WINTON INAUGURAL SYMPOSIUM

ENERGY EFFICIENCY...

...fundamental physical limits

Cambridge,

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Limits to efficiency of photovoltaic energy conversion

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The Centre for Plastic Electronics

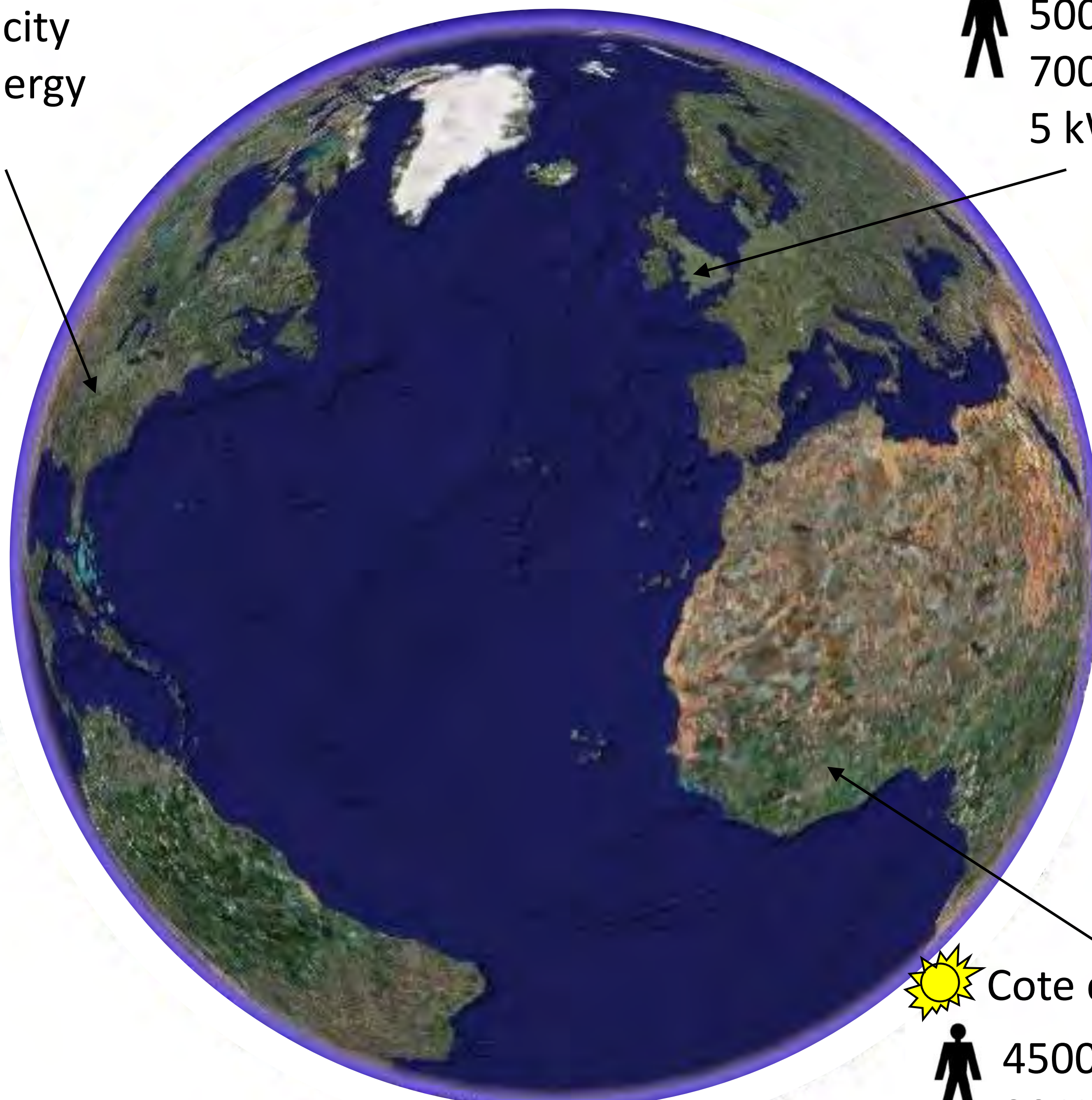
Energy from the Sun

USA: ~200 Wm^{-2}

6500 kW solar resource
1500 W electricity
10 kW total energy

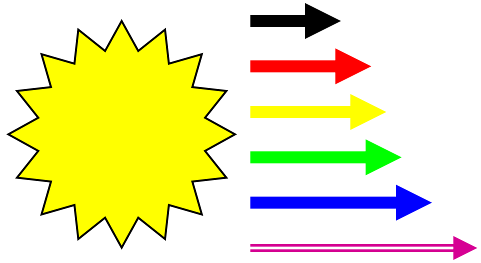
UK: 125 Wm^{-2}

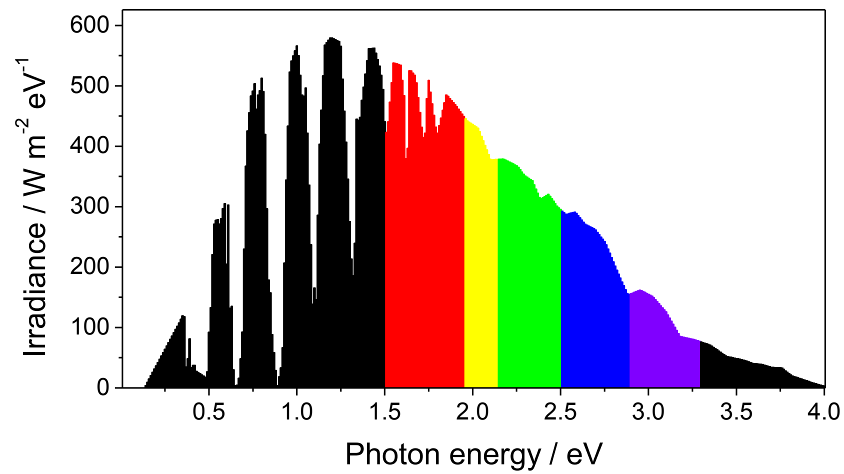
500 kW solar resource
700 W electricity
5 kW total energy

