Week 2-9

Optical Detectors 4

Multijunction cells

Singlet Fission

Light trapping

Reliability

Ch. 7.5 - 7.7

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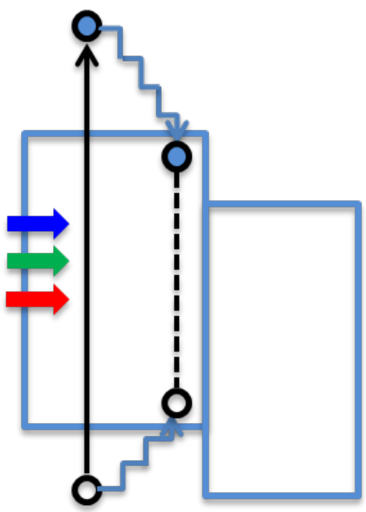
Multijunction OPV cells: The Most Effective Way to Increase Efficiency

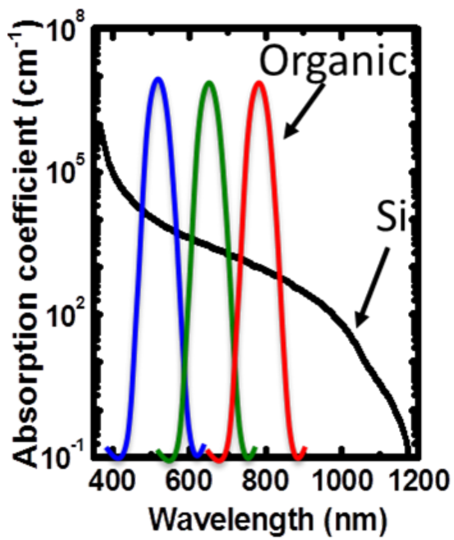
Can significantly exceed the thermodynamic limit of single junction cells

Major issues of single junction OPV:

(a) Thermalization loss

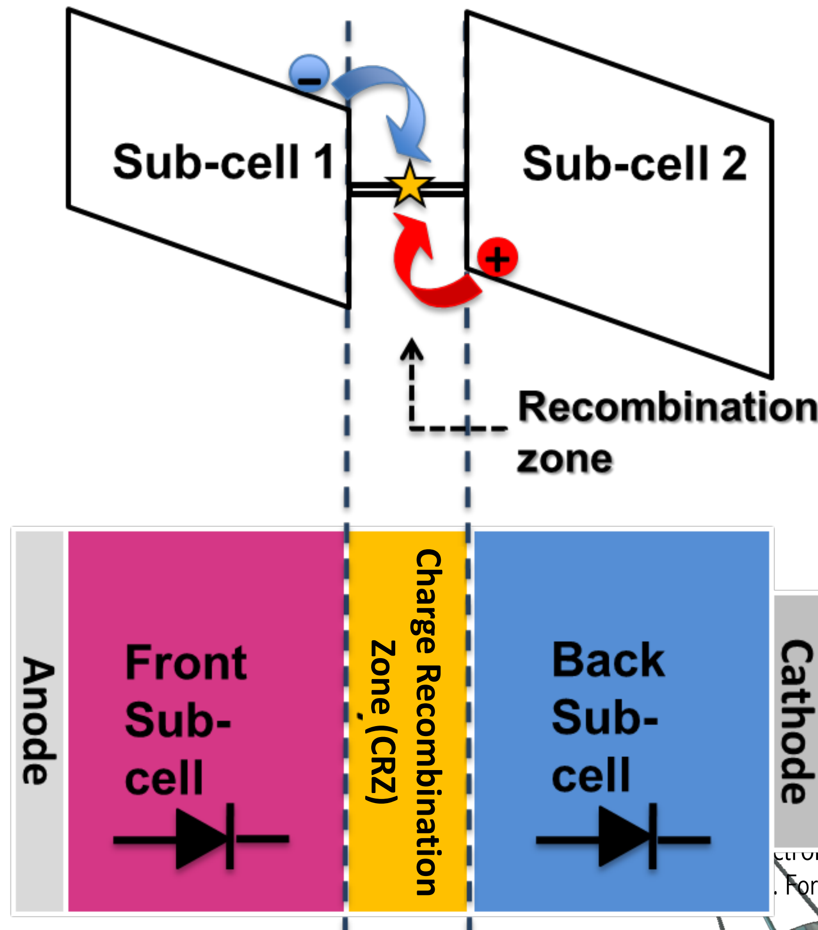


(b) Narrow absorption range

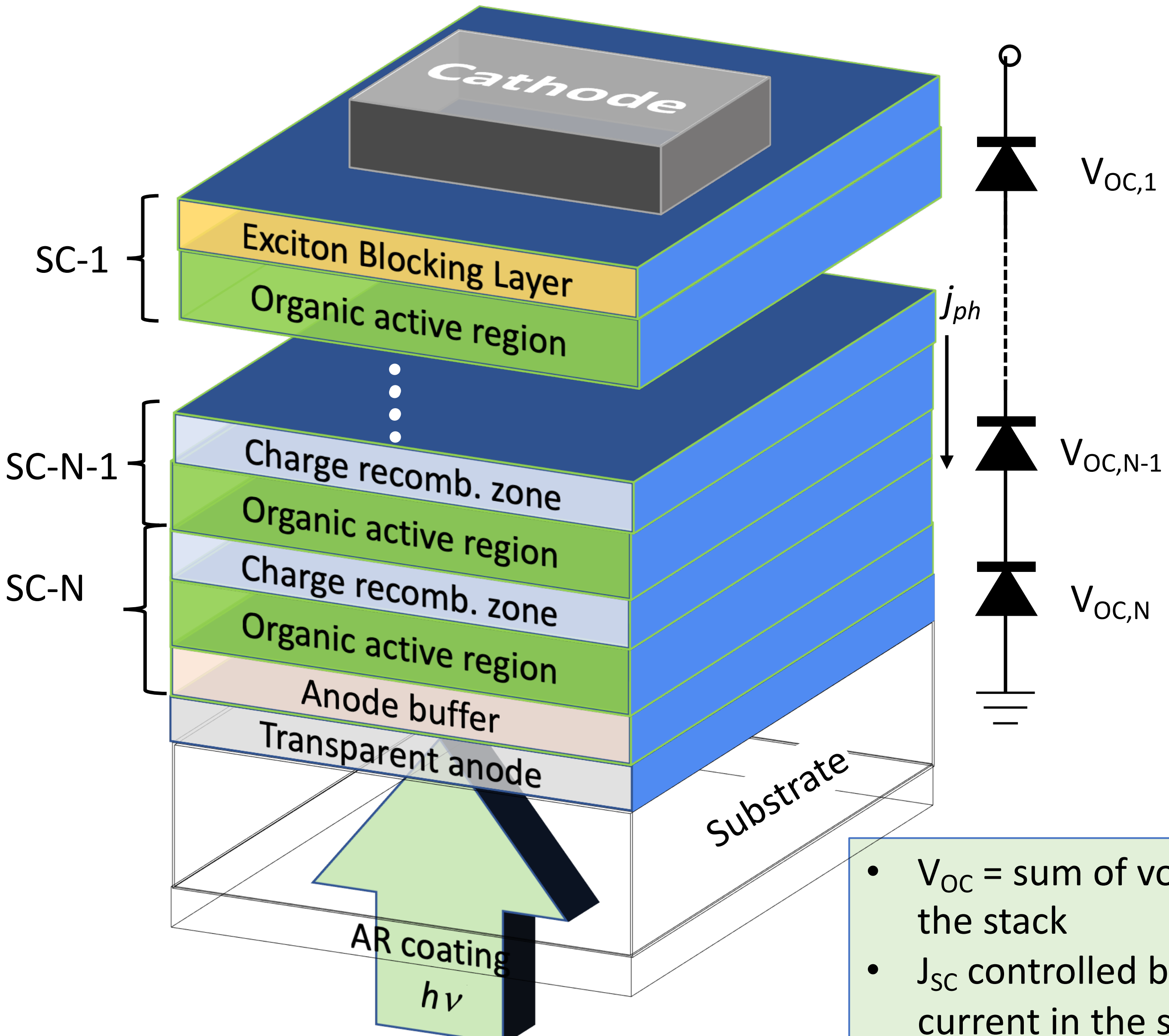


Advantages of multijunction cells:

- Decrease thermalization losses
- Cover a broad spectral range

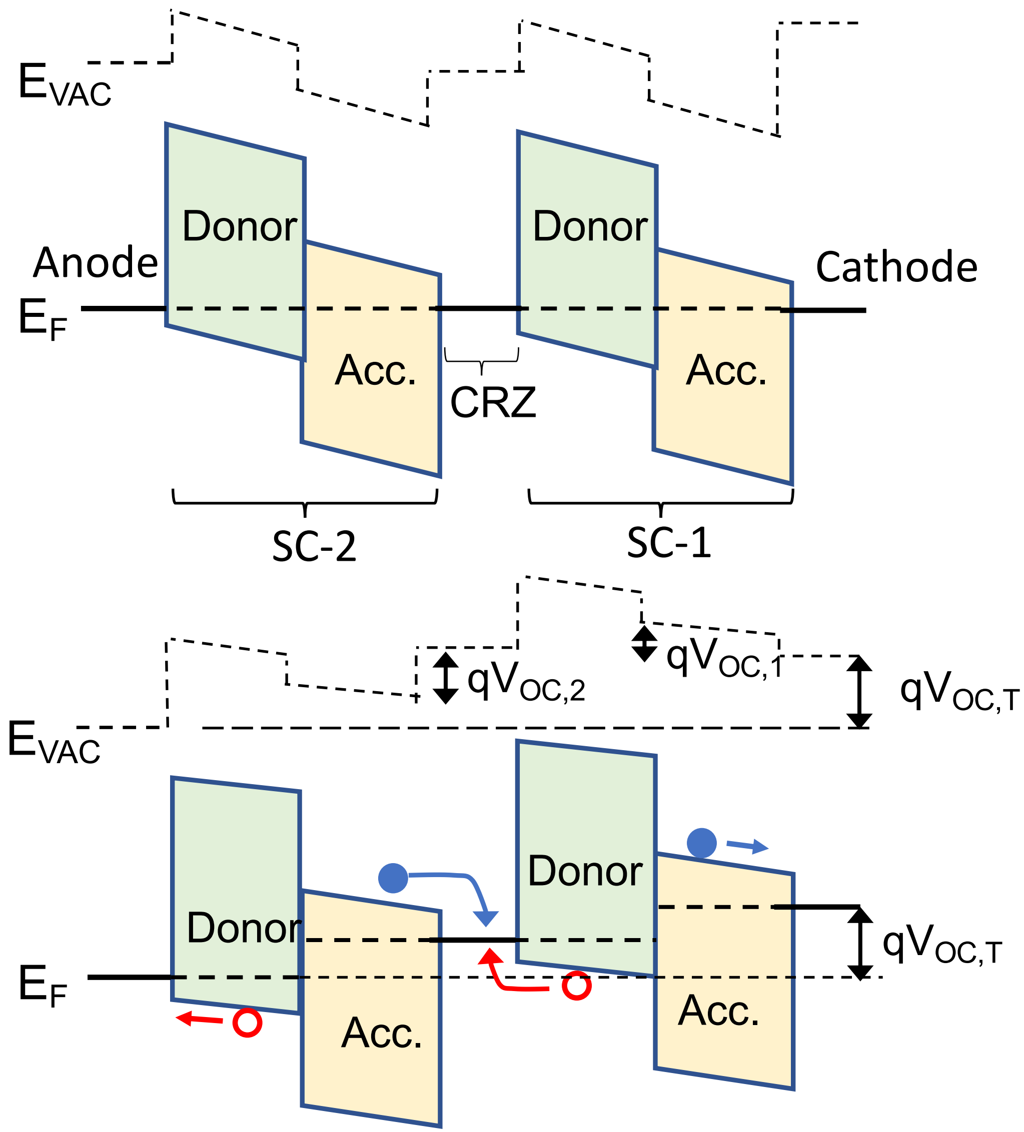


Tandem Cell Designs: Series Stacking



- V_{OC} = sum of voltages of the subcells in the stack
- J_{SC} controlled by the lowest subcell current in the stack

