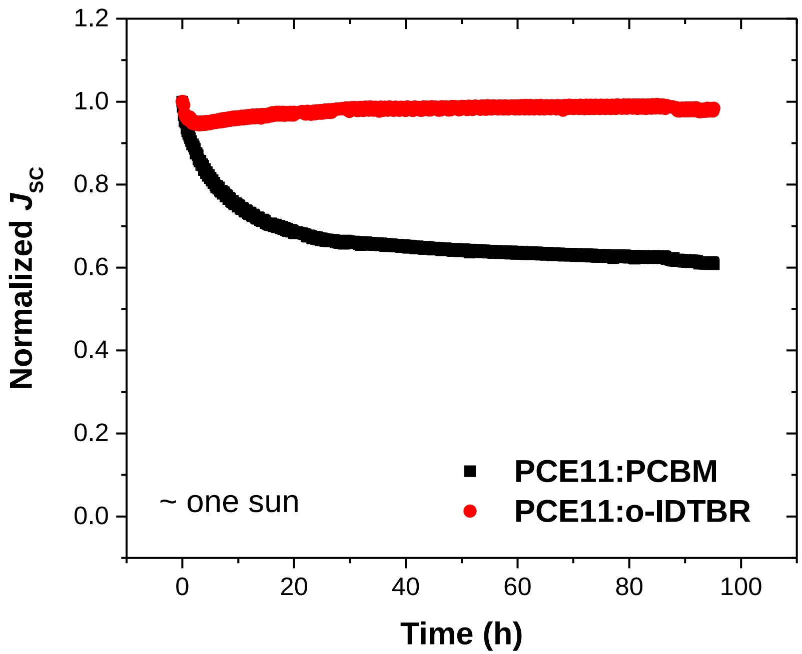
technology: *Prediction of HSP, miscibility & stability of blends*

- Having learned that „demixing“ is the major cause for **burn-in**
  - (1) exclusively use **miscible systems**
  - (2) learn to **stabilize** instable microstructures – **e.g. vitrification**

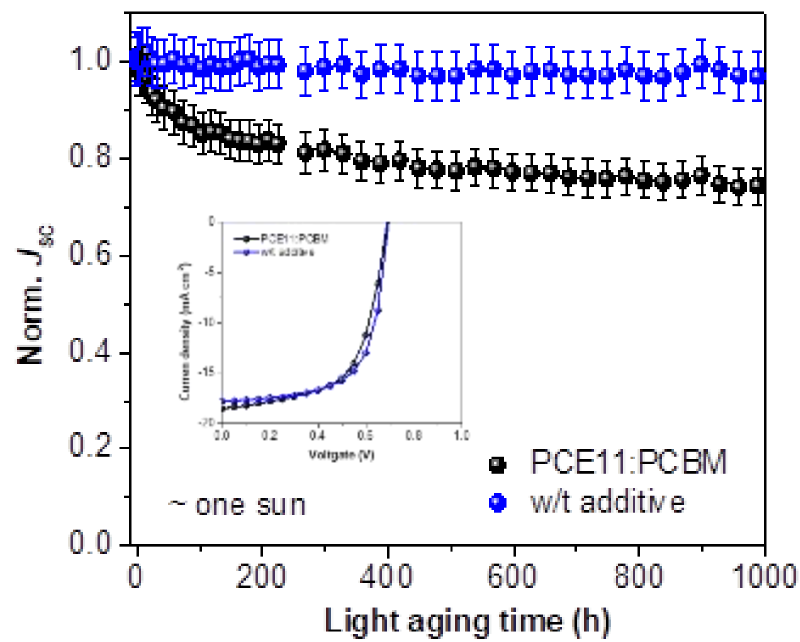


FBT-Th$_4$(1,4)   PffBT4T-2OD

(1)

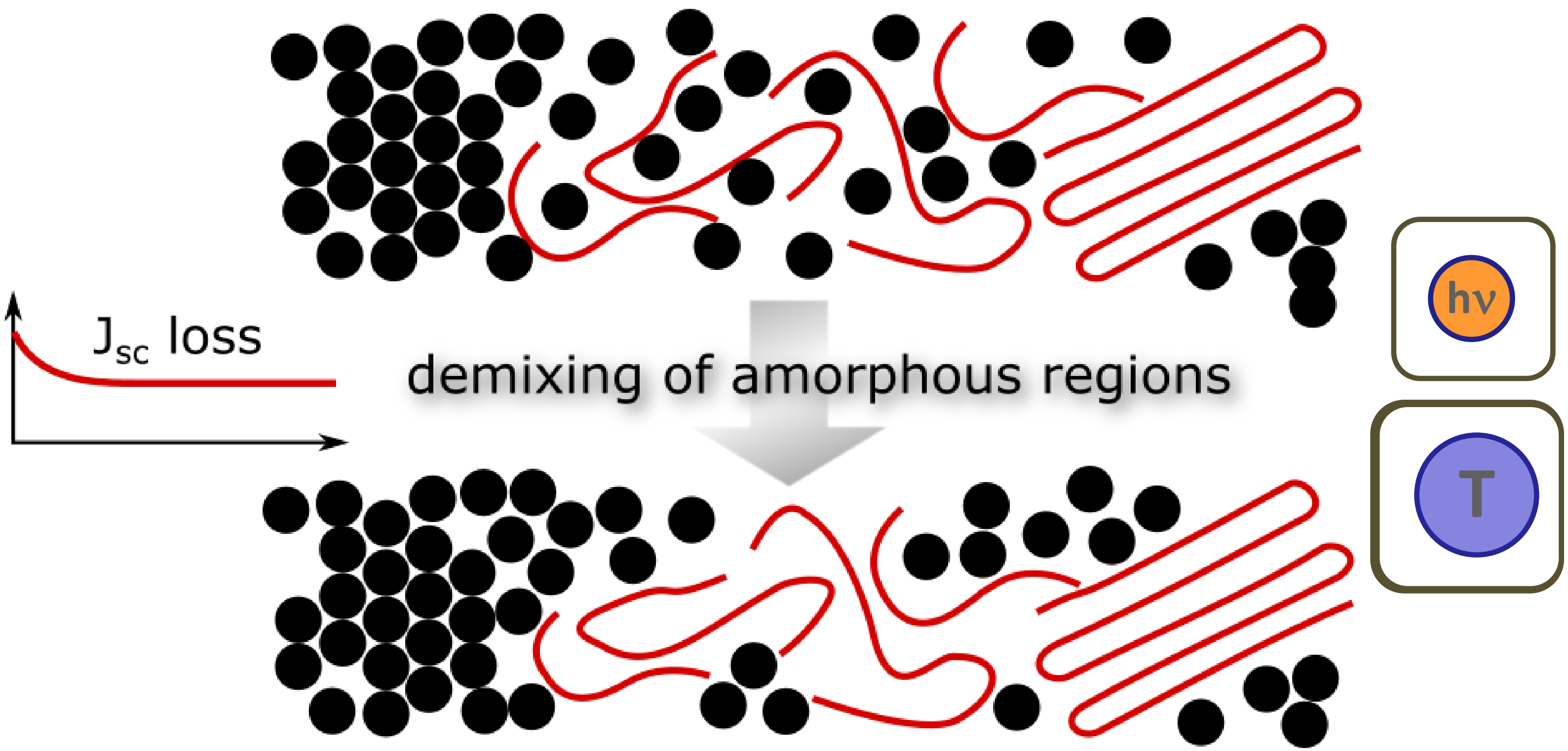


(2)