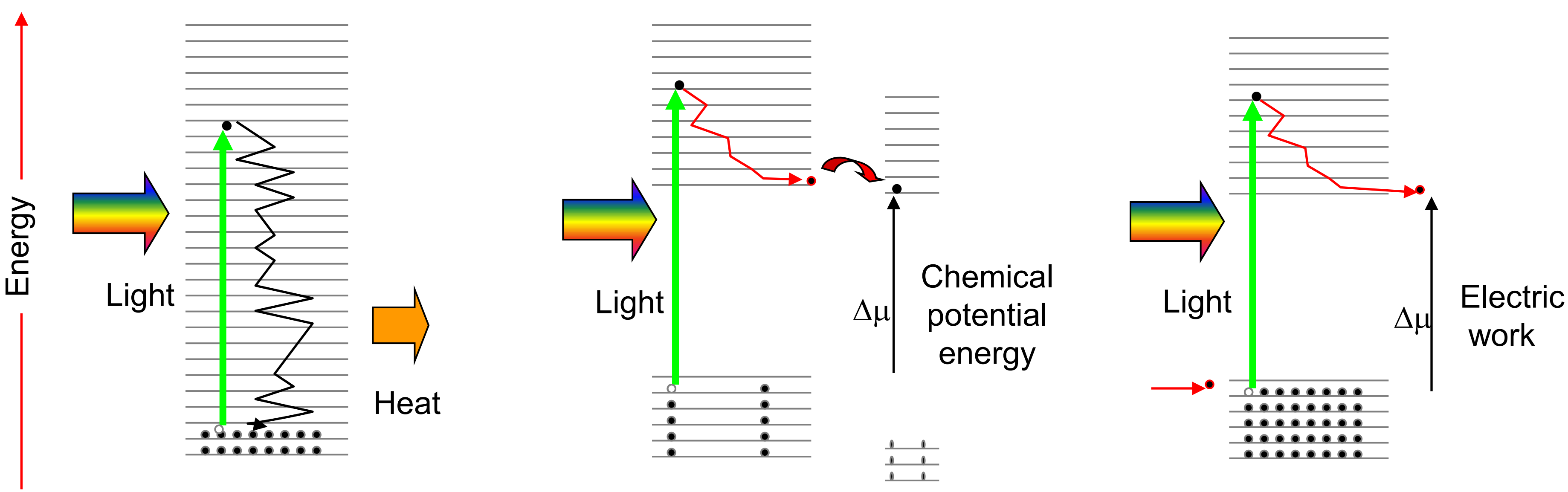


Cote d'Ivoire: ~250 Wm^{-2}

4500 kW solar resource
20 W electricity
0.5 kW total energy





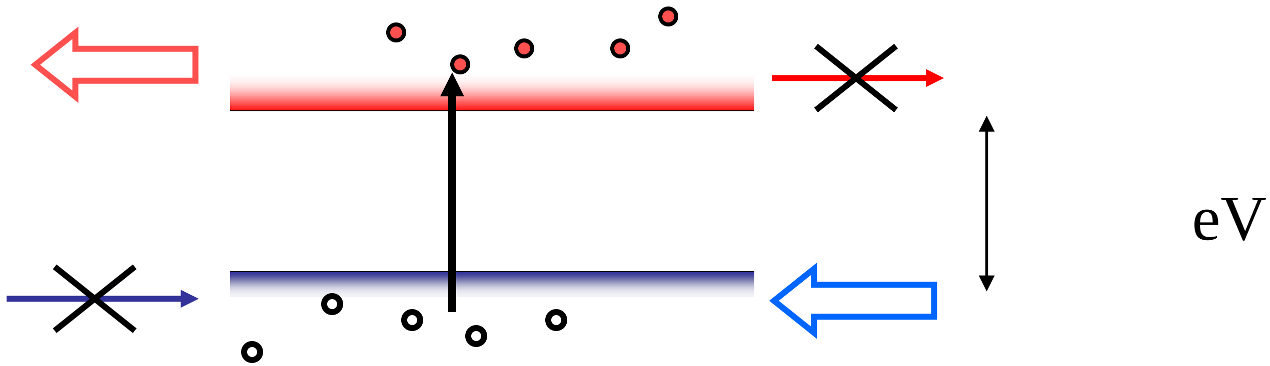


Solar thermal

Solar chemical

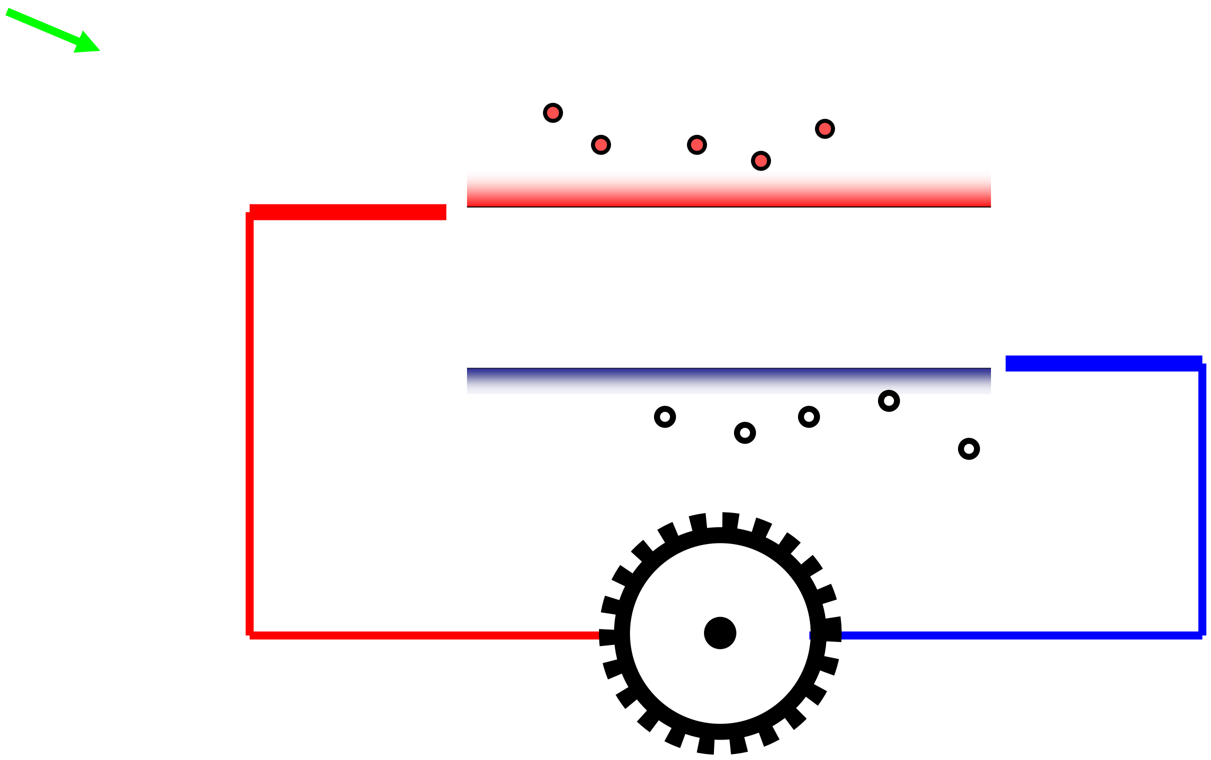
Solar photovoltaic

Photons in, electrons out

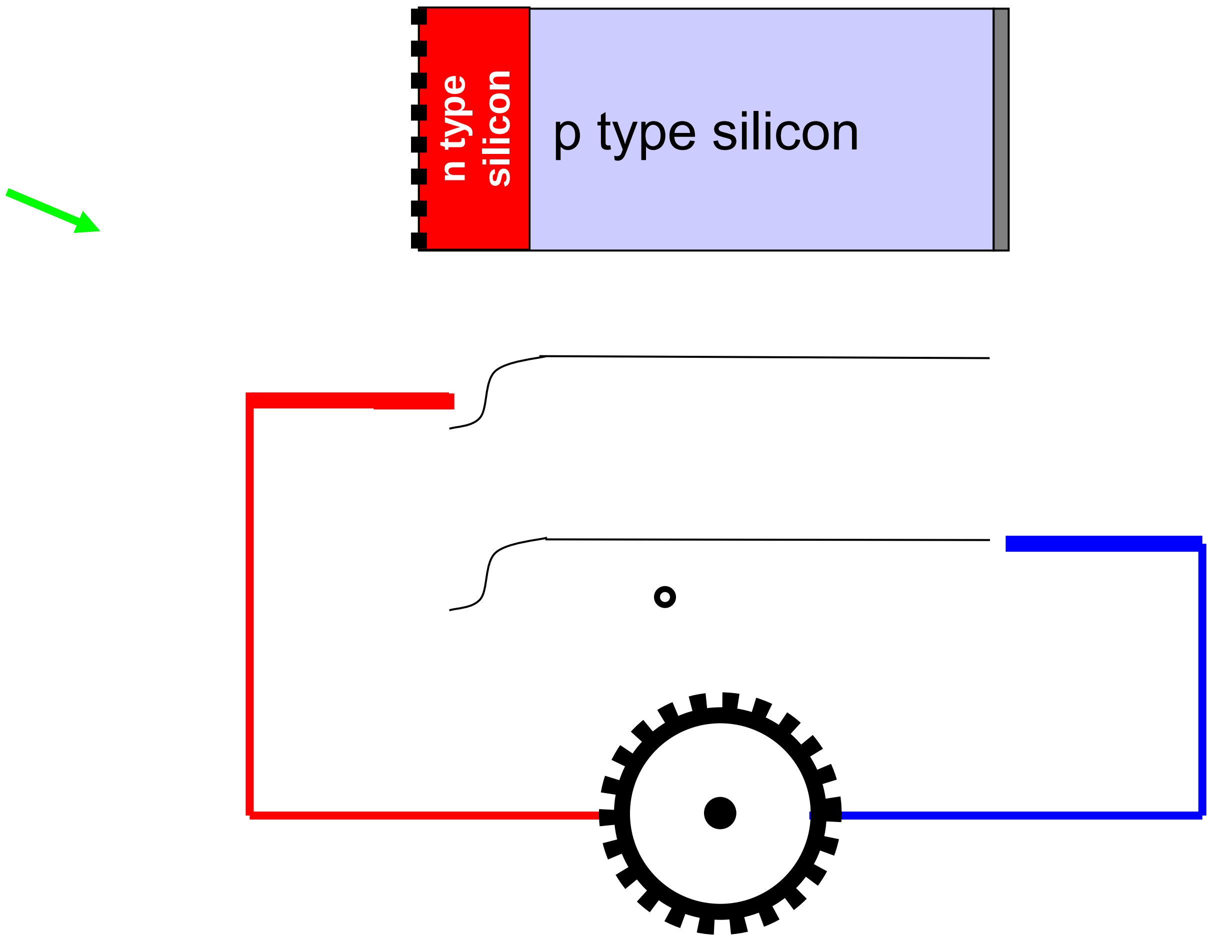


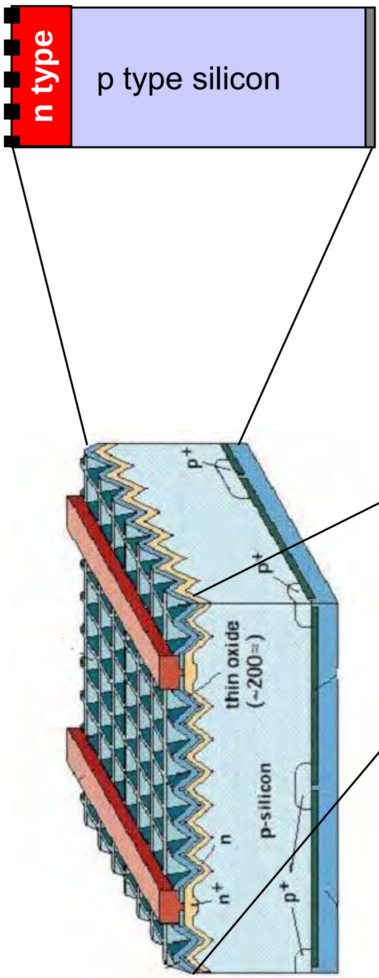
- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - separation of photogenerated charges
  - asymmetric contacts to an external circuit

