Improving the light-harvesting of thin-film solar cells with photochemical upconversion

T. F. Schulze, Y. Y. Cheng, R. W. MacQueen, B. Fückel, J. Czolk, A. Danos, T. Khoury, M. J. Crossley, A. Colsmann, U. Lemmer, B. Stannowski, K. Lips, and T. W. Schmidt

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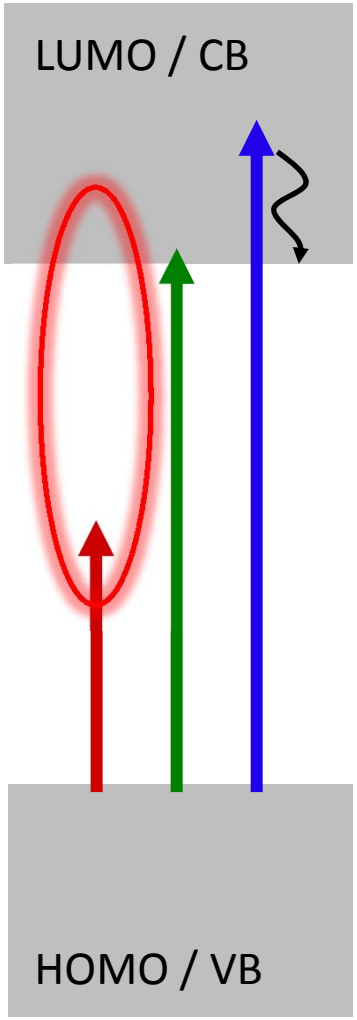
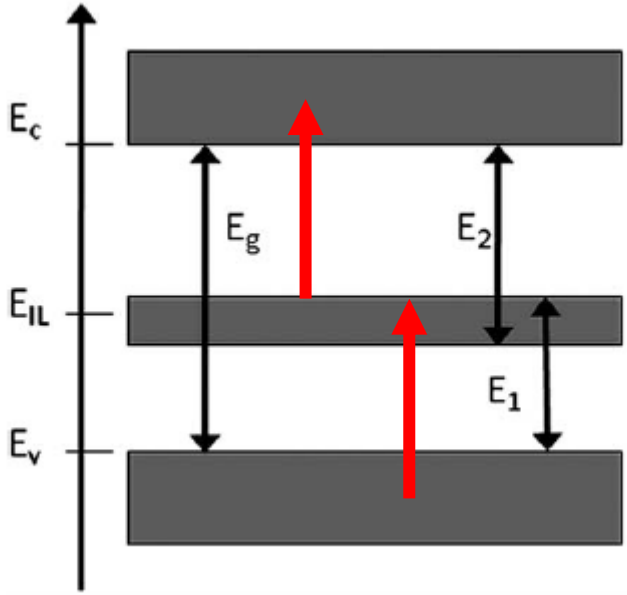
Harvesting sub-bandgap photons

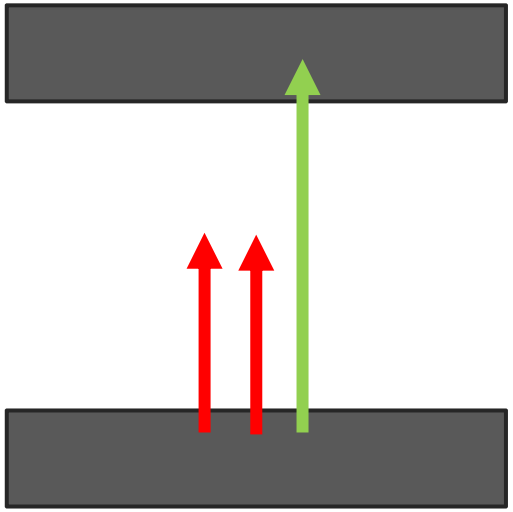


1) Intermediate band SC



Restructuring of electronic bands,
→ Re-engineering of solar cell

2) Photon Upconversion (UC)



Spectral conversion by add-on unit
→ Augmentation of existing solar cell technology

Options for photon upconversion

Coherent UC

Two-photon absorption

Coherent effect
Extremely high light intensity
$\Rightarrow$ $MWcm^{-2}$ – $GWcm^{-2}$
$\Rightarrow$ 10^7suns

Incoherent UC

Energy Transfer Upconversion (ETU)

QE of a few % is useful
Lanthanide-doped crystals and glasses
Applicable in a solid state concept

Shalav et al., Appl. Phys. Lett. **86** (2005) 013505

Photochemical Upconversion (UC)

Figure of merit about three orders of magnitude better than Er-based UC

Triplet-Triplet Annihilation (TTA)
Non-coherent UC
Potential at one sun?

Baluschev et al. Phys. Rev. Lett. **97** 143903 (2006)

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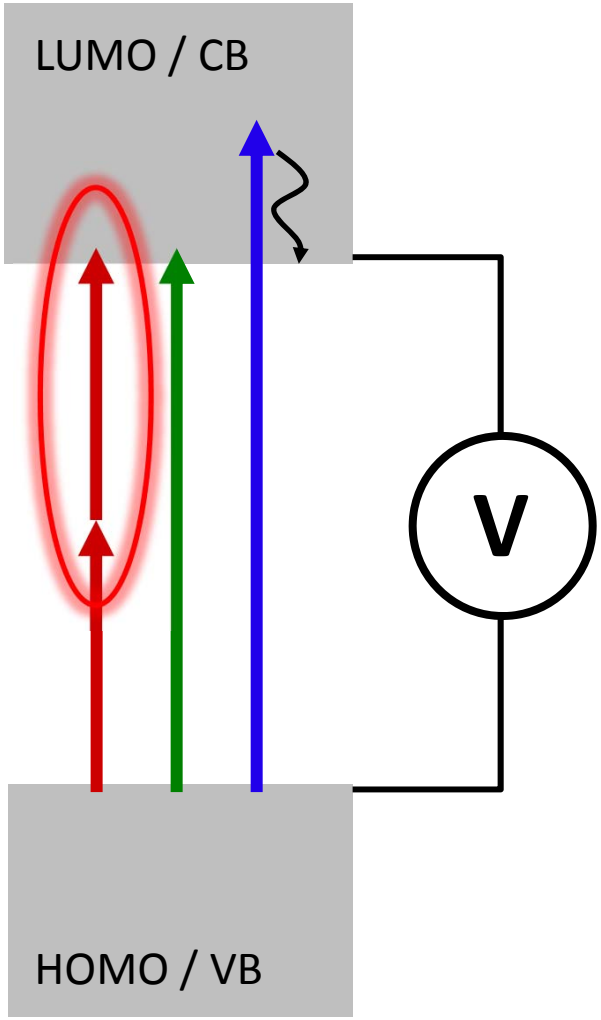
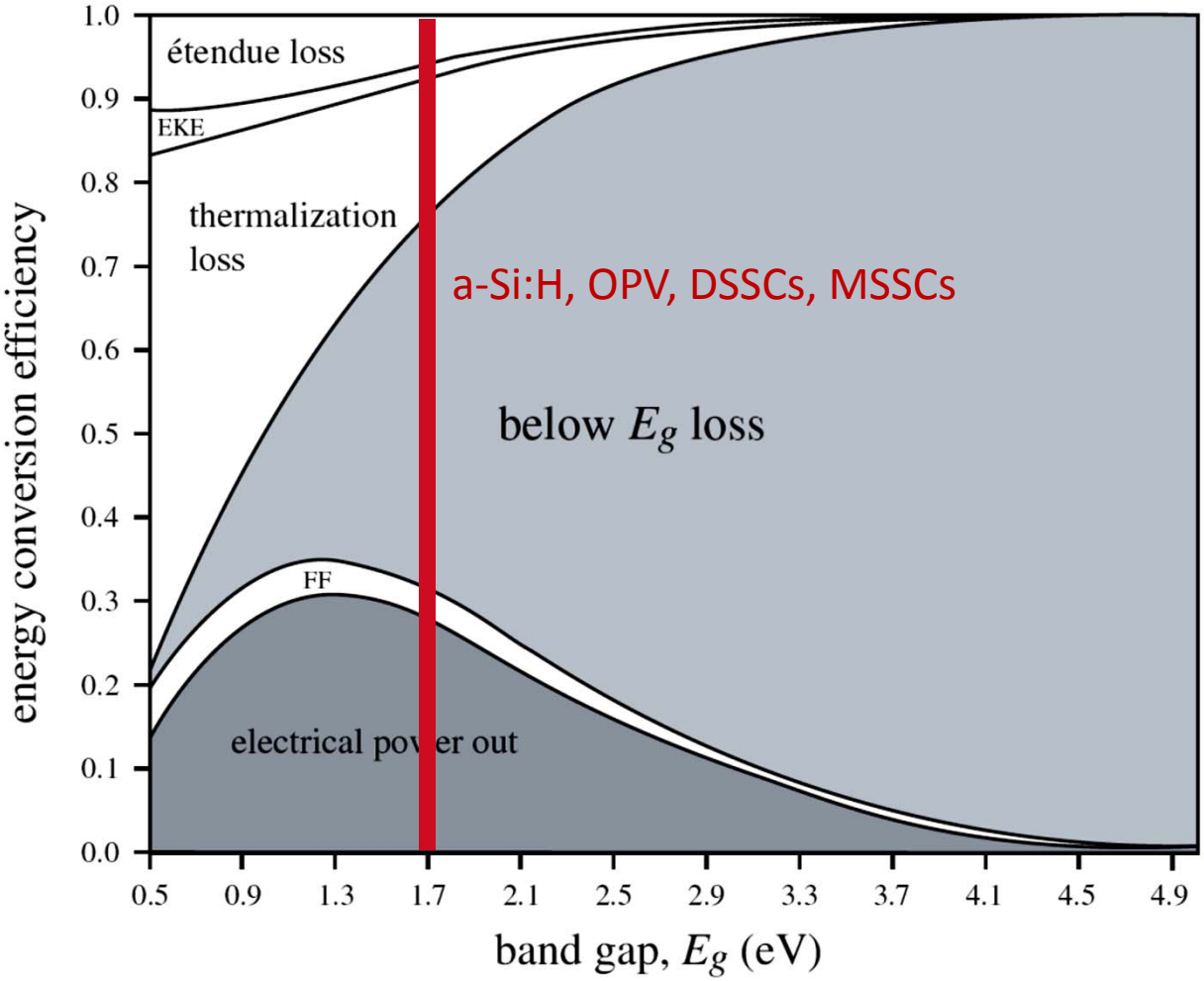
Outline

1. Efficiency gains by upconversion
2. What is triplet-triplet annihilation?
3. Spin physics and rate equations
4. State-of-the-art in device application
5. How to further improve ΔJ_{SC}
6. Outlook

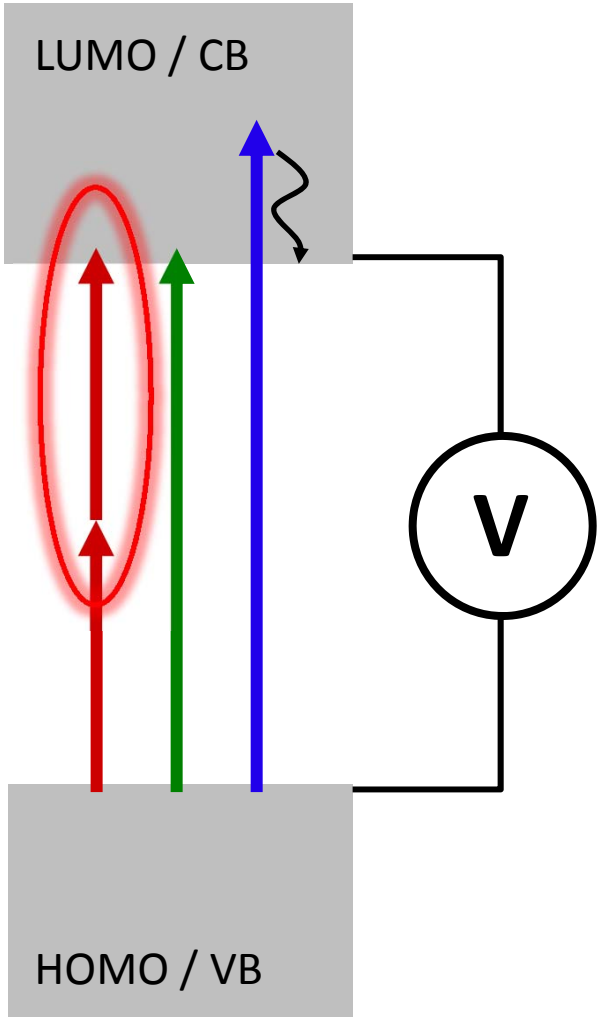
Efficiency limits of single-threshold solar cells