Tandem Cell Energetics

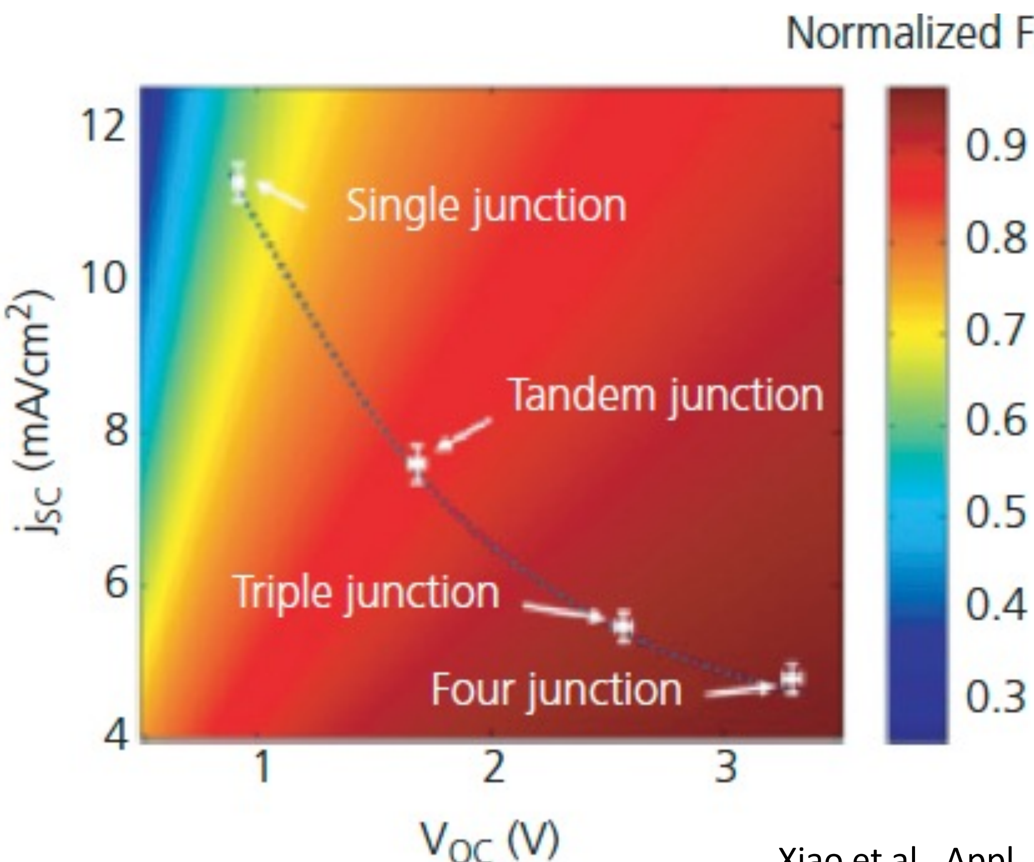


Adding Voltage and Reducing Current in Series Stacked Cells

- Reduced current

  ⇒reduced Joule (I^2R) losses

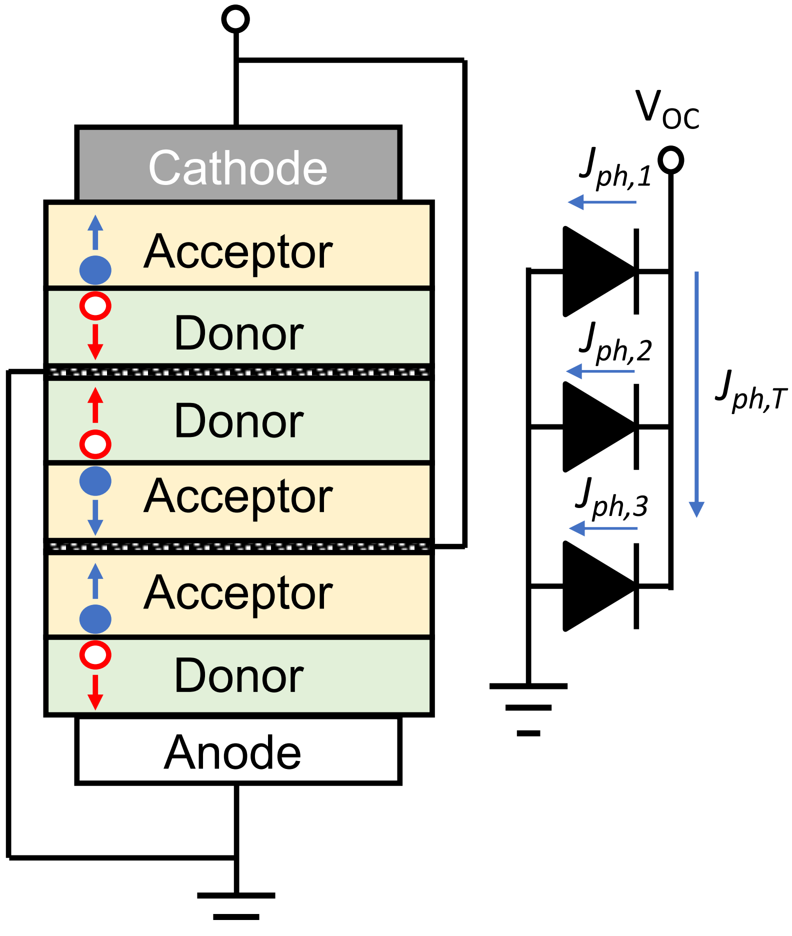
  ⇒increased FF

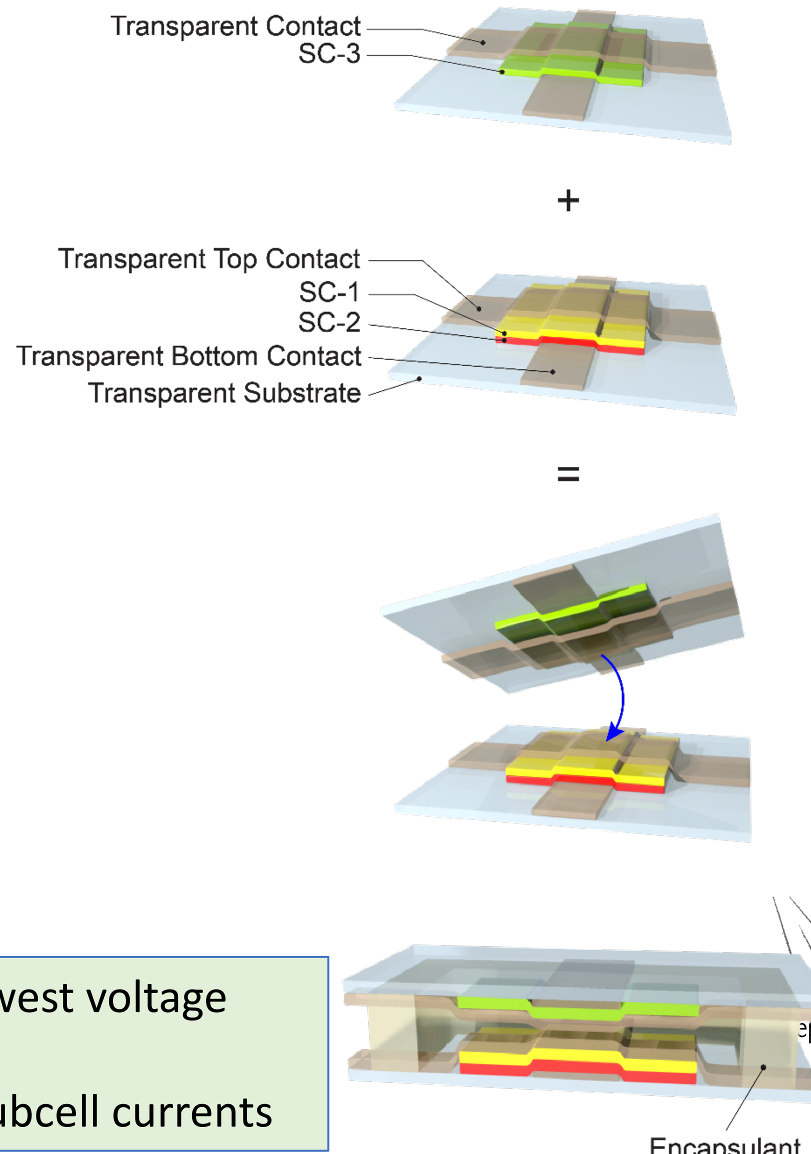


Multijunction cells comprising DTDCTB and DBP donors, and C_{70} acceptors

Xiao et al., Appl. Phys. Lett., 106, 203301 (2015)

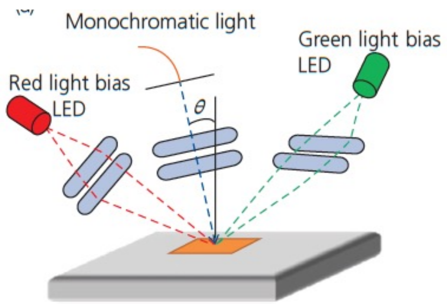
Tandem Cell Designs: Parallel Stacking





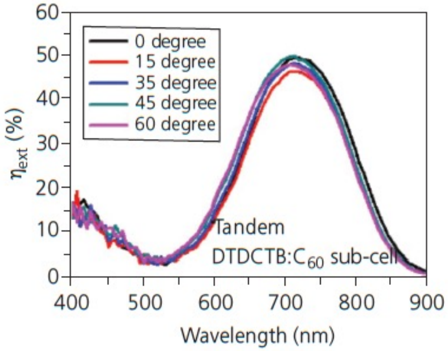
- V_{OC} controlled by the lowest voltage element in the stack
- J_{SC} = sum of individual subcell currents

Multijunction Cells are Microcavities

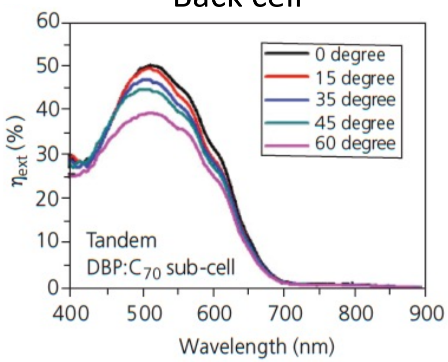


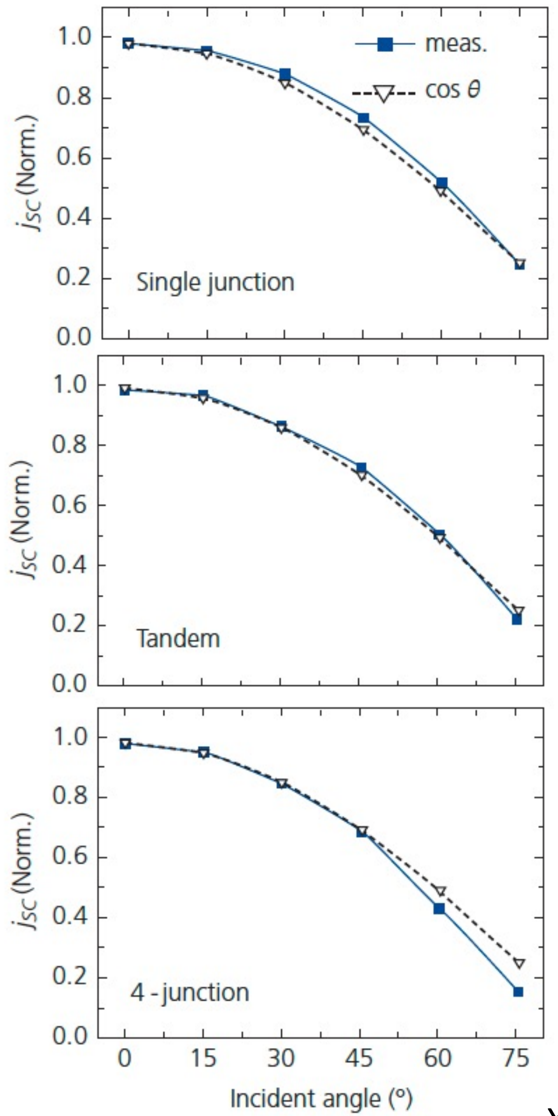
(c)

Front cell



Back cell





Angle dependence of efficiency is small due to thickness of stack needed for efficient absorption

Front cell (near ITO anode) less angle dependent than back cell due to longer λ absorption

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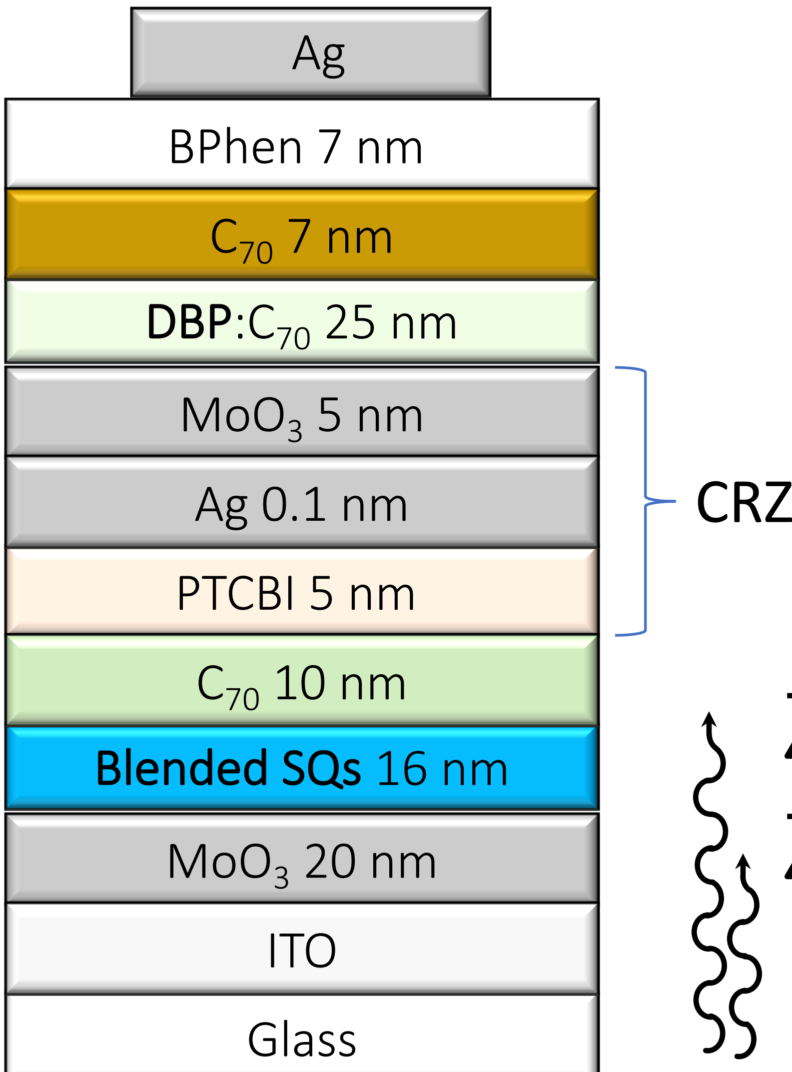
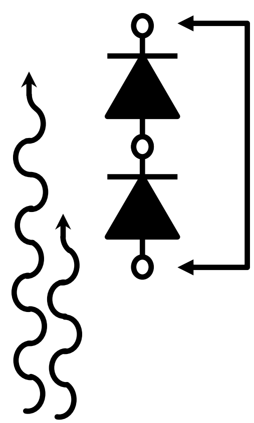
X. Che, PhD Thesis, U. Mich. (2018)

An Example Tandem Cell Structure

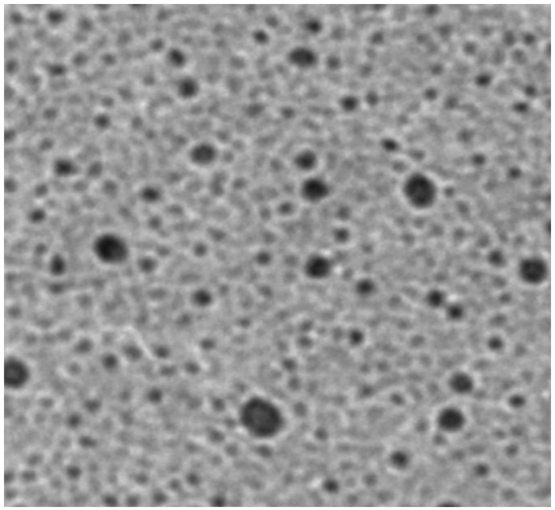




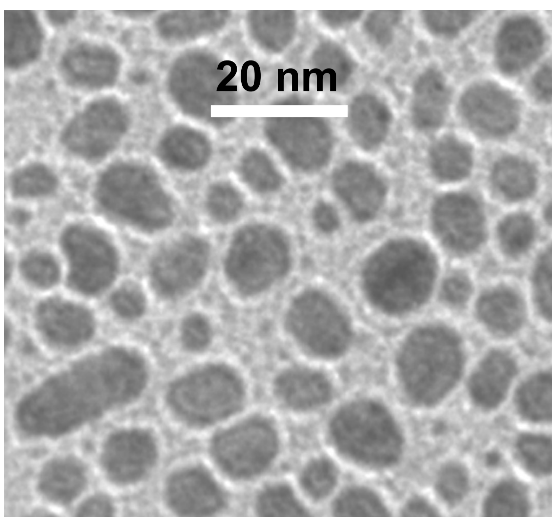
- Thinner cells have higher IQE.
- Stacking cells in series improves the total absorption.
- Addition of the photovoltage increases V_{OC}.
- Ag nanoclusters provide efficient charge recombination.