Burn-in in the dark*: the role of microstructure*

- **Summary**: demixing of **amorphous BHJ regime** causes burn-in
- **Statement**: **developing strategies to stabilize** instable microstructures



①	Introduction:	1st chapter	Measuring Degradation
②	Overview:	Next chapter	Fundamental Aspects
③	Technology:	Next chapter	Microstructure Degradation
④	Technology:	Next chapter	**Chemical Degradation**
⑤	Technology:	Next chapter	Interface Degradation
⑥	Technology:	Next chapter	Spectrally Induced Degradation
⑦	Outlook:		Accelerated Degradtion - towards 100.000 hrs operation

Chemical Degradation*: ITIC derivatives*

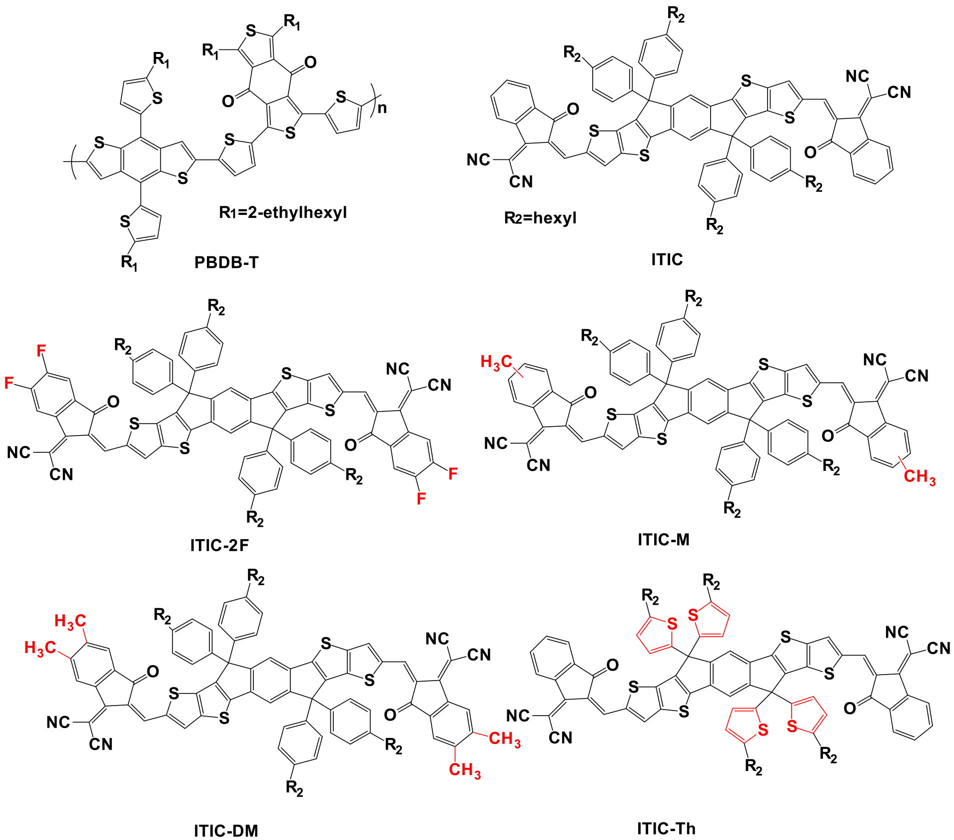
Motivation

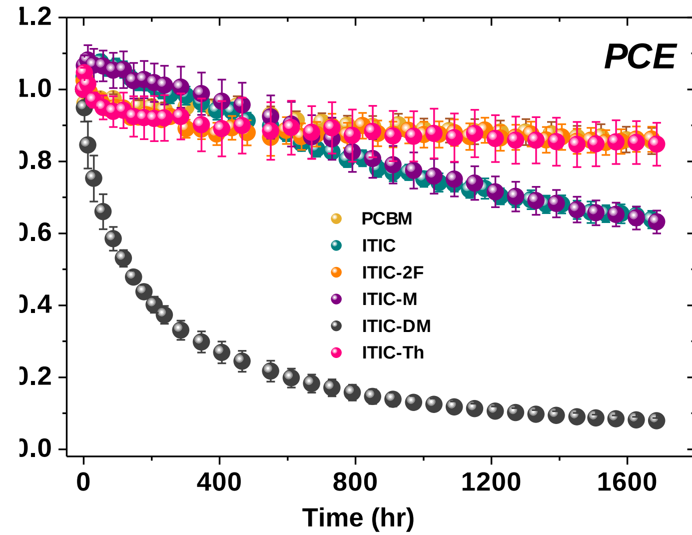
Technology

Outlook

Conclusion

- **5 ITIC variations**: **stability** with PBDB-T
- **Efficiencies** of various combinations: about **8 – 10 %**
- **ITIC-DM** has a totally **different trend – why?**