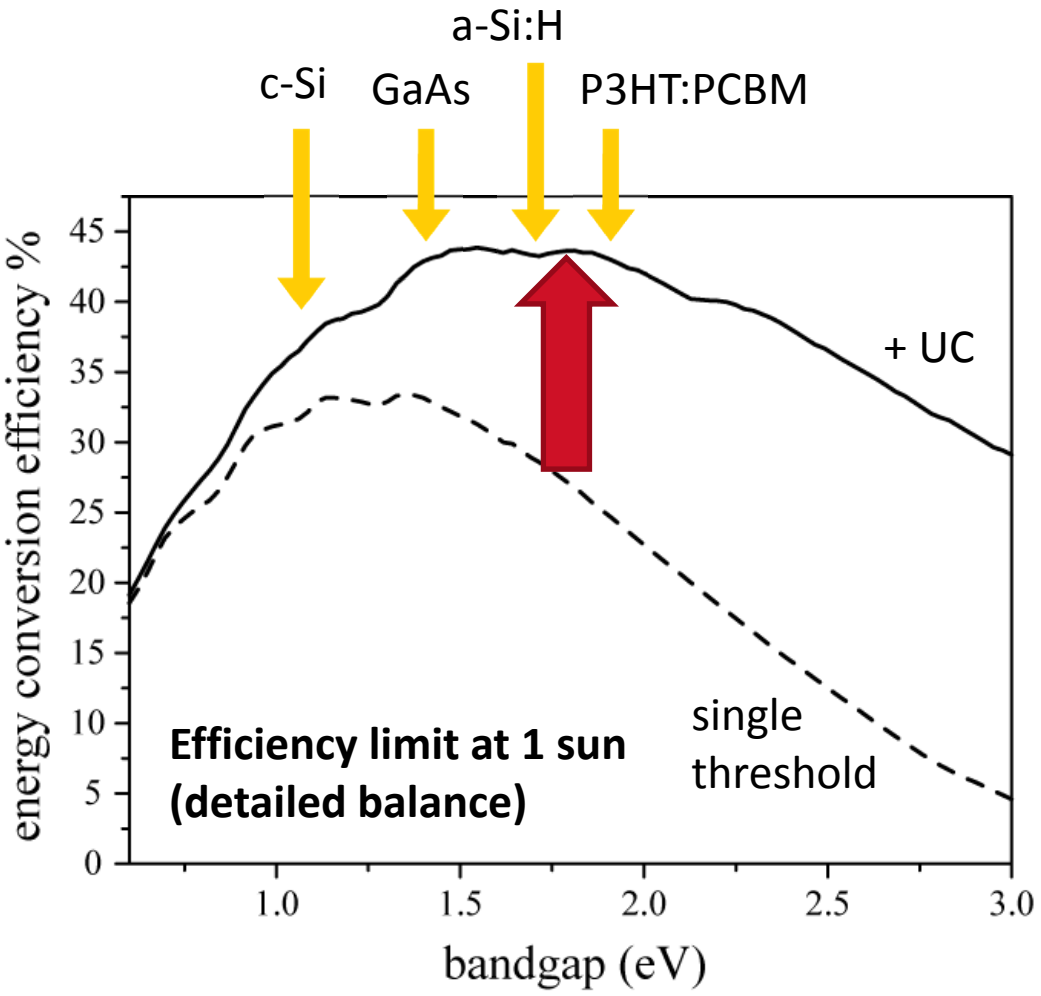




L. Hirst and N. Ekins-Daukes, Prog PV **19**, 286 (2011)

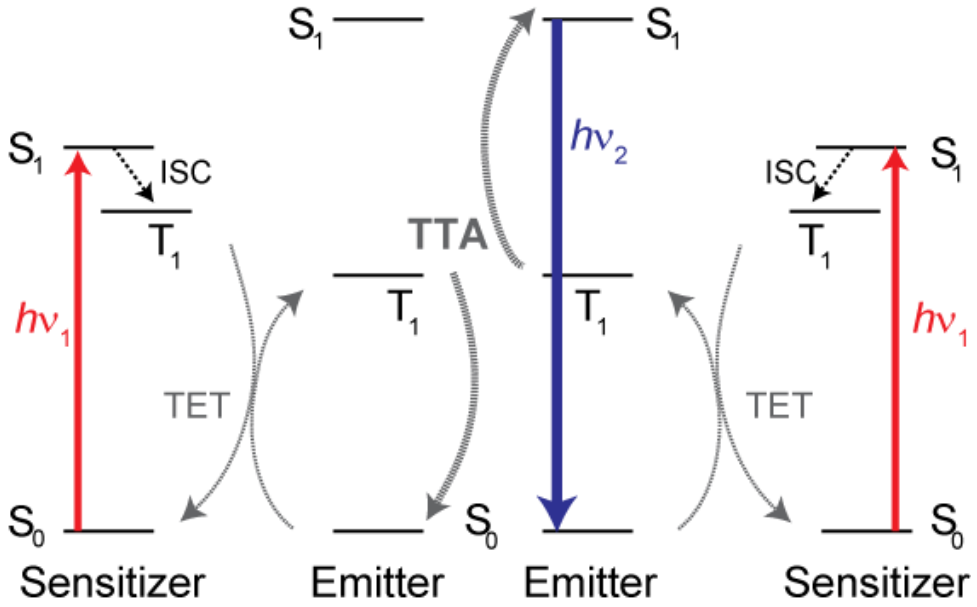
Efficiency limits of single-threshold solar cells

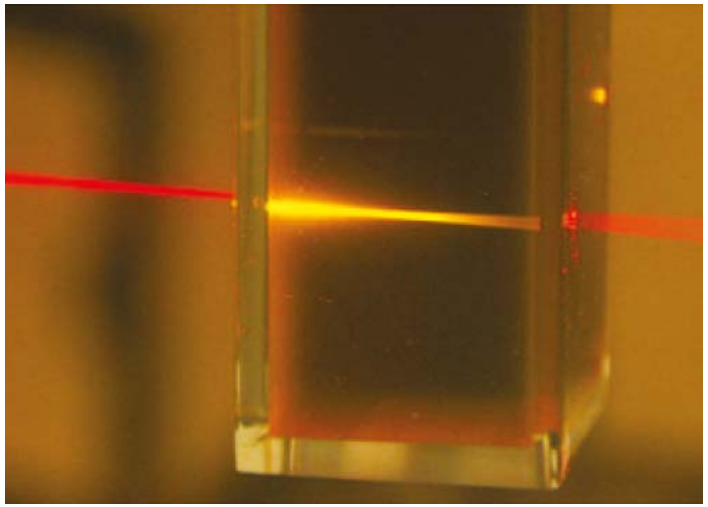


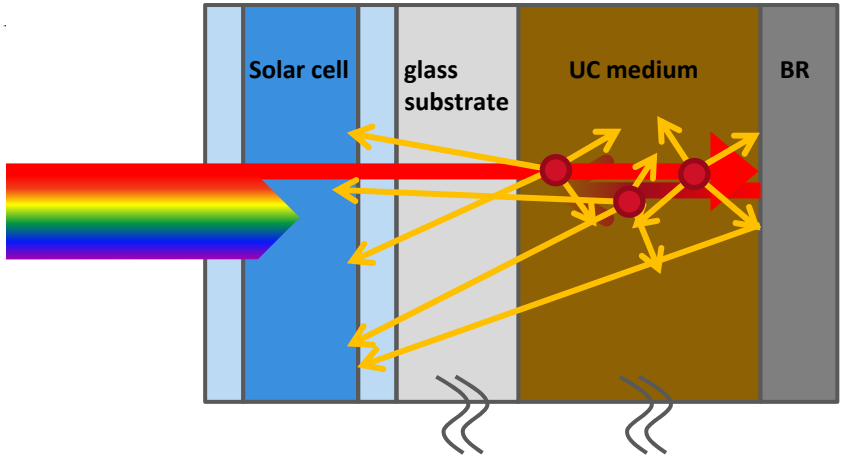


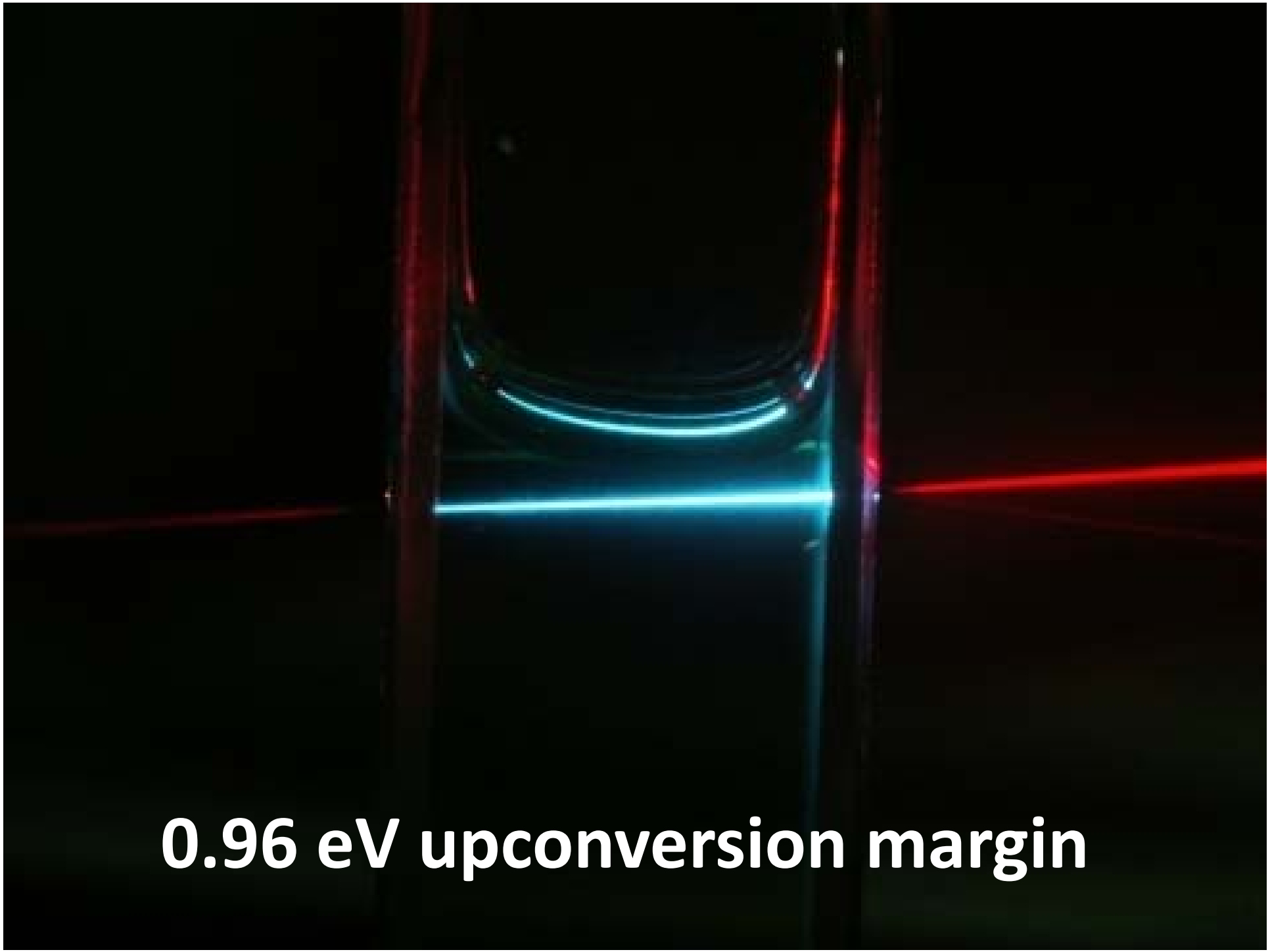
M. J. Y. Tayebjee and T. W. Schmidt, *in Comprehensive Renewable Energy, Elsevier 2012*

Triplet-triplet annihilation upconversion

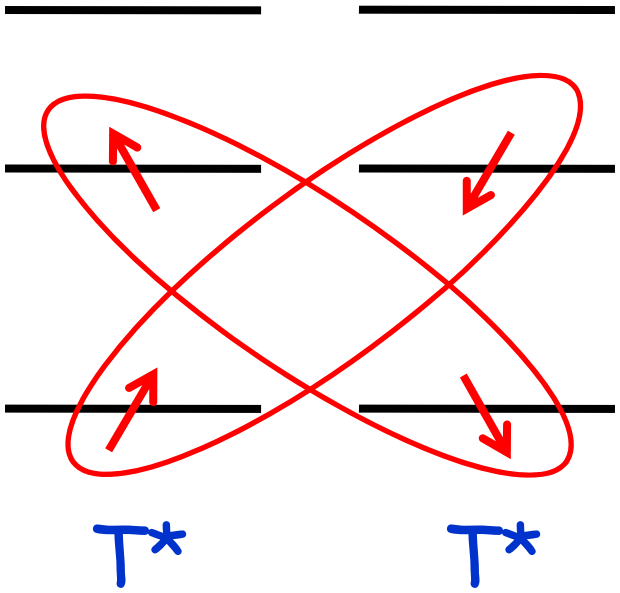






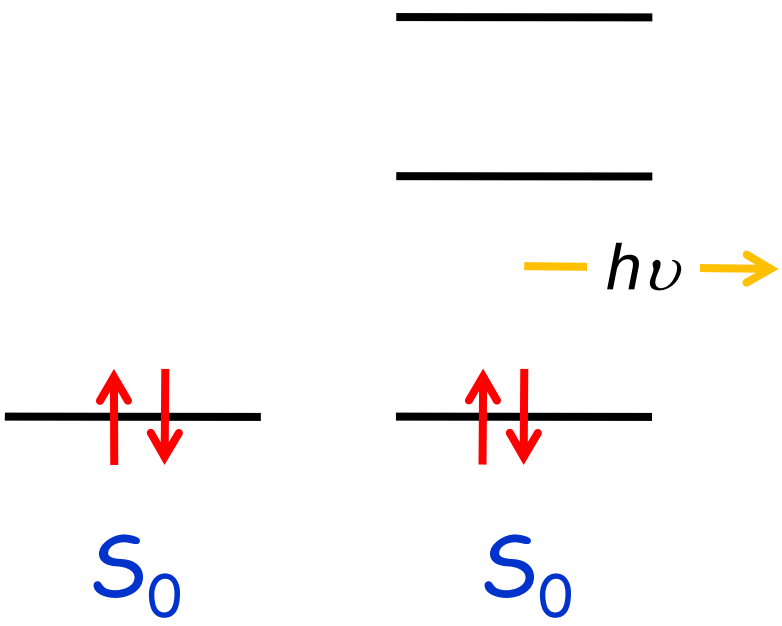

0.96 eV upconversion margin

TTA efficiency: Spin statistics



J. L. Charlton, et al. J. Am. Chem. Soc. 105 (1983) 3473

TTA efficiency: Spin statistics



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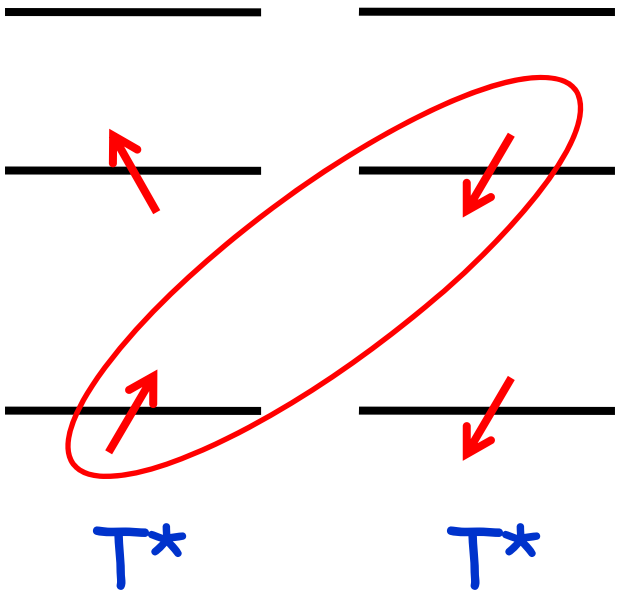

