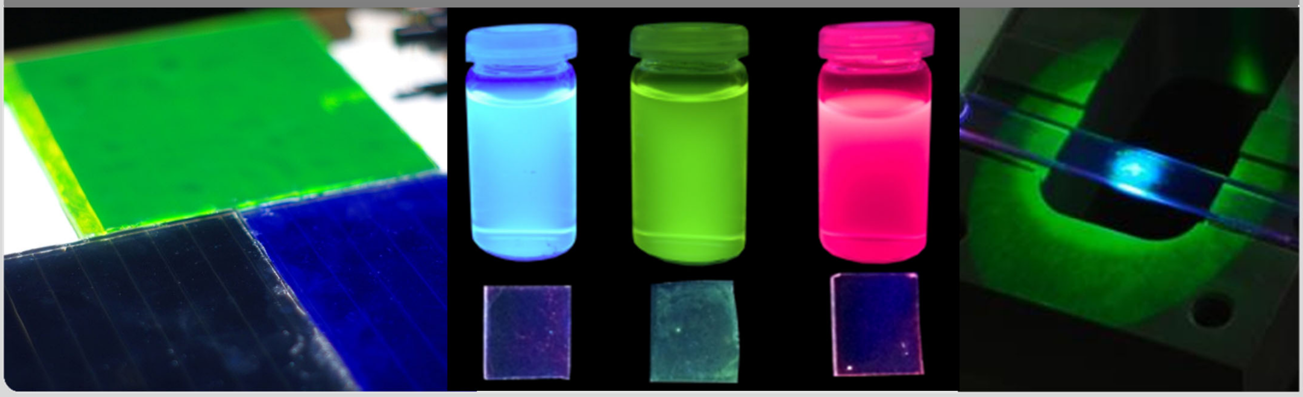
"Solar Energy" WS 2021/2022

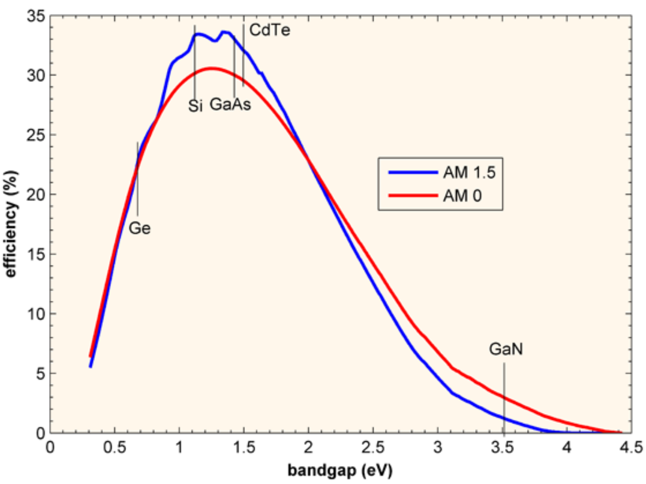
Lecture 14: Luminescent Materials for Photovoltaics

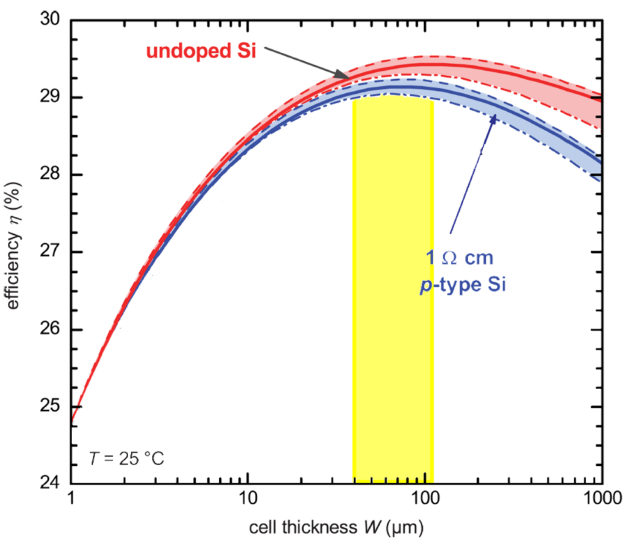
Dr. Andrey Turshatov and Prof. Dr. Bryce S. Richards
Institute of Microstructure Technology (IMT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen
Light Technology Institute (LTI), Engesserstrasse 13, Building 30.34, 76131 Karlsruhe



Single-Junction PV

- Maximum theoretical efficiency of c-Si solar cell: earlier 33%, revised in 2013 to be 29.4% under one-sun
- Ideal Si wafer thickness 40-100μm

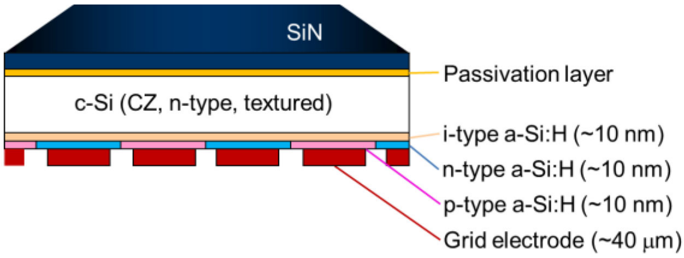


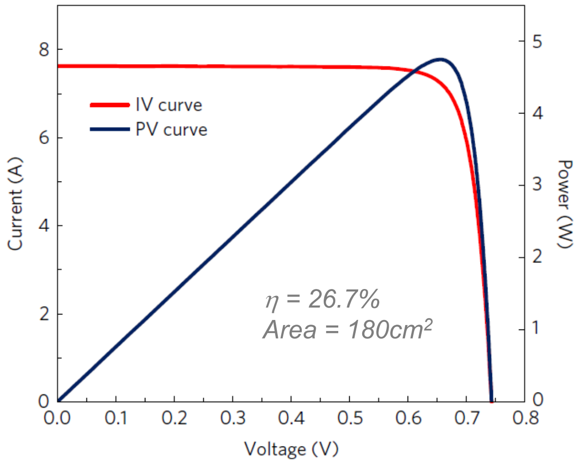


Sources: Richter et al. IEEE J. Photovolt. 3 (2013) 1184-1191
http://www.pveducation.org/pvcdrom/solar-cell-operation/detailed-balance

Single-Junction PV

- Record Si solar cell:
  - η = 26.7% for c-Si/a-Si *pin*-heterojunction



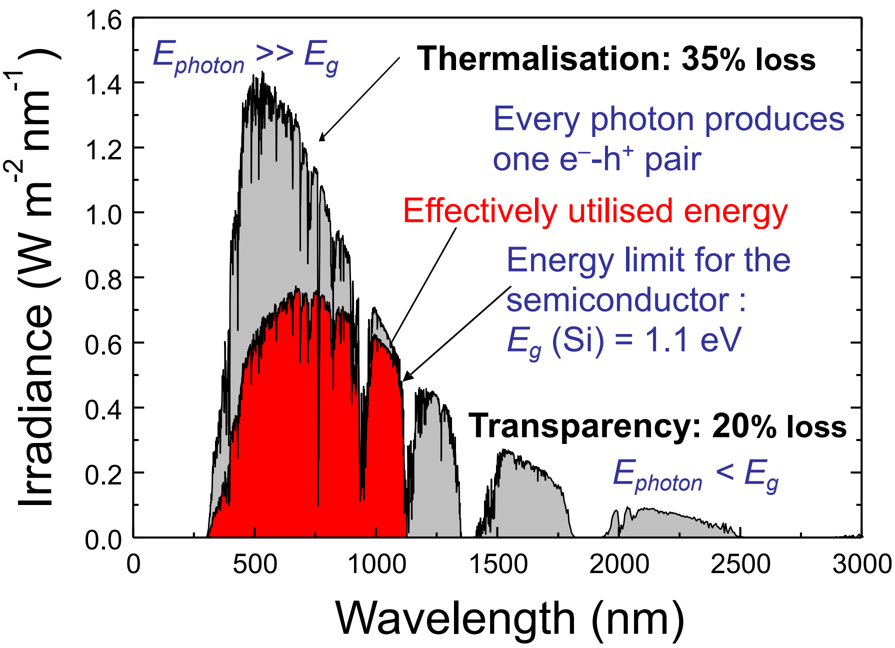


- What 3rd generation PV technologies can we pair together with c-Si?

Sources: Masuko et al., IEEE PVSC (2014); Yoshikawa et al., Nature Energy 2 (2017) 17032

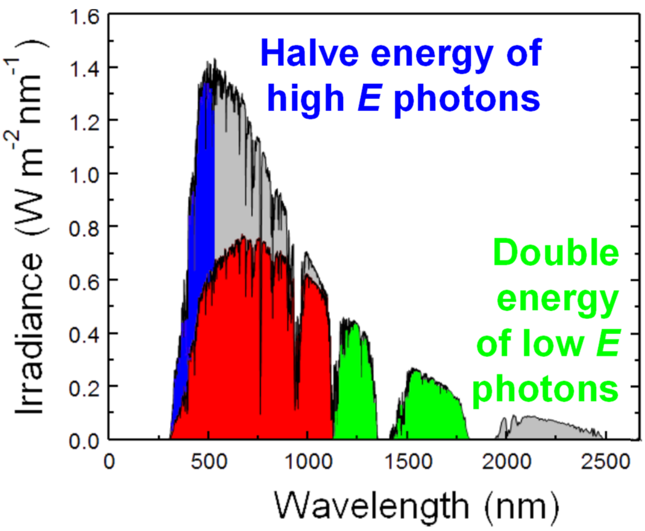
3rd Gen PV

- Harvesting significant thermalisation & transparency losses



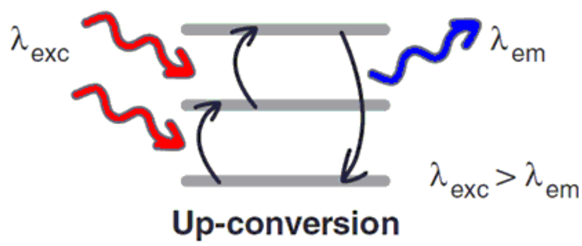
Spectral Conversion

- Use of **luminescent materials** to change wavelengths of sunlight
- Address thermalisation and transparency losses
- Still rely on a single-junction solar cell