X. Du et al, Joule 2018

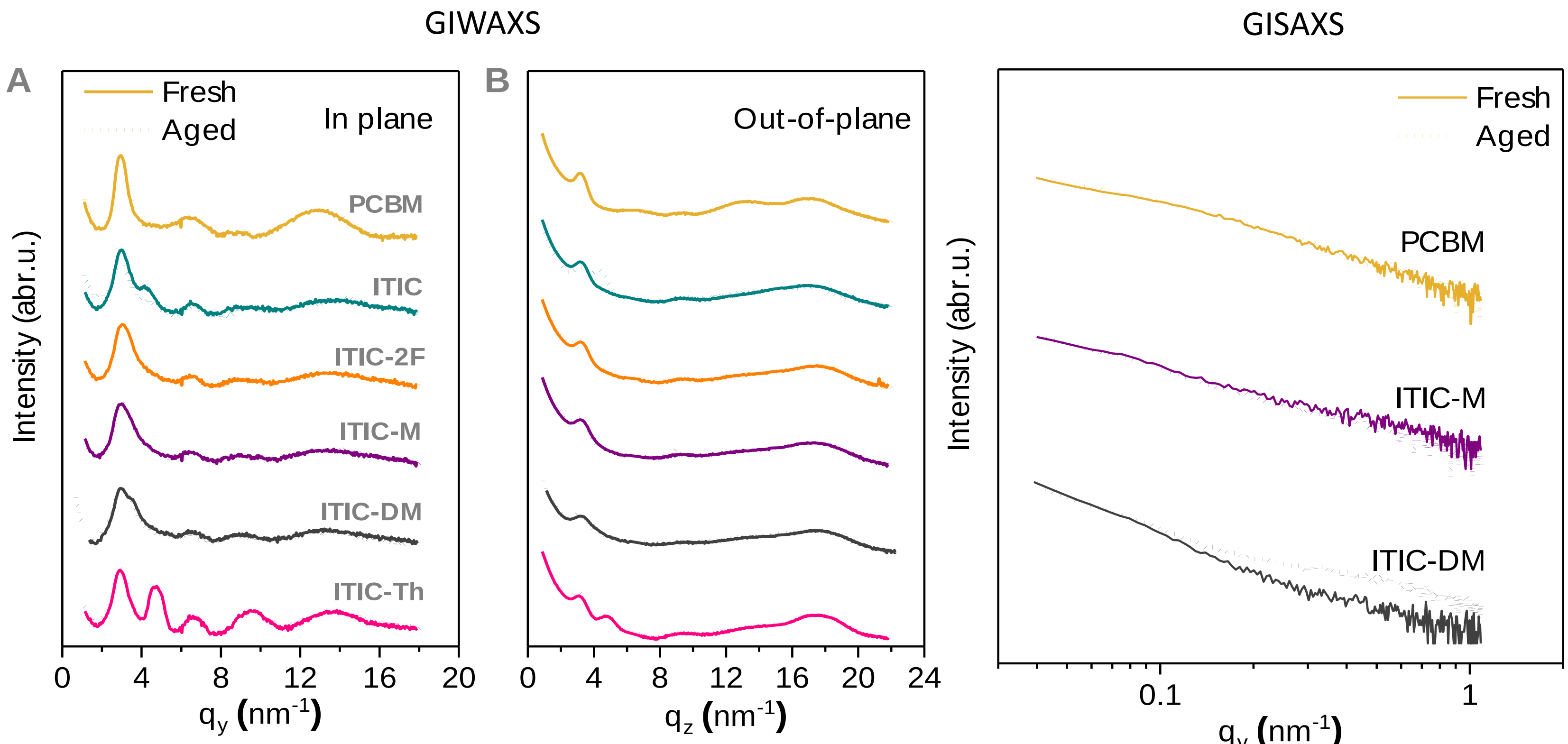
ENERGIE CAMPUS NÜRNBERG

ZAE BAYERN

Chemical Degradation: *ITIC derivatives*

ITIC variations show **different stability trends**: is this **microstructure?**

- **Microstructure changes** for **PBDB-T/ITIC-DM –** demixing in the amorphous regime



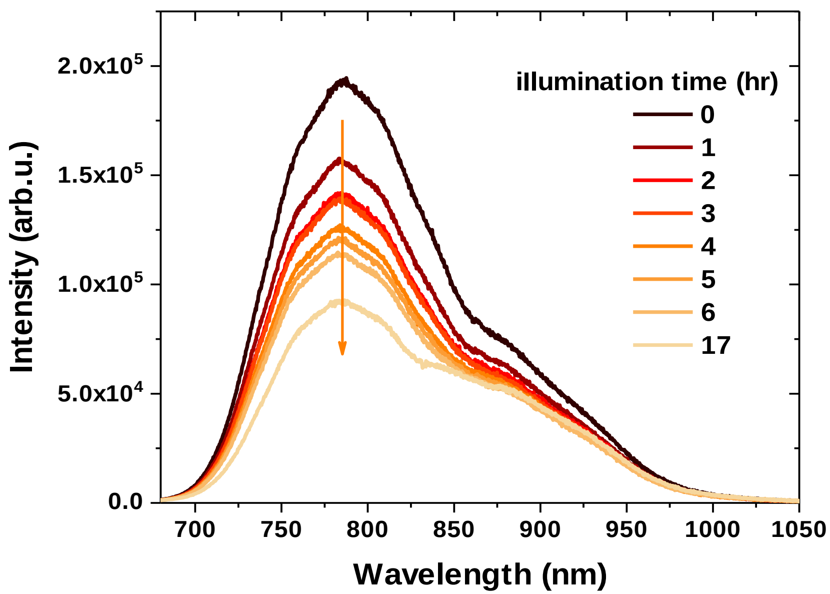
Aging under N2, 1 sun conditions, 500 hrs

X. Du et al, Joule 2018

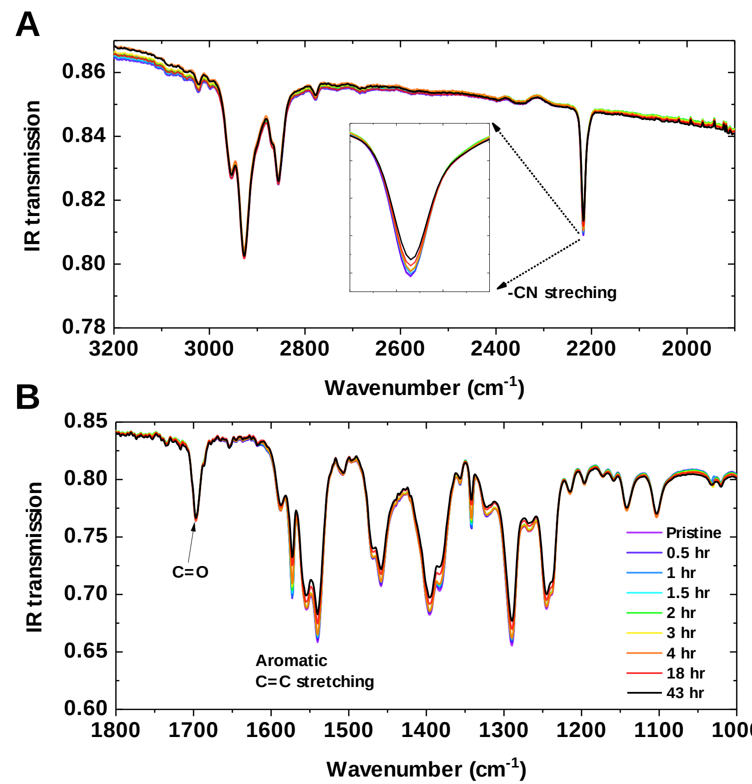
Chemical Degradation: *ITIC derivatives*

Is **demixing explaining all observiations? NO!**

- **Surprisingly - ITIC-DM** is unstable under illumination!
- **No photooxidation!** We observe **photodegradation** of the endgroup