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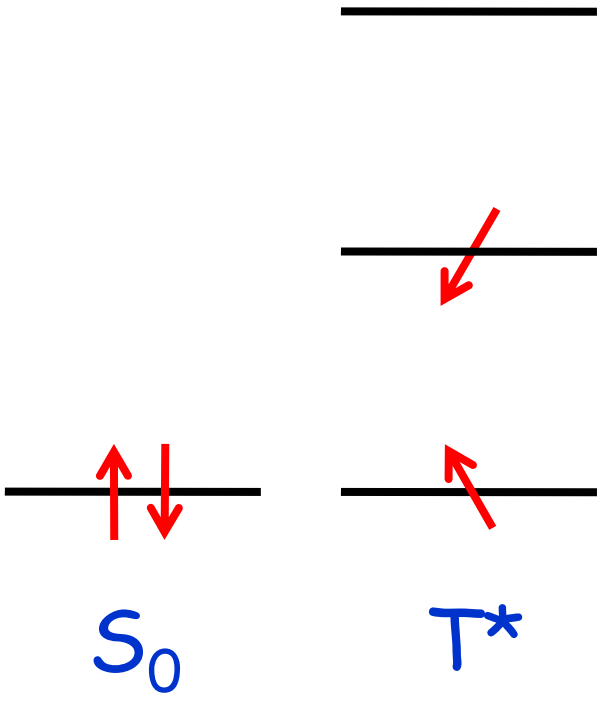


S	T	Q
T	T	Q
Q	Q	Q

Simple reasoning: Only 1 out of 9 collisions statistically gives a singlet !

=> 11% conversion efficiency

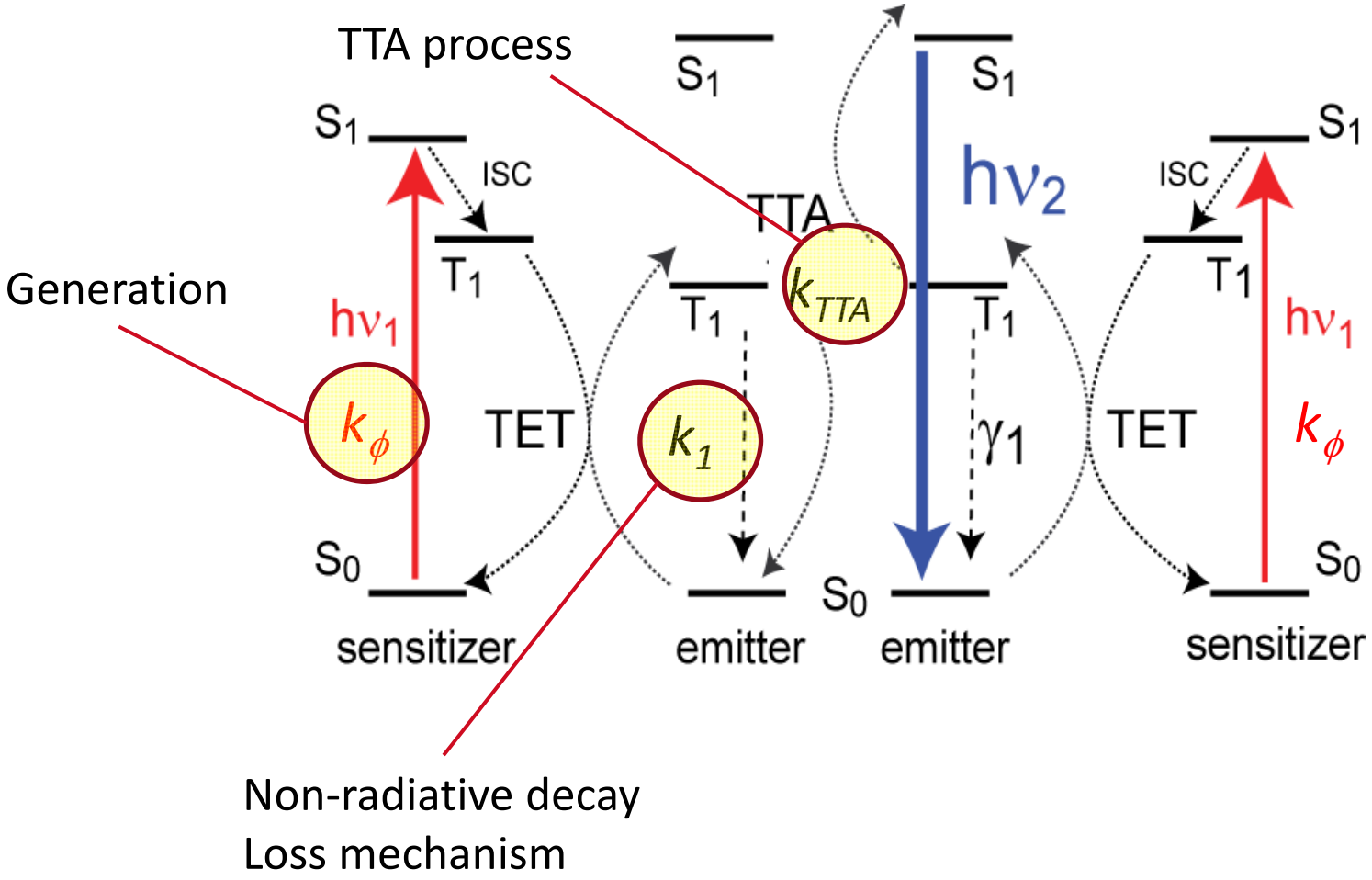
Experiment: 60% conversion eff.

Quintet states cannot be populated!

Triplet channel barely open, one T* recovered!

Cheng et al., J. Phys. Chem. Lett. 1, 1795 (2010)

TTA dynamics: Rate equations



TTA dynamics: Rate equations

Rate equations

$$0 = \frac{dN_T}{dt} = k_\phi N_S - k_1 N_T - k_{\mathrm{TTA}} N_T^2$$

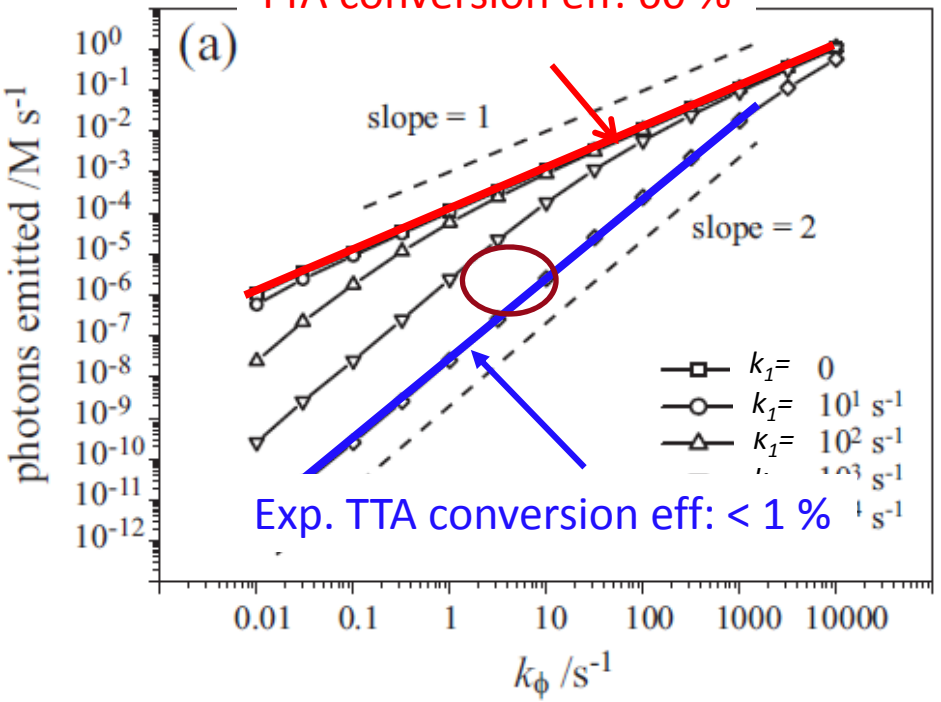
$$f = \frac{k_{\mathrm{TTA}} N_T}{k_1 + k_{\mathrm{TTA}} N_T}$$

Fraction of emitters undergoing TTA

$$N_T = \frac{k_\phi N_S}{k_1}$$

Emitter triplet concentration

TTA conversion eff: 60 %



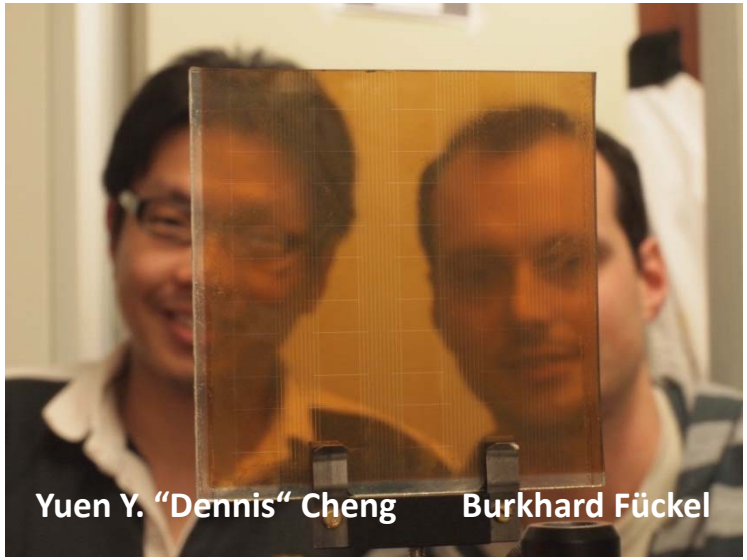
Exp. TTA conversion eff: < 1 %

Auckett et al., J. Physics: Conference Series 185, 012002 (2009)

Concentrate light!
Back-reflectors
Micro-focussing
Near-field effects,…

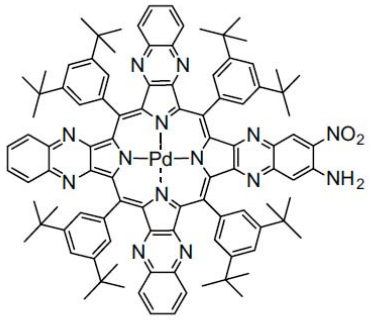
Concentrate sensitizers!
Solid-state approaches
Adsorbates,…

Choice of materials & Spectra



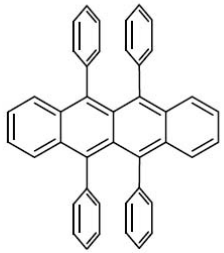
Bifacial, transparent a-Si:H pin solar cell prepared at HZB's Photovoltaic Competence Center Berlin (PVcomB), conversion efficiency = 7.5 %.