- DBP:C_{70} green absorber.
- Blended squaraine/C_{70} red/NIR absorber.

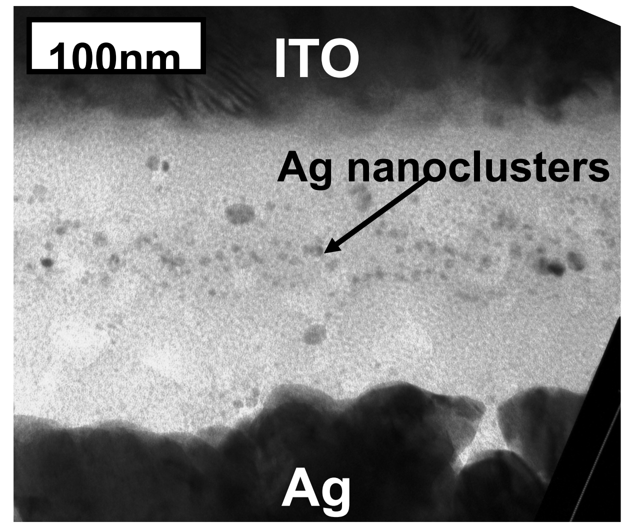
Charge Recombination Zone: Ag Nanoclusters



0.5 nm



45 nm



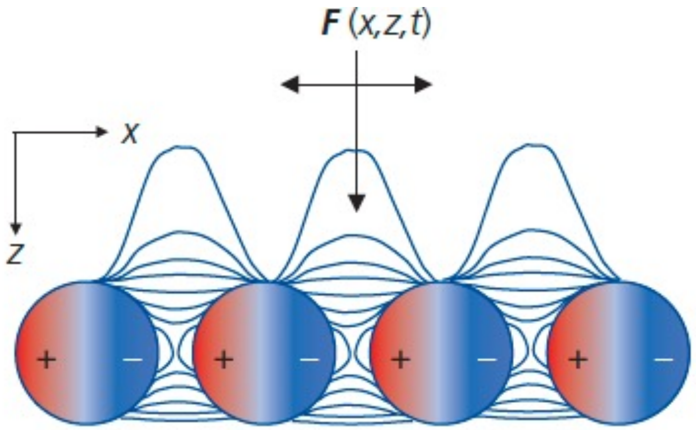
Nanoclusters give rise to surface plasmons

Plamsons reradiate field into thin active region

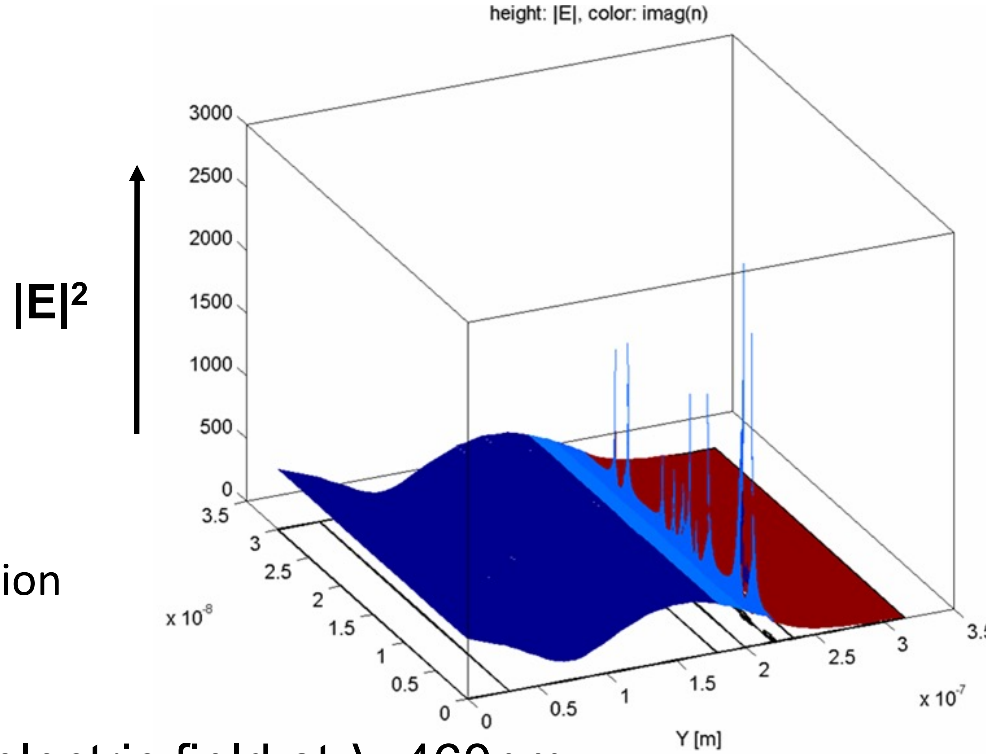
Increase in efficiency >50%

Yakimov & Forrest, *Appl. Phys. Lett.*, 80 1667 (2002)

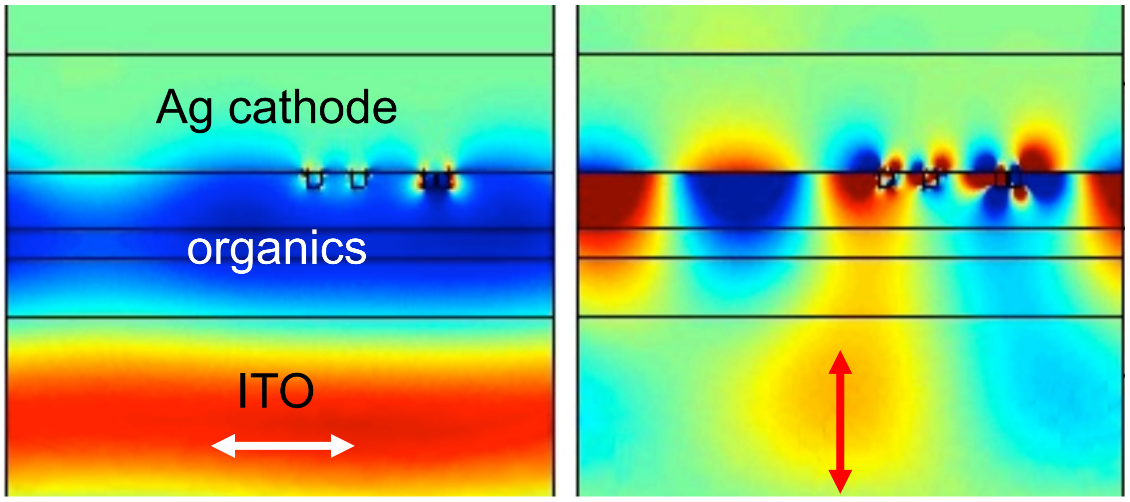
Rough interface: Surface plasmon excitation



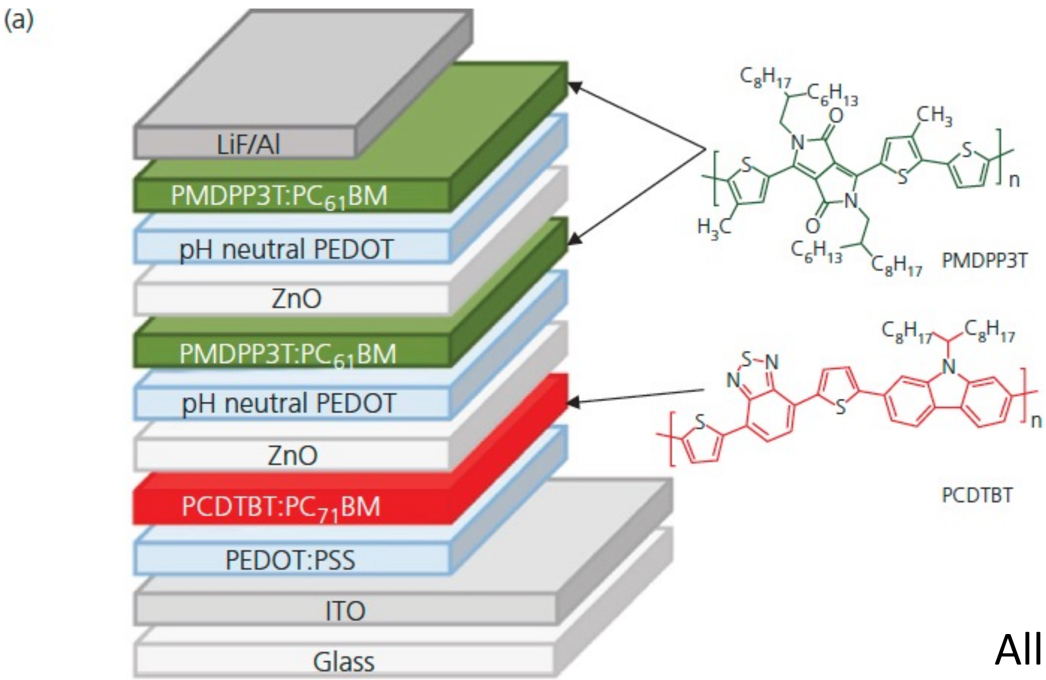
Surface plasmons intensify near field absorption

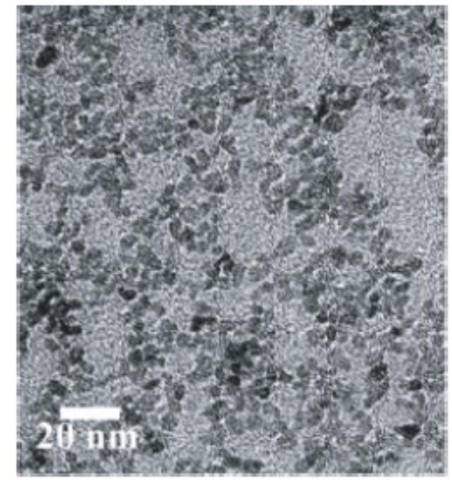


Calculation of optical electric field at λ=460nm



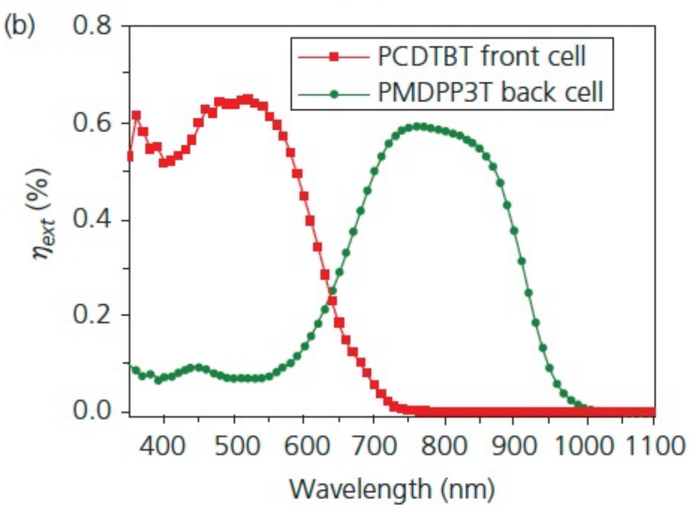
ZnO NP Layer: Alternative to Ag NPs





ZnO NP Layer

Beek et al.,J. Phys. Chem. B, 109, 9505 (2005)



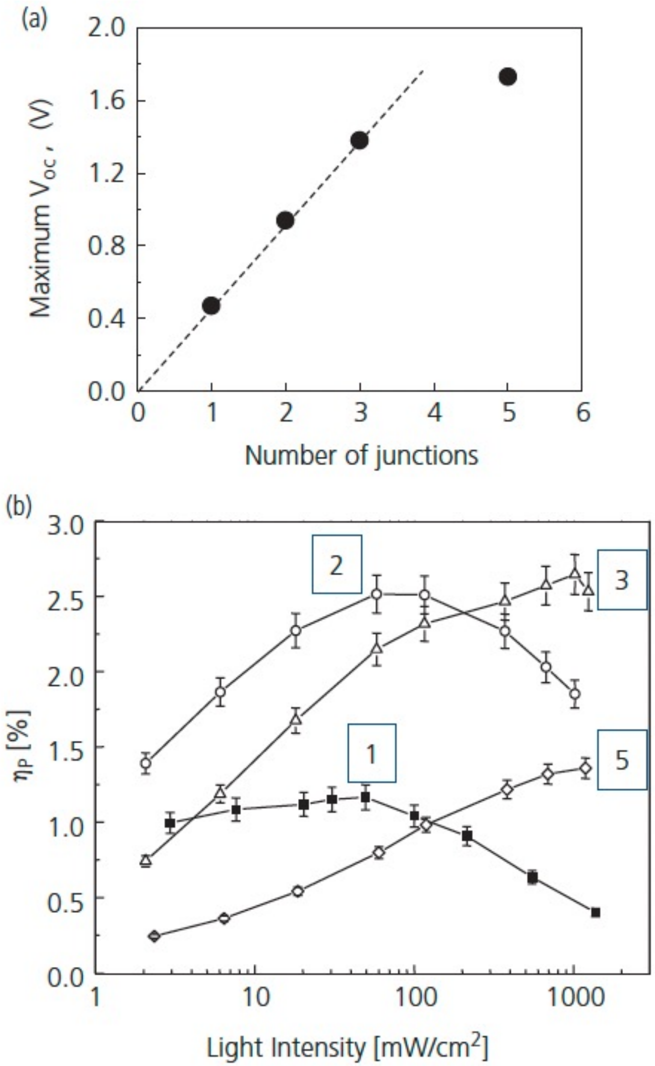
All solution processing

Cells	j_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η_P (%)
PCDTBT:PC_{71}BM	9.76	0.87	0.56	4.73
PMDPP3T:PC_{61}BM	15.3	0.61	0.65	6.00
Tandem	9.58	1.49	0.62	8.90
Triple	7.34	2.09	0.63	9.64