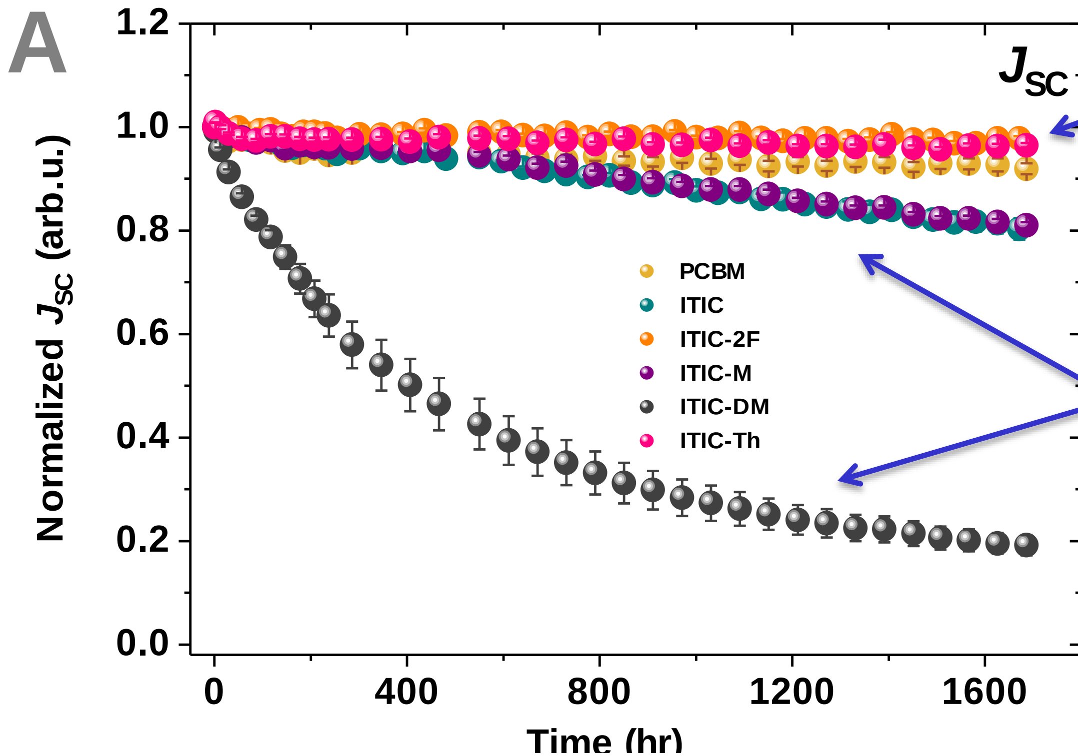


Aging under N2, 1 sun conditions, 20 hrs



Chemical Degradation: *ITIC derivatives*

- **Minisummary**:
  - **burn-in** (due to demixing) has to flatten out
  - If not – other effects may be dominant



This is a minor burn-in due to demixing

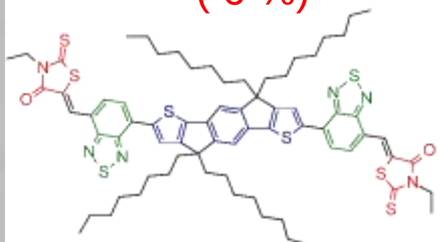
This is something else – in this case, probably **photochemical degradation**

①	Introduction:	1st chapter	Measuring Degradation
②	Overview:	Next chapter	Fundamental Aspects
③	**Technology:**	Next chapter	Microstructure Degradation
④	Technology:	Next chapter	Chemical Degradation
⑤	Technology:	Next chapter	Interface Degradation
⑥	Technology:	Next chapter	**Spectrally Induced Degradation**
⑦	Outlook:		Accelerated Degradtion - towards 100.000 hrs operation

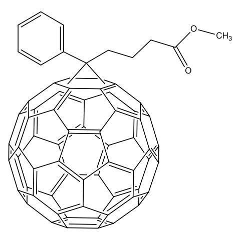
spectral degradation: *UV sensitivity*

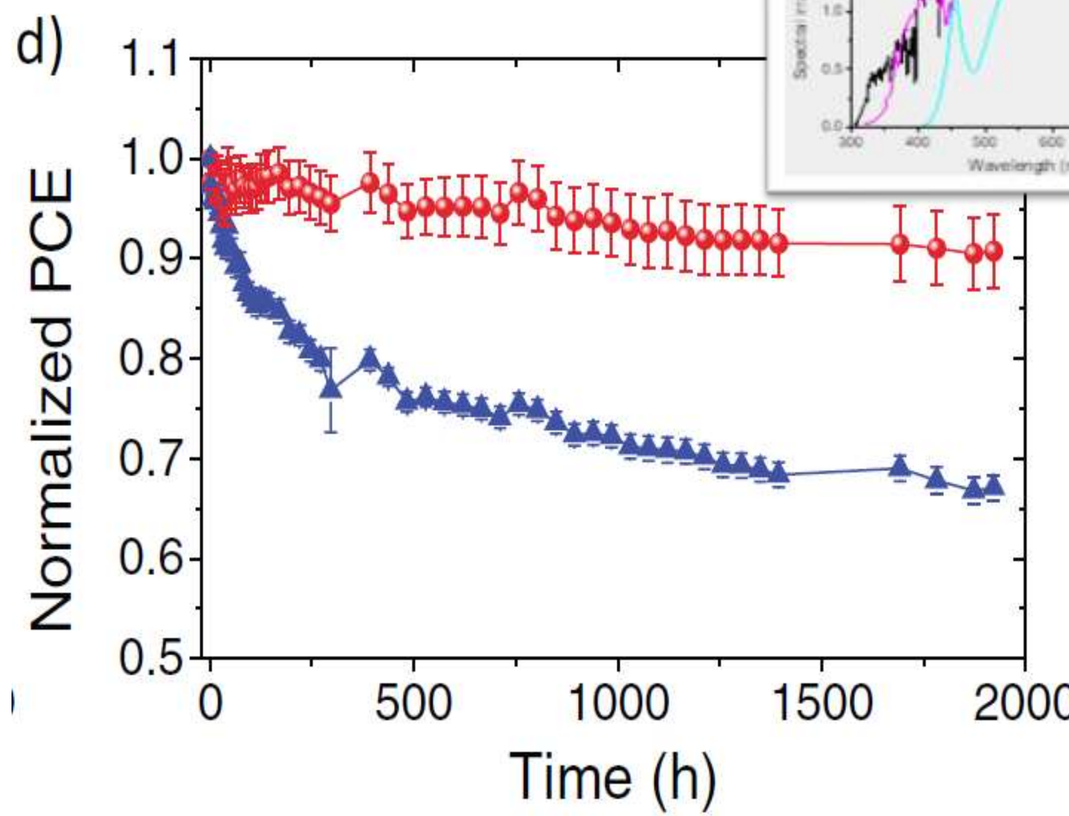
- What do we **know** about the **UV stability** ?
- Two different acceptors – PCBM vs IDTBR

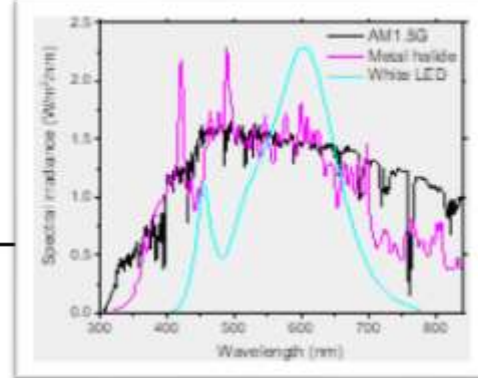
P3HT: IDTBR
(6 %)