Sensitizer



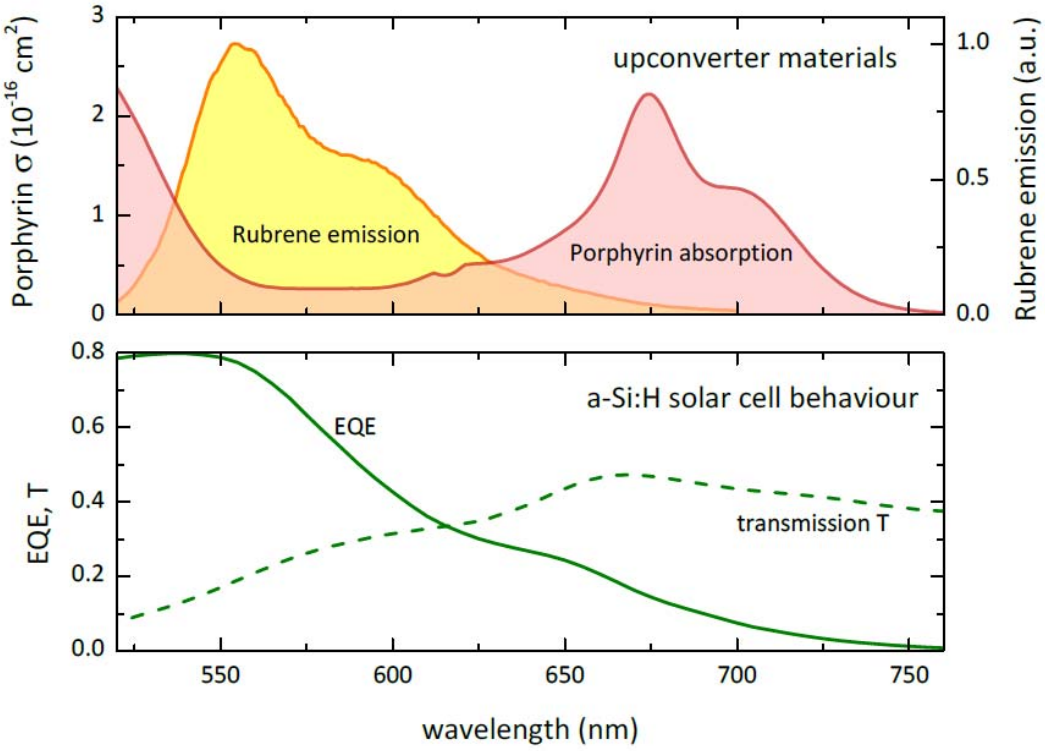
PQ_4PdNA

Emitter

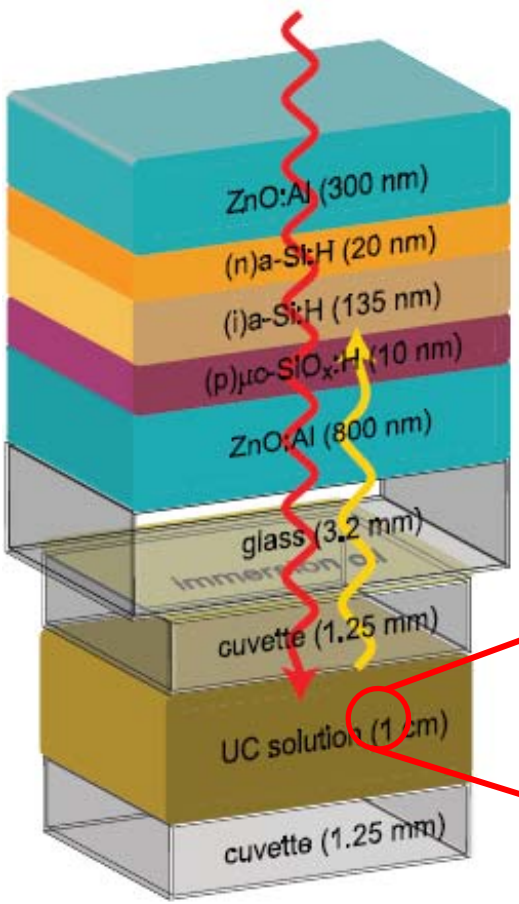


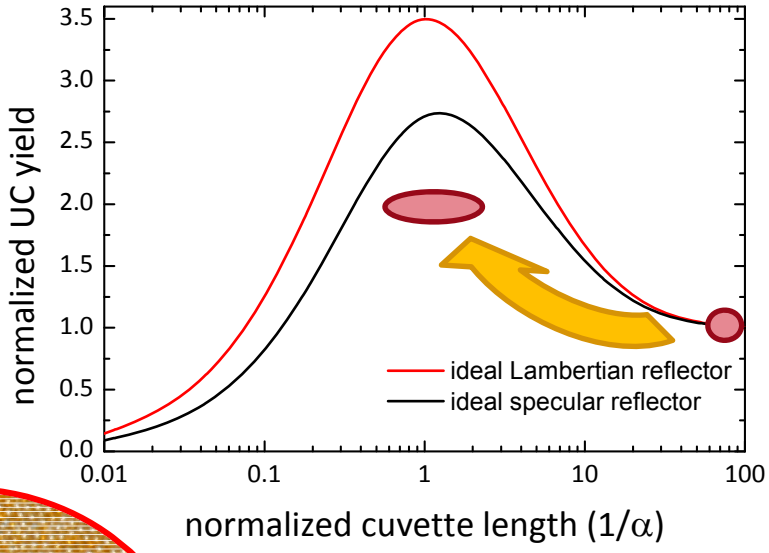
rubrene

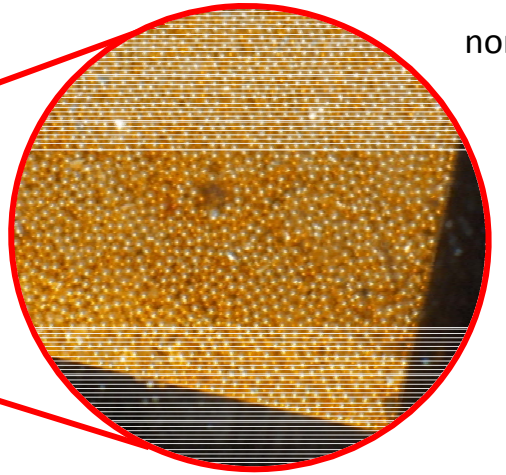
Solvent: Toluene



Optical configuration







$\eta_{\downarrow}$ = 3.9 %

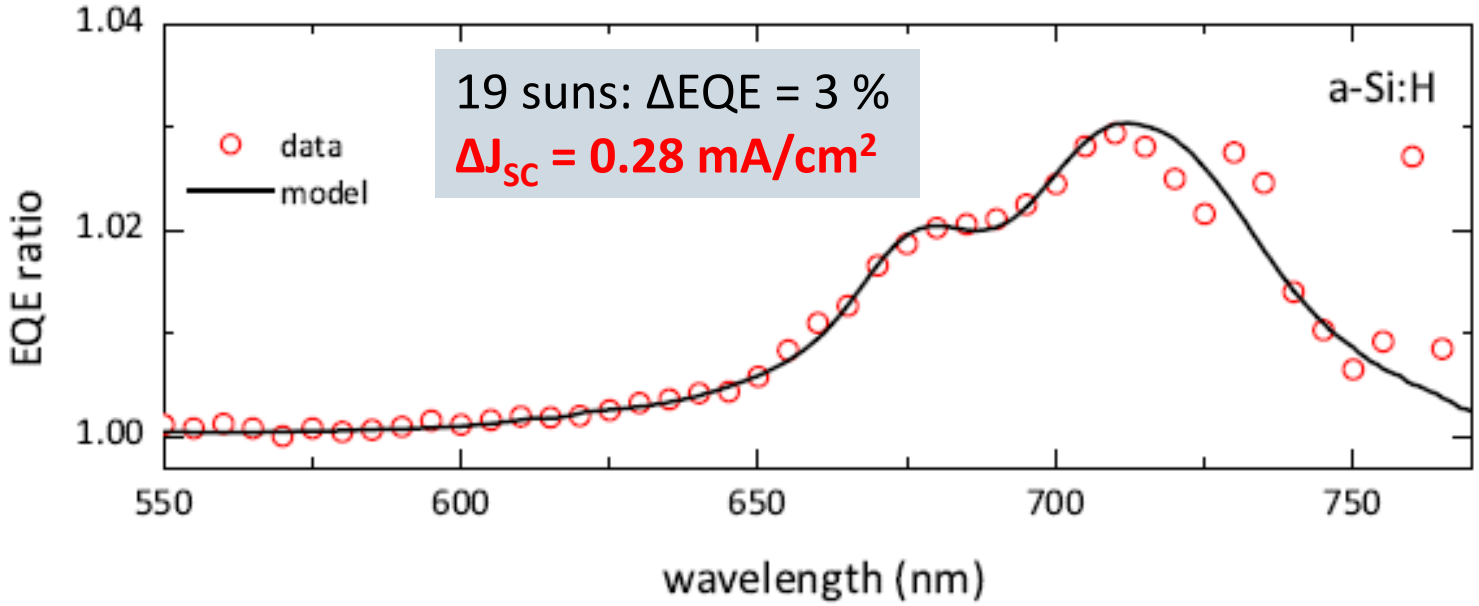
$\eta_{\uparrow}$ = 7.5 % (w. reflector)

Cheng, Schulze et al., Energy Environ. Sci. 5, 6953–6959 (2012)

Schulze et al., Aust. J. Chem. 65, 480–485 (2012)

UC effect seen in solar cell EQE

a-Si:H pin cell
w. back reflector
(Ag-coated beads)



Lines are model fits for UC effect in EQE:

$$\frac{\mathrm{EQE_{UC}}(\lambda)}{\mathrm{EQE_0}(\lambda)} = 1 + \chi \times \frac{T_{\mathrm{SC}}(\lambda)}{\mathrm{EQE_0}(\lambda)} \frac{\sigma(\lambda)\sigma_b}{\sigma(\lambda)+\sigma_b}$$

Efficiency of UC

Opt. cross section of UC

Transmission of SC/UC unit

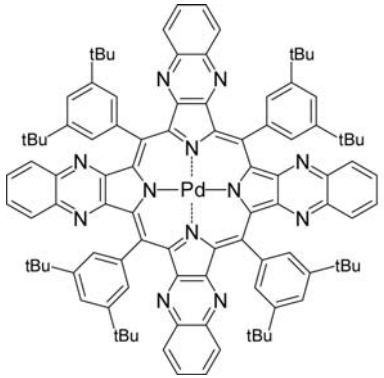
Opt. cross section of UC for bias light

Schulze et al., J. Phys. Chem. C, online (2012)

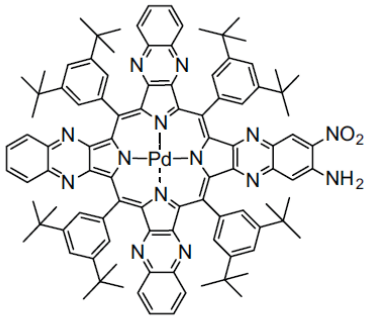
…as compared to very first results

170 suns

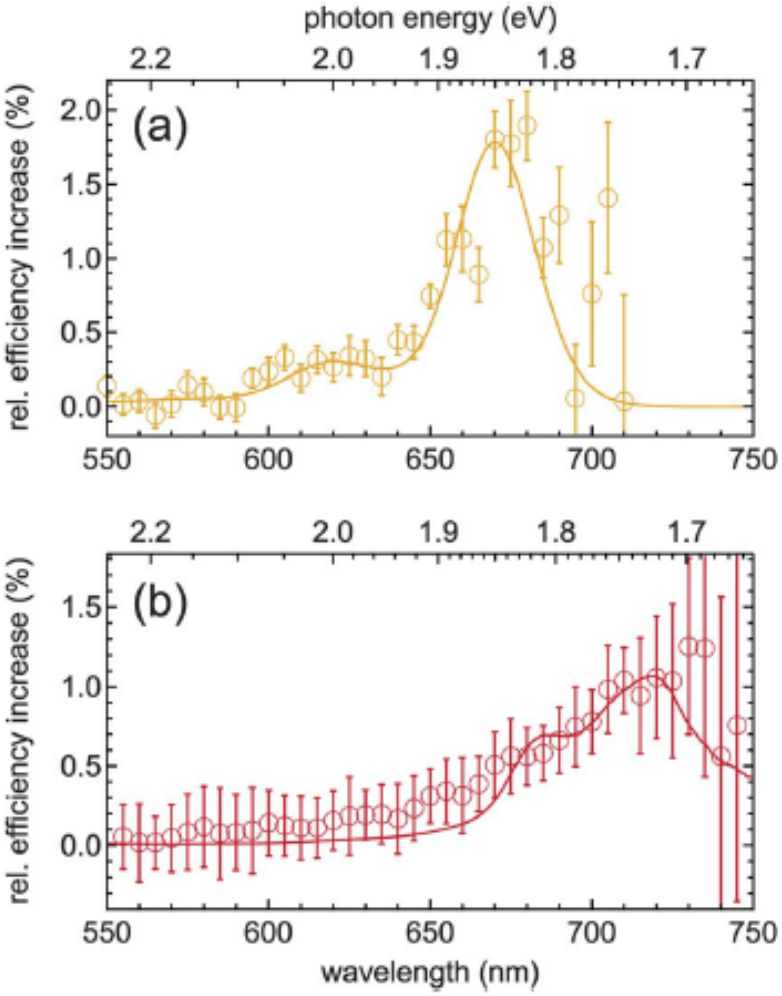
PQ_4Pd



50 suns



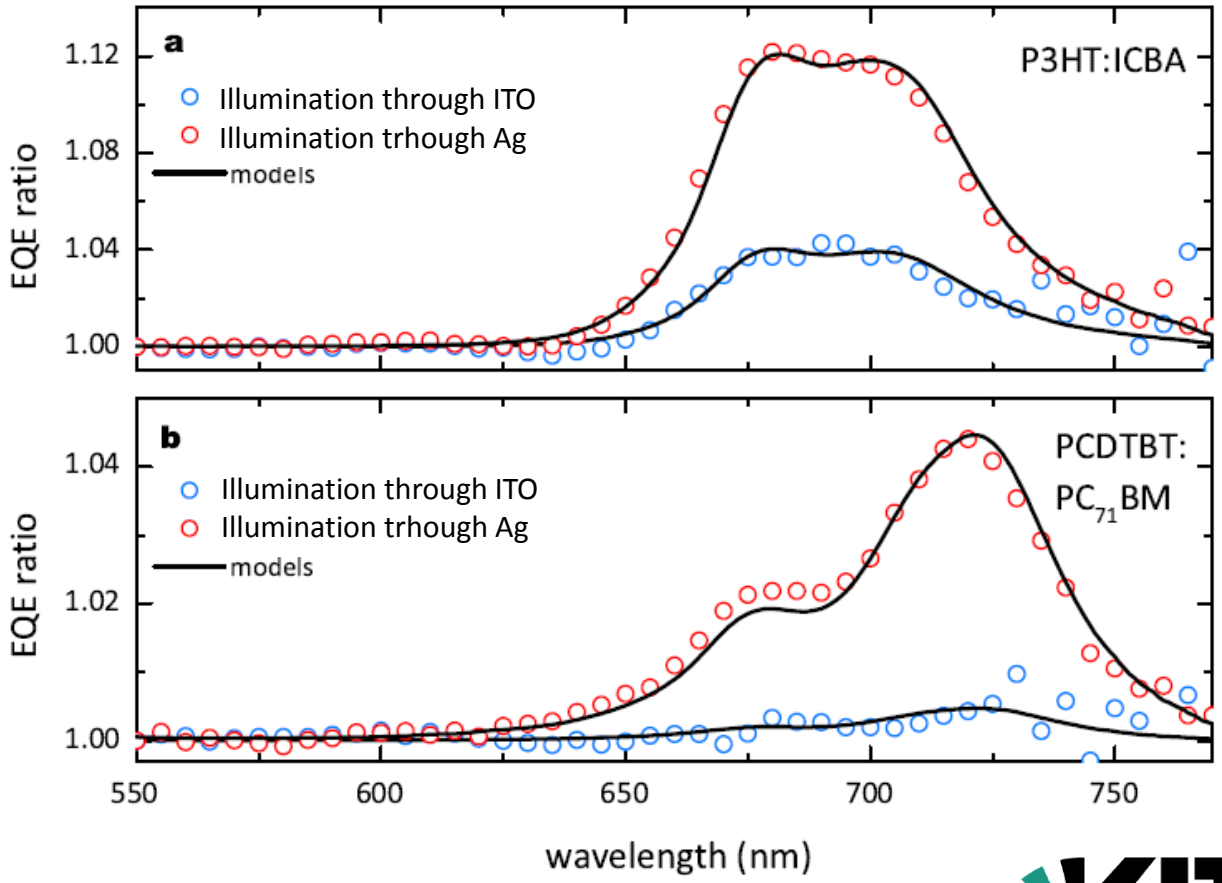
PQ_4PdNA



Cheng, Schulze et al., Energy Environ. Sci. 5, 6953–6959 (2012)