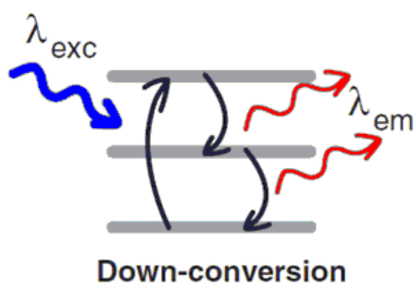


Spectral Conversion

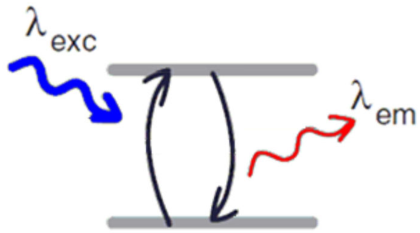
- Up-conversion (UC) of 2 low-energy photons to give 1 higher-energy photon
  $\Rightarrow$ addresses sub-bandgap losses



- Down-conversion (DC) a.k.a. quantum cutting, is where 1 high-energy photon is 'cut' into 2 lower-energy photons
  $\Rightarrow$ addresses lattice thermalisation losses



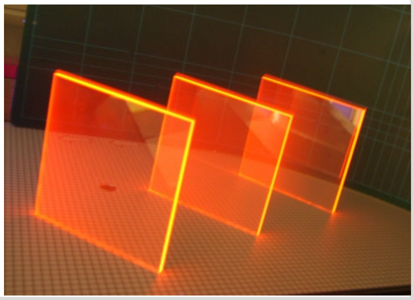
Spectral Conversion



- <u>Luminescent down-shifting</u>: standard photoluminescence (Stokes) process
- Doesn't address thermalisation or sub-bandgap losses, but:

⇒ can still enhance performance of solar cells with poor external quantum efficiency (EQE)

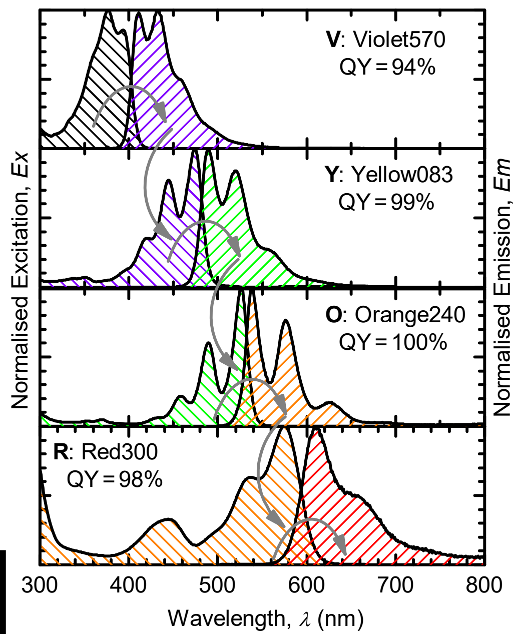
⇒ waveguiding of PL is principle behind the <u>luminescent solar concentrator</u> (LSC)

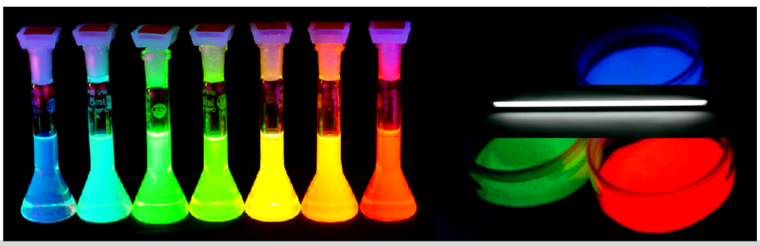


Source: *Moudam et al., Chem. Comm. 2009, 6649 -6651*

Luminescent Materials

- Wide range of luminescent materials available
- Inorganics: lanthanide phosphors and semiconducting nanoparticles (quantum dots)
- Fluorescent organic dyes: strong absorption and high photoluminescence quantum yields (PLQY)



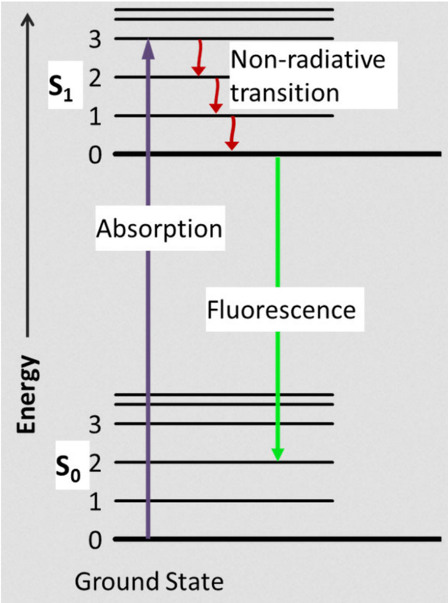


Source: *Richards and McIntosh, Prog. Photovolt. 15 (2007) 27–34*

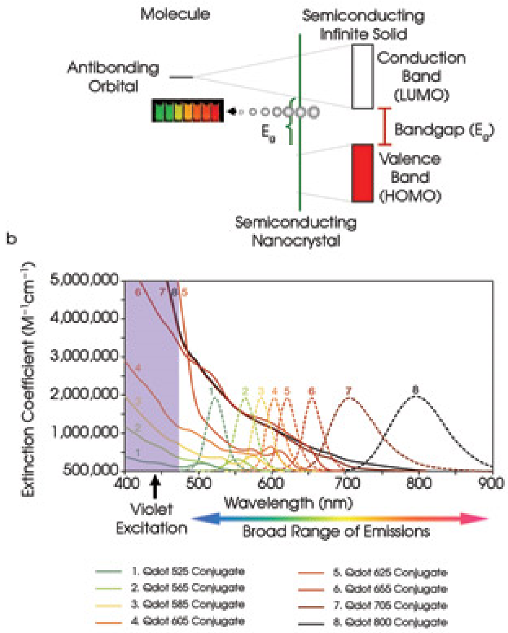
Luminescent Materials

Karlsruher Institut für Technologie

- Organic dyes



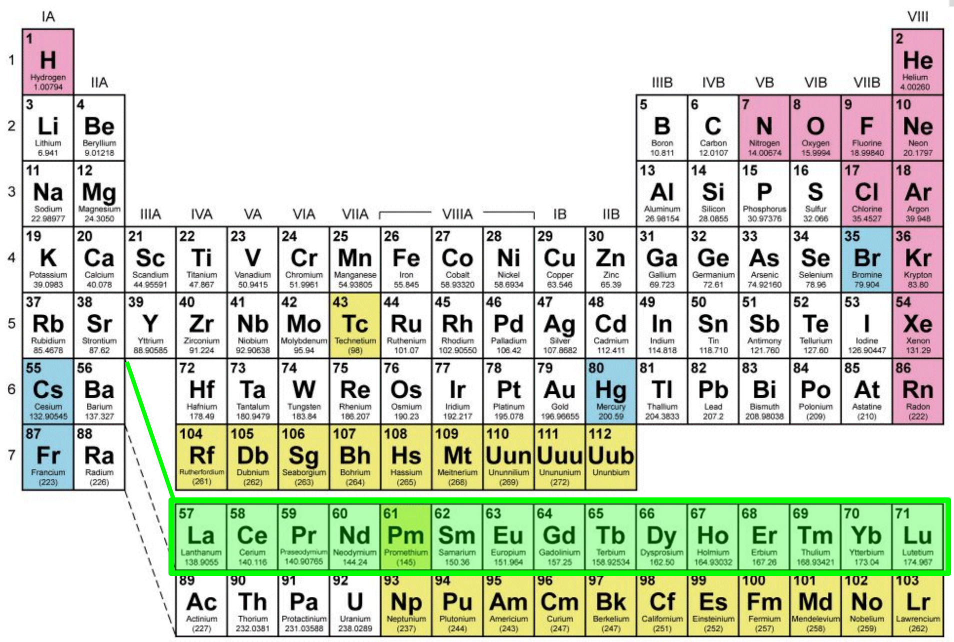
Quantum dots



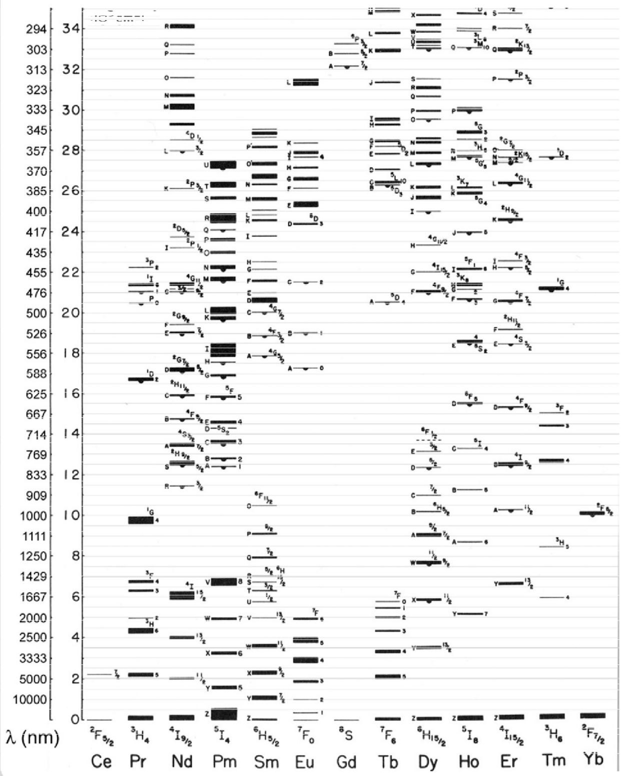
Materials for Up- and Down-Conversion

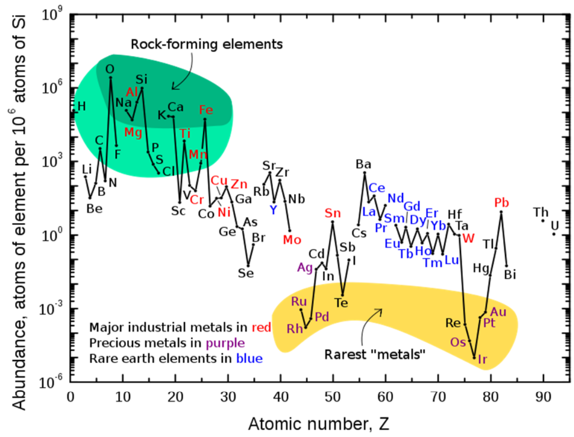
Karlsruher Institut für Technologie

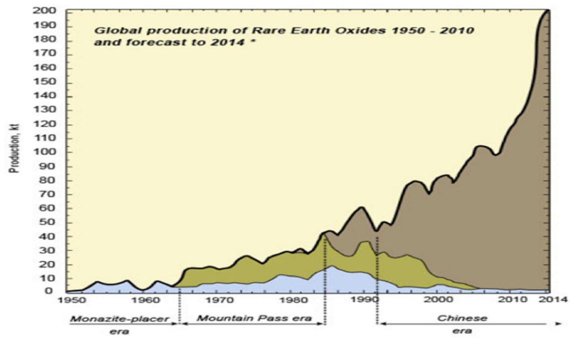
- Rare-earth elements (lanthanides): La – Lu
- Partially filled *4f* e⁻ shell
  ⇒ unique energy levels
  ⇒ unique optical properties
- Non-toxic
- Stable
- Low-cost