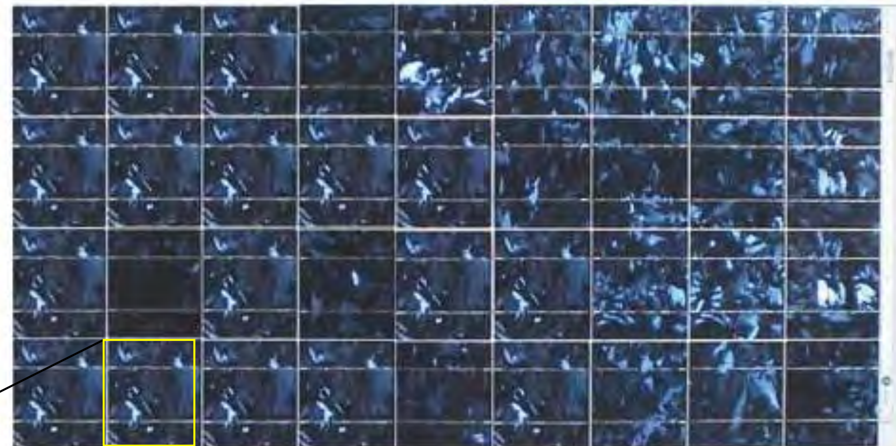
Photons in, electrons out



Photons in, electrons out







efficiency
~ 15-20%

power rating
~ 100-200 W_p

Applications, large and small

CIS Tower, Manchester
0.4 MW_p
(Solar Century)

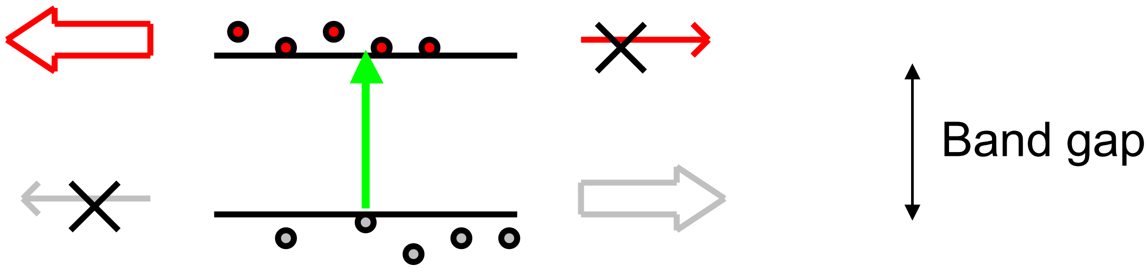
Solar powered refrigeration
~100 W_p

~1 mW_p

Outline

- Photovoltaic energy conversion
- Limiting efficiency of solar cells
- Where next?
- Routes to more work per photon
- Molecular solar cells

Detailed balance limit



(i) One electron hole pair per photon with $h\nu > E_g$,

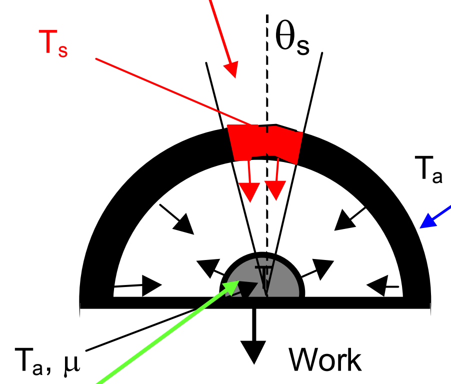
(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta\mu$.

(iii) All electrons extracted with same electrochemical potential $\Delta\mu = eV$

(iv) Only loss process is spontaneous emission

Detailed balance limit

A fraction Xβ of the "sky" emits solar radiation at a black body temperature of T_{sun}

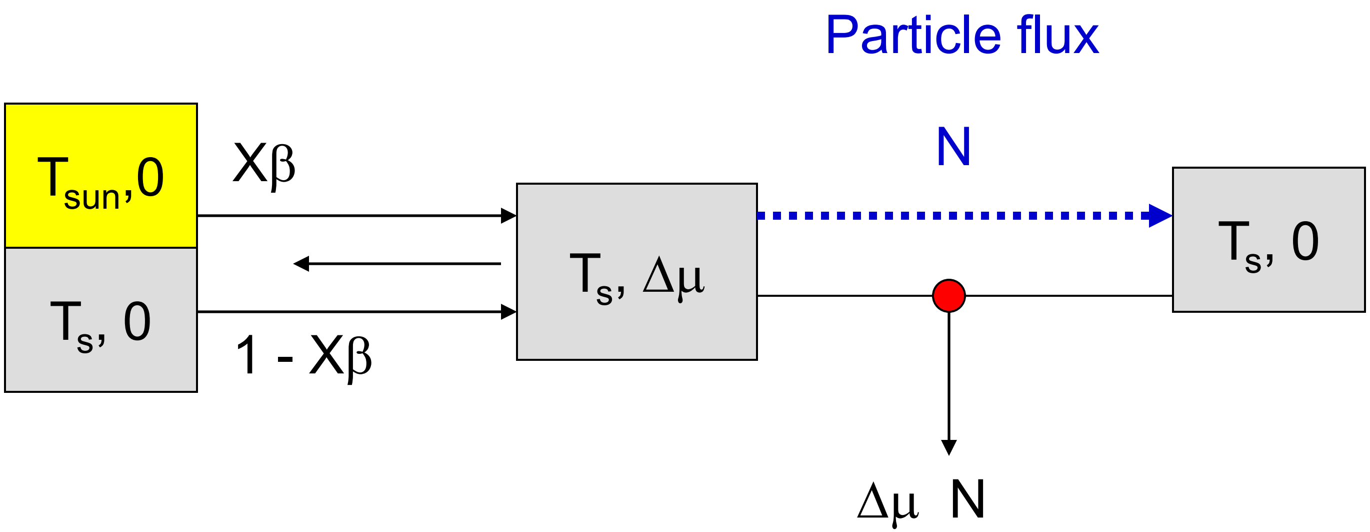


A fraction (1 - Xβ) of the "sky" emits ambient radiation at a black body temperature of $T_{ambient}$

The photovoltaic energy converter emits ambient radiation at a black body temperature of $T_{ambient}$ and a chemical potential of $\Delta\mu$

The remaining charge pairs provide a current of electrons with chemical potential of $\Delta\mu$

Calculation of limiting efficiency

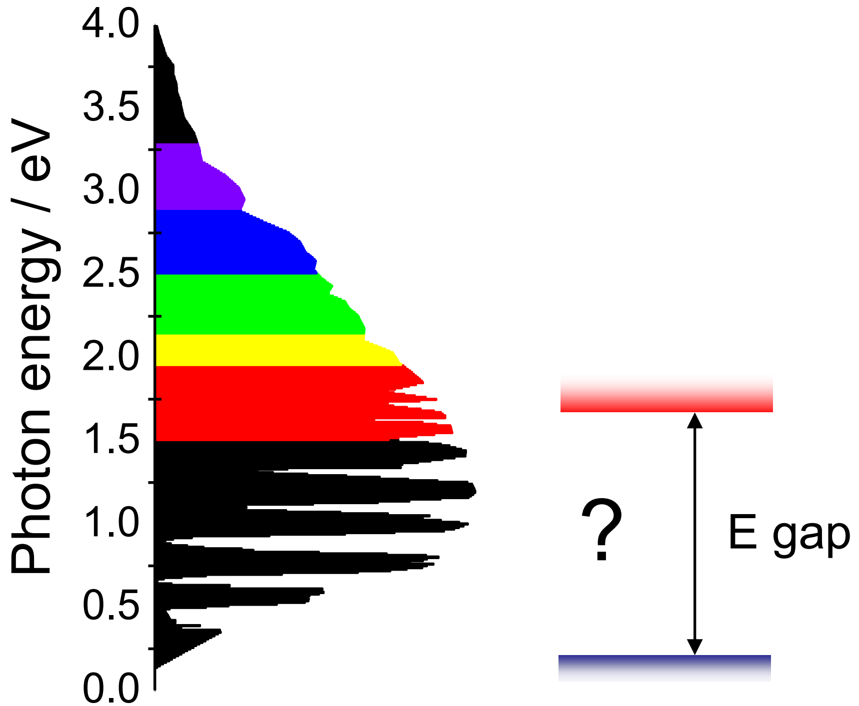


$$\frac{J}{e} = X\beta \int_{E_g}^{\infty} b_{sun}(E)dE + (1 - X\beta)\int_{E_g}^{\infty} b_{ambient}(E)dE - e^{\Delta\mu / kT} \int_{E_g}^{\infty} b_{ambient}(E)dE$$