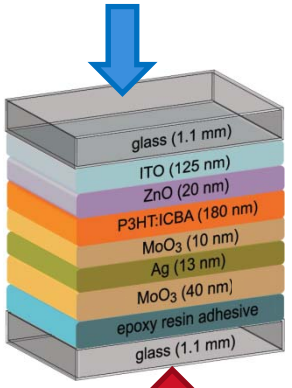
Experimental results on OPV

UC signal in EQE of OPV cells

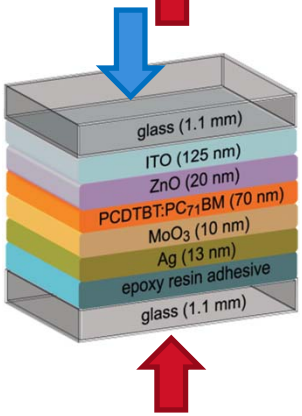


Schulze et al., J. Phys. Chem. C, online (2012)

Eff. solar conc.:
29 suns



$\eta_{\downarrow}$ = 3.1%
$\eta_{\uparrow}$ = 1.7%



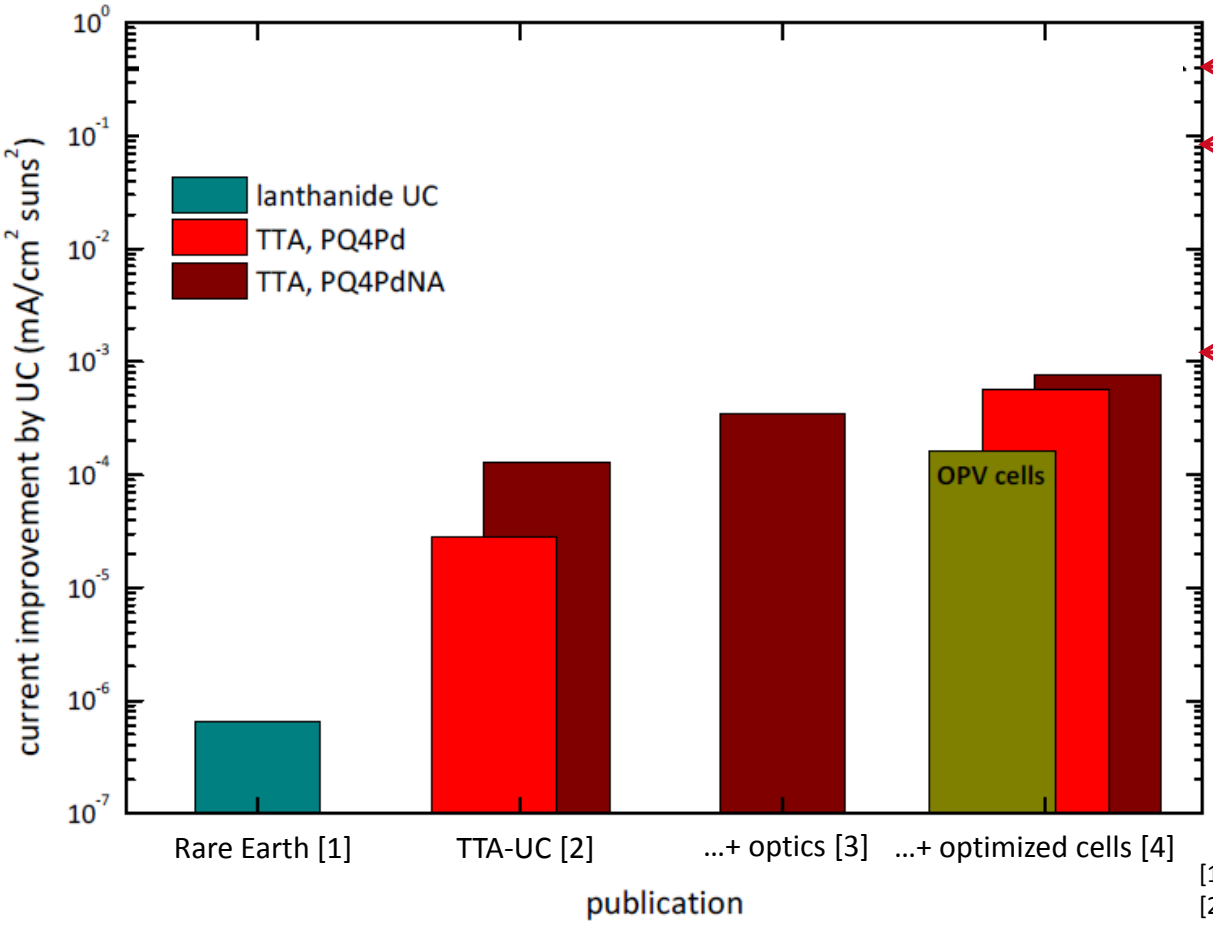
$\eta_{\downarrow}$ = 3.6%
$\eta_{\uparrow}$ = 2.3%

Karlsruhe Institute of Technology

Cells designed & produced by
J. Czolk & A. Colsmann at KIT

Prospects for TTA-upconversion

Analyzing the figure of merit: Current enhancement at 1 sun for a-Si:H cells



Yield at maximum η_{UC}

100 x $C_{Sensitizer}$, optimized optics

current concentrations, optimized optics

FOM = $\Delta j_{sc} / C^2$

[1] De Wild et al., Sol. Energ. Mat. Sol. C. 94, 2395–2398 (2010)
[2] Cheng et al., Energy Environ. Sci. 5, 6953–6959 (2012)
[3] Schulze et al., Aust. J. Chem. 65, 480–485 (2012)
[4] Schulze et al., J. Phys. Chem. C, online (2012)
Schulze et al., J. Photonics for Energy, submitted (2012)

Crucial quantities for optimization

Rate equations

$$0 = \frac{dN_T}{dt} = k_\phi N_S - k_1 N_T - k_{\mathrm{TTA}} N_T^2$$

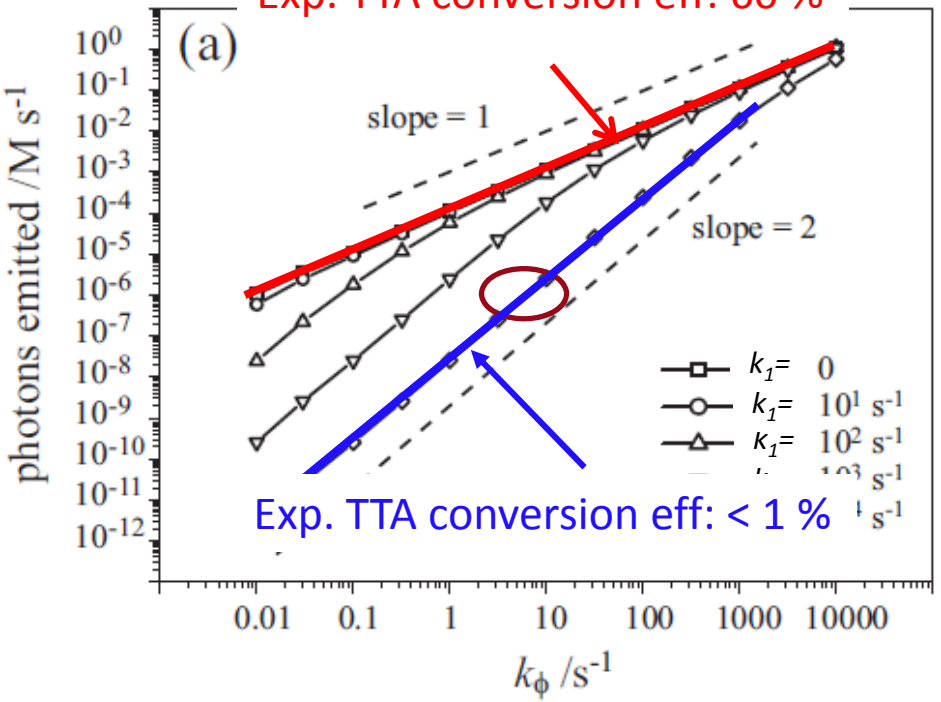
$$f = \frac{k_{\mathrm{TTA}} N_T}{k_1 + k_{\mathrm{TTA}} N_T}$$

Fraction of emitters undergoing TTA

$$N_T = \frac{k_\phi N_S}{k_1}$$

Emitter triplet concentration

Exp. TTA conversion eff: 60 %



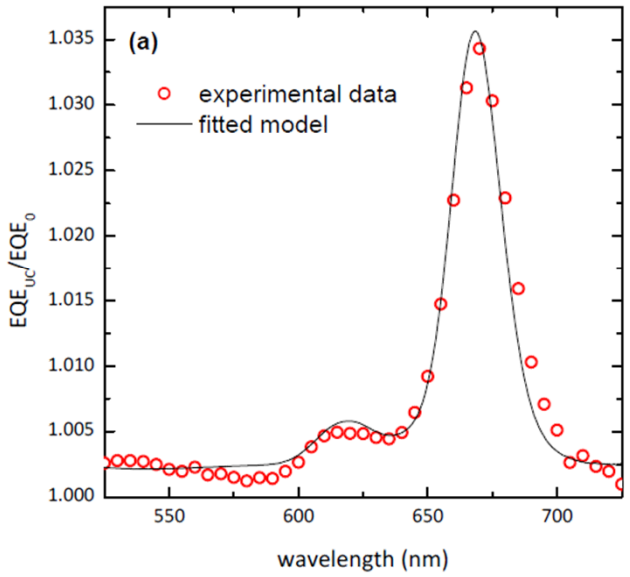
Exp. TTA conversion eff: < 1 %

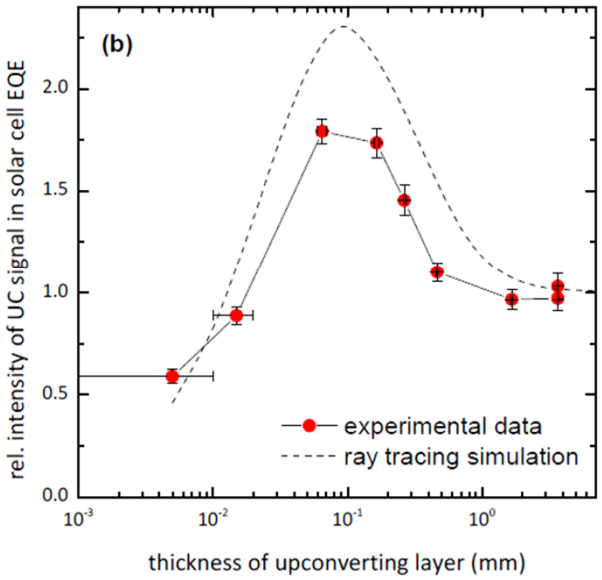
Auckett et al., J. Physics: Conference Series 185, 012002 (2009)

Concentrate light!
High transmission of SC back-reflector
near-field effects?