Li et al. J. Am. Chem. Soc. 135, 5529 (2013)

Surface Plasmonic Field Focusing in Multijunction Cells

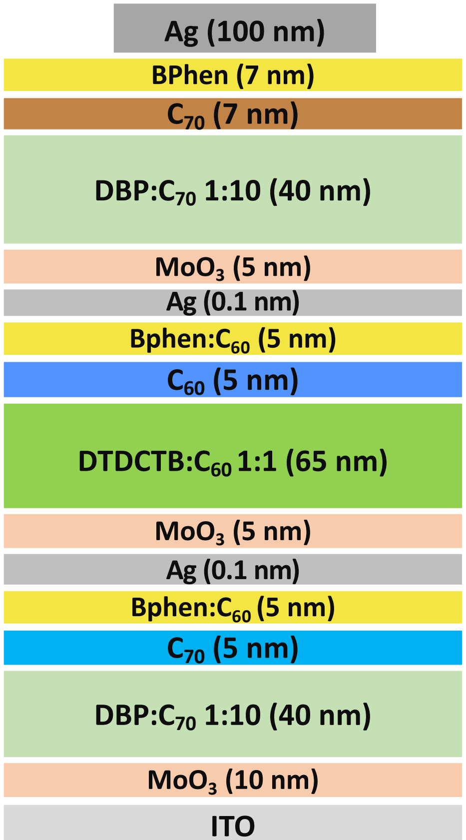
Series stacked PTCBI:CuPc cells



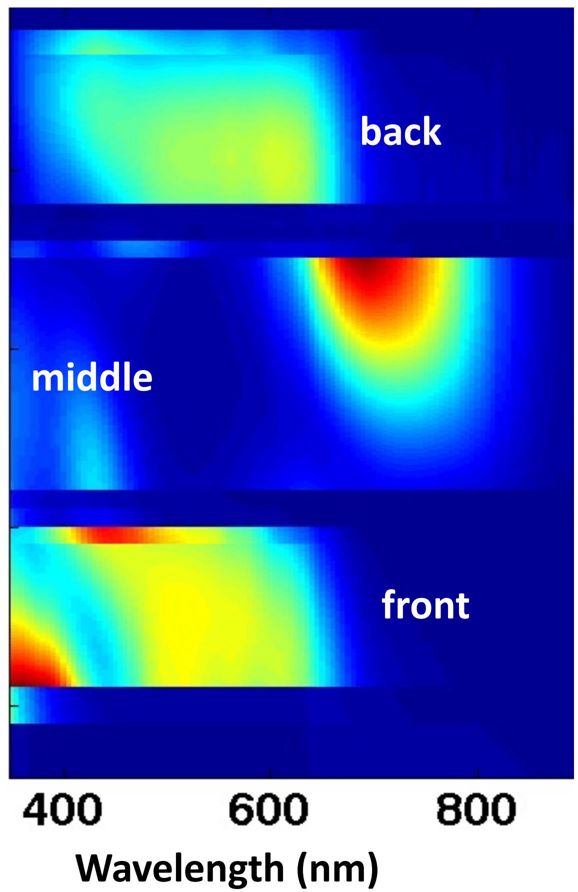
- Tandem cell efficiency is >2X single junction efficiency
  - ⇒plasmonic field focusing increases absorption
- Increased number of subcells
  - ⇒peak efficiency at increasing intensity
  - ⇒loss of intensity in the upper cells
- Optimal efficiency at 1 sun intensity for tandem
  - ⇒individual subcells too thin to absorb >50% light
- Voltage is linear function of number of subcells
  - ⇒nearly lossless CRZ using Ag NPs

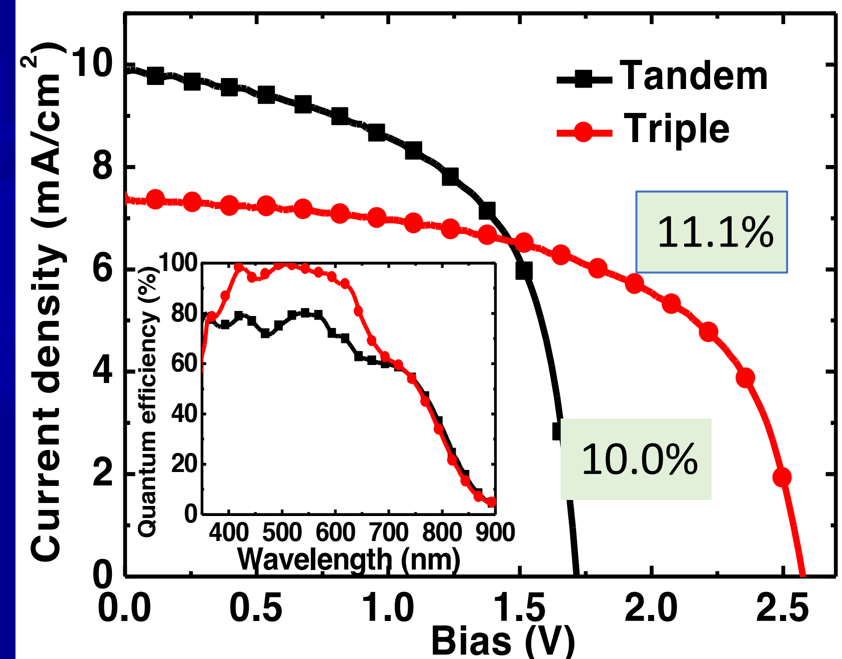
Yakimov & Forrest, *Appl. Phys. Lett.*, 80 1667 (2002)

High Efficiency Triple Junction Cell



Optical field distribution

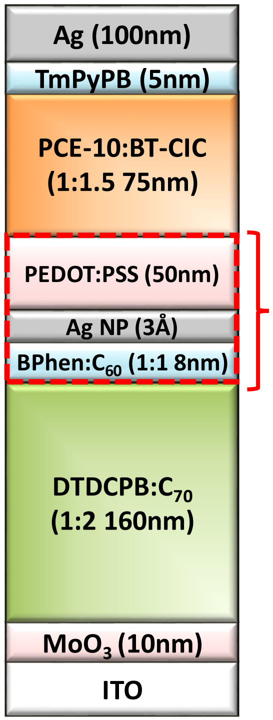


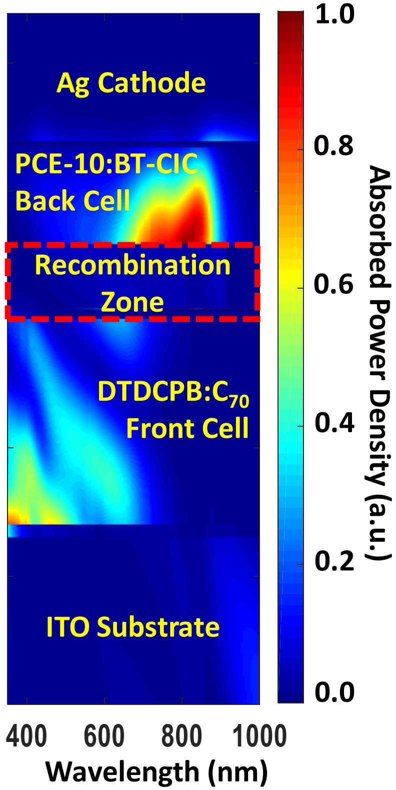


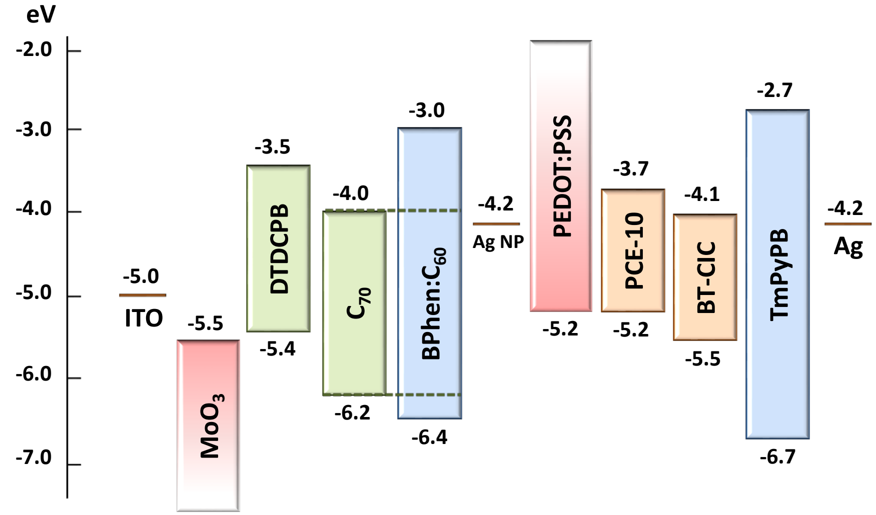
Transfer matrix calculations of optical field required to ensure current generated in every subcell is equal

X. Che, et al. Adv. Energy Mater., 4, 568 (2014)

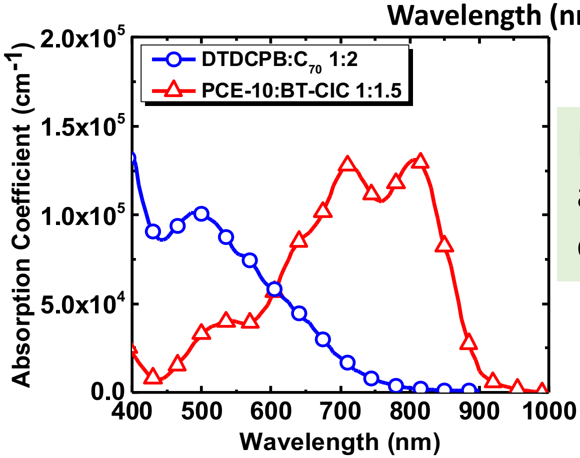
Combining Solution Processed Back Cell with Vapor Deposited Front Cell



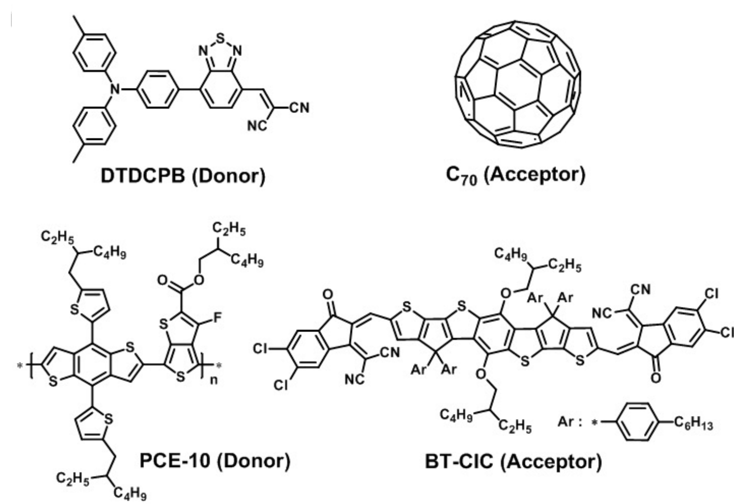




CRZ must be lossless, but also must protect front cell from damage due to deposition of back cell

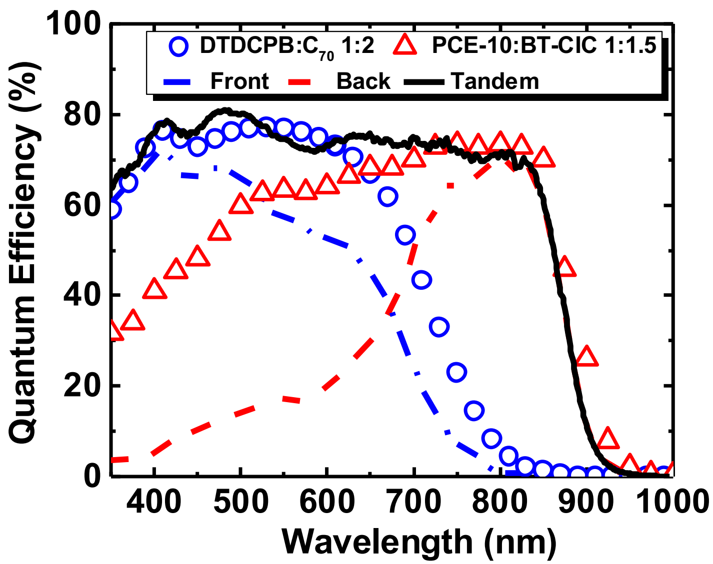


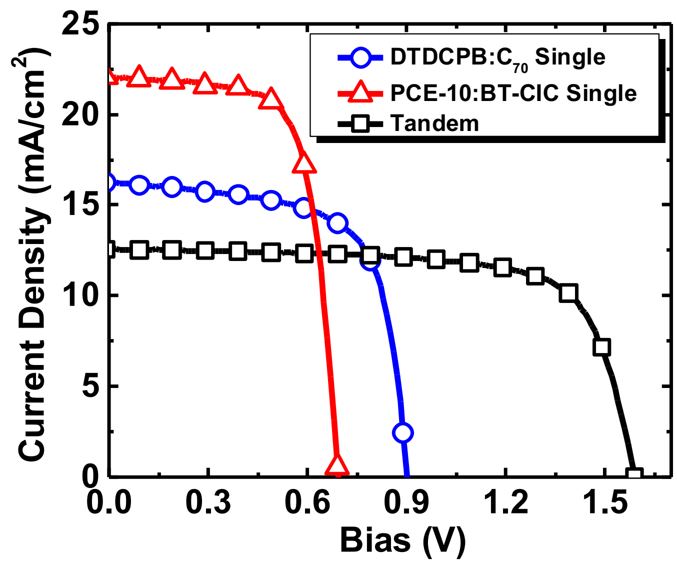
Minimal overlap of front and back spectra ensures current balance



Che et al., Nature Energy, 3, 422 (2018)

High Efficiency Tandem Results





Device	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η_P (%)
[Back] PCE-10:BT-CIC	22.1	0.69	0.70	10.7
[Front] DTDCPB:C_{70}	16.2	0.90	0.67	9.8
Tandem	12.7	1.59	0.71	14.3
Tandem (w/ARC)	13.3	1.59	0.71	15.0
Tandem (1 cm^2, w/o ARC)	12.6	1.58	0.57	11.5

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Che et al., Nature Energy, 3, 422 (2018)