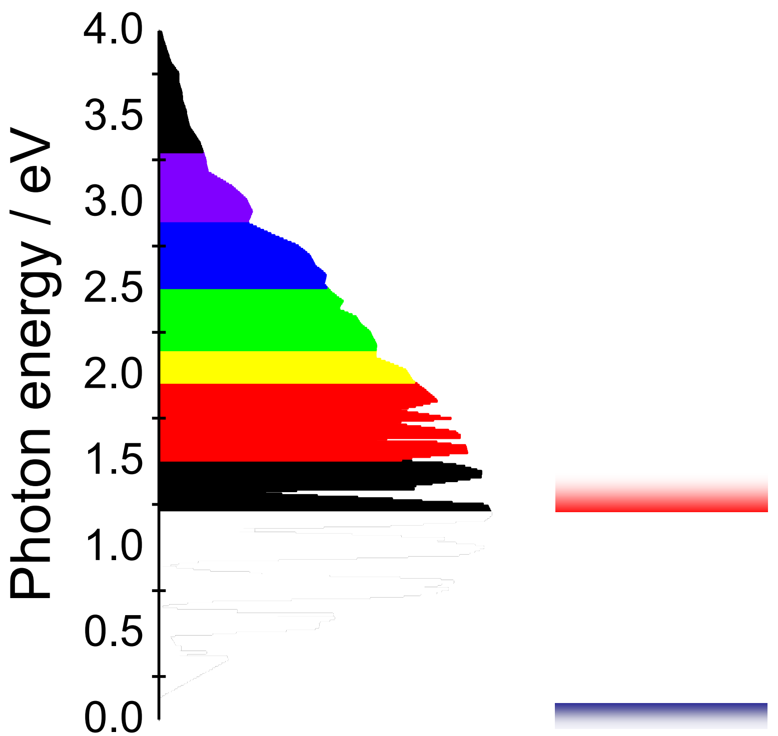
$$J = J_{sc} - J_0\left(e^{eV/kT} - 1\right)$$