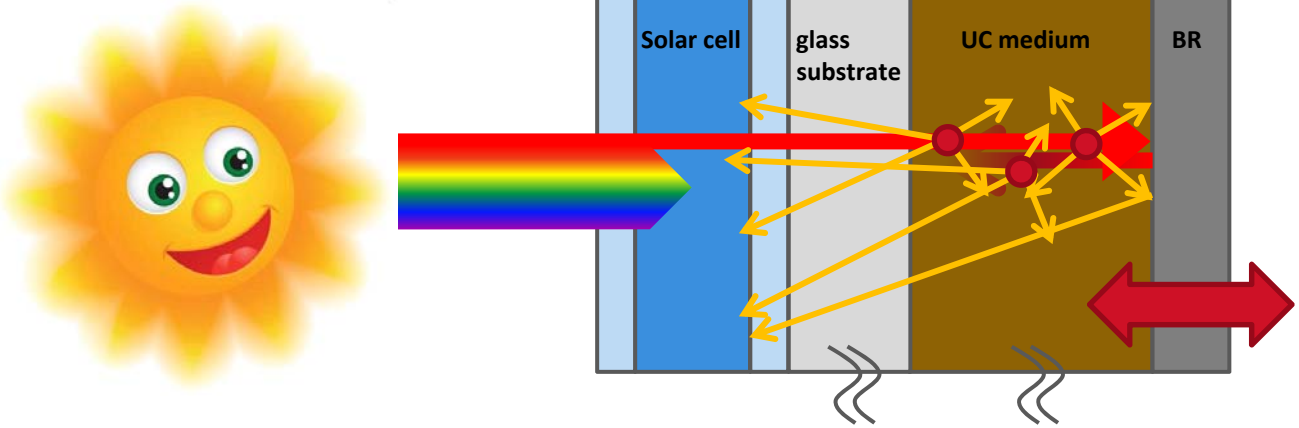
Concentrate sensitizers!
Solid-state approaches
Adsorbates,…

Thickness variation of UC layer with reflector





Schulze et al.,
J. Photonics for Energy,
submitted (2012)

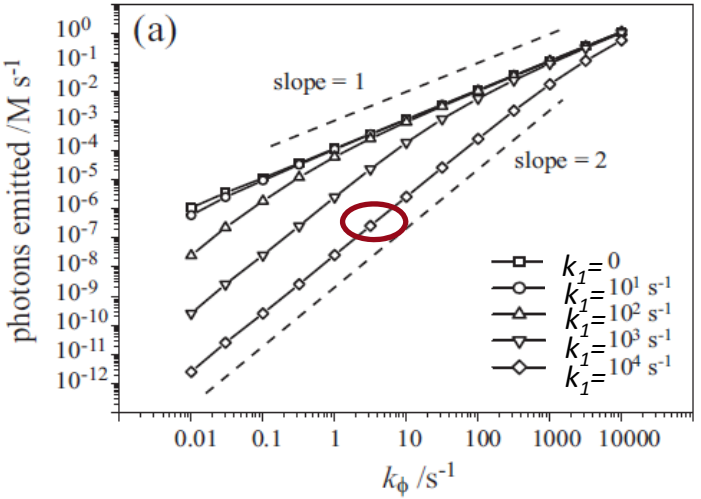


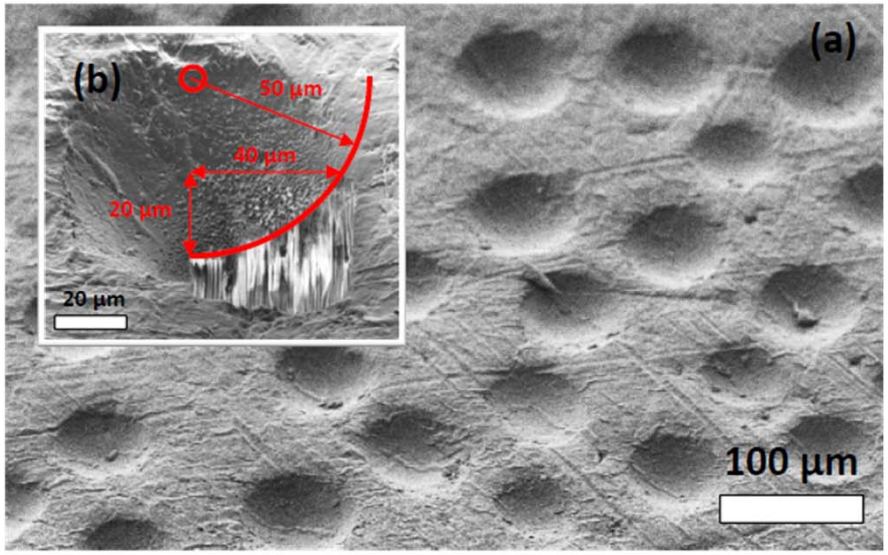
Step 1: Tuning k_Φ – local focussing of light

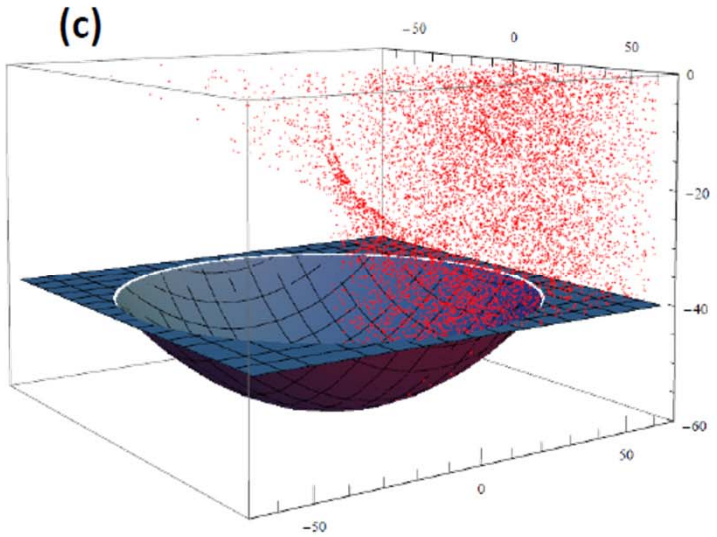
Exploiting the nonlinearity of UC response

Nonlinearity → gain by focussing

- Hot embossing of PTFE foil with silica beads
- Successively Al coating for reflectance
- Measurement in the half cuvette







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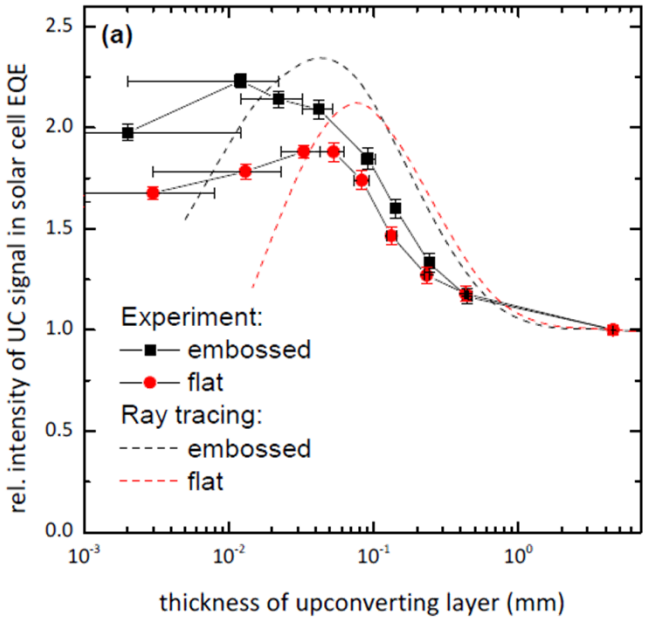
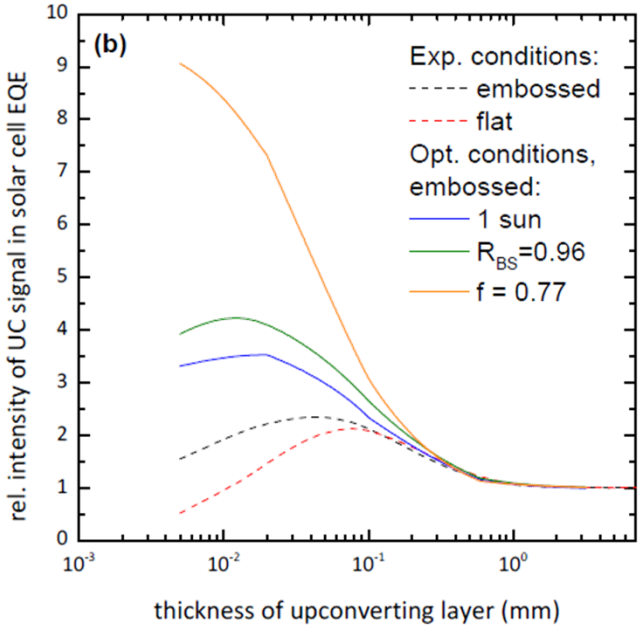
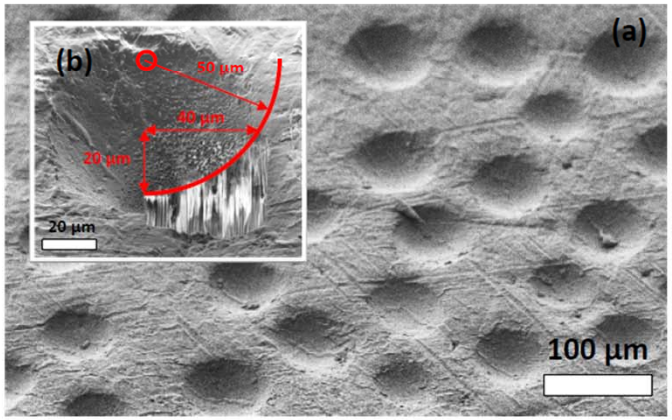
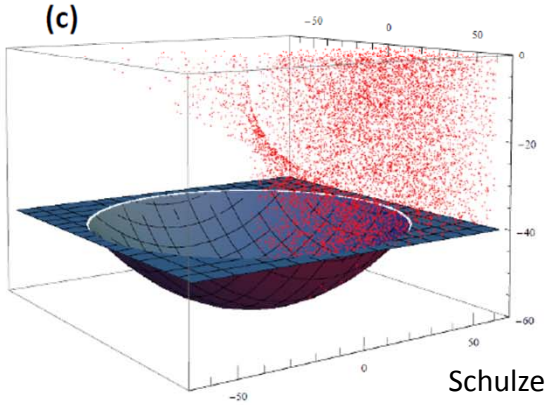








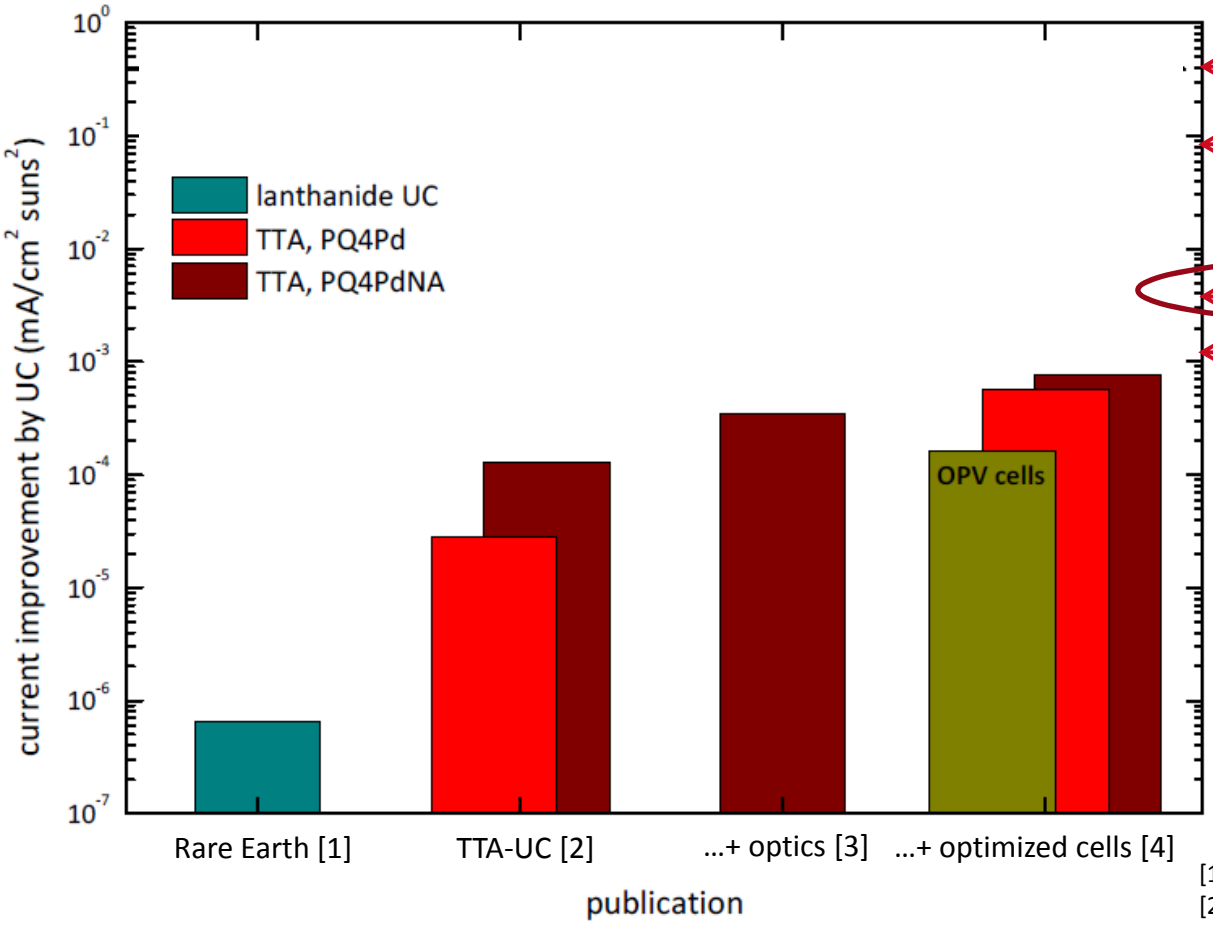
Results:

- Moderate gain (25%)
- Factor of up to 9 promised for optimized conditions (fill factor, reflectance)

Schulze et al., J. Photonics for Energy, submitted (2012)

Prospects for TTA-upconversion

Analyzing the figure of merit: Current enhancement at 1 sun for a-Si:H cells



Yield at maximum η_{UC}

100 x $C_{Sensitizer}$, optimized optics

…with micro-focussing current concentrations, optimized optics

FOM = $\Delta j_{sc} / C^2$

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[2] Cheng et al., Energy Environ. Sci. 5, 6953–6959 (2012)
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Schulze et al., J. Photonics for Energy, submitted (2012)

Step 2: Increasing C_{Sens} – All solid upconverter

Materials Views
www.MaterialsViews.com

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Energy Upconversion via Triplet Fusion in Super Yellow PPV Films Doped with Palladium Tetraphenyltetrabenzoporphyrin: a Comprehensive Investigation of Exciton Dynamics

Vygintas Jankus, Edward W. Snedden, Daniel W. Bright, Victoria L. Whittle, J. A. G. Williams, and Andy Monkman*

SY before energy transfer can occur. It has been shown that during this migration in PdTPBP aggregates, 76-99% triplets in PdTPBP are lost due to triplet annihilation in PdTPBP.