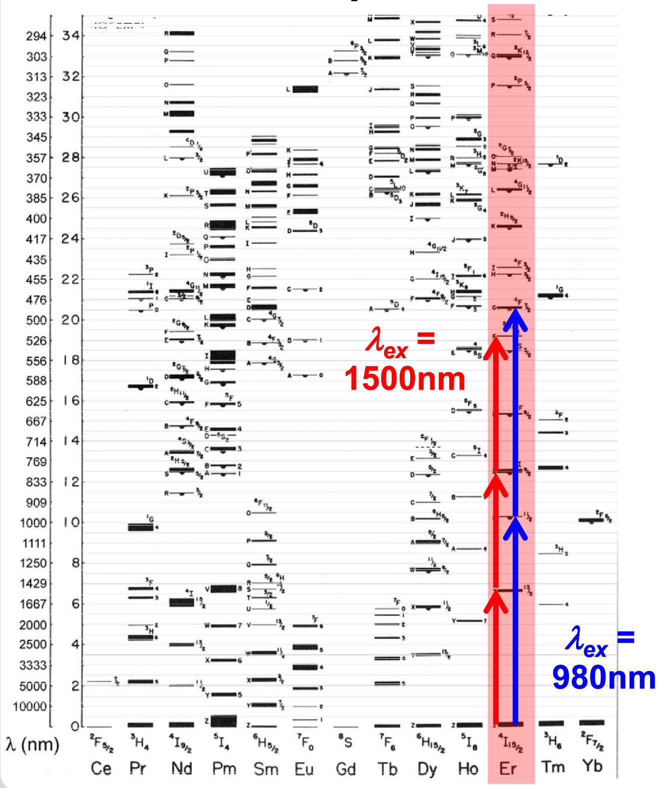
Materials for Up- and Down-Conversion

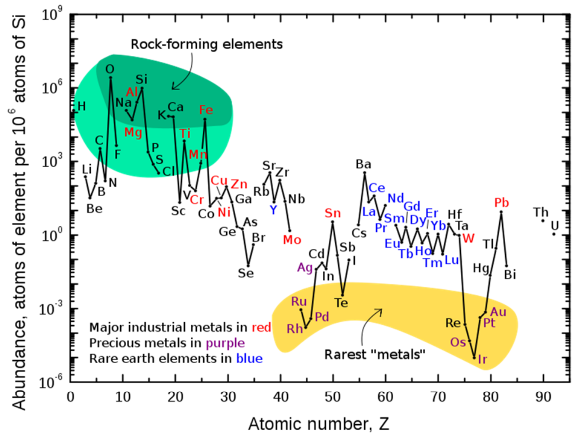


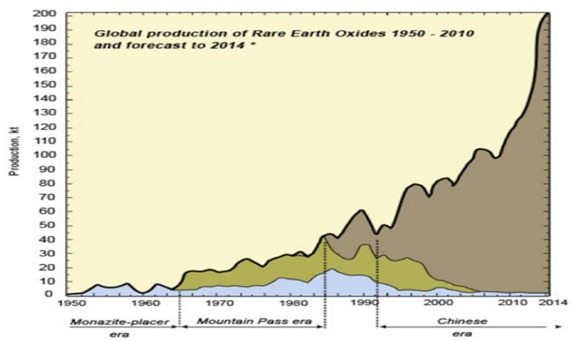




Materials for Up- and Down-Conversion

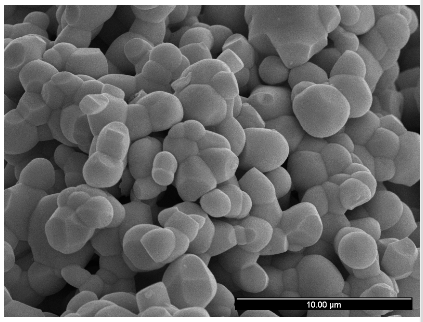


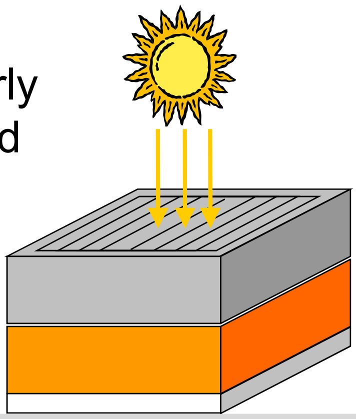




Up-Conversion

- Sub-bandgap photons harvested via UC layer at rear of *bifacial* Si solar cell
- Er-doped fluoride based phosphors ($NaY_{1-x}F_4:Er_x$)
- Luminescence emitted isotropically ⇒ rear reflector ensures nearly all UC light is collected
- Theoretical efficiency limit of UC with Si solar cell = 40% (one-sun)





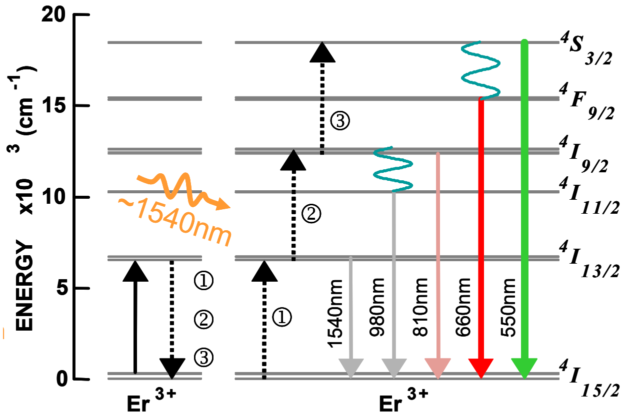
Bifacial Si solar cell η = 15%

UC: $NaYF_4:Er^{3+}$ in polymer

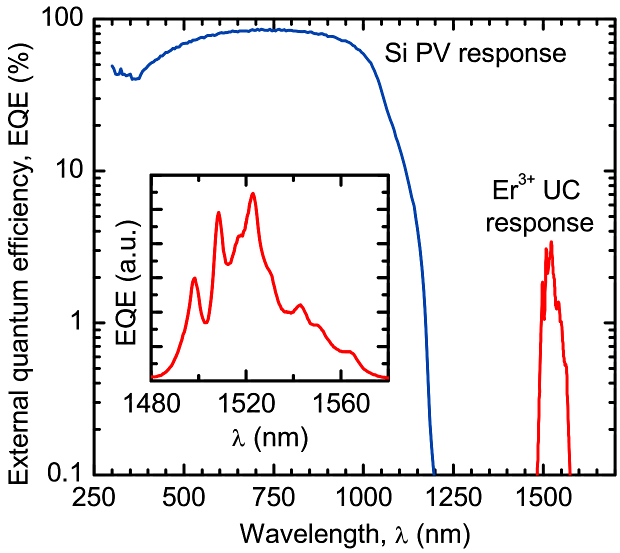
Rear reflector

Up-Conversion

- Non-linear process!



Energy Transfer Up-conversion (ETU)

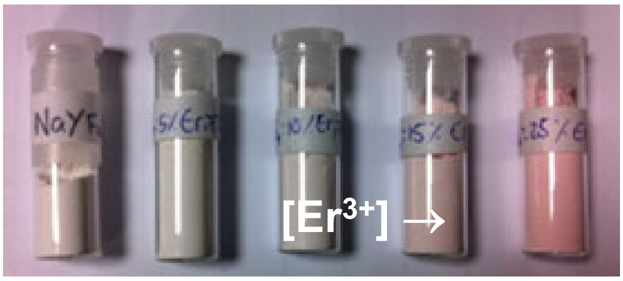


- Best performance of UC-PV device with $[Er^{3+}]$ = 20% ⇒ EQE = 3.4% @ 1523nm

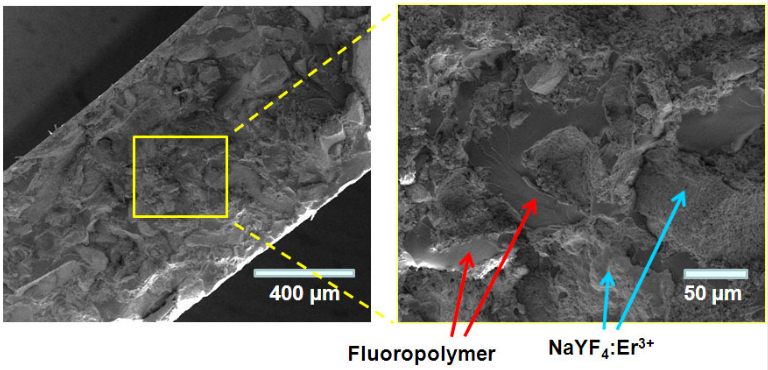
Source: Shalav, Richards, et al., Appl. Phys. Lett. 86 (2005) 103505
Richards, Shalav, IEEE TED. 54 (2007) 2679