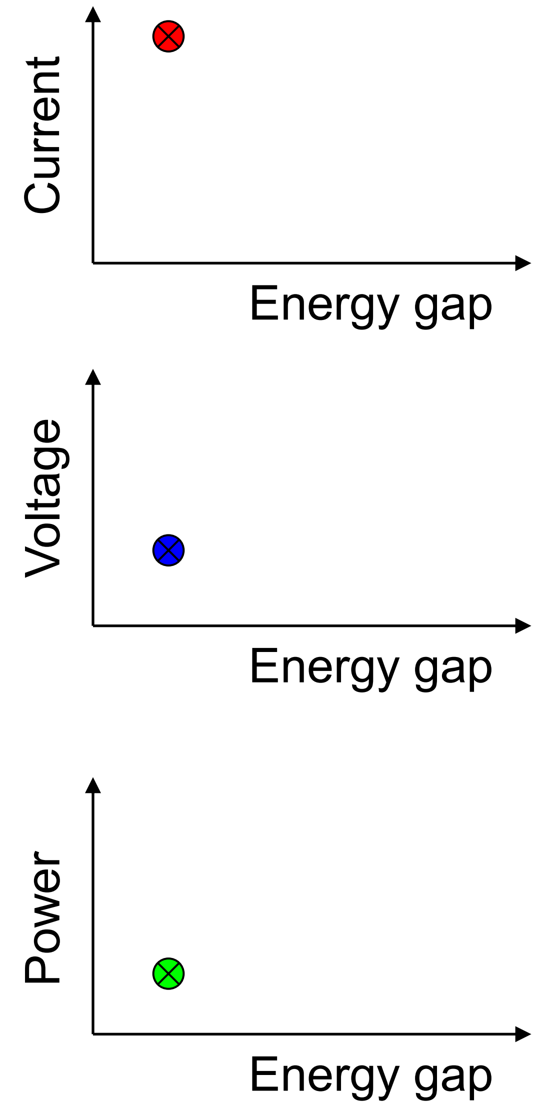
$$P = JV$$

Limit to efficiency: the Goldilocks story

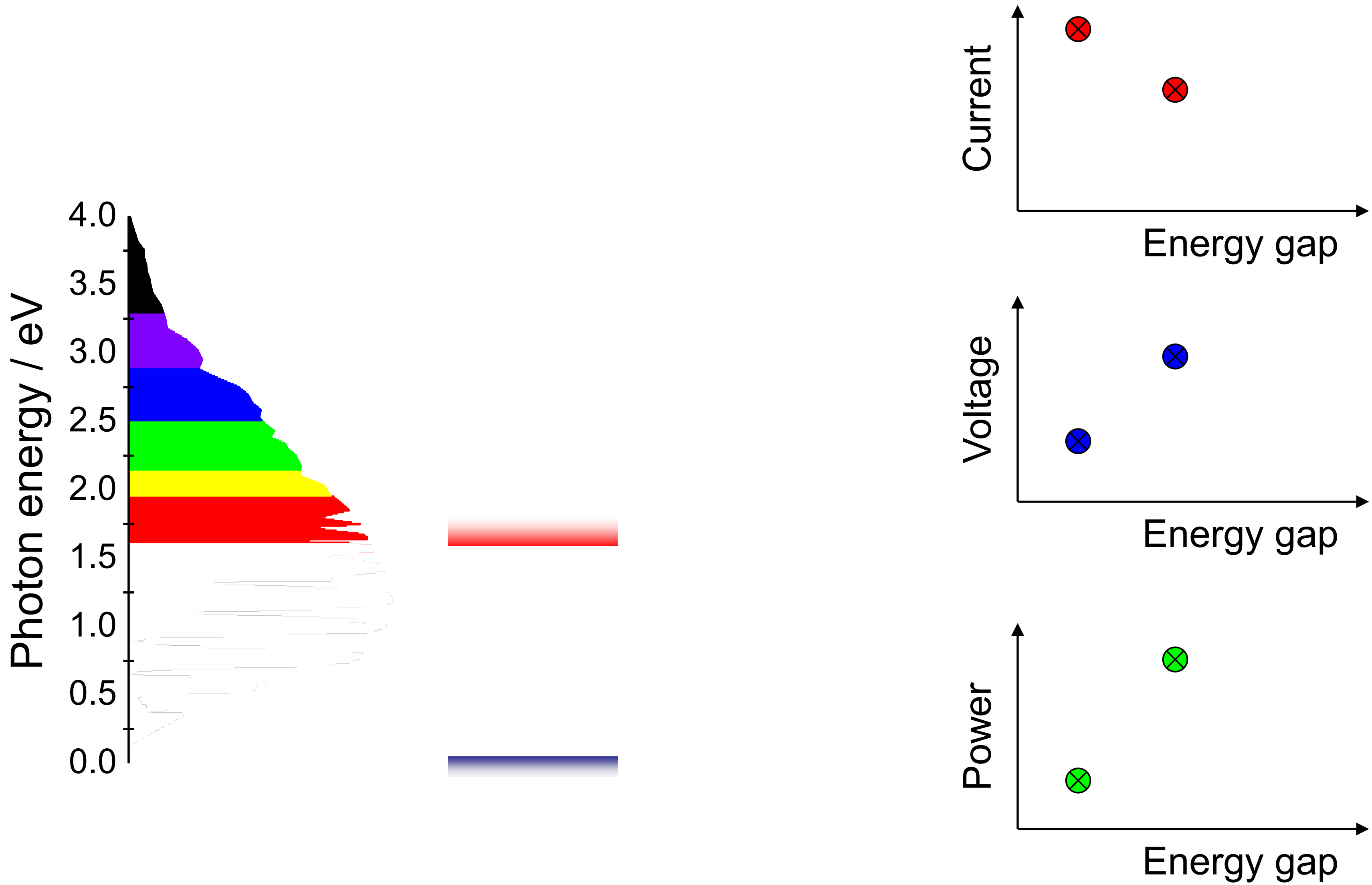


Limit to efficiency: the Goldilocks story

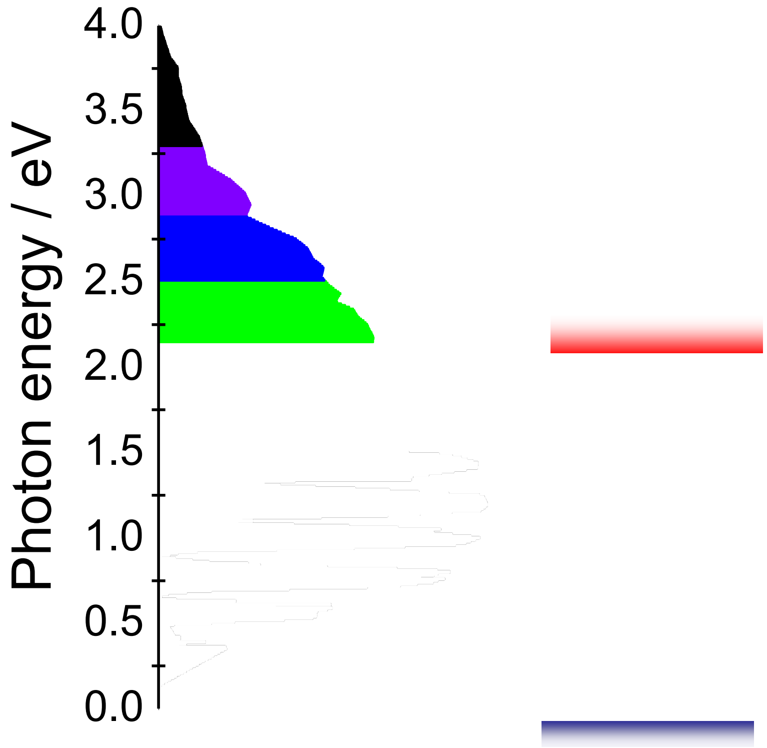


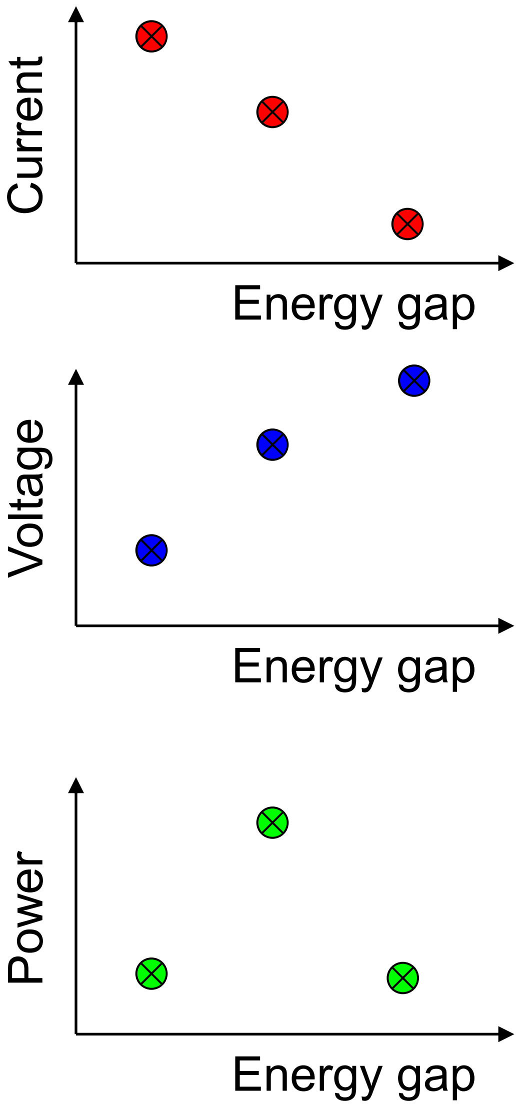


Limit to efficiency: the Goldilocks story

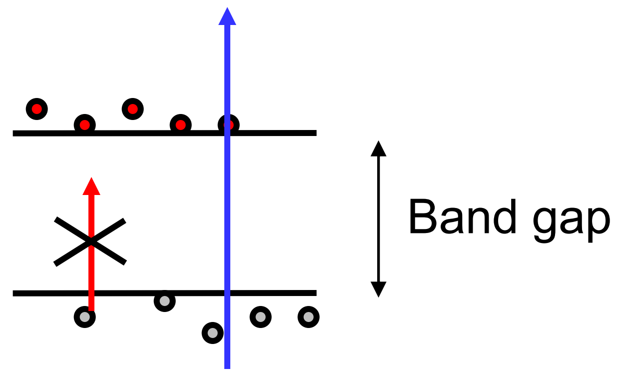


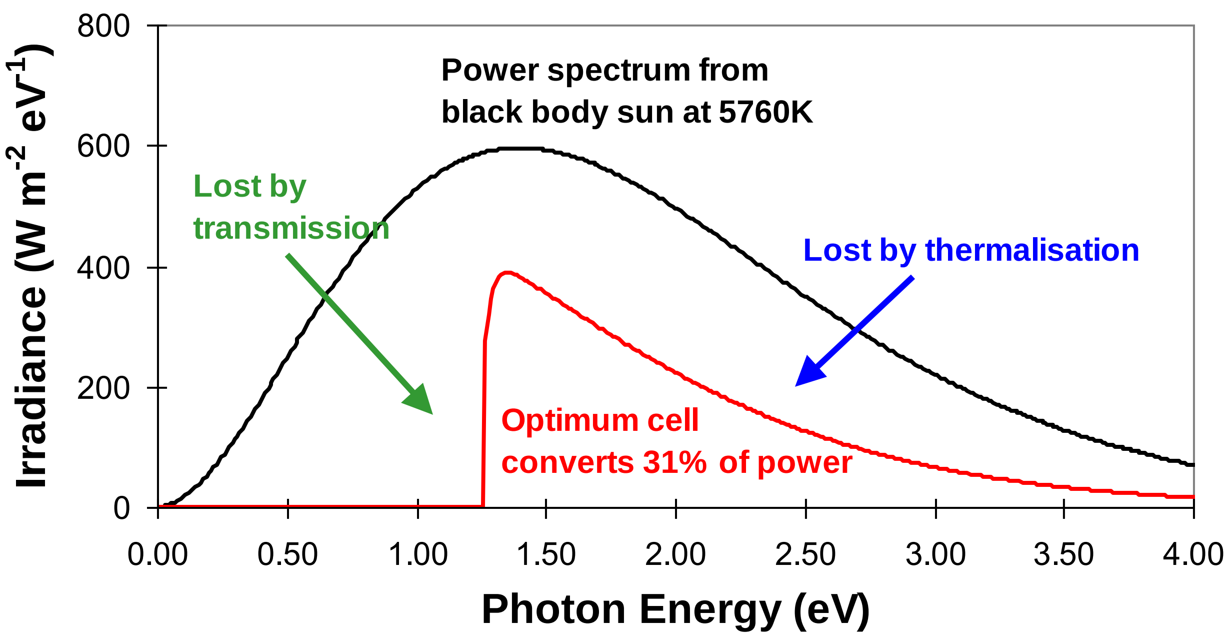
Limit to efficiency: the Goldilocks story