P3HT:$PC_{60}BM$
(3,5 %)







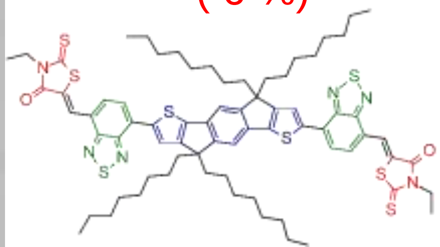
Under white light LED illumination (no UV < 400 nm)

N. Gasparini, AEM 2017
A. Classen, T. Heumüller, et al, unpublished

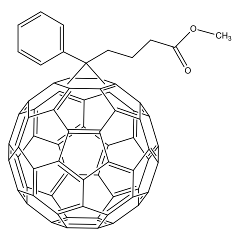
spectral degradation: *UV sensitivity*

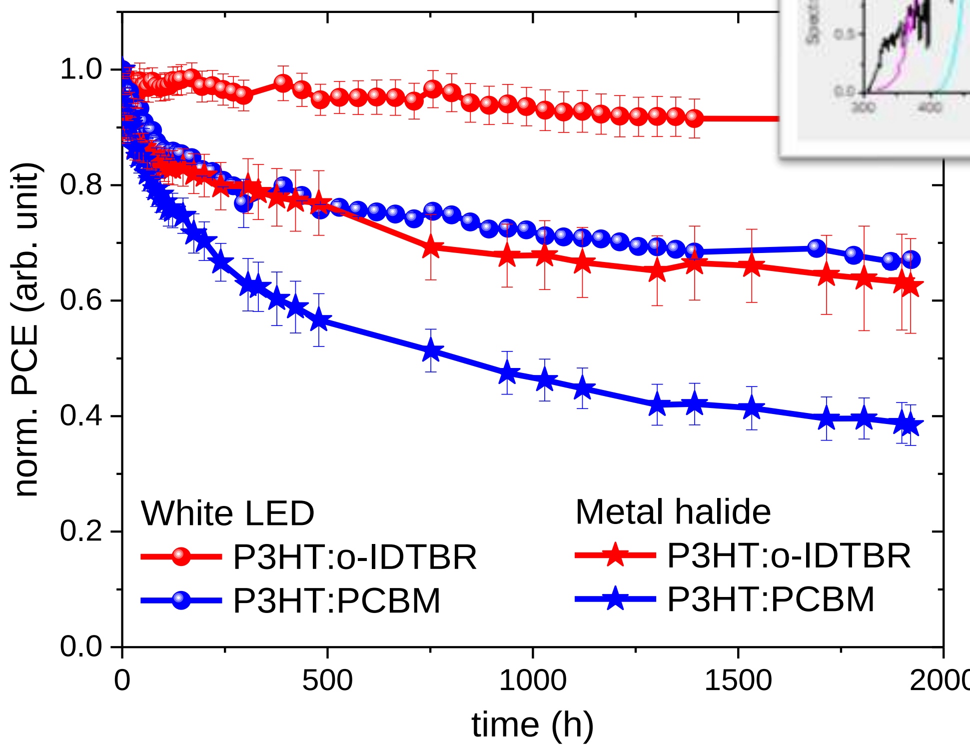
- What do we **know** about the **UV stability** ?
- P3HT is probably **not UV stable**!

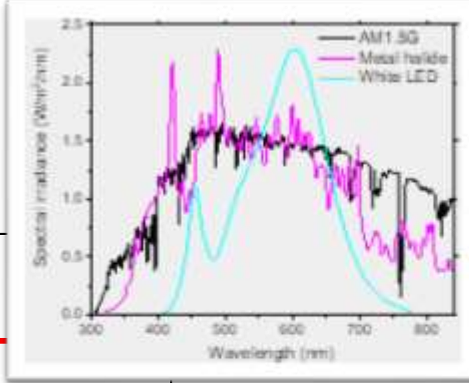
P3HT: IDTBR
(6 %)



P3HT:$PC_{60}BM$
(3,5 %)







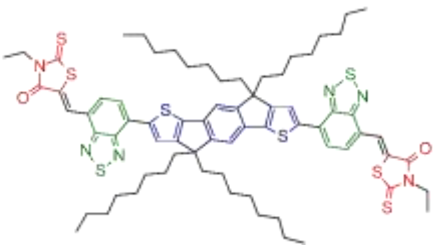
Under metal halide lamp (UV onset at < 330 nm)

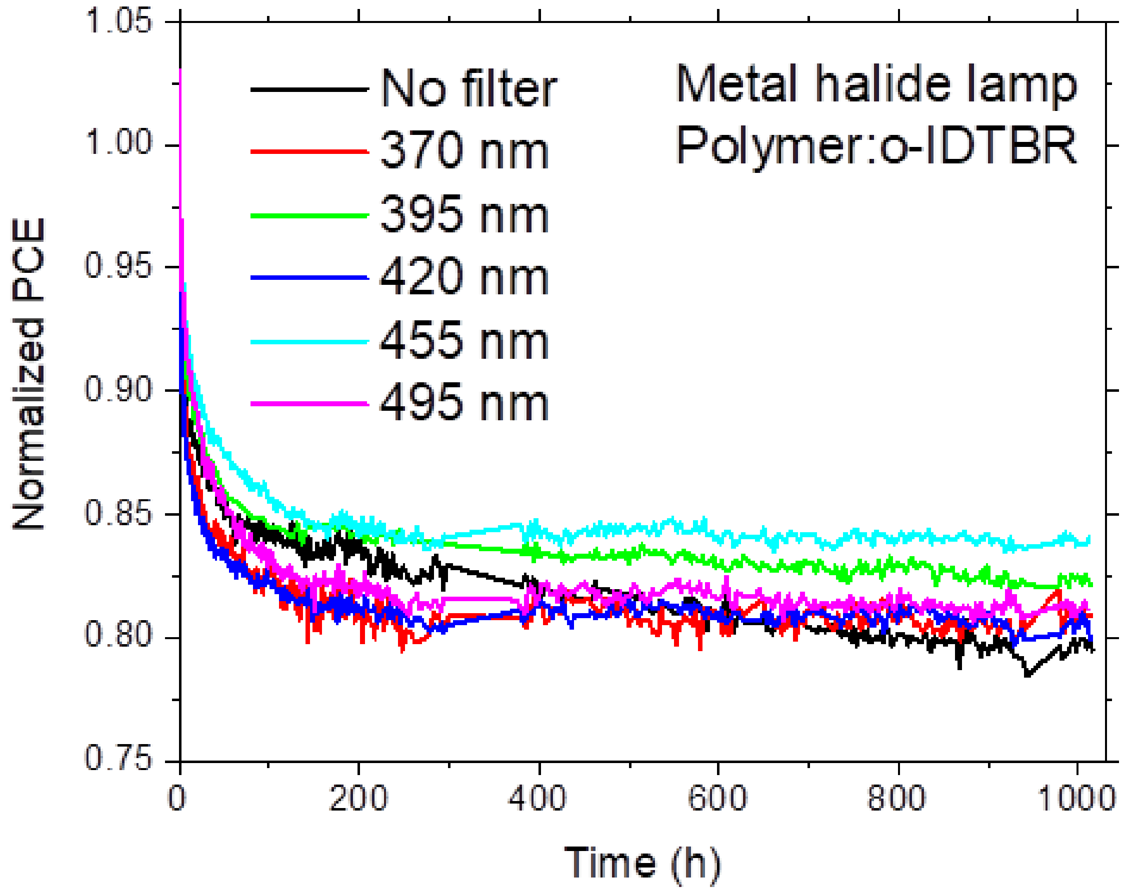
N. Gasparini, AEM 2017
A. Classen, T. Heumüller, et al, unpublished