Up-Conversion

- Optimisation of [Er^{3+}] doping concentration 5% – 75%

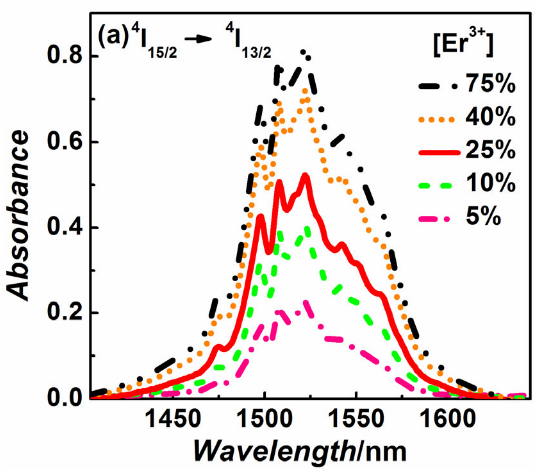


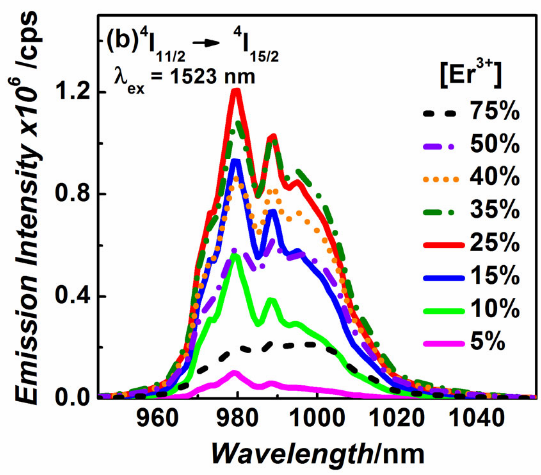
- UC layer: micro-phosphor powder doped into 1mm thick polymer layer @ up to 85% w.w. ⇒ ideal *n*, low α, reduced C-H vibrations



Up-Conversion

- Optimum [Er^{3+}] = 25% ⇒ trade-off between i) higher concentrations absorbing more but ii) also emitting less due to cross-relaxation (non-radiative recombination)

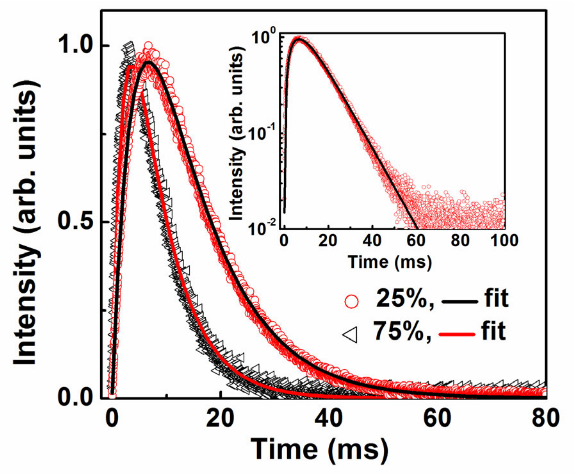


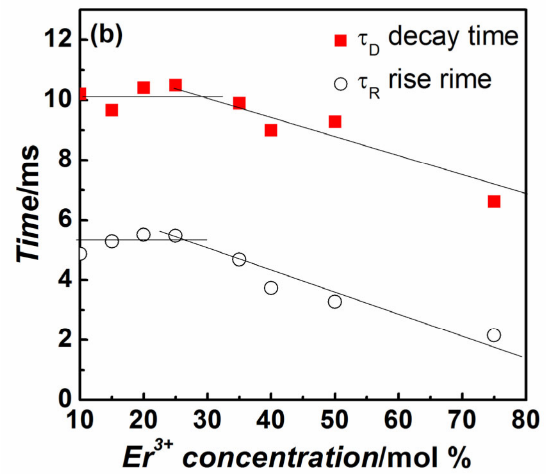


Source: Ivaturi et al., Journal of Applied Physics 114 (2013) 01350

Up-Conversion

- Time resolved PL (980 nm emission) ⇒ clear rise in PL intensity before decaying ⇒ evidence of ETU (energy transfer between states takes time)
- Decreases in τ for $[Er^{3+}]$ > 25% ⇒ concentration quenching



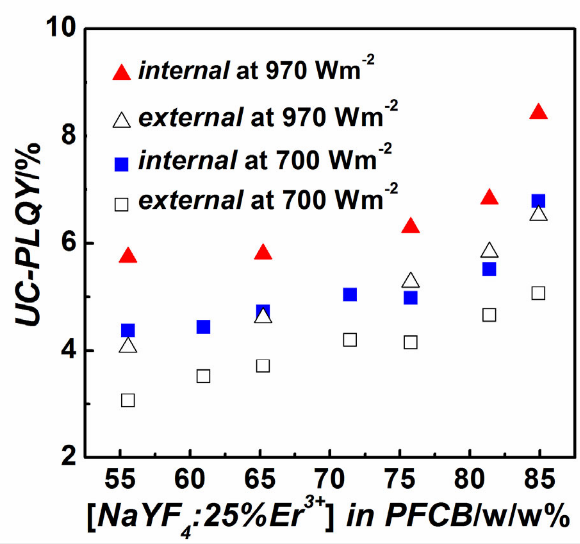


17

Source: Ivaturi et al., Journal of Applied Physics 114 (2013) 01350

Up-Conversion

- Max $PLQY_{int}$ = 8.4% ($PLQY_{ext}$ = 6.5%) measured at highest concentrations of [β-$NaYF_4$:Er] in PFCB host
- Increase in PLQY at high [β-$NaYF_4$:Er] driven by anomalous ↓ in absorption
- When coupled with Si solar cell can expect device with EQE of 5-6% at 1523nm (@ 970 W/m^2)

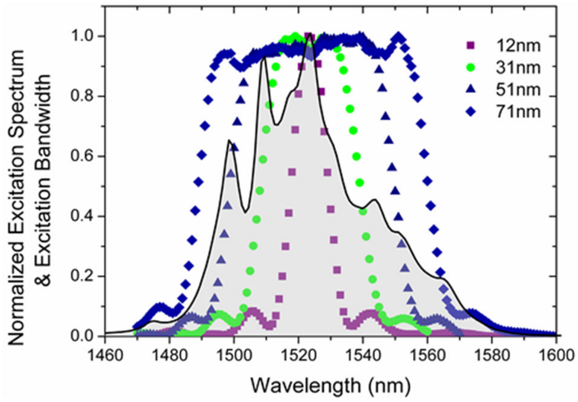


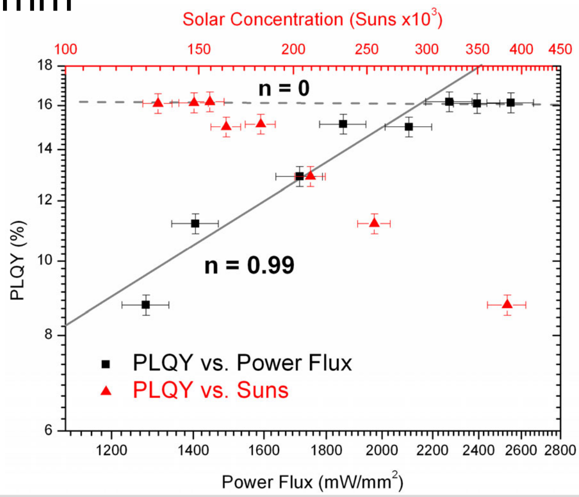
18

Source: Ivaturi et al., Journal of Applied Physics 114 (2013) 01350

Up-Conversion

- Goal: move to broadband excitation of Er^{3+} UC materials
- White-light laser: up to 80nm FWHM $\Rightarrow$ span full Er^{3+} absorption band
- Max $PLQY_{int}$ = 16.2% @ >2.2 W/mm^2





Source: *MacDougall et al., Optics Express 20 (2012) A879*

Up-Conversion

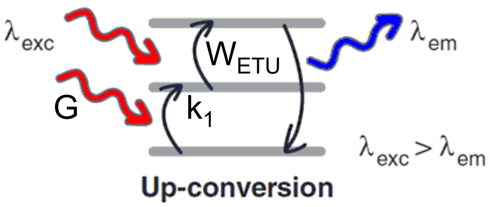
- The rule of thumb for effective UC

$$k_1 < \sqrt{\frac{GW_{ETU}}{10}} \text{ or } W_{ETU} > \frac{10k_1^2}{G}$$

k_1 (experimental) – 12 ms

W_{ETU} (experimental) – 2.4×10^{-15} cm^3 s^{-1}

G – generation rate;
W_{ETU} – rate of energy transfer
k_1 – decay rate of the intermediate state

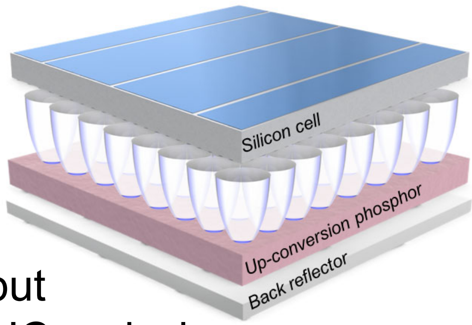


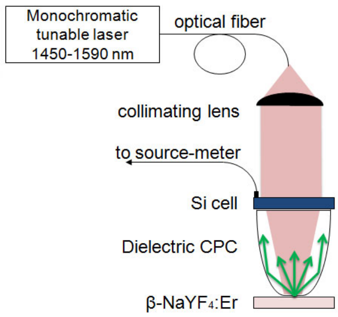
- UC can work under 10-100 sun
- Challenge: UC materials efficiently working under 1 sun are unknown

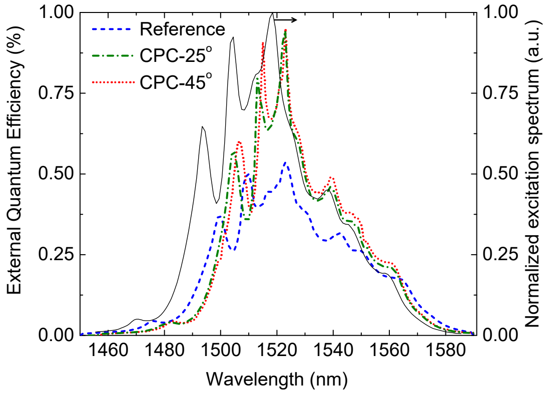
Source: *Richards et al. Chemical Review (2021), 9165–9195*

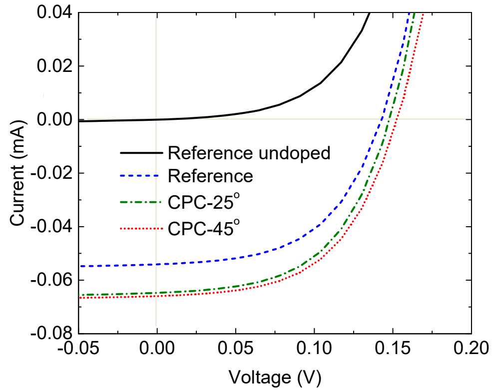
Up-Conversion

- Secondary concentrators
- Gains made by concentrating light, but poorer collection of UC emission