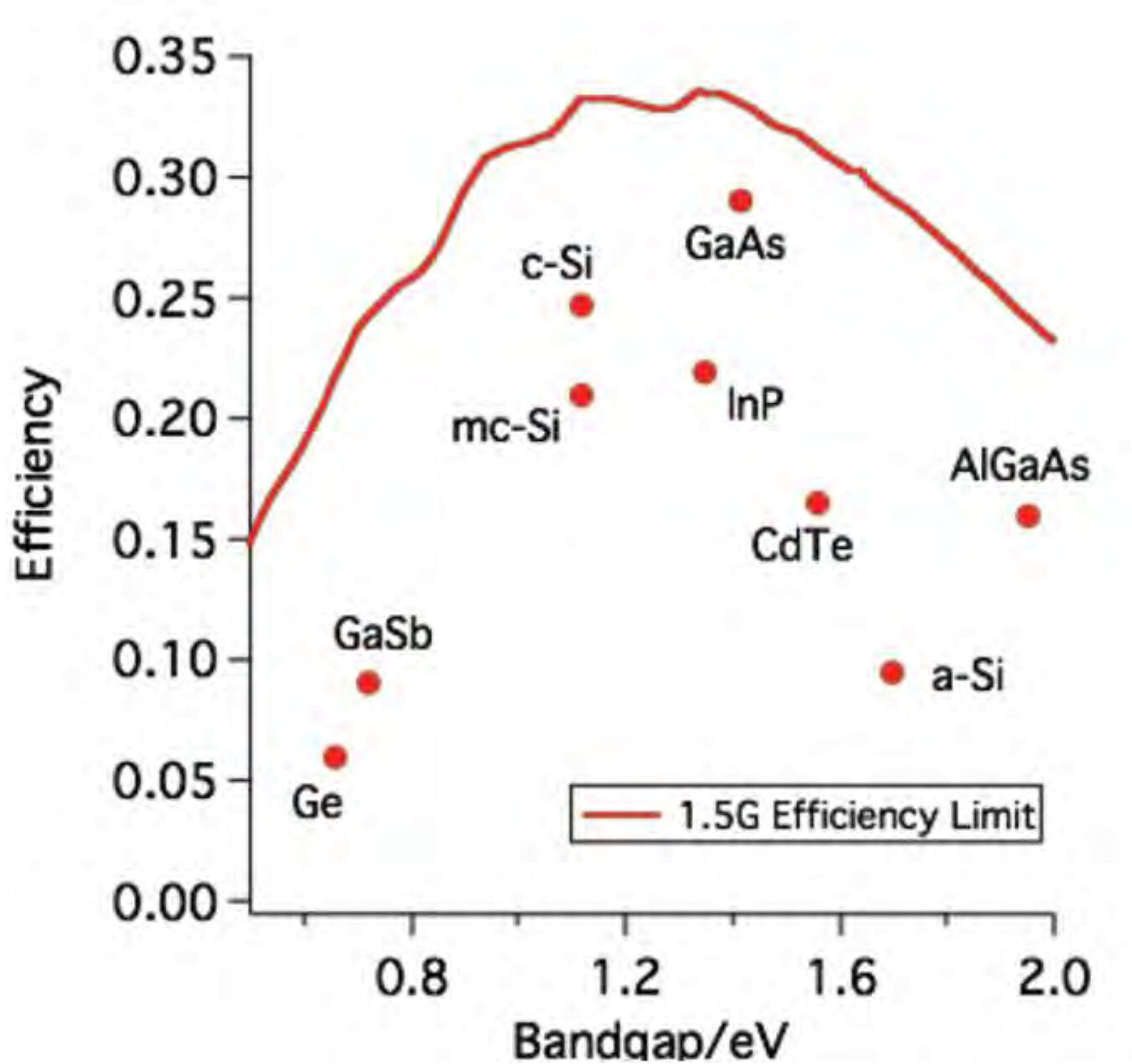


Limiting efficiency of single band gap cell





Practical and limiting efficiencies



Courtesy:Ned Ekins-Daukes

How bad are the assumptions?

(i) One electron hole pair per photon with $h\nu > E_g$,

Overestimate current by 10-20%

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta\mu$.

~ OK

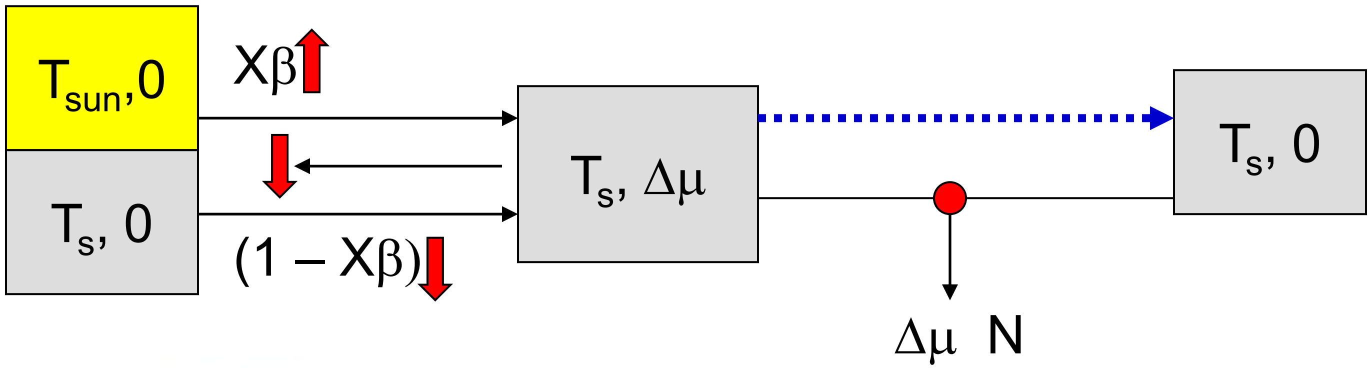
(iii) All electrons extracted with same electrochemical potential $\Delta\mu = eV$

Overestimate eV_{oc} by O(0.1 eV)

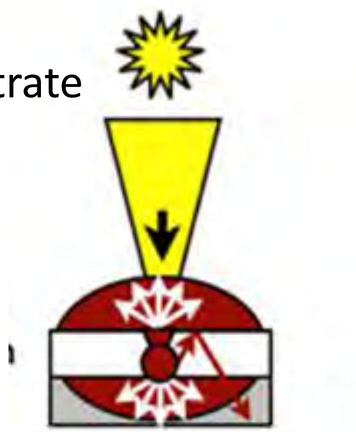
(iv) Only loss process is spontaneous emission

Overestimate eV_{oc} by few 0.1 eV
Overestimate fill factor

Highest efficiency single junction: thin film GaAs



Device with absorbing substrate



Limiting efficiency: 30.4 %
Actual efficiency: 24.8 %

Spire Corp, IEEE Tr. Electron Dev. 37, 469 (1990)

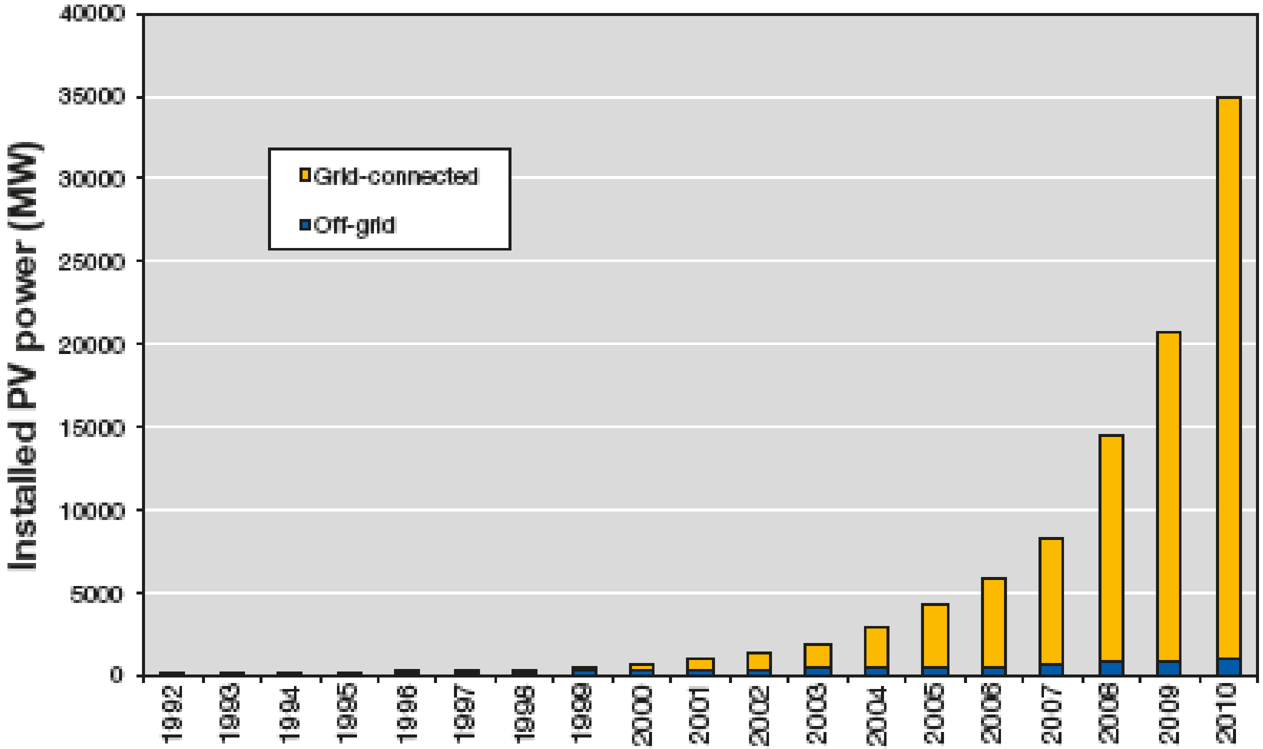
Thin-film device

Limiting efficiency: 32.4 %
Actual efficiency: 28.8 %

Alta Devices, Prog. Photovoltaics 20, 606 (2012)

Outline

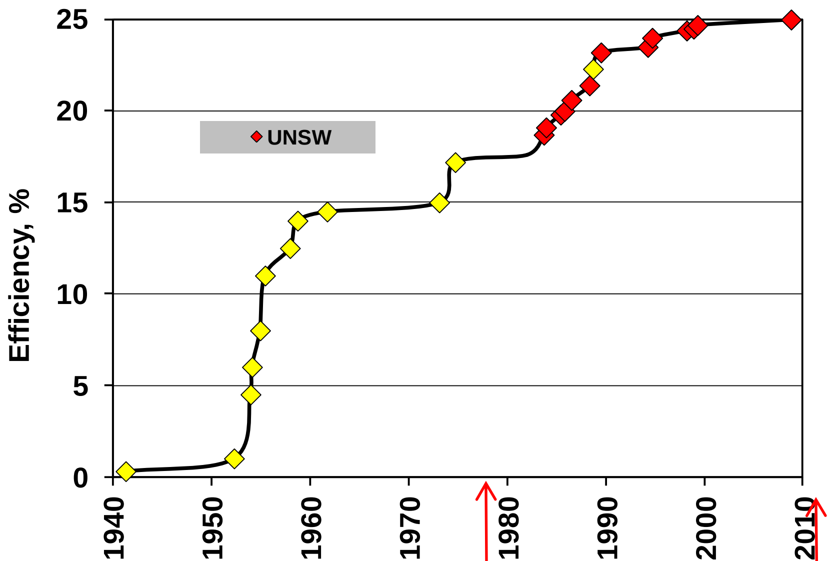
- Photovoltaic energy conversion
- Limiting efficiency of solar cells
- **Where next?**
- Routes to more work per photon
- Molecular solar cells

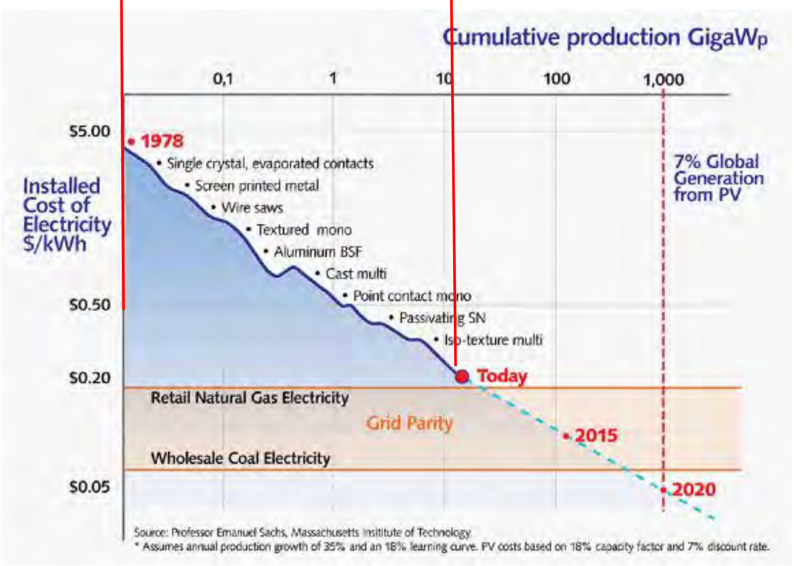


IEA PVPS 2011

- Installed PV capacity growing at > 30% per annum for ~15 years
- Mainly based on crystalline Si technology

- Where next?





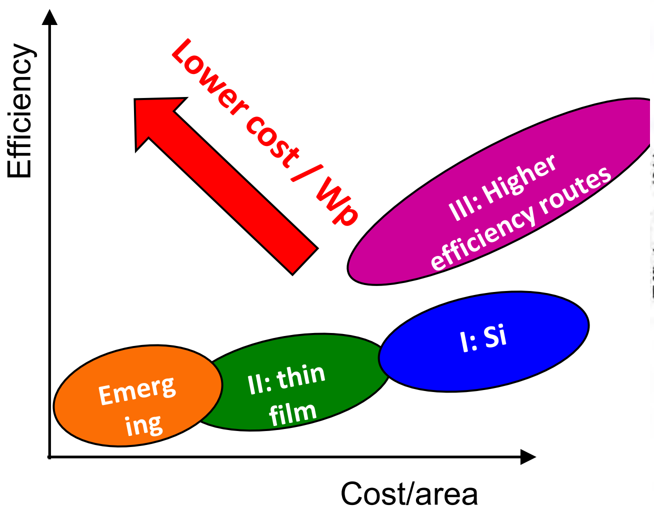
Courtesy: Martin Green

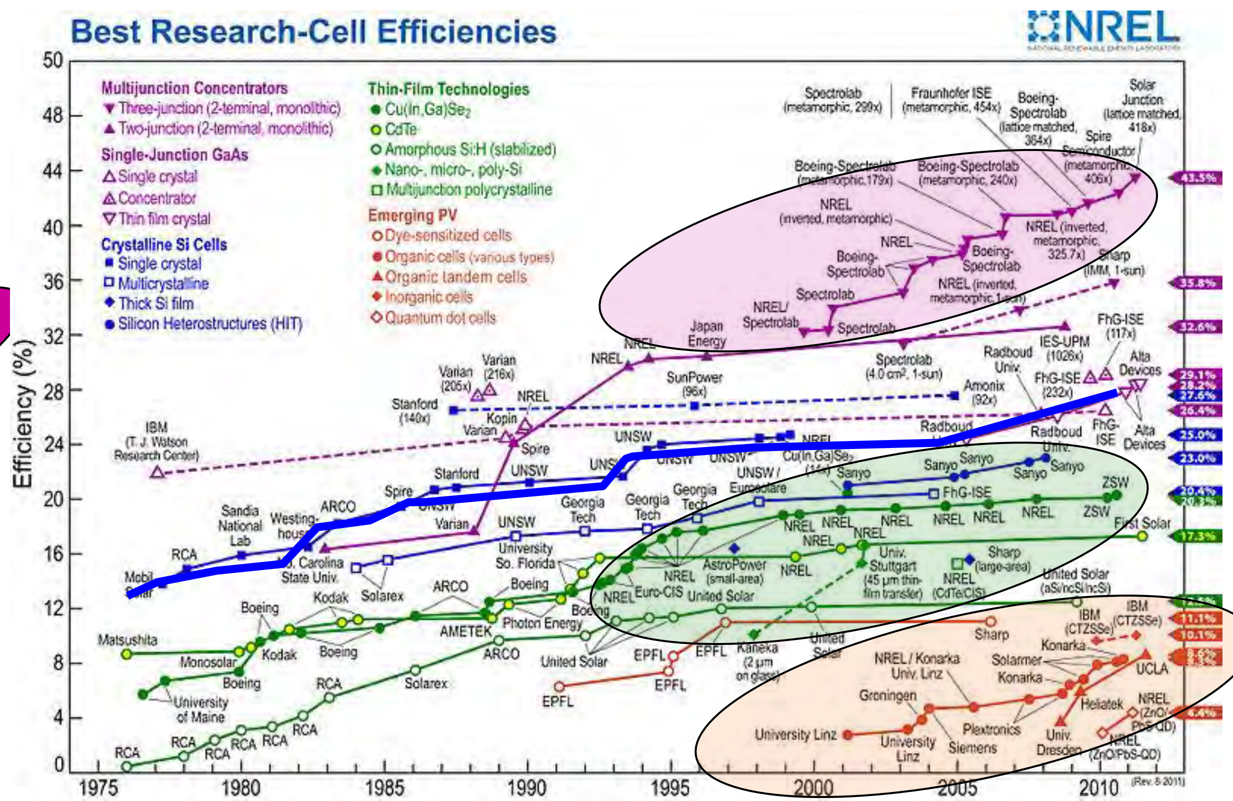
Cost reductions follow maturing of Si technology through innovations in manufacturing and design.

Cost evolution typical of a semiconductor technology not a conventional energy technology

Role for technical innovation?

PV technologies





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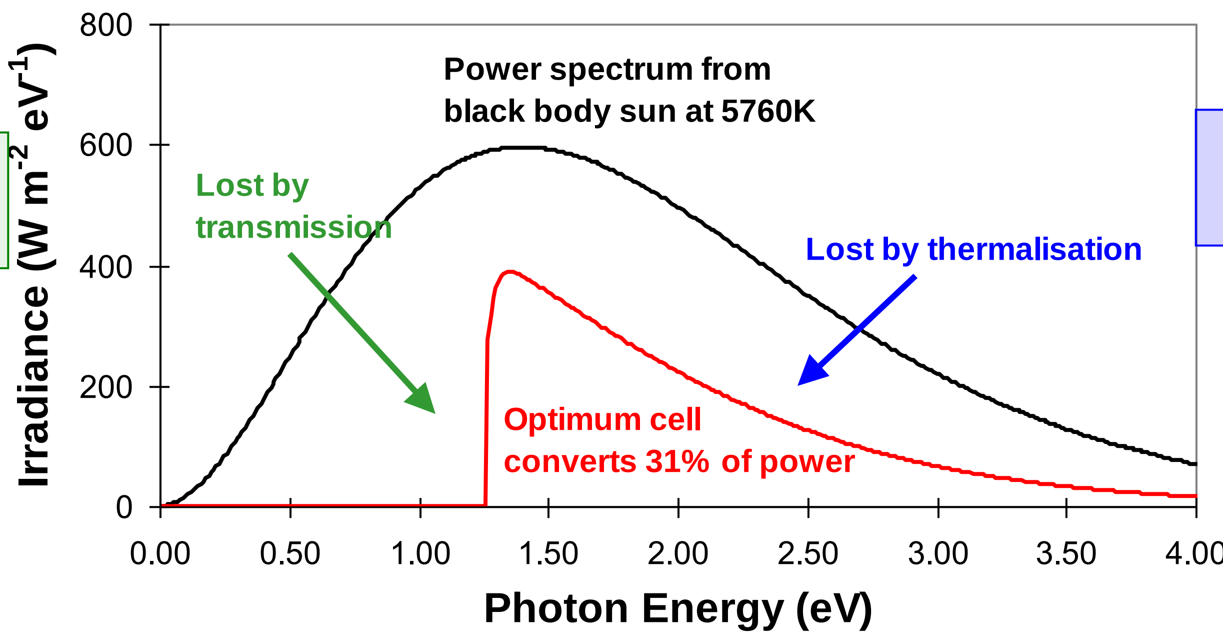
- **Routes to more work per photon**
- Molecular solar cells