Unoptimized microstructure

Outlook – Plasmonic Magic

IOP Publishing — Journal of Optics
J. Opt. **14** (2012) 024008 (7pp) doi:10.1088/2040-8978/14/2/024008

Toward high-efficiency solar upconversion with plasmonic nanostructures

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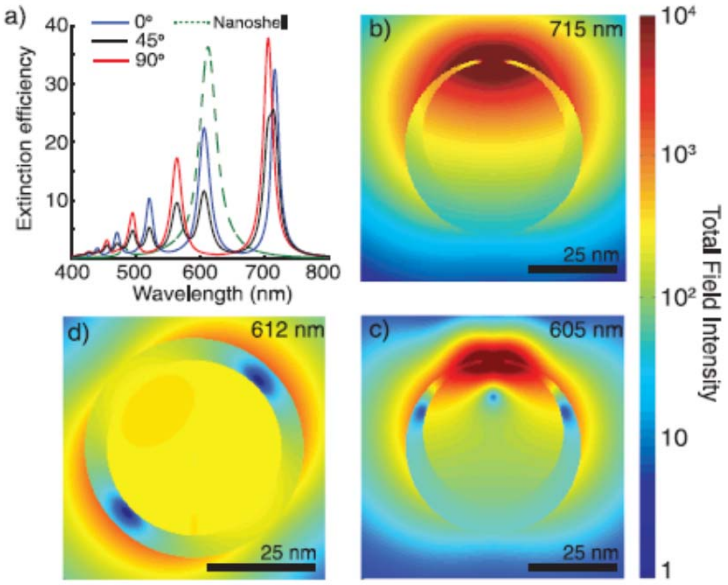


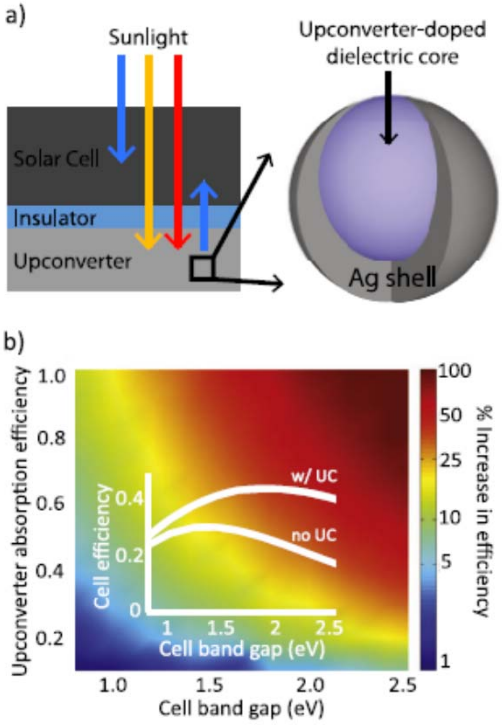
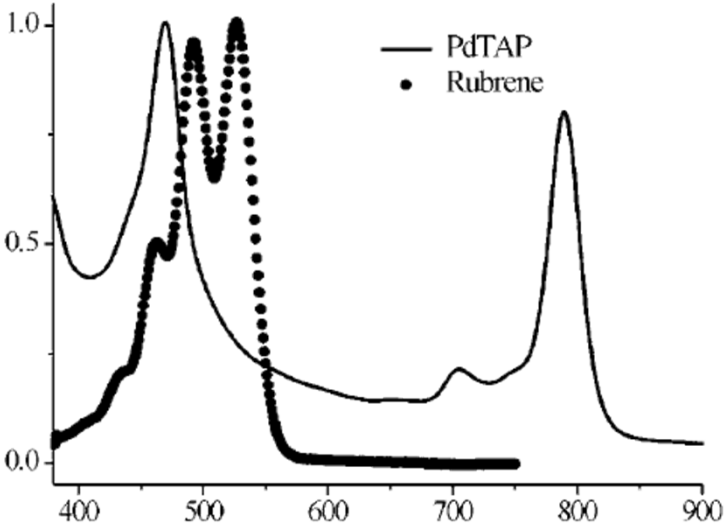
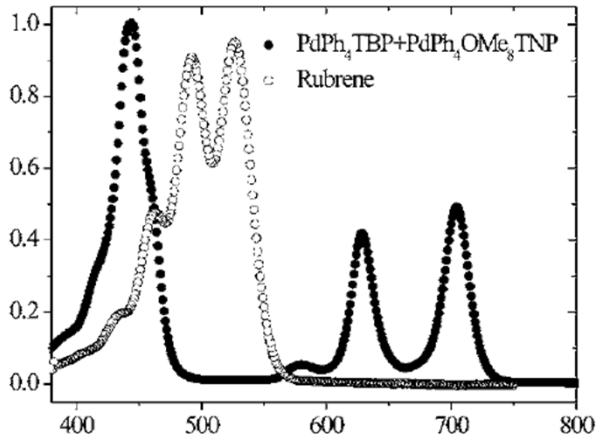


Figure 1. (a) Schematic diagram of the solar cell–upconverter system. Above-bandgap light is absorbed by the solar cell, while sub-bandgap light is absorbed in the upconverter layer. The upconverter consists of metal–dielectric core–shell nanocrescents, in which the core is doped with the upconverting material. (b) An upconverter (UC) can significantly increase the efficiency of an ideal single-junction solar cell. This relative increase is greatest when the upconverter absorption efficiency and cell bandgap are high. The inset shows the absolute efficiency for an ideal solar cell both with and without an ideal upconverter.

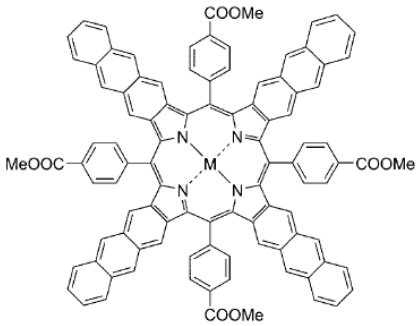
Outlook

Tuning the absorption range

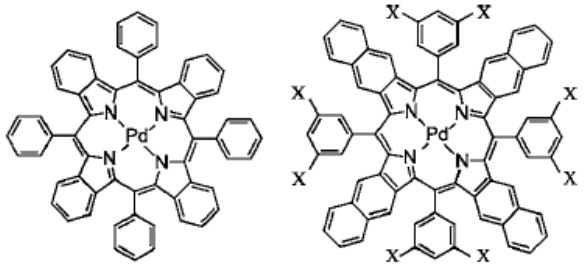




→ molecular engineering & multiple sensitizers



Baluschev et al., APL 90, 181103 (2007)



Yakutkin et al., Chem. Eur. J. 14, 9846 (2008)

World Map

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FUNDING:

Australian Solar Institute
Australian Research Council
NSW Government
The University of Sydney
Deutsche Forschungsgemeinschaft (DFG)
Alexander-von-Humboldt foundation

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ISBN 1-86500-168-6

On my own behalf… introducing the Energy Materials In-situ Lab Berlin (EMIL)

Unsolved Questions

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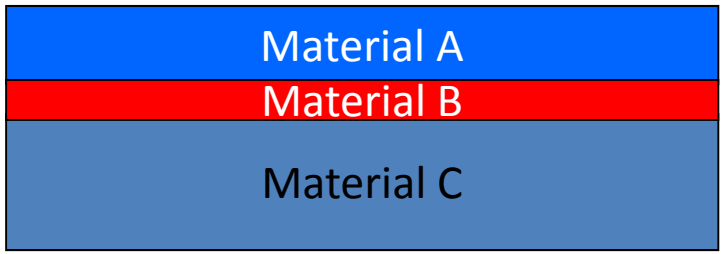
What is the impact of structure, stoichiometry and electronic properties on material quality and device performance?

- Stoichiometry, interdiffusion
- Homogeneity
- Oxidation, contamination
- Structure, grain boundaries
- Interface passivation
- Light harvesting



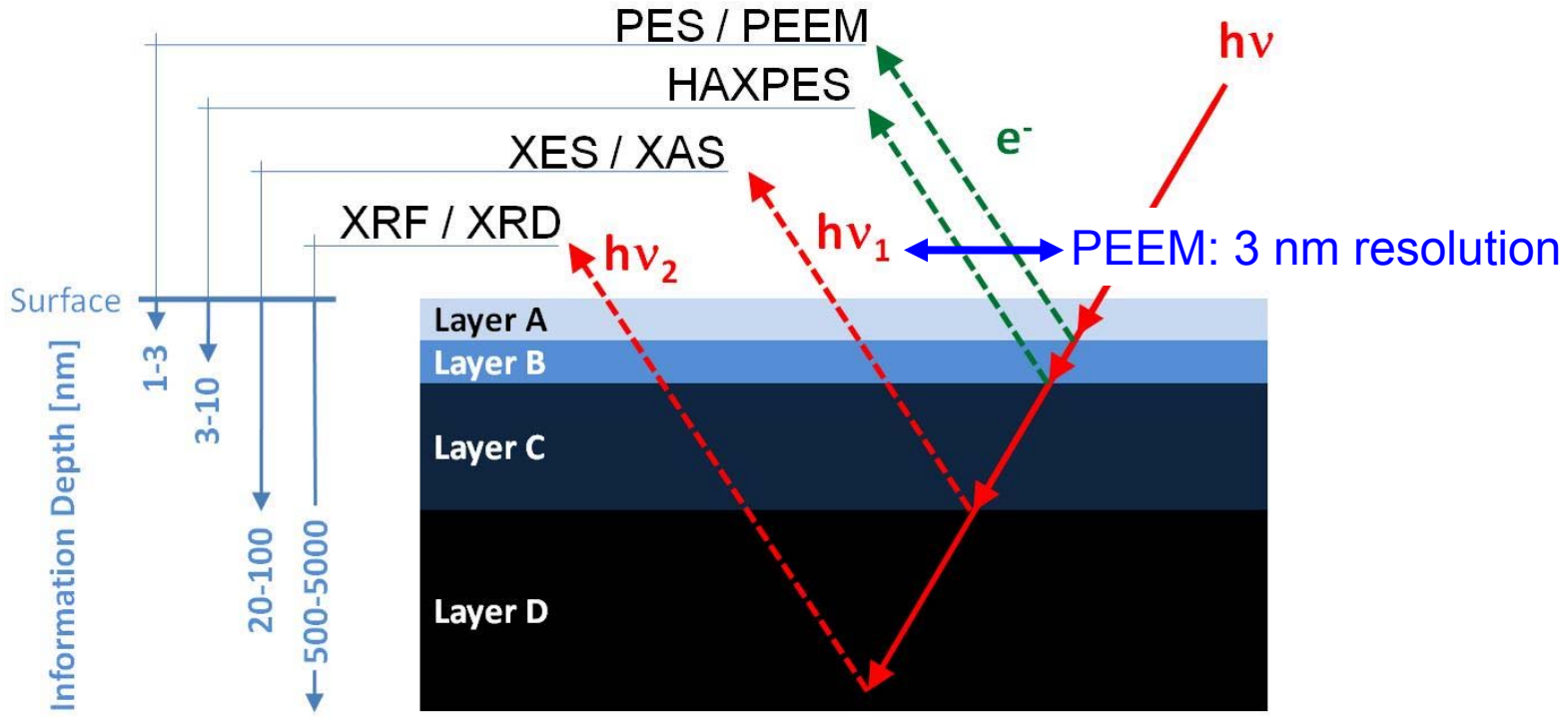
Thin-film solar cell

→ Elucidate chemical/electronic structure:

A knowledge-based solar cell improvement requires...

- Fast measurements on large sample series
- Material properties must relate to device
- *In-situ* deposition/preparation/manipulation on sample areas 100 cm^2 (boundary effects, compatibility to industrial processes)

Synchrotron-based X-Ray Spectroscopy



PES – Photoelectron spectroscopy
PEEM – Photoemission electron microscopy
HAXPES – Hard X-ray PES
XES – X-ray emission spectroscopy
XAS –X-ray absorption spec.
XRF – X-ray fluorescence spec.
XRD – X-ray diffraction spec.