Multiexciton Generation via Singlet Fission

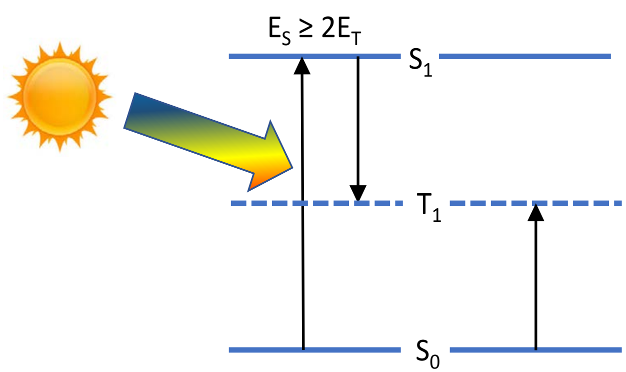
Recall from Ch. 3:

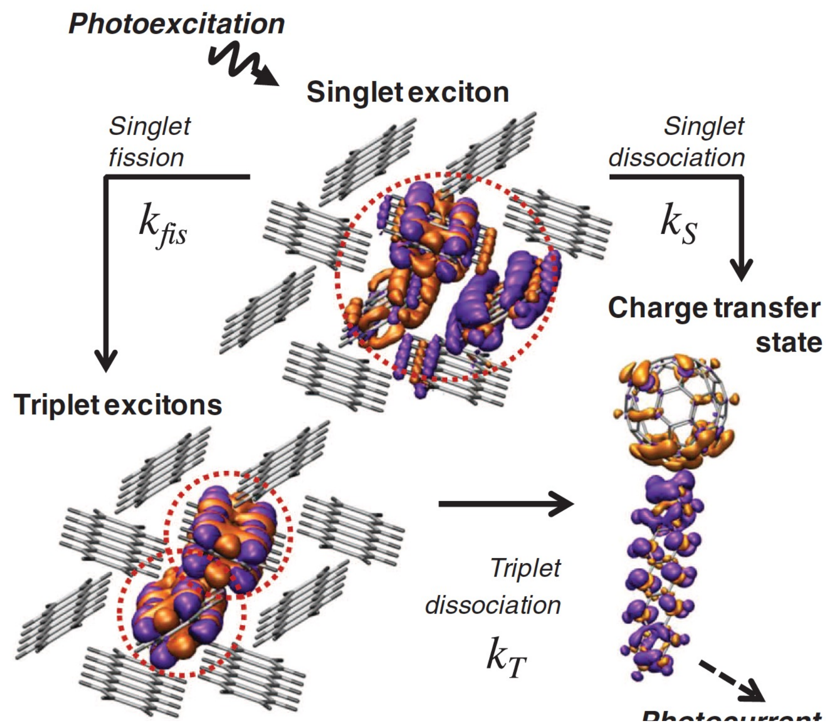
> 1 singlet can generate 2 triplets by fission when $E_S \geq 2E_T$

via the reaction: $$S_0 + S_0 + h\nu \rightarrow S_1 + S_0 \underset{k'_{fis}}{\overset{k_{fis}}{\rightleftharpoons}} {}^1(TT) \underset{k'_T}{\overset{k_T}{\rightleftharpoons}} T_1 + T_1$$

Precursor triplet pair with singlet symmetry

at rate: $$\frac{k'_{fis}}{k_{fis}} = \frac{9}{2}\exp\left[-\left(2E_T - E_S\right)/k_B T\right]$$





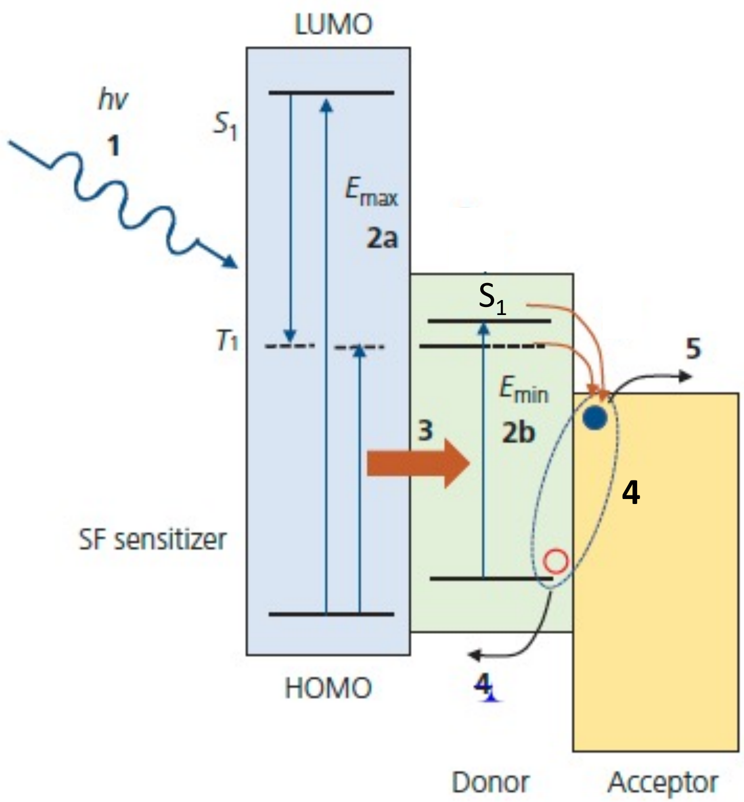
Example singlet fission on pentacene followed by dissociation at a pentacene/C_{60} HJ

Congreve, et al. Science, 340, 334 (2013)

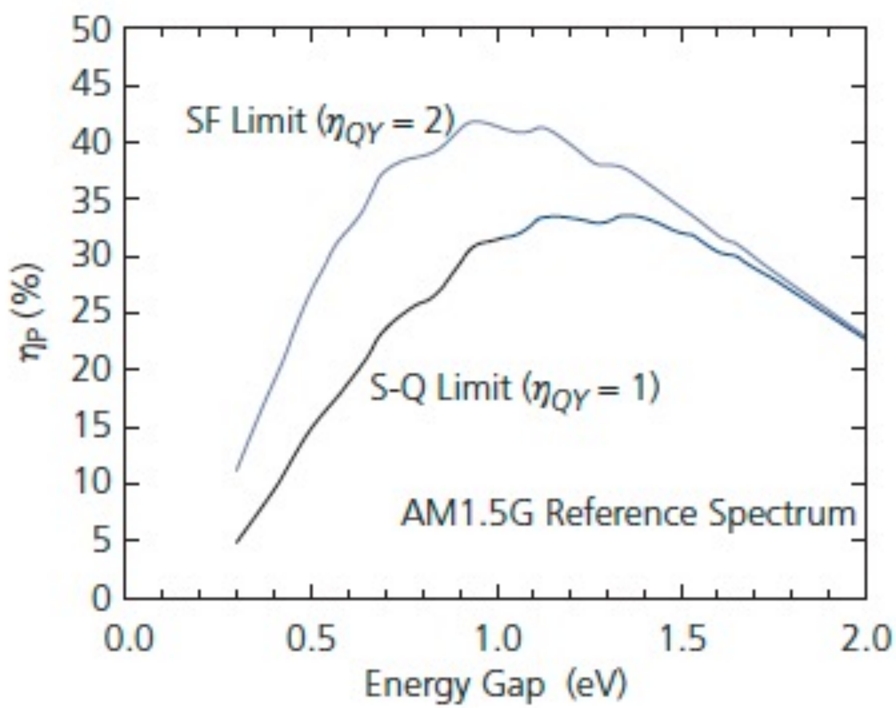
Benefits to Employing MEG in PV Cells

- Up to 2X current due to two exciton generation
- But voltage (and hence η_P) is unchanged
- When combined with a lower energy D-A HJ, thermalization losses can be reduced

Fission Process in an OPV



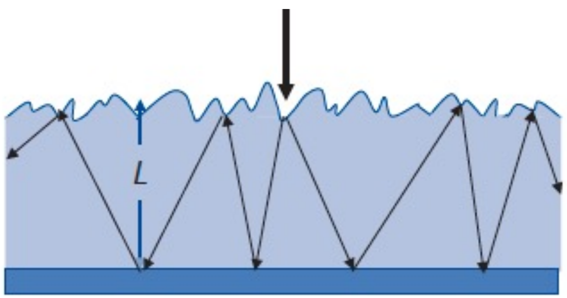
Thermodynamic Limits to SF



Hanna & Nozik J. Appl. Phys. 100, 074510 (2006)

Increasing Efficiency By Light Trapping

- We have shown that the best detector materials are the most radiative due to reduced non-radiative recombination
- Thin film cells often do not absorb all the light in one pass
- Strategies to recapture radiated or unabsorbed photons increase cell efficiency

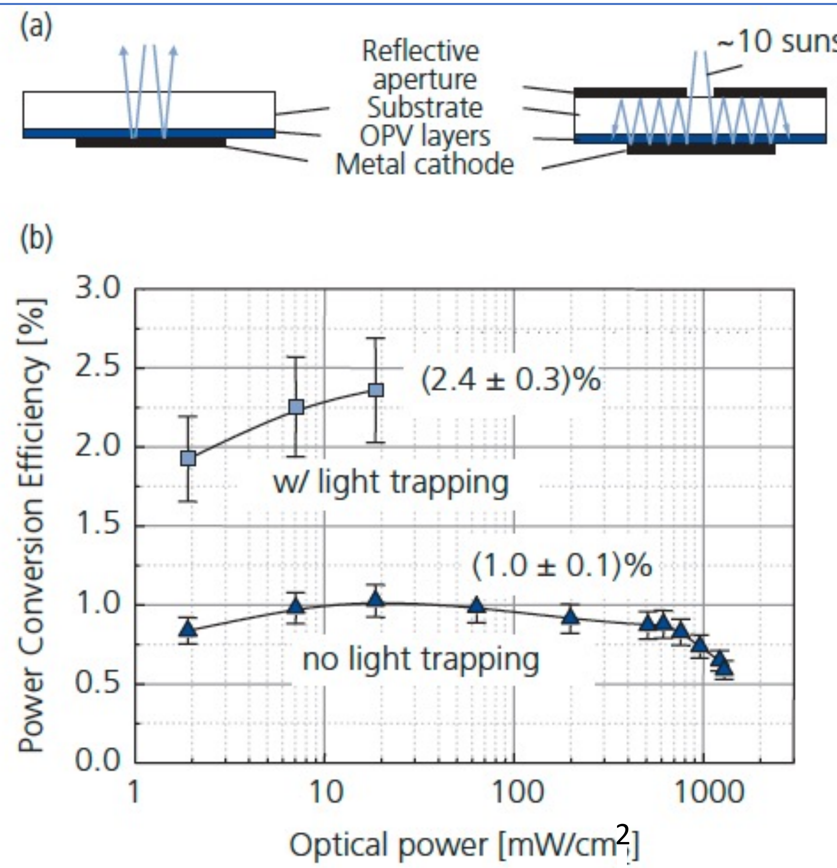


The light intensity trapped in the medium is amplified by its high index of refraction:

$$I_{medium} = 2n^2 \alpha L I_{inc}$$

assuming there is a back surface reflector

Example: CuPc/PTCBI OPV with front and back surface reflectors

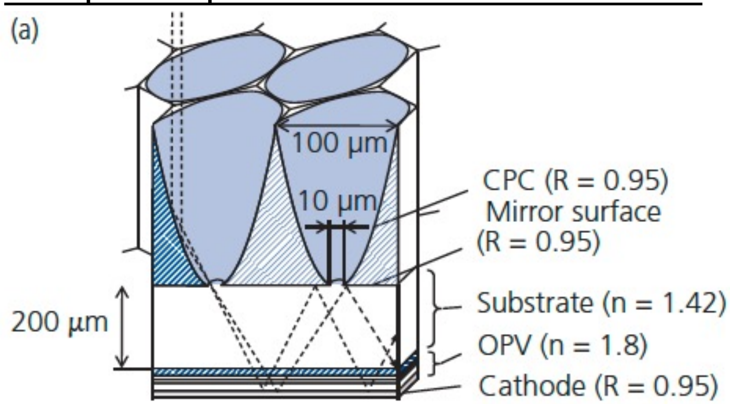


Peumans et al. Appl. Phys. Lett. 76, 2650 (2000)

Other Light Trapping Strategies

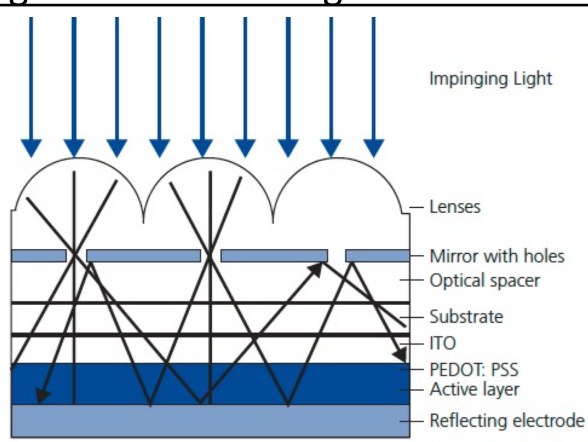
- Most light trapping strategies involve concentration
- Concentration requires solar tracking
- Solar tracking can be expensive

Compound parabolic mini-concentrators



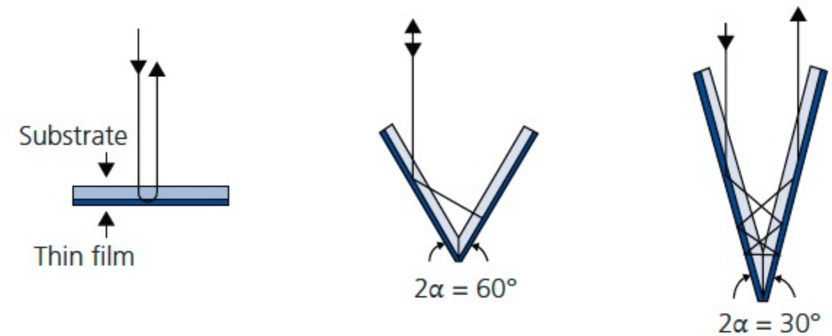
Peumans et al. Appl. Phys. Lett. 76, 2650 (2000)