spectral degradation: *UV sensitivity*

- **UV stability has to be determined for every new compound!**

polymer: IDTBR
(from Xyl, 8-9 %)





N. Gasparini, AEM 2017
A. Classen, T. Heumüller, et al, unpublished

spectral degradation: *UV sensitivity*

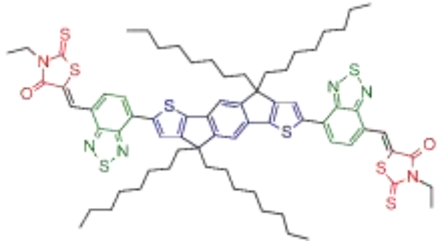
- What do we **know** about the **UV stability** ?
- P3HT is probably not UV stable!

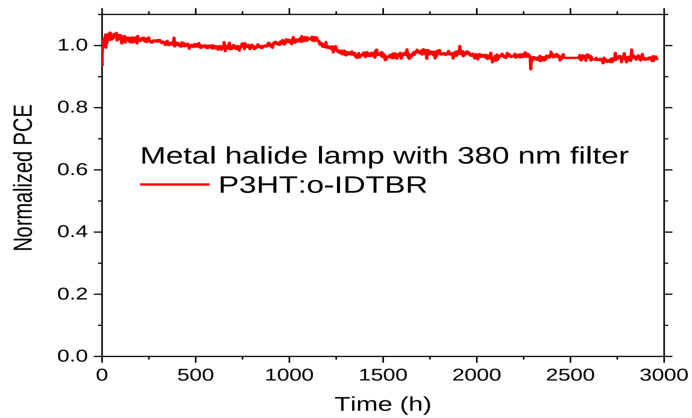
Technology

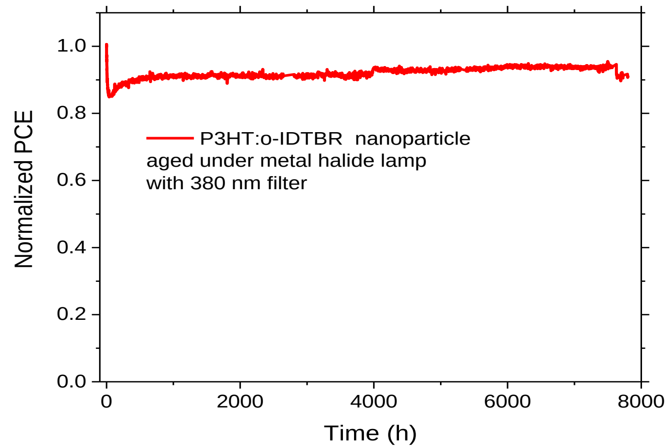
Outlook

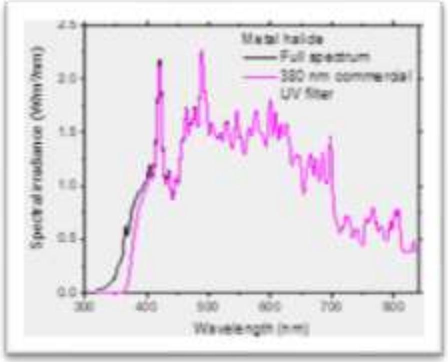
Conclusion

P3HT: IDTBR
(from Xyl, BrAni 6 %)

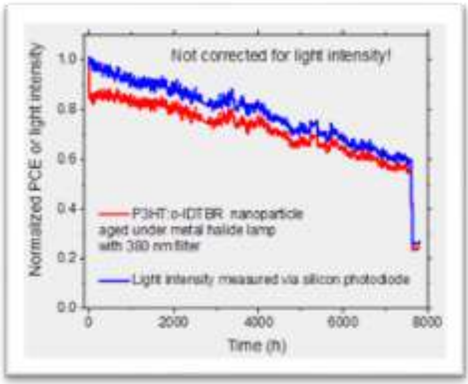








Under metal halide lamp with UV filter (380 nm onset) and lamp correction



P3HT: IDTBR
(from water, 4 %)