Wide X-ray energy range needed (80 eV - 10keV)

EMIL: Energy research at the synchrotron BESSY II

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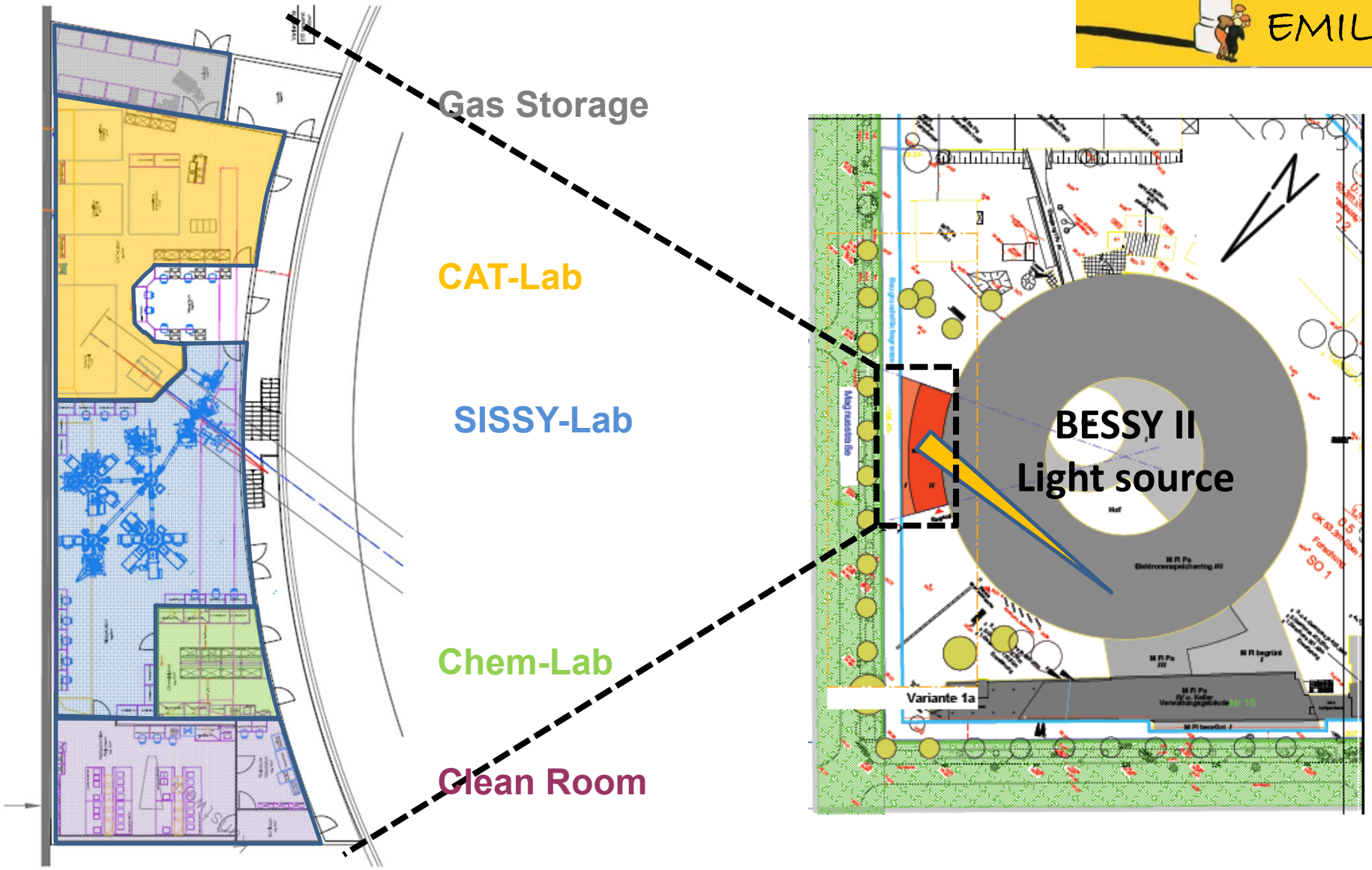
EMIL



BESSY II: 3rd-gen storage ring (d=80m, 1.7GeV), operating since 1998

EMIL‘s Building: An Extension to BESSY II

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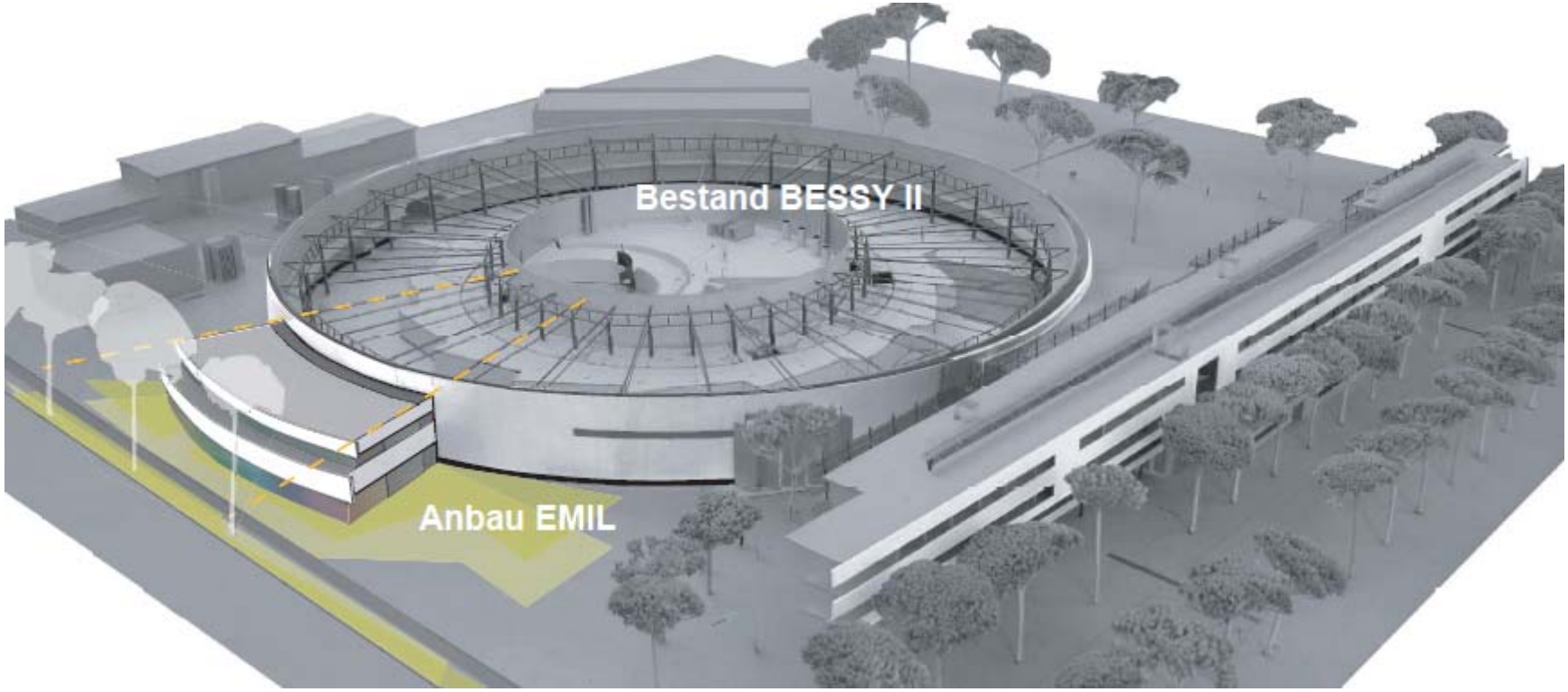

Available Lab Space at EMIL > 600 m^2

DEPOSITION and UHV- TRANSPORT

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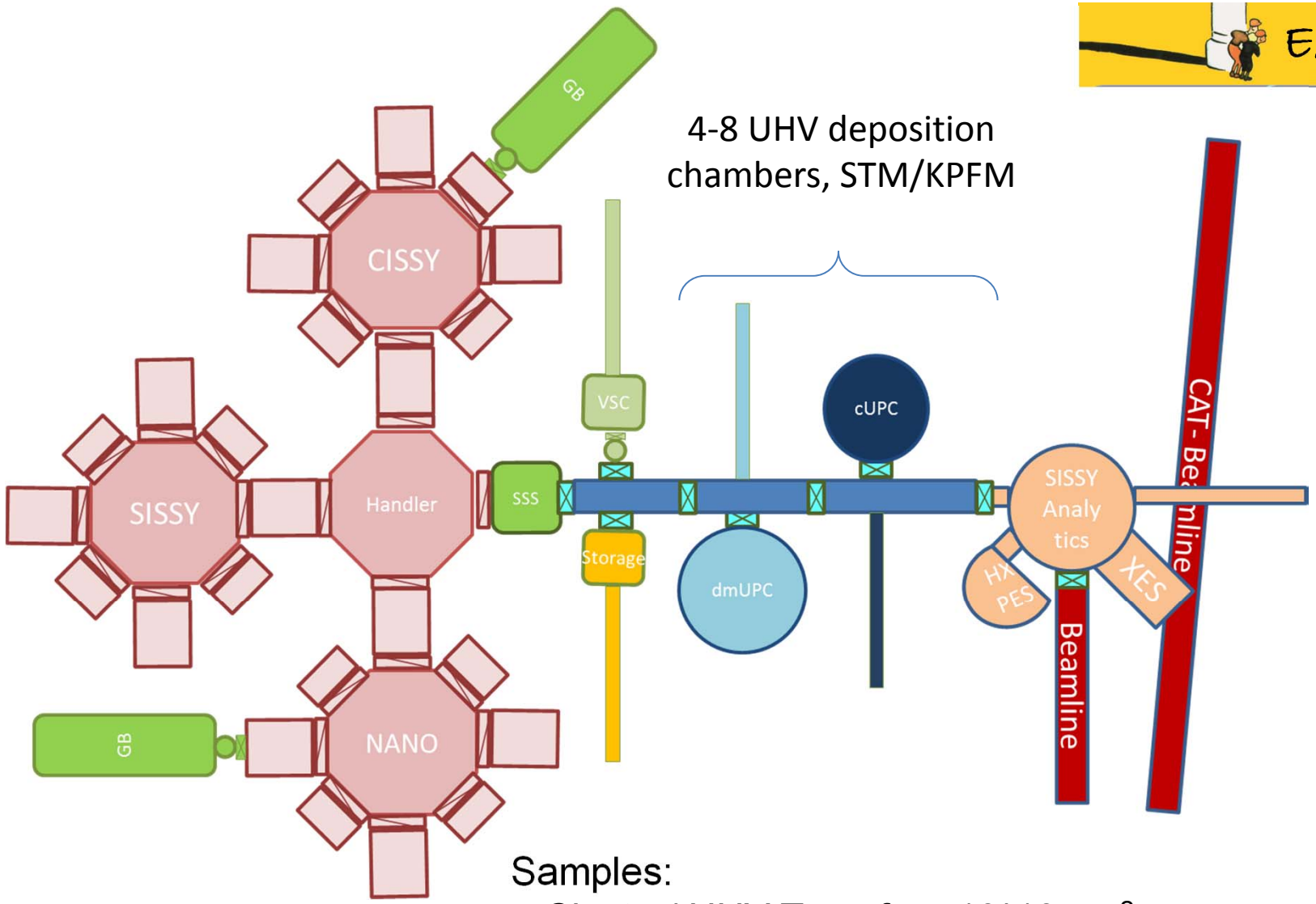


4-8 UHV deposition chambers, STM/KPFM

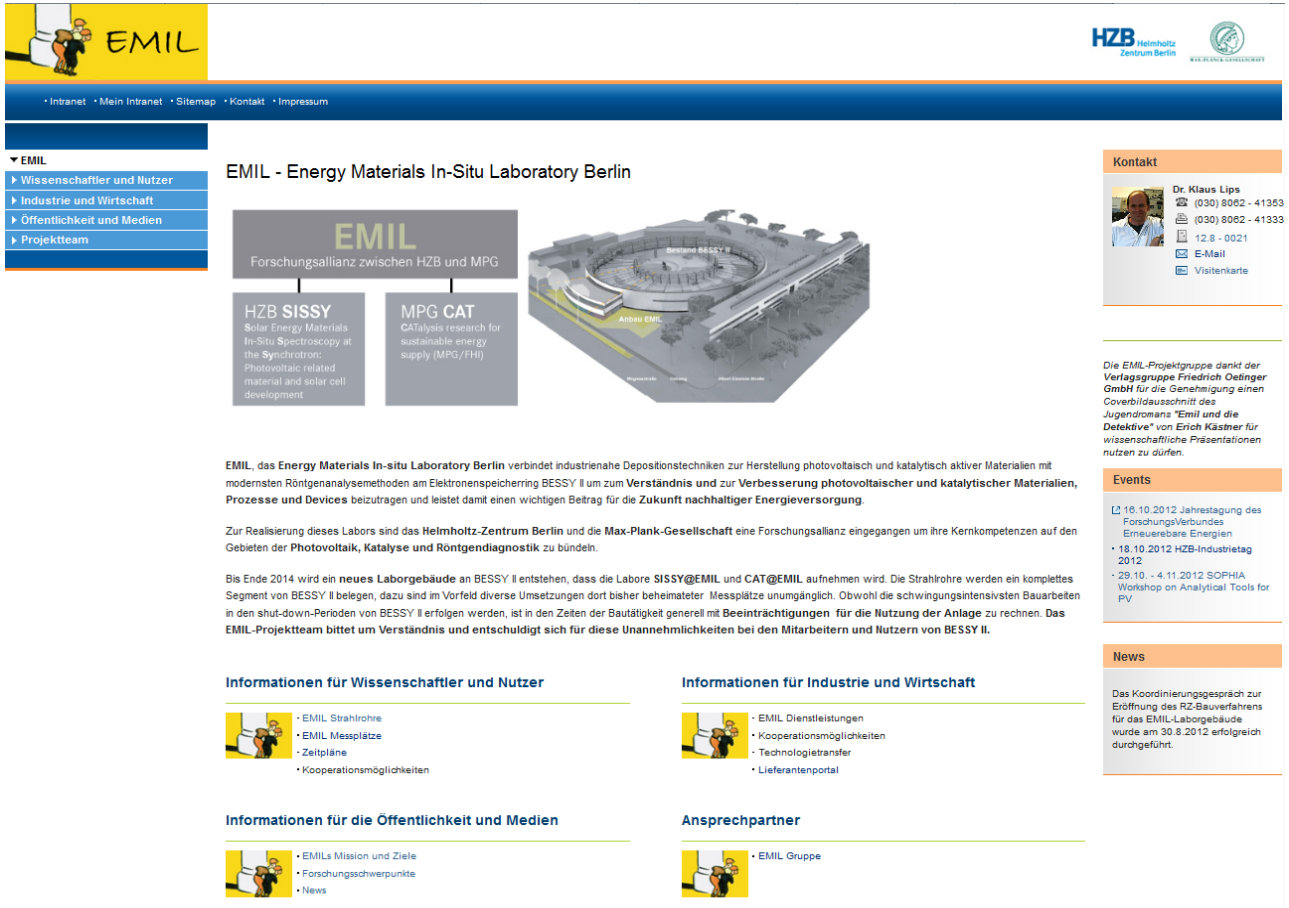
Samples:

Cluster/ UHV Transfer : 10*10 cm^2

Analytics: 2.5*2.5 cm^2

EMIL facts

- Research alliance between HZB and Max-Planck Society
- Total funding secured: 26.6 Mio EUR
- First beam: End of 2014, fully operational by mid-2015.
- **Will be a user facility!**
- Stay tuned: EMIL website to be launched soon…



Thank you for your attention!

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