Self-aligned concentrating microlens arrays



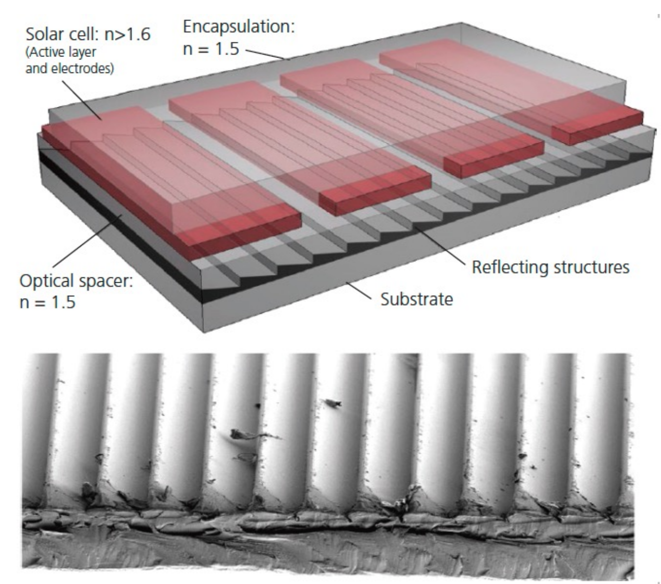
Tvingstedt et al. Opt. Express, 16, 21608 (2008)

V-traps



Kim et al. Opt. Express, 21, A305 (2013)

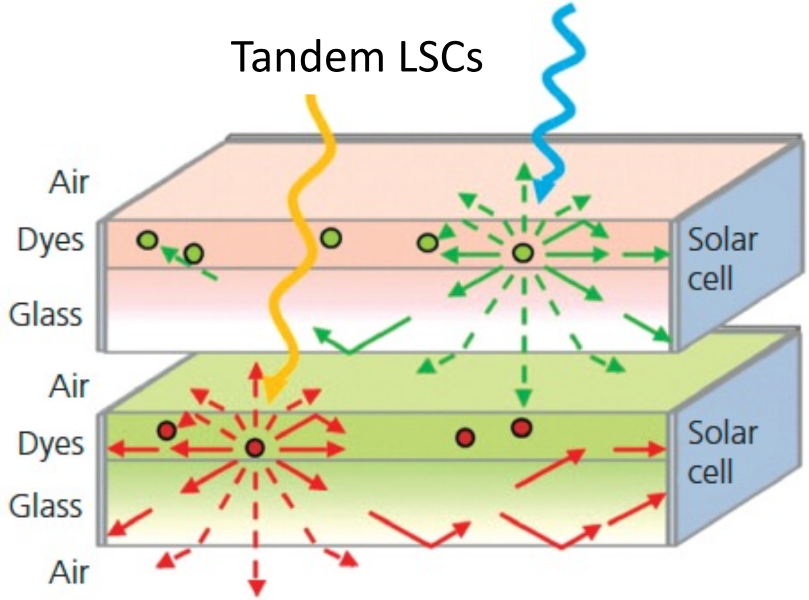
Echelle reflectors



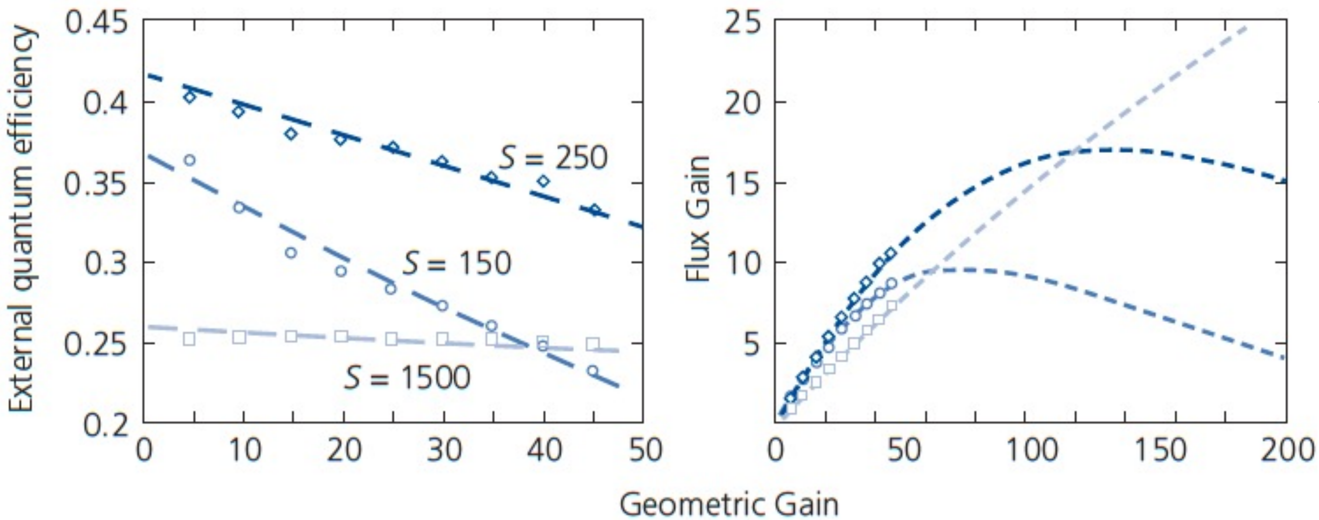
Tvingstedt et al. Appl. Phys. Lett., 101, 163902 (2012)

Luminescent Solar Concentrators: An omnidirectional approach

Tandem LSCs



- Light absorbed in waveguide (plastic) sheet loaded with luminescent organic dyes
- Re-emission trapped within the sheet. Only light emitted at θ > total internal reflection angle lost
- Waveguided light concentrated on solar cells (organic, Si, GaAs, etc.) on slab periphery
- Primary loss: Re-adsorption by insufficiently Stokes-shifted fluorophores
- Solution: Dexter transfer light to lower energy triplet state in a co-doped phosphor



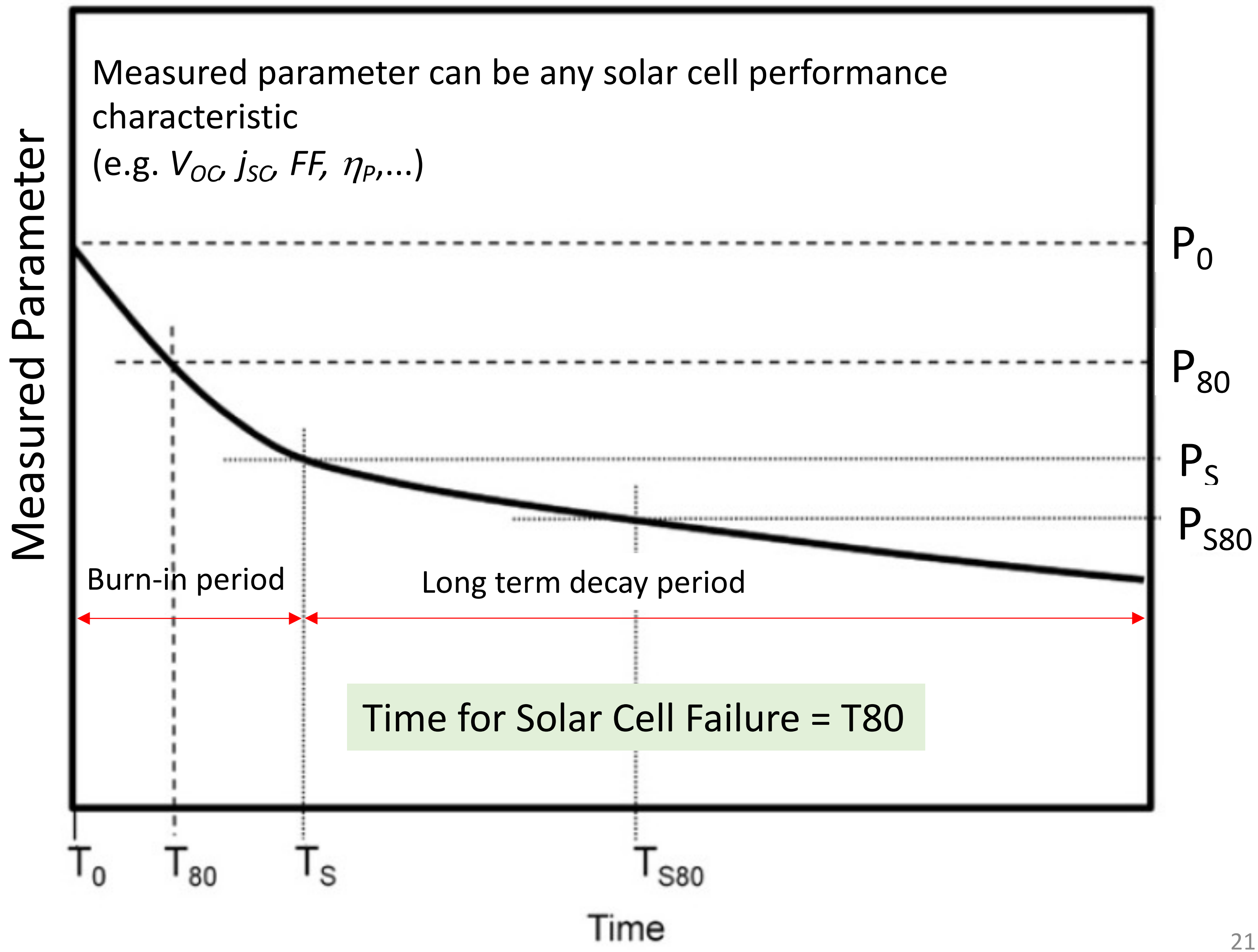
S = ratio of emission from phosphor to abs. of light by fluorophore

Geometric gain = ratio of concentrator to the cell areas

Flux gain = Geometric gain × propagation loss

Currie et al. Science 321, 226 (2008)

Quantifying OPV Lifetimes



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Analytical Approaches to Failure

(see also Ch. 6.7)

Burn in — Long term loss

Sum of Exponentials: $$P(t) = P_0 \exp(-t/\tau_1) + P_{ex} \exp(-t/\tau_2)$$

Stretched Exponential: $$P(t) = P_0 \exp\left[-(t/\tau_1)^{\beta}\right]$$

Degradation rate: $$k_{deg} = 1/\tau \;= k_0 \exp(-E_a/k_B T)$$

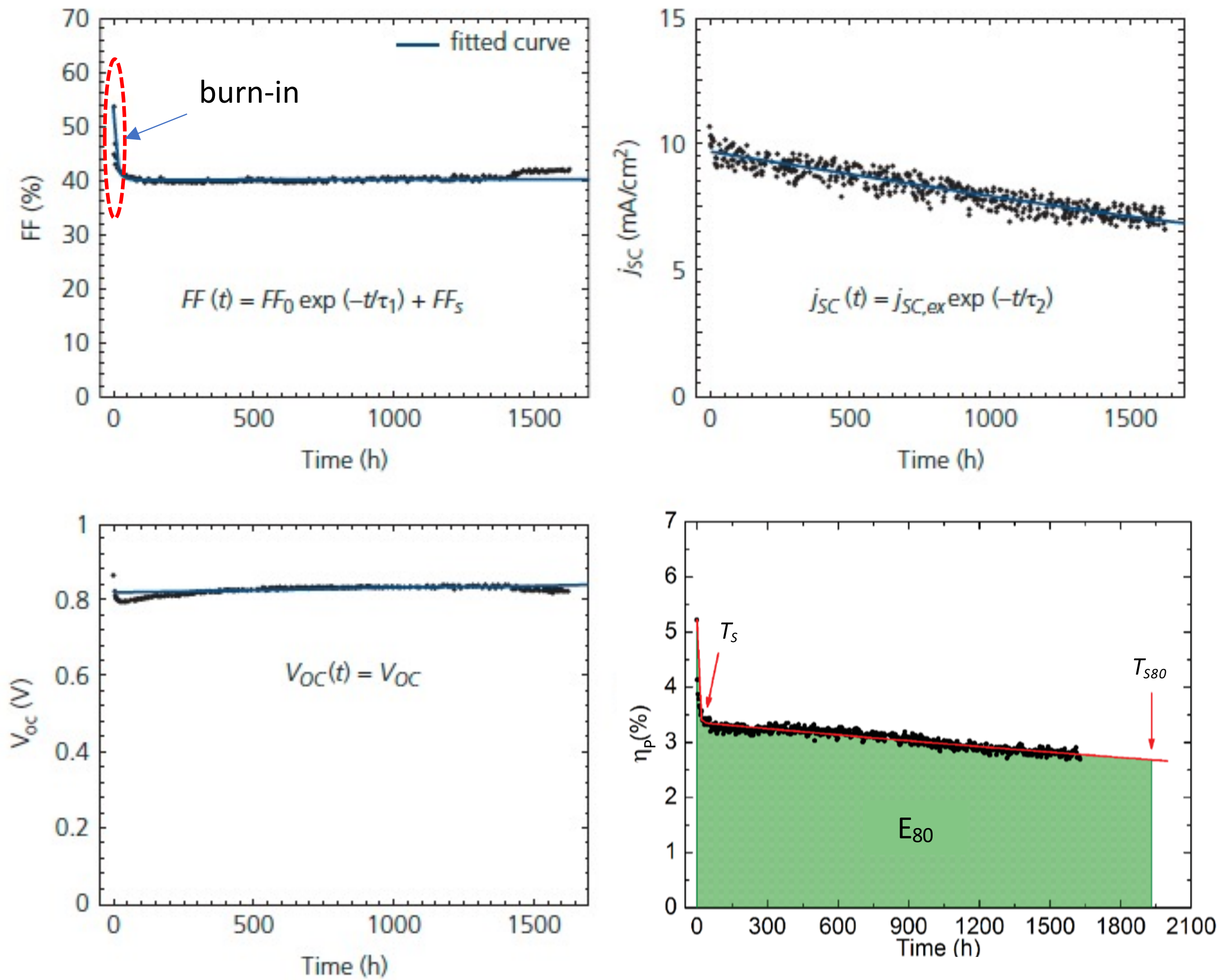
E_a = thermal activation of degradation rate, k_{deg}

Acceleration Factor: $$\mathcal{A} = \left(\frac{P_{inc}^1}{P_{inc}^2}\right)^{\gamma} \exp\left[-\frac{E_a}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

Total energy generated during cell useful life: $$E_{80} = \int_{t=0}^{T_{S80}} \eta_P(t) P_{inc}\, dt$$