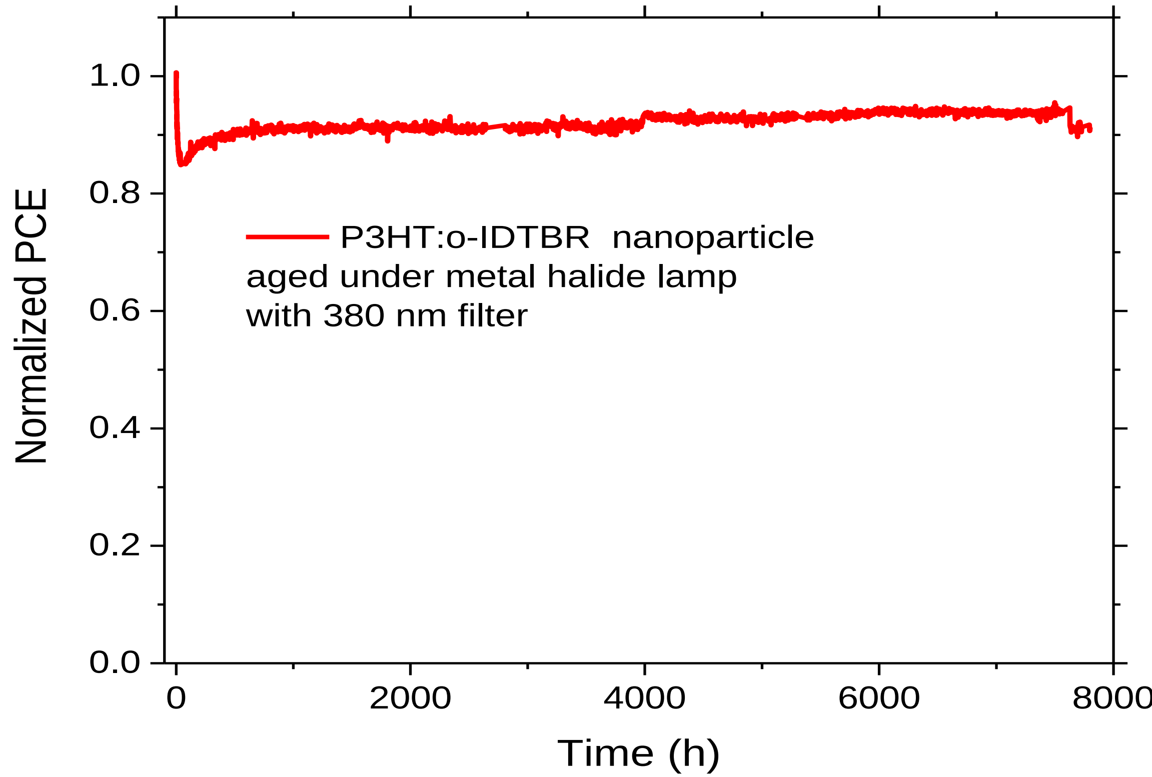
spectral degradation: *UV sensitivity*

- **Minisummary**:
  - **Controlling spectrum is essential -** can´t compare lifetime from LED and metal halide illumination
  - **Correcting lamp degradation** is essential

This is the baseline we want to see!

Organics can be fully stable for 10.000 hrs

Now – towards 100.000 hrs!



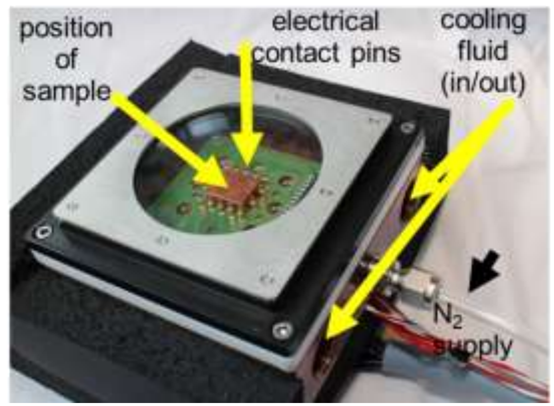
① Introduction:	1st chapter	Measuring Degradation
② Overview:	Next chapter	Fundamental Aspects
③ **Technology:**	Next chapter	Microstructure Degradation
④ Technology:	Next chapter	Chemical Degradation
⑤ Technology:	Next chapter	Interface Degradation
⑥ Technology:	Next chapter	Spectrally Induced Degradation
⑦ Outlook:		**Accelerated Degradation - towards 100.000 hrs operati**

Chemical Degradation: *ITIC derivatives*

- **How to go from 10.000 hrs to 100.000 hrs?**
- **Acceleration!**

- **Previous studies** suggest **no correlation** to 1 sur
- We **developed a protocol highly ALT testing**.

T-controlled cell holder



Developed cooling system for T regulation inside the cell

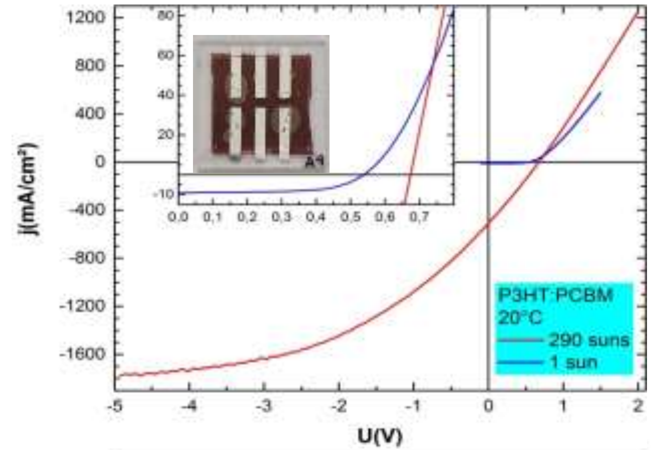
Cooling System

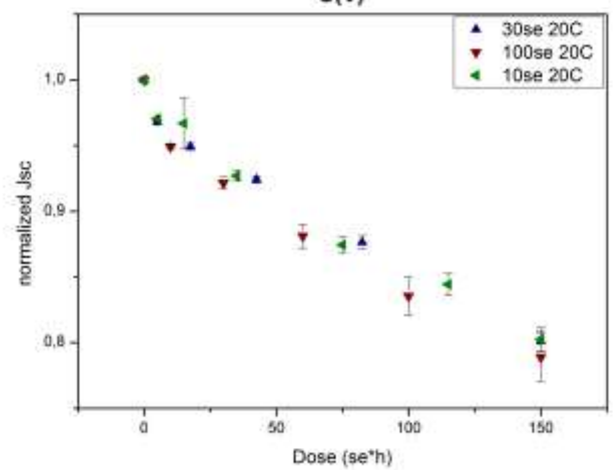
Chemical Degradation: *ITIC derivatives*

- How to go from 10.000 hrs to 100.000 hrs?
- **Acceleration at 300 suns – the case of P3HT:PCBM**

  - Setup must allow to measure jV characteristics to understand ageing
  - P3HT:PCBM has a photocurrent of **1.8 A/cm2 at ~ 300 sun.**

- Degradation (in Jsc) is independent from concentration factor
- Data plotted as function of **"Sun Equivalent Hours"** (se*h)