Routes to more work per photon

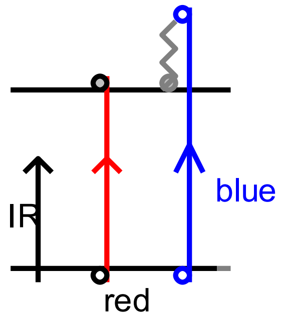
Spectral conversion



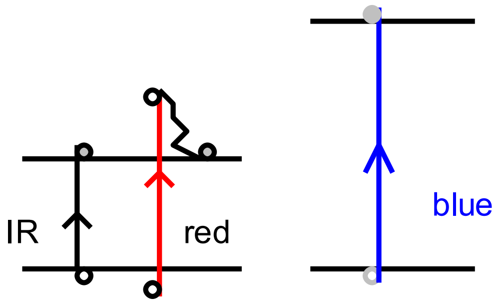
Slow carrier cooling

More band gaps

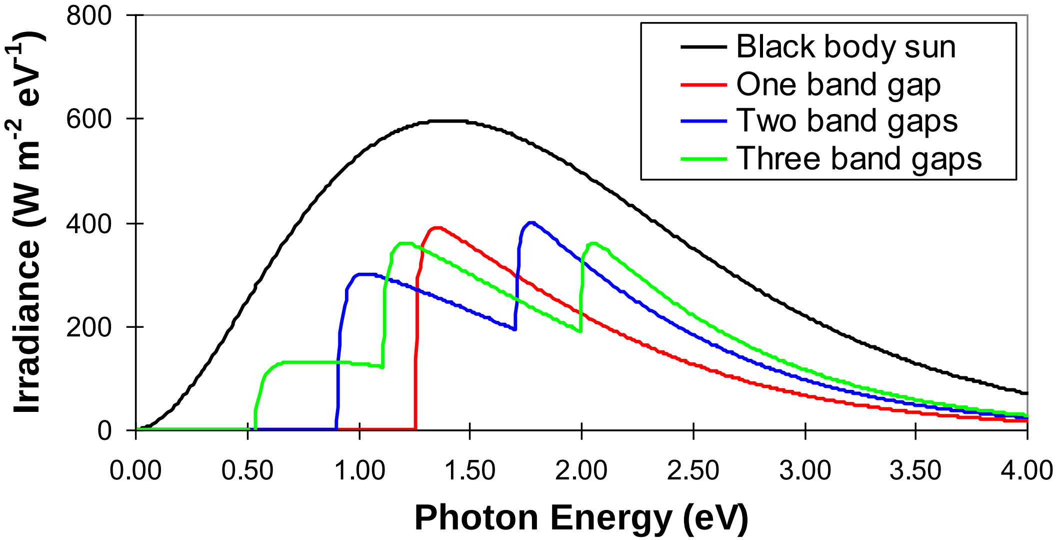
Route 1: Multiple band gaps



Single band gap

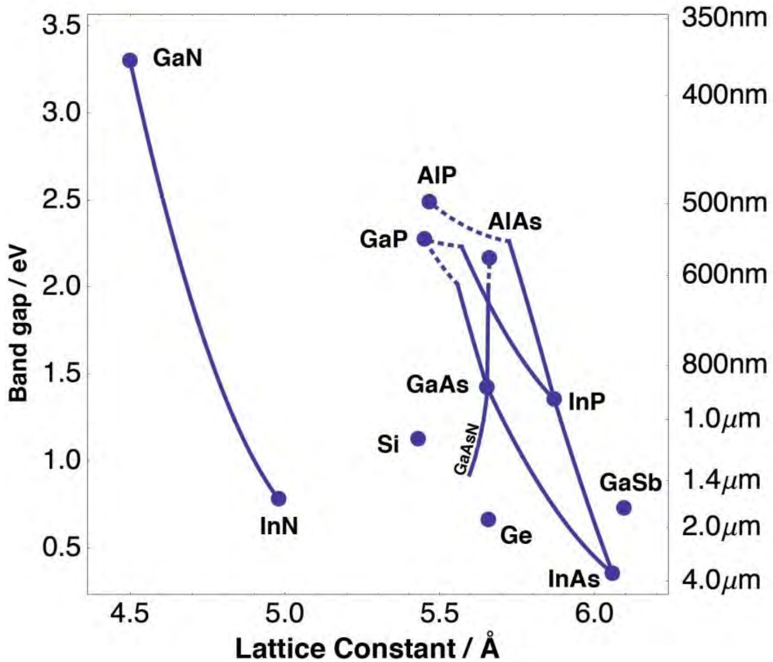


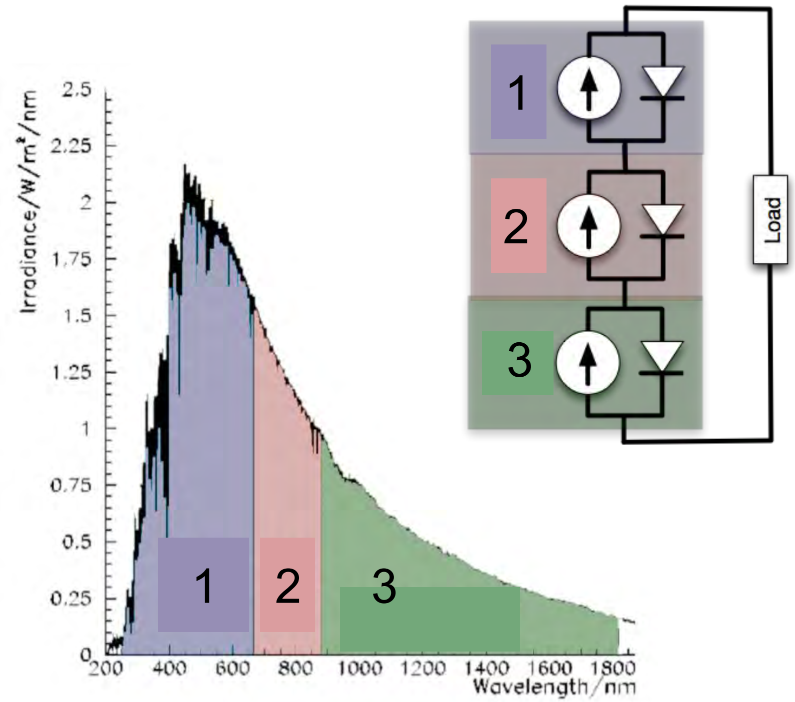
Two band gaps



- Multi-junction structures or spectral splitting

III-V Multi-Junction Solar Cells

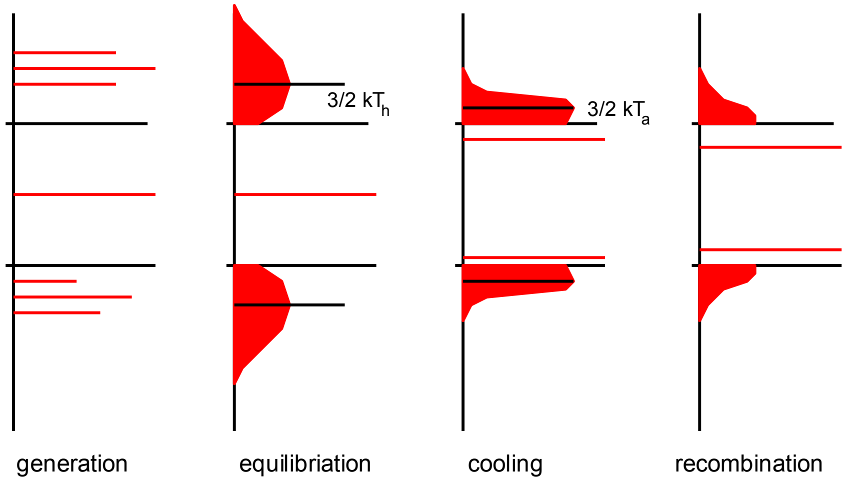