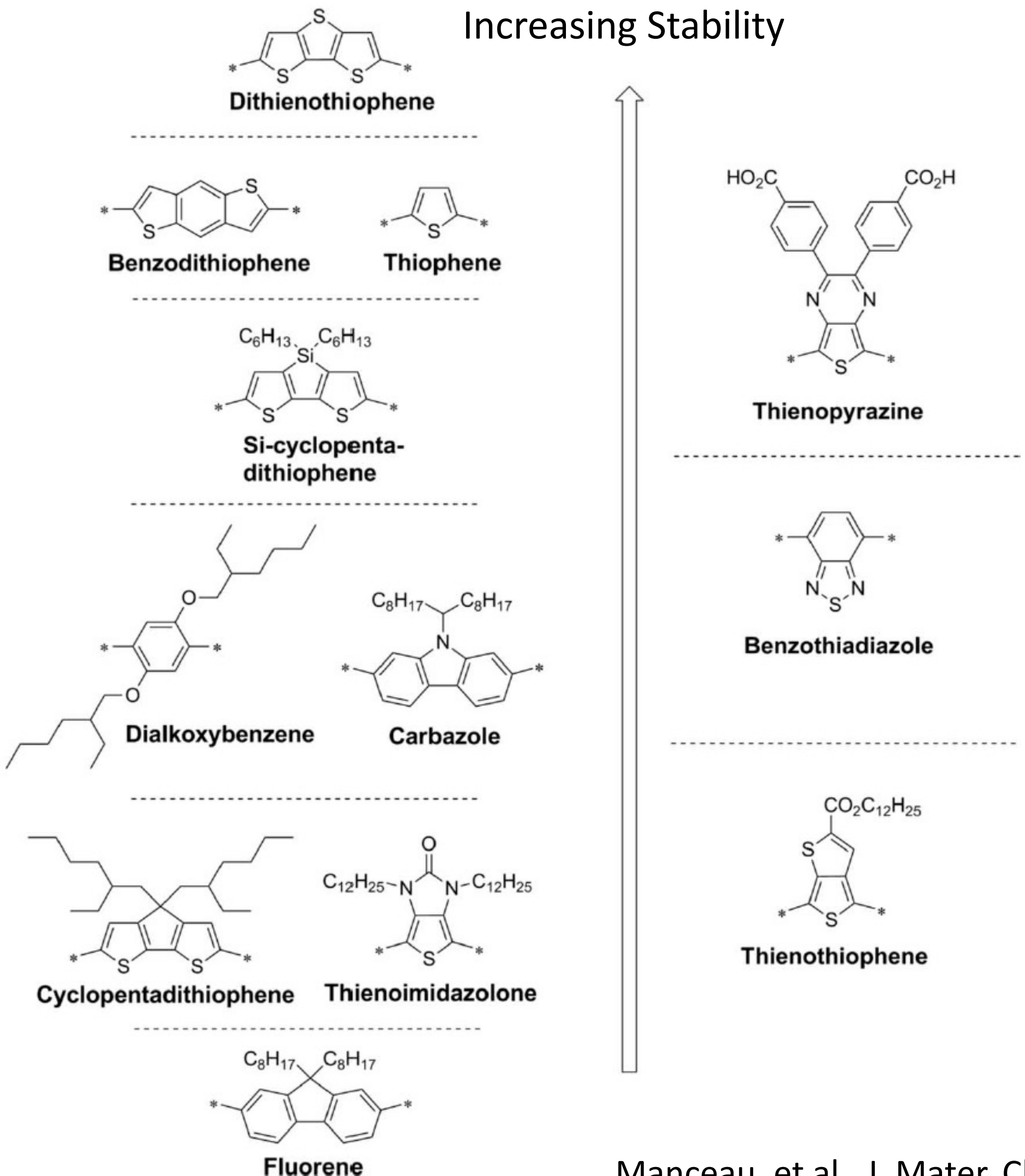
(assumes life begins after burn-in)

A Characteristic Data Set



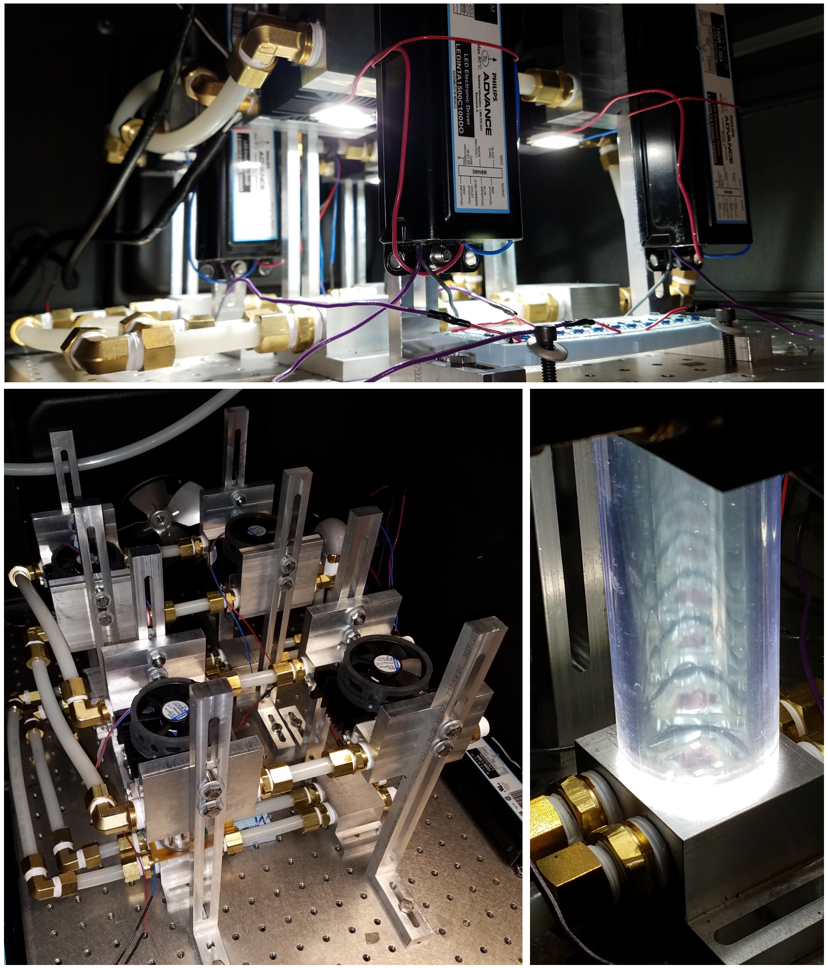
Roesch et al. Adv. Energy Mater. 5, 1501407 (2015)

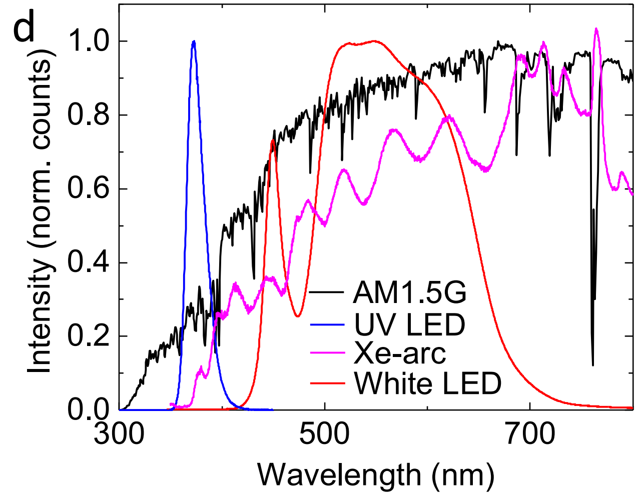
Choice of Molecules Impacts Stability

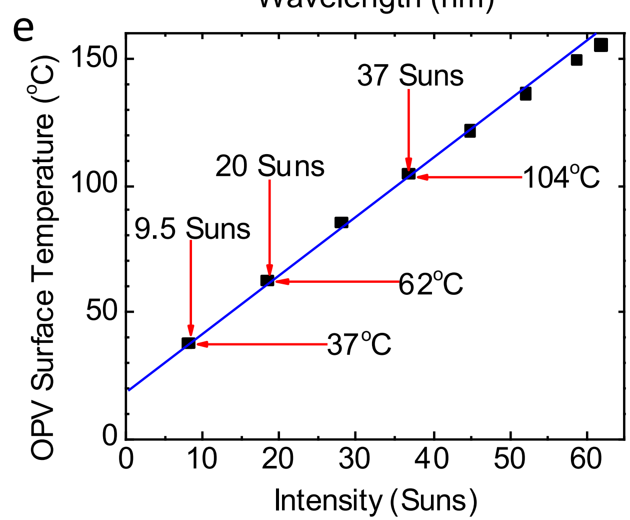


Manceau, et al., J. Mater. Chem., 21, 4132 (2011).

Test set up for Accelerated Aging





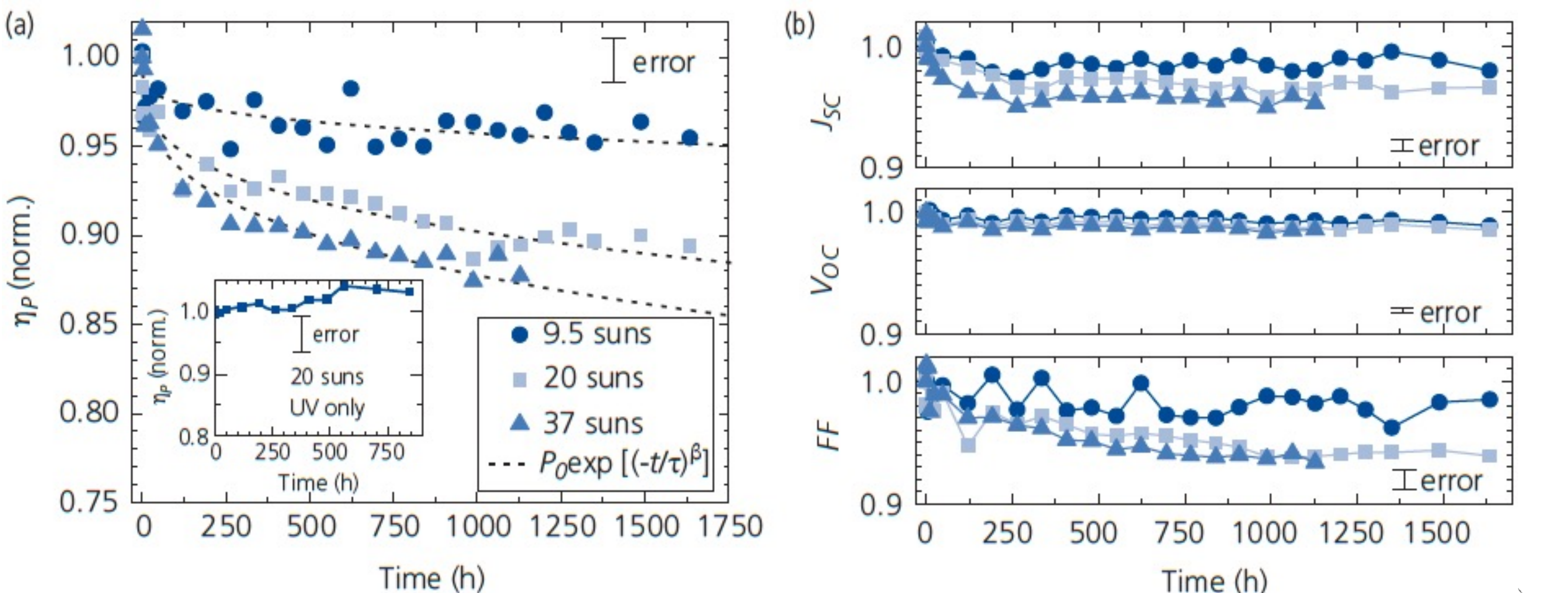


Populations of devices under very high intensity illumination using LEDs

Need to separate effects of temperature and intensity acceleration factors

Data for Extremely High Reliability DBP:C_{70} OPVs

Aging accelerated at high intensity



Q. Burlingame, et al., (2019),Nature, 573, 394.

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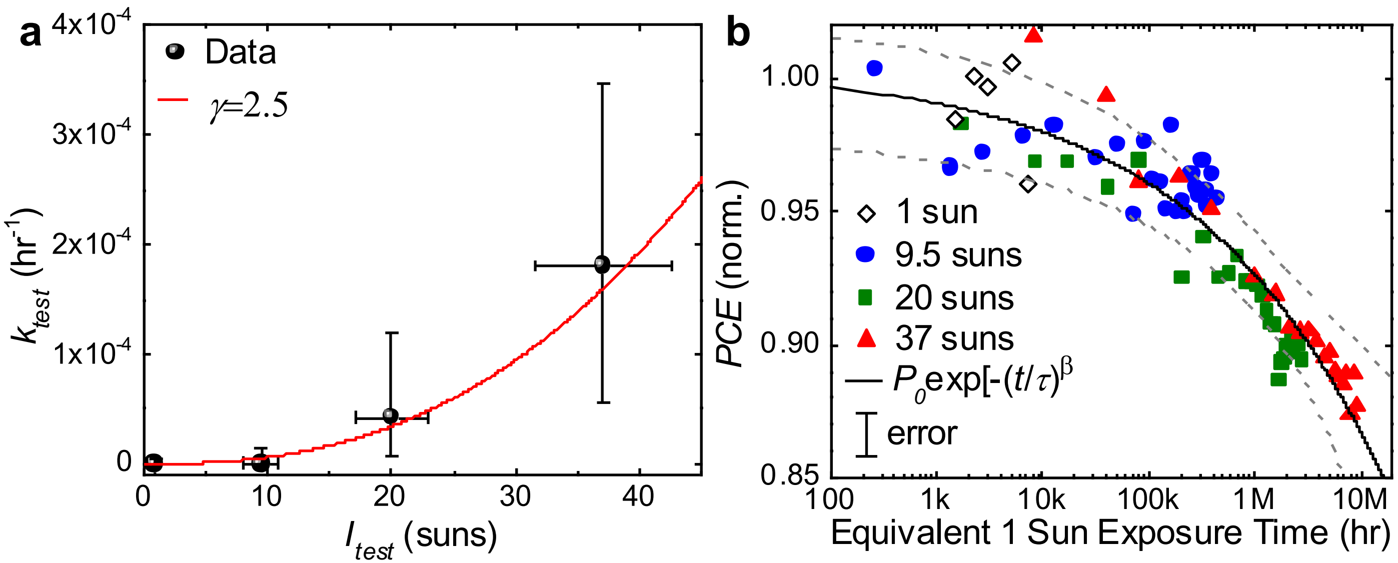
Stephen R. Forrest