Chemical Degradation: *ITIC derivatives*

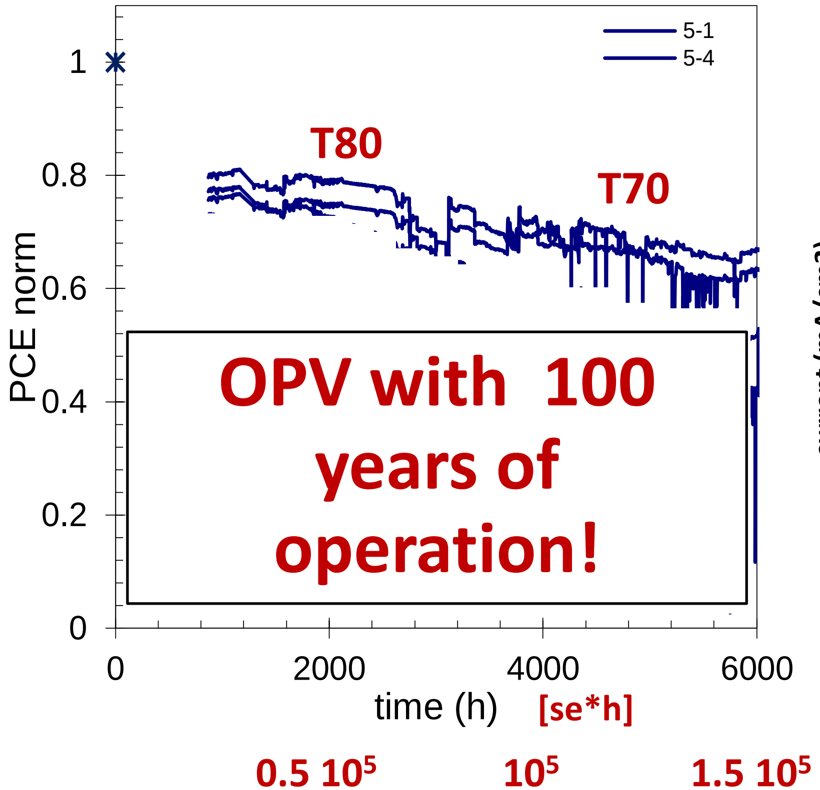
Technology

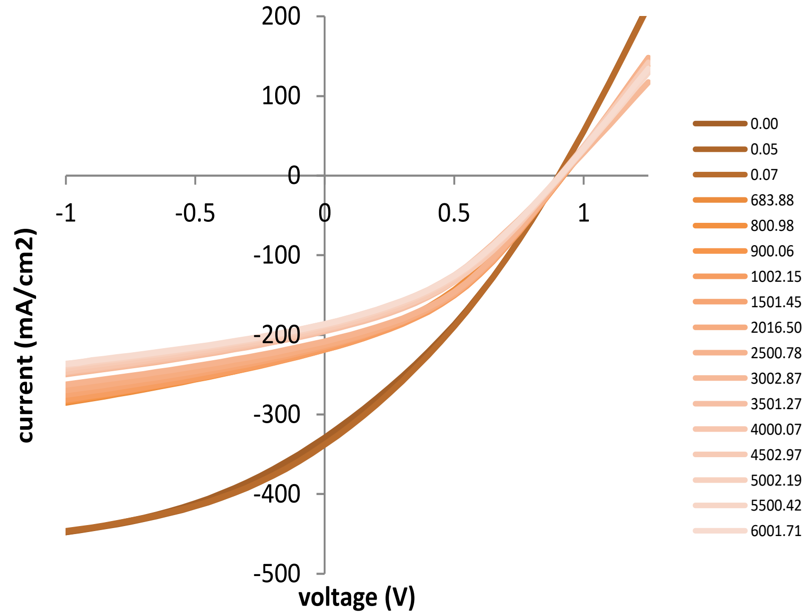
Outlook

Conclusion

- **Contolled degradation under 25 x concentration,** no UV, T ~ 40° C
- **OPV46: IDTBR (8 - 10 %)** – a **rather stable system** with some burn-in

- **25 sun equivalents for 6000 hrs -> 150.000 se*h**

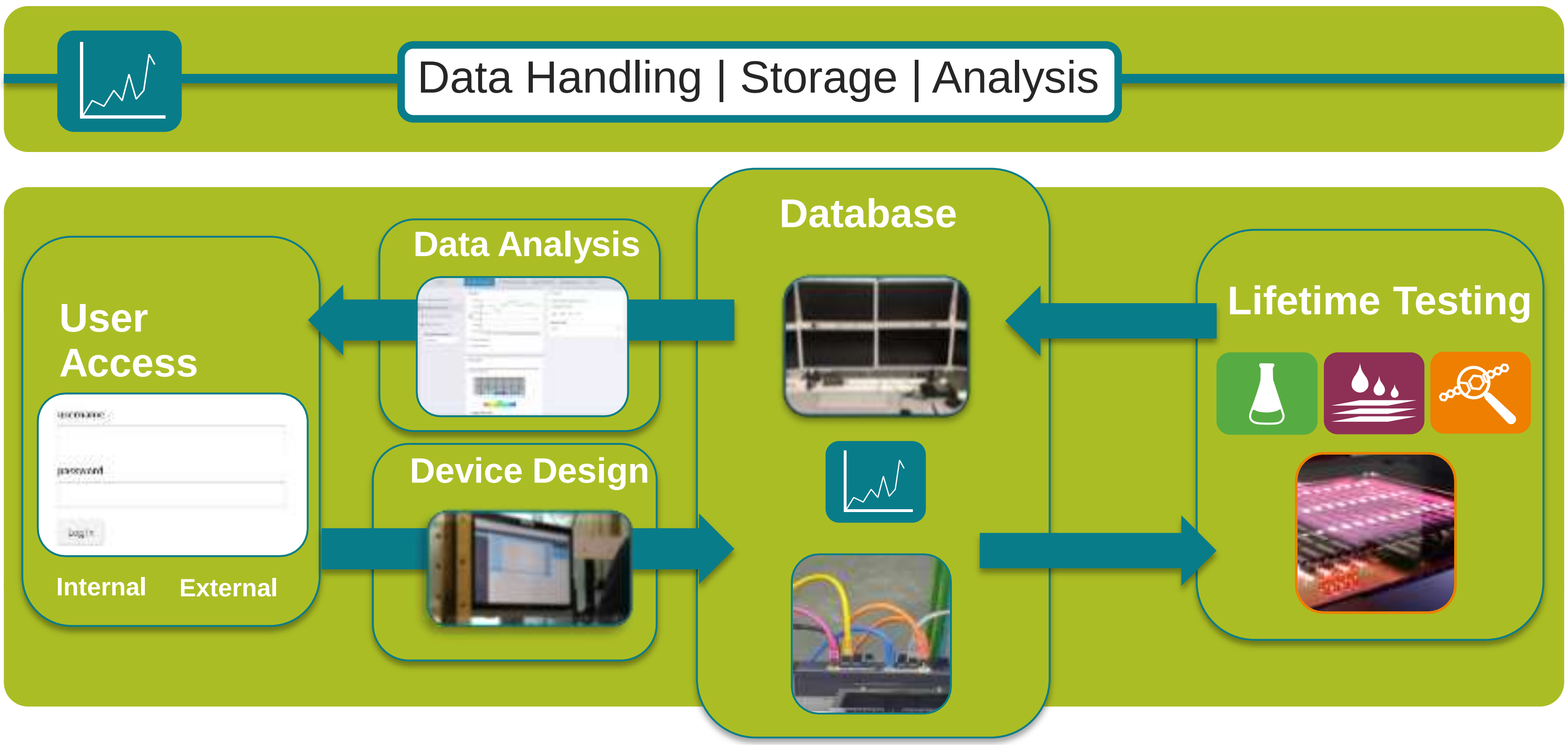




T. Heumüller, unpublished

Chemical Degradation: *ITIC derivatives*

- **Opening our lifetime / X-ALT lab to the public as user facility**
- **Possibility to testing novel materials for 10.000 (100.000) se*h**



- **Measuring degradation**: Organics are probably more stable than initial thought
- **1st data up to 150.000 se*h operation**

- **Degradation requires outmos**
  - Temperature
  - Spectrum (UV part
  - Light intensit
  - Interfa

- **Degradation:** ultimate tool to get ight into potential long term stable aterials

Thank you for your attention