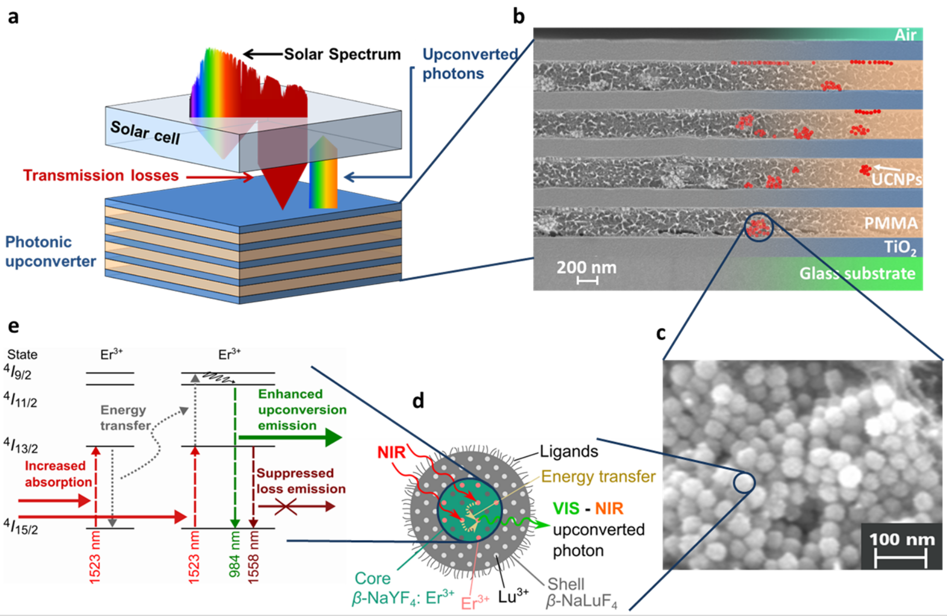




Source: Arnaoutakis et al. Sol. En. Mat.& Solar Cells 140 (2015) 217–223

Up-Conversion

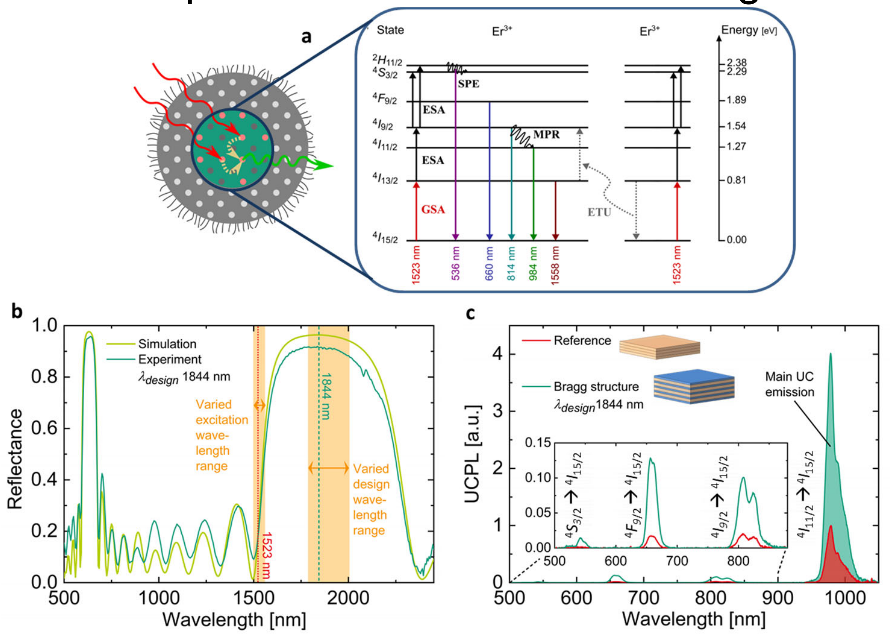
- Enhancement of UC via Bragg-stack (1D photonic crystal):
  - Irradiance enhancement
    ⇒ enhances absorption ∴ exploits non-linear efficiency increase of UC
  - Vary local density of photon states (LDOS)
    ⇒ enhance desired radiative transitions and suppress others



Source: Hofmann et al. Nature Communications (2021) 12, 104

Up-Conversion

- Materials: ALD TiO_2 + PMMA doped with $NaYF_4$:Er^{3+} NPs
- 2-3x enhancement of UC performance… still not enough



Source: Hofmann et al. Nature Communications, doi: 10.1038/s41467-020-20305-x

Up-Conversion (science meets economical aspects)

- Rooftop scenario -

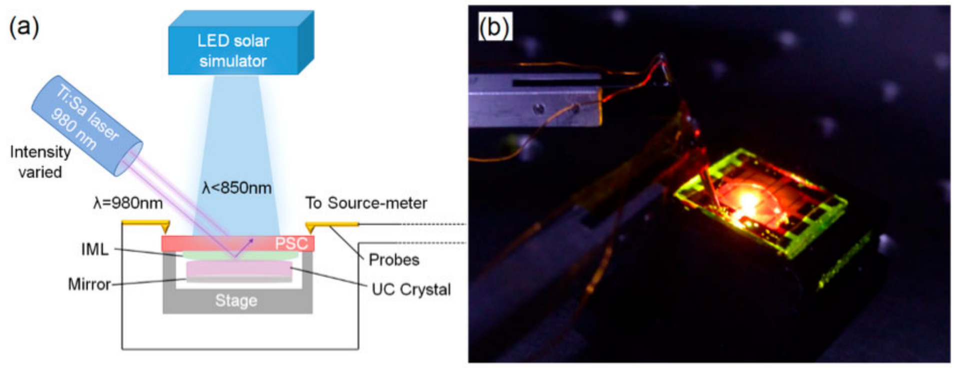
Best commercially available c-Si solar cells (Sunpower Maxeon Gen III, with η = 24.3% and an area of ~153 cm^2) will generate 3.7 W total power (achieved with a current density of
38.5 mA cm^{-2} at a voltage of 0.63 V) – cost US$0.41

UC can add 0.26 W (best case scenario) and therefore, to remain competitive will need to cost less than US$0.028 or US$14 kg−1 vs cost of raw material Er_2O_3 – US$20 kg^{-1}

- Solar farms scenario – for semi-transparent solar cell, the impact of reflected light is ~ 10% or (~ 3-4 mA cm^{-2}). The additional UC layer should bring more, that currently is possible only under 100 – 1000 sun
- Current status: UC will in the near-term remain unattractive for mass market PV power generation

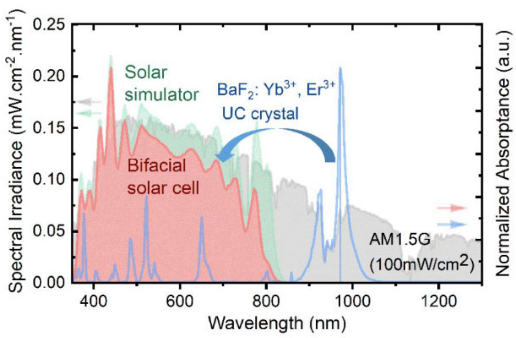
Up-Conversion perspectives for other PV technologies

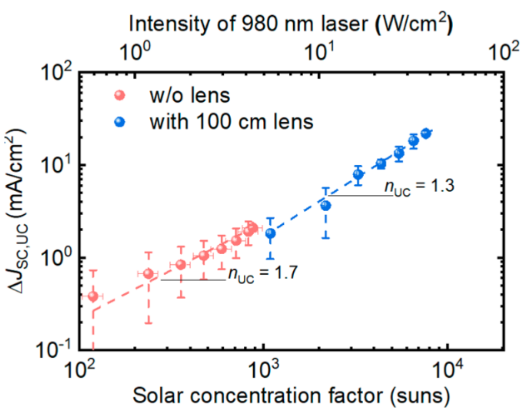
- Harvesting Sub-bandgap Photons via Upconversion for Perovskite Solar Cells
- Up-conversion 980 nm → visible



Source: Singh et al. ACS Appl. Mater. Interfaces (2021), 54874–54883

Up-Conversion



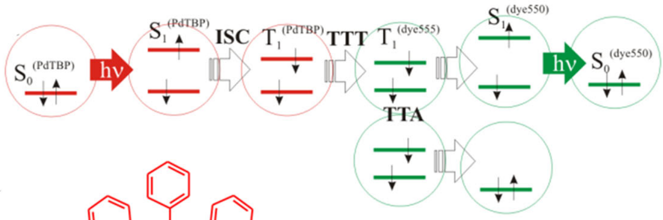


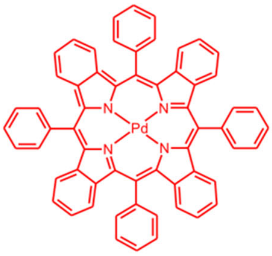
- J_{SC} lost by going from a rear gold electrode to a transparent conducting oxide is on the order of ~1.5 mA/cm^2
- ~ 0.5 mA/cm^2 @ 100 sun
  ~ 2 mA/cm^2 @ 1000 sun
- More efficient UC is required

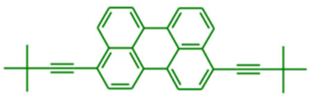
Source: Singh et al. ACS Appl. Mater. Interfaces (2021), 54874–54883

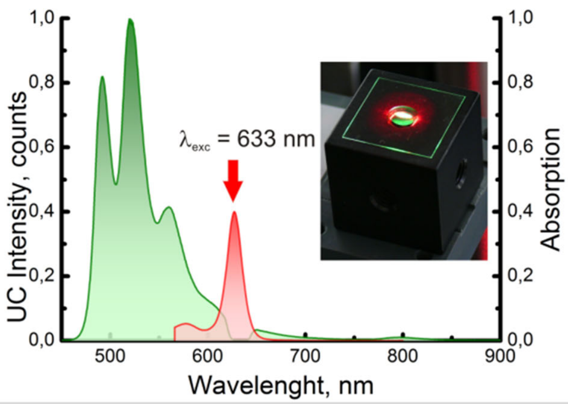
Up-Conversion (triplet-triplet annihilation UC)

- Alternate approach to UC using organic molecules
- 633 nm absorption of palladium-based porphyrin ⇒ intersystem crossing (ISC) ⇒ triplet-triplet transfer (TTT) across to perylene derivative ⇒ triplet-triplet annihilation (TTA) ⇒ energy from two triplets added to promote e⁻ to singlet state ⇒ 550 nm UC emission





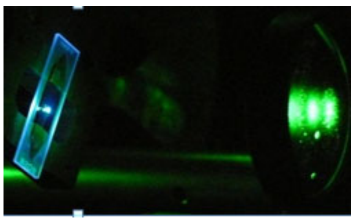




TTA Up-Conversion

- Can work with ~ 10 % quantum efficiency under 1 sun
- However, taking into account spectral response can be used only with DSSC, organic or perovskite solar cells – not mass market product yet
- TTA-UC is extremely oxygen sensitive – long lifetime of the device is questionable
- Performs in solid devices with lower efficiency then in solution

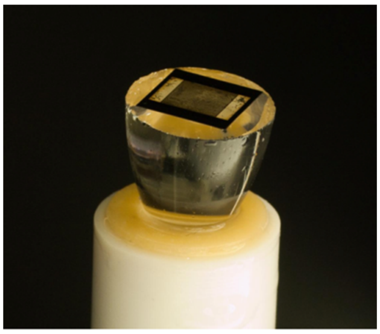
Green to blue UC with ~2% PLQY



Source: Turshatov, Howard, Richards, patent application

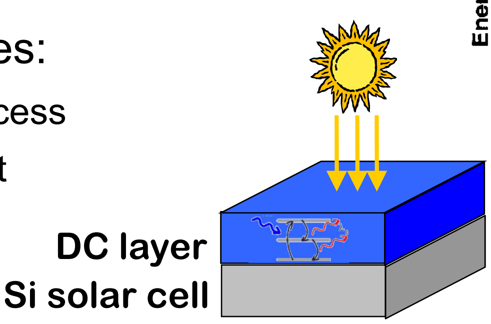
Up-Conversion
Future & Challenges

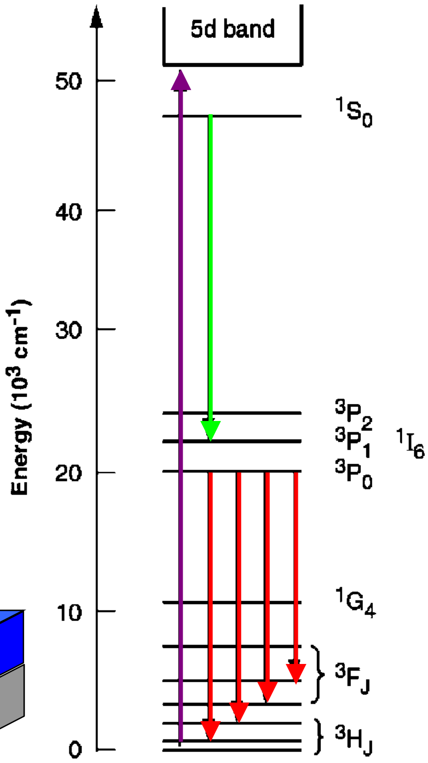
- Concentration of light, not only via geometrical optics but also via nanophotonic structures
  ⇒ enhance localised electric fields
- Plasmonic structures ⇒ increase weak absorption
- Inorganic materials challenges:
  - Nanocrystals ⇒ open up new device structures but challenging due to surface recombination
  - Sensitisation via other metal ions
  - Hosts with ideal phonon energy & defects
- Organic materials challenges: extend into NIR, working in polymer, avoid O_2
- Broadband excitation, low UC thresholds



Down-Conversion

- DC pursued for other applications
- Fluorescent lamp phosphors based on Pr^{3+} ion achieve PLQYs of 140%, several challenges for PV:
  - No 185nm light in solar spectrum!
  - Lanthanide ions are weak absorbers
    ⇒ current layers would be ~1cm thick
- Some advantages:
  - DC is linear process
  - Don't care about colour of light

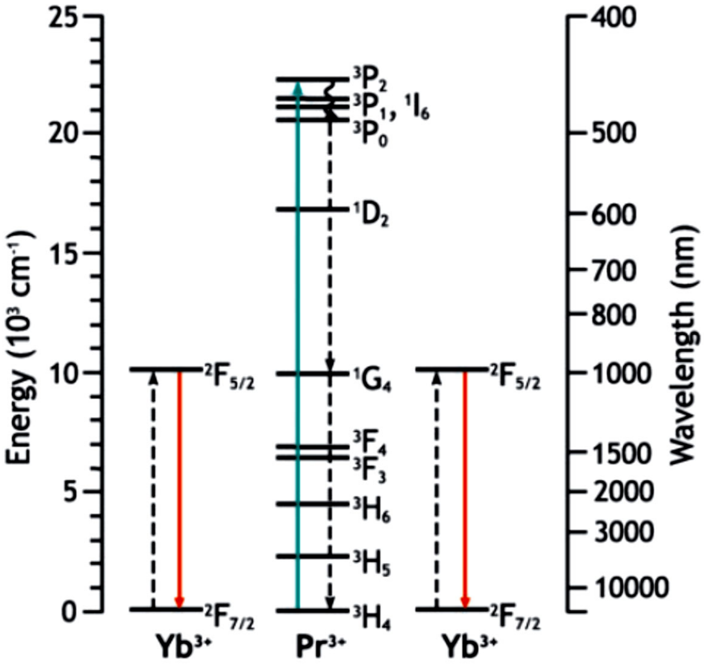




Source: adapted from Ronda, J. Alloys Comp. 225 (1995) 534

Down-Conversion

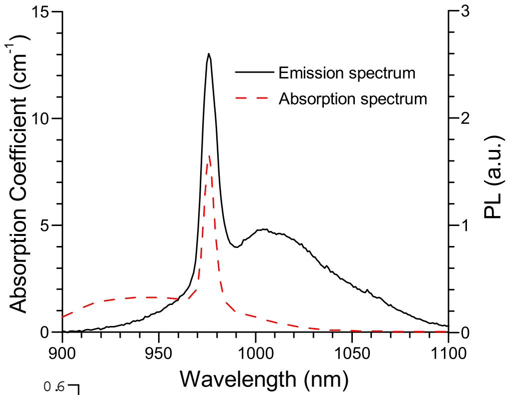
- DC of UV/blue light to NIR via co-doping with Yb^{3+} emitter ⇒ *internal* PLQYs of 200% (absorption very weak)
- Theoretical efficiency limit of DC with Si solar cell = 40% ⇒ motivation to pursue further

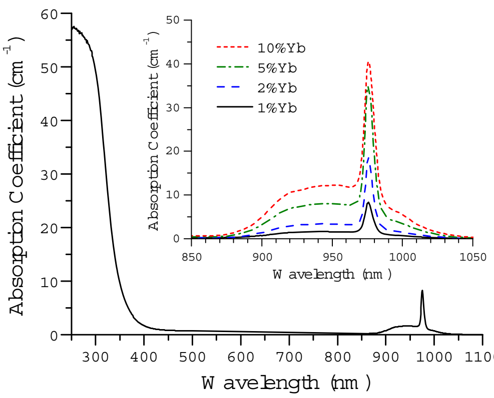


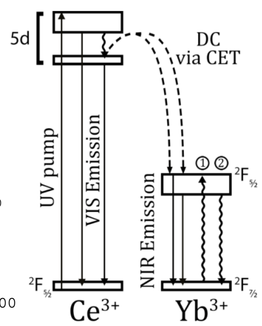
Source: Ende et al., Phys.Chem.Chem.Phys. 11 (2009) 11081

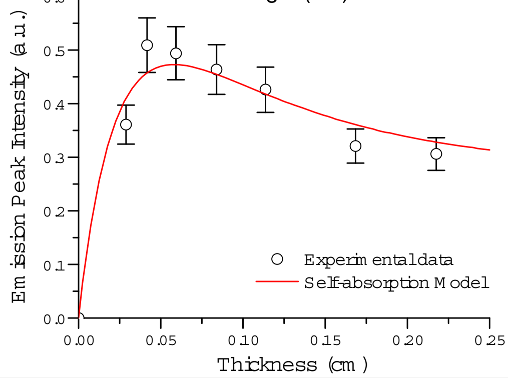
Down-Conversion

- DC via Ce^{3+}-Yb^{3+} ion pair
- Optimise DC layer thickness to maximise absorption but still avoid self-absorption









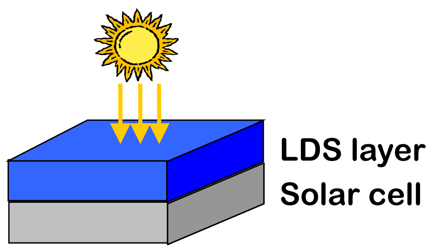
Source: Boccolini et al., Sol. En. Mat. & Solar Cells 122 (2014) 810

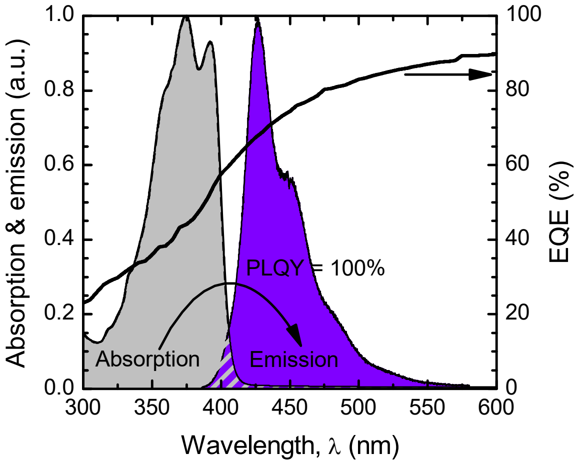
Down-Conversion
Future & Challenges

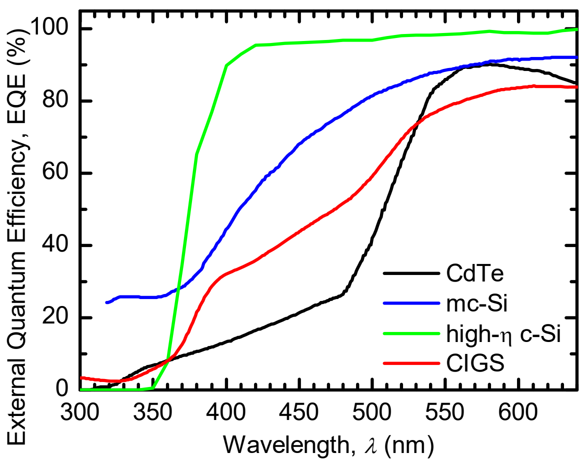
- Challenge of achieving strong absorption
  ⇒ sensitisation via Ce^{3+}, Eu^{2+}, or Bi^{3+}
- Low phonon energy host materials required to minimise non-radiative recombination
- Self-absorption can be minimised but not avoided
- Avoid parasitic absorption ⇒ material should remain totally transparent in the 500 – 950nm range
- Actual demonstration of >100% solar cell EQE's still to be achieved
- "Singlet fission" also possible – injection of two triplets from an organic material into c-Si

Luminescence Down-Shifting

- Many of today's commercial PV modules exhibit poor response to short wavelength light



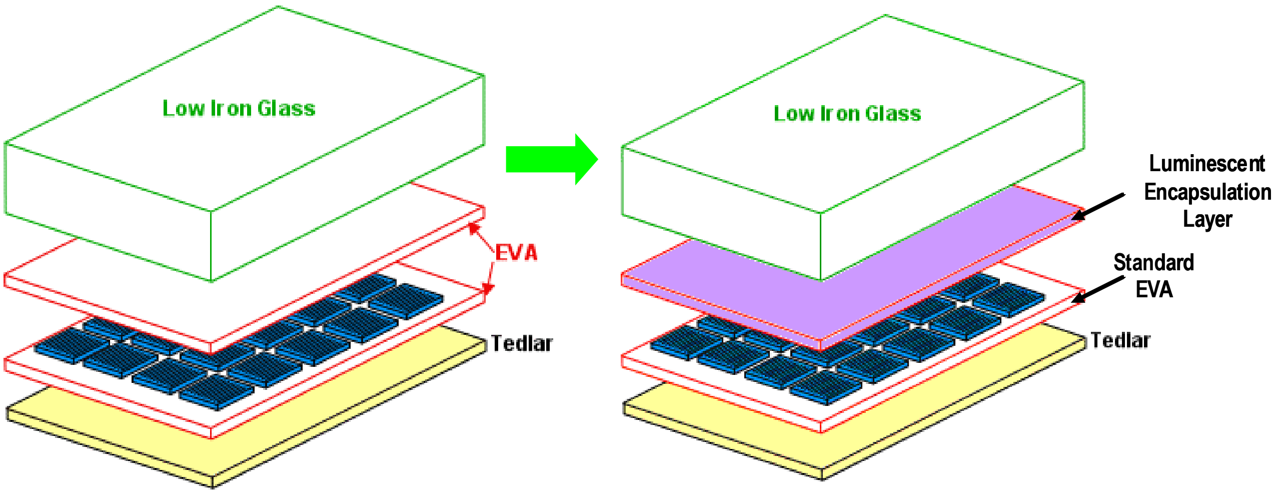




Source: adapted from: Klampaftis et al. Prog. Photovolt. 19 (2010) 345–351
Klampaftis et al. Sol. En. Mat. & Solar Cells 93 (2009) 1182–1194

Luminescence Down-Shifting

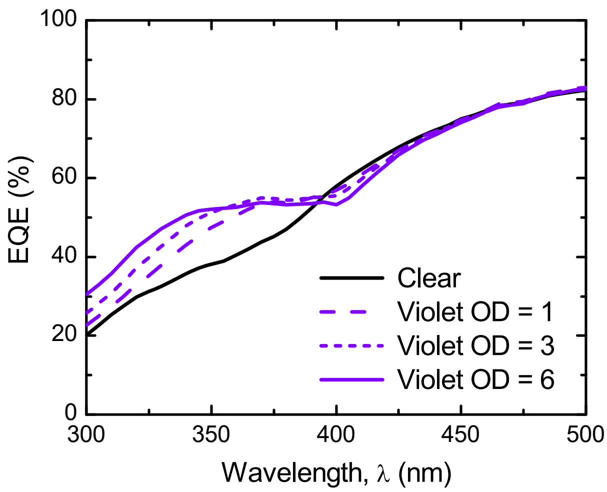
- Add luminescent materials to pre-existing ethylene vinyl acetate (EVA) encapsulation layer
  $\Rightarrow$ no additional production steps!



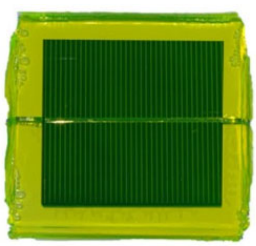
Source: adapted from: Boehm, Grimm, Richards, patent number WO/2008/110567

Luminescence Down-Shifting

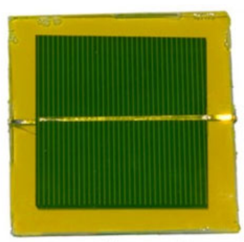
- Demonstrated $\Delta\eta_{abs}$ = 0.2 – 0.3% increase in efficiency of a multicrystalline Si solar cell



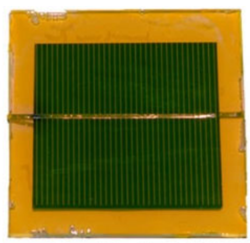
mc-Si with EVA/V570



mc-Si with EVA/Y083



mc-Si with EVA/Y170

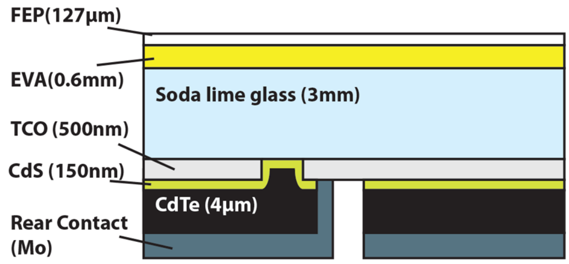


mc-Si with EVA/O240

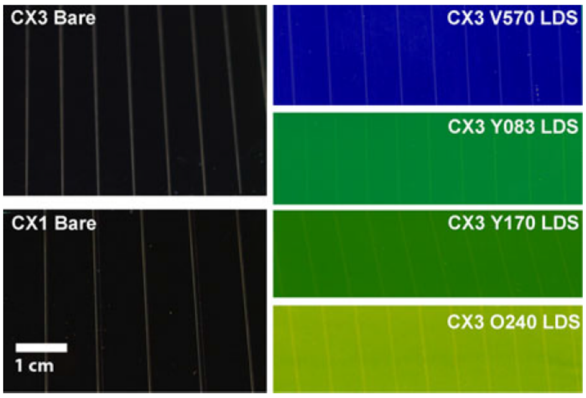
Sources: Klampaftis, Richards, Prog. Photovolt. 19 (2011) 345 – 351; Klampaftis, Richards, Photovolt. Int. 11th ed.: 104 – 109

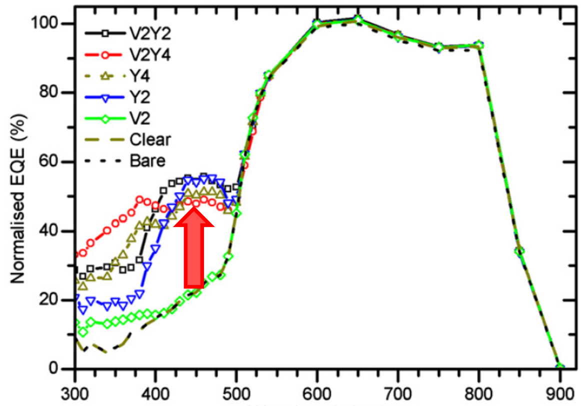
Luminescence Down-Shifting

- EVA + dye mechanically mixed & extruded ⇒ 0.6mm sheet
- Fluoropolymer top sheet



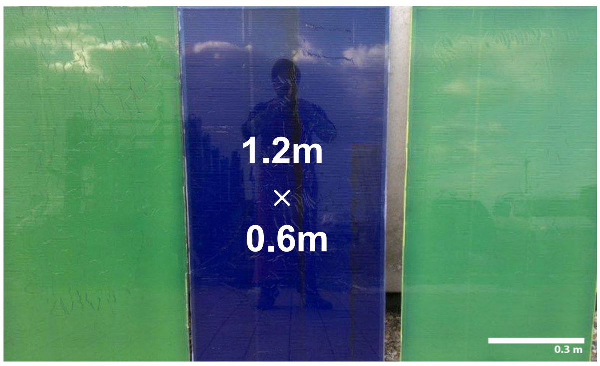
- $\Delta\eta_{rel}$ = 9% performance increase for V570 + Y083 dye mix



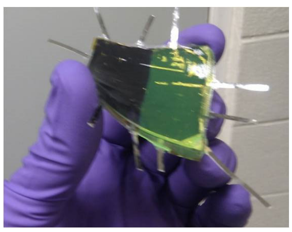


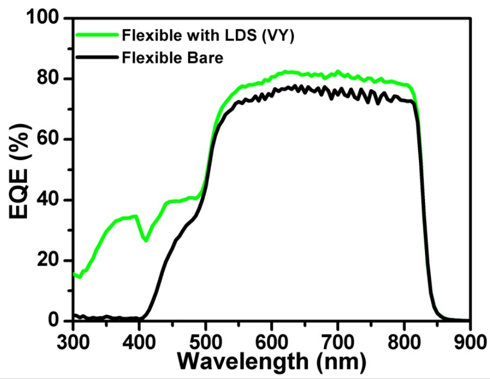
Source: *Ross et al., Sol. En. Mat. & Solar Cells 103 (2012) 11–16; Ross et al., IEEE J. Photovolt. 4 (2014) 457–464*

Luminescence Down-Shifting



- $\Delta\eta_{rel}$ = 4% increase for full-size CdTe PV module
- Flexible CdTe devices on polyimide foil ⇒ ΔJ_{sc} = 12%
- Gains due to LDS plus also better optical coupling:
  n_{FEP} ~1.35
  n_{EVA} ~1. 5
  n_{PI} ~1.7





Source: Ross et al., IEEE J. Photovolt. 4 (2014) 457–464

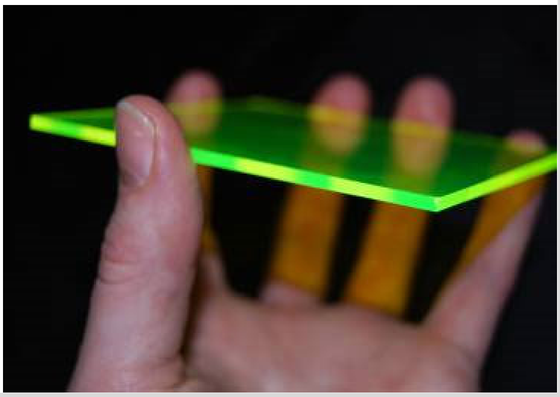
Luminescence Down-Shifting
Future & Challenges

- LDS greater gains when cell exhibits poor EQE
- LDS can be integrated into encapsulation or cover sheet
- EQE of production solar cells improving over time
- Enhancing life of organic PV devices
- Development of stable, large Stokes shift and high PLQY materials

Source: Klampaftis et al., IEEE J. Photovolt. 5 (2015) 584

Luminescent Solar Concentrators

- Concept: replace expensive solar cells with low cost materials, e.g. costs for optical PMMA €2-3/kg & dyes ~€5/g
  ⇒ waveguide luminescence to solar cells placed at edges
- Static concentrator:
  ⇒ can even concentrates diffuse sunlight!
  ⇒ no tracking required
- Improved thermal performance of solar cells under “cold light”
- Solar concentrations of 5 –10X
- BIPV product as “electric window”
  ⇒ different sizes/forms possible
  ⇒ adds colour as well!



Luminescent Solar Concentrators

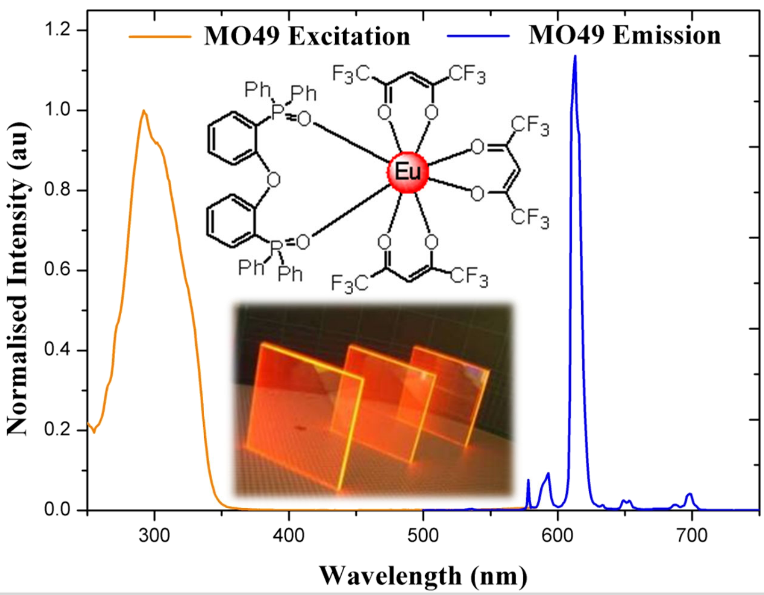
- Ideally LSC material would fulfil all of the following criteria (for Si solar cell):

Criterion	Organic	Inorganic Ln† / QD‡	Hybrid?
Absorb sunlight all λ < 900nm	✗	✗ / ✓	>✓
Emission peak λ ~ 950nm	✗	✓ / ✓	✓
Large Stokes shift (low self abs.)	✗	✓ / ✗	✓
PLQY > 90%	✓	✓ / ✗	✓
20yr stability	~ *	✓ / ✗	✓
Low cost	✓	✓ / ✗	✓

** 10yr max † Lanthanide-based nanoparticles ‡ PbS or PbSe quantum dots*

Luminescent Solar Concentrators

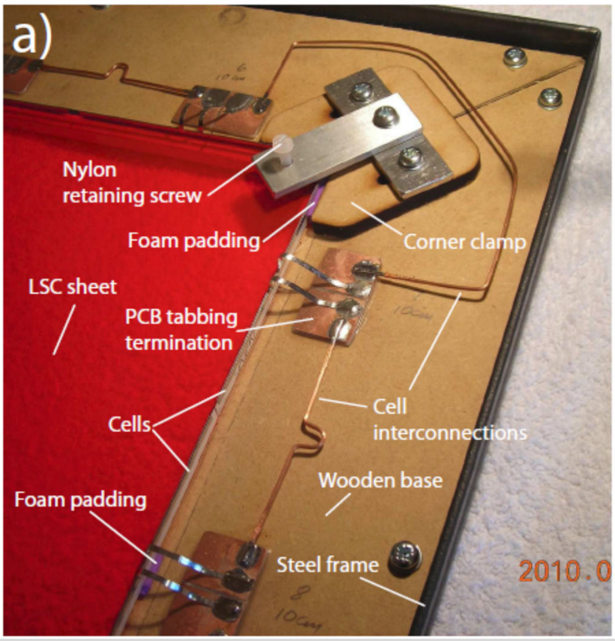
- Large Stokes shift via lanthanide complexes: organic chromophore transfers energy to emitting Eu^{3+} ion
- PLQY = 85% in PMMA
- Large Stokes shift
  ⇒ no re-absorption
- Absorption range not broad enough
- Stability
  - UV
  - Thermal



Source: Moudam et al., Chem. Comm. 2009, 6649-6651
Klampaftis et al. IEEE Journal of Photovoltaics 1 (2011) 29-36

Luminescent Solar Concentrators

- Large areas possible (60cm × 60cm, η = 2%)

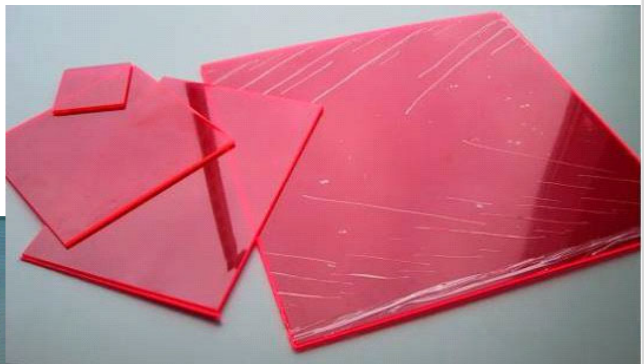


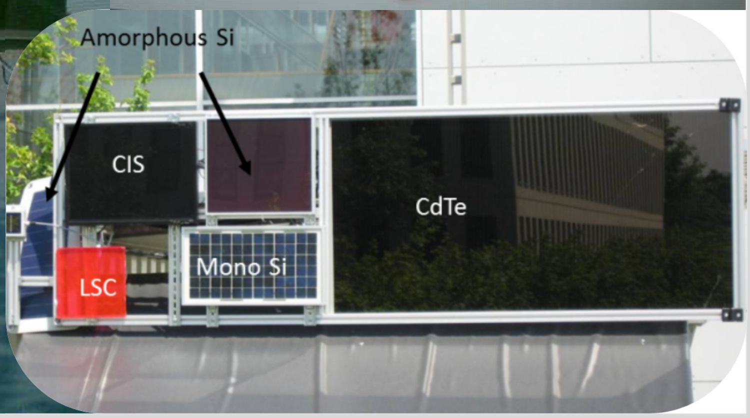
<u>LSC materials</u>:
- cast PMMA
- 400ppm Lumogen Red300
- 10cm × 0.3cm c-Si solar cells

Source: Wilson, PhD thesis (2010)

Luminescent Solar Concentrators

- 3D LSCs also possible (roof tile)

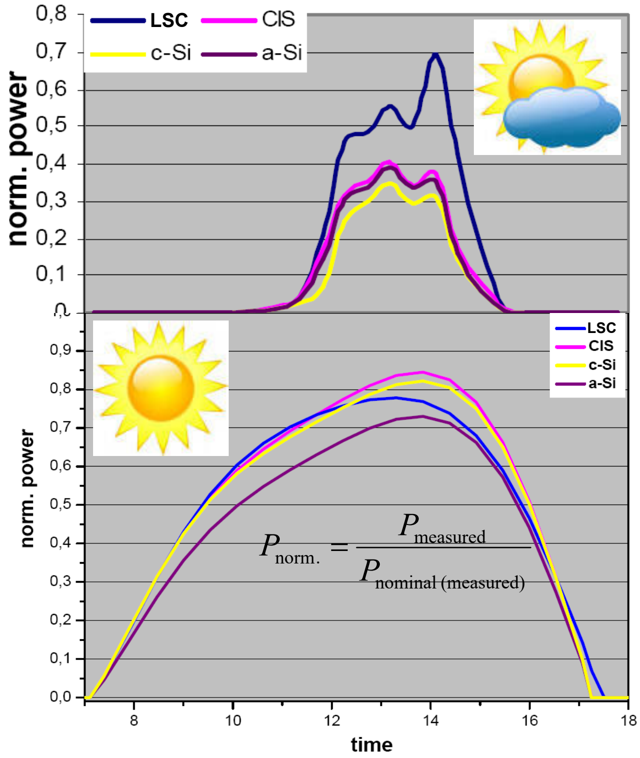




Source: collaboration with GE Global Research, Garching

Luminescent Solar Concentrators

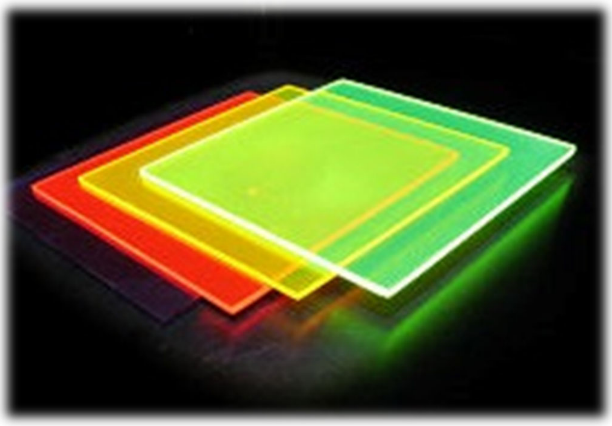
- Outdoor façade: performance of different PV technologies measured at same angle (Munich, July 2007): a-Si, CIS, c-Si, LSC
- Sunny day: all technologies exhibited similar behaviour
- Cloudy day: LSC performed significantly better!



Source: unpublished – collaboration with GE Global Research, Garching

Luminescent Solar Concentrators
Future & Challenges

- Marrying of absorption window of host material (polymer, glass,…) with luminescence peaks and solar cell EQE
- Alignment of dye molecules within ordered porous hosts
- Development of luminescent materials with:
  - broad absorption range,
  - large Stokes shift,
  - high PLQY,
  - >10y life,
  - … and low cost!



Conclusions

- For UC and DC, huge potential enhancement ⇒ further materials development work needed
- Enhanced sensitisation and emission (non-linear)
- LDS can be applied to large areas ⇒ small enhancement in solar energy conversion demonstrated
- LSC able to concentrate diffuse light ⇒ better performance under cloudy conditions
- Potential of integrating colour and PV into built environment
- Lots more R&D needed! (incl. MSc projects!)