Extracting Lifetime from Aging Data & Acceleration Factors



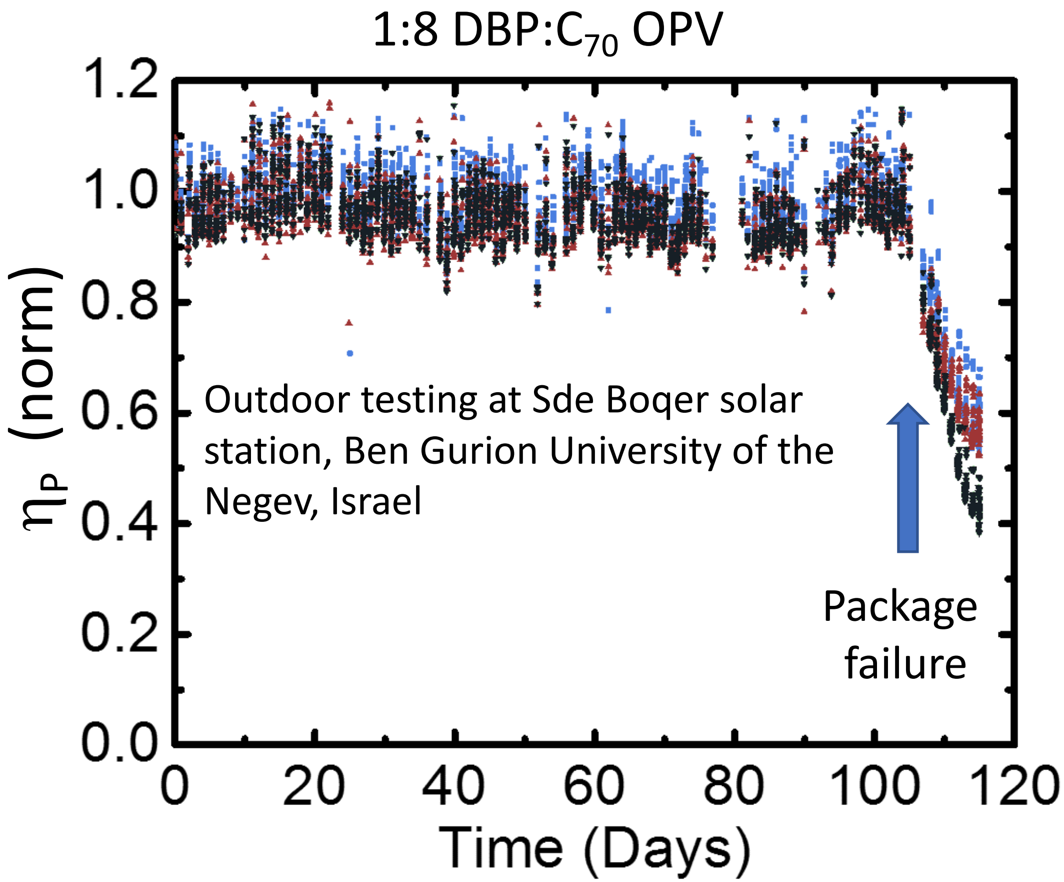
Extrapolated *intrinsic* lifetime: >10^4 years!

Metric for failure: T80; 5 h = 1 day solar equivalent

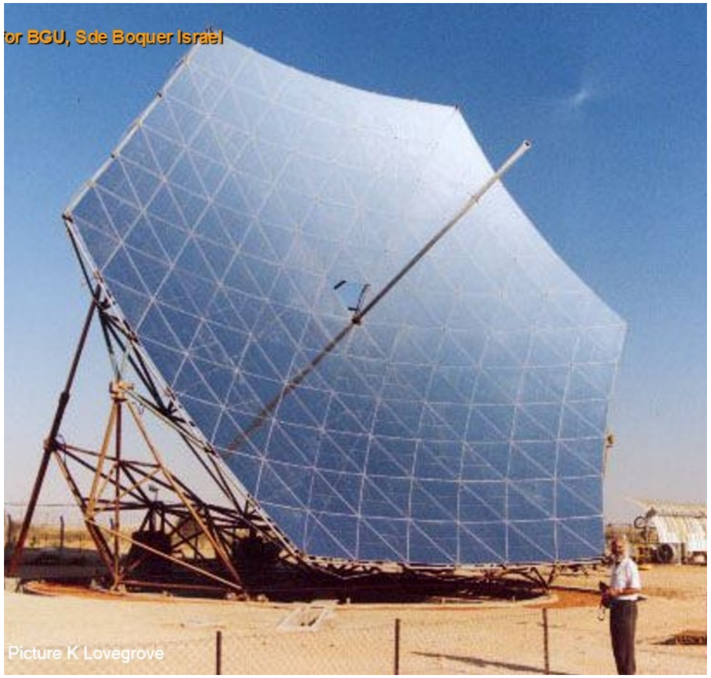
Q. Burlingame, et al., (2019),Nature, 573, 394.

What happens outdoors

Examining reliability in a real operating environment



Package failed after rain event



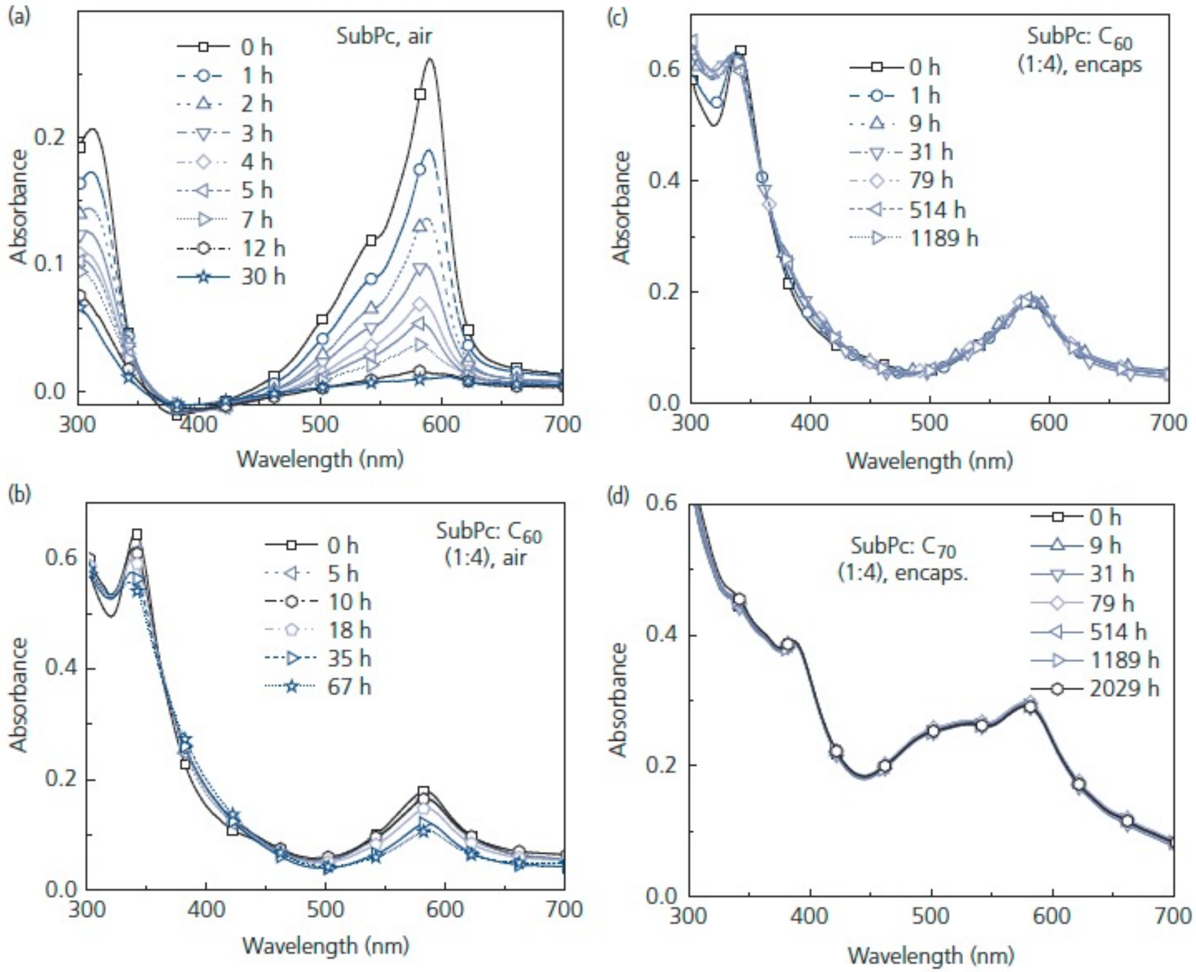
Solar concentrator system

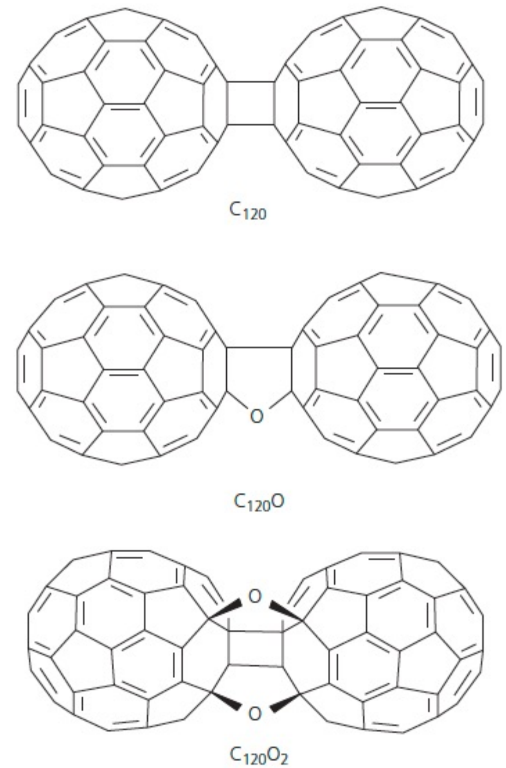
Ultimately, solar cell reliability depends on materials, morphologies and test conditions in actual environments

Burlingame et al. *Organic Electronics*, 41, 274 (2016).

Seeking the Chemical Origins of Failure

Absorbance changes of molecules and blends





C_{60} oligomerization implicated in photodegradation

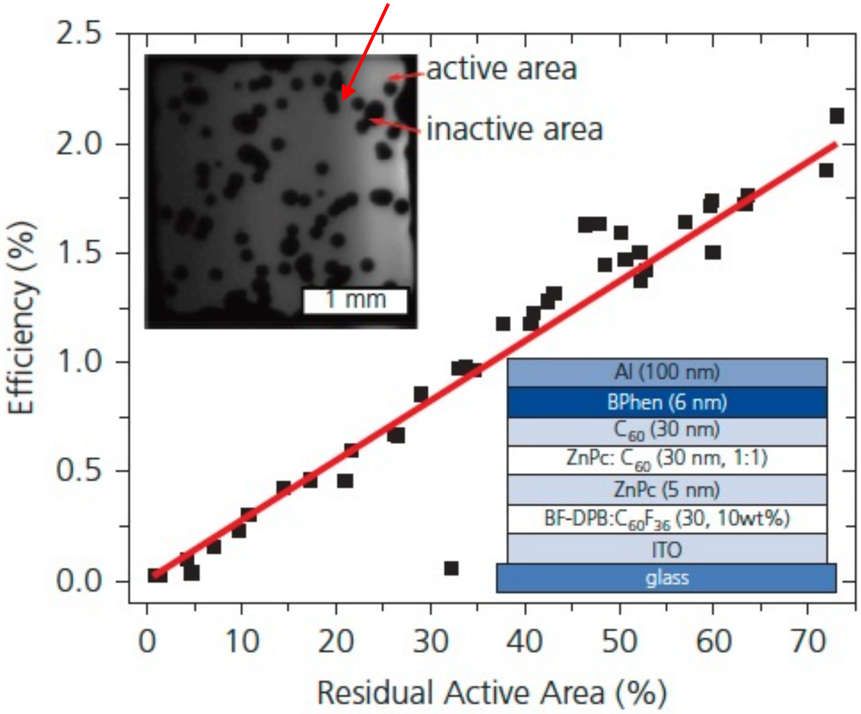
- Both SubPc and C_{60} degrade in air
- Degradation reduced for SubPc when encapsulated in N_2, but C_{60} still decays
- Blends show reduced decay rate: excitons in blends extremely short lived
- ⇒excitons and oxygen promote molecular destruction

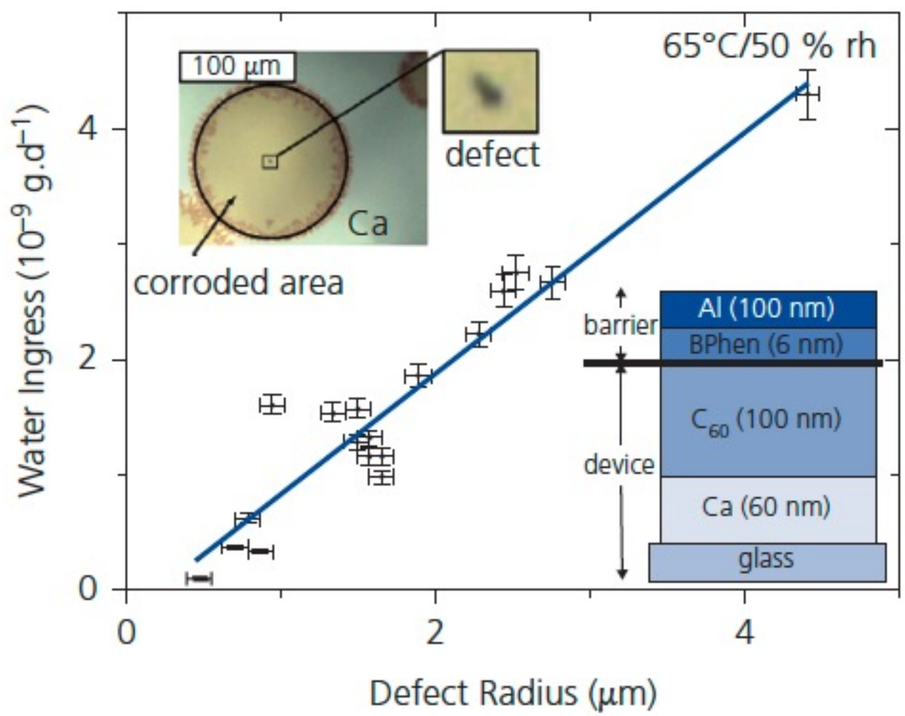
Wang et al. Solar Cells, 125, 170 (2014)

Dark Spots On Contacts

Similar to dark spot formation in OLEDs

EL image of contact





Device epoxy “sealed” to PET lid
Active device area equal to emissive area
Dark spots grow with time

WVTR vs. Defect radius shows defect growth with water exposure
Corroded area much larger than defect⇒penetration by dust?
Barrier formed by top contact

Klumbies et al. Solar Energy Mater. Solar Cells 120, 685 (2014)

Stress due to heating can damage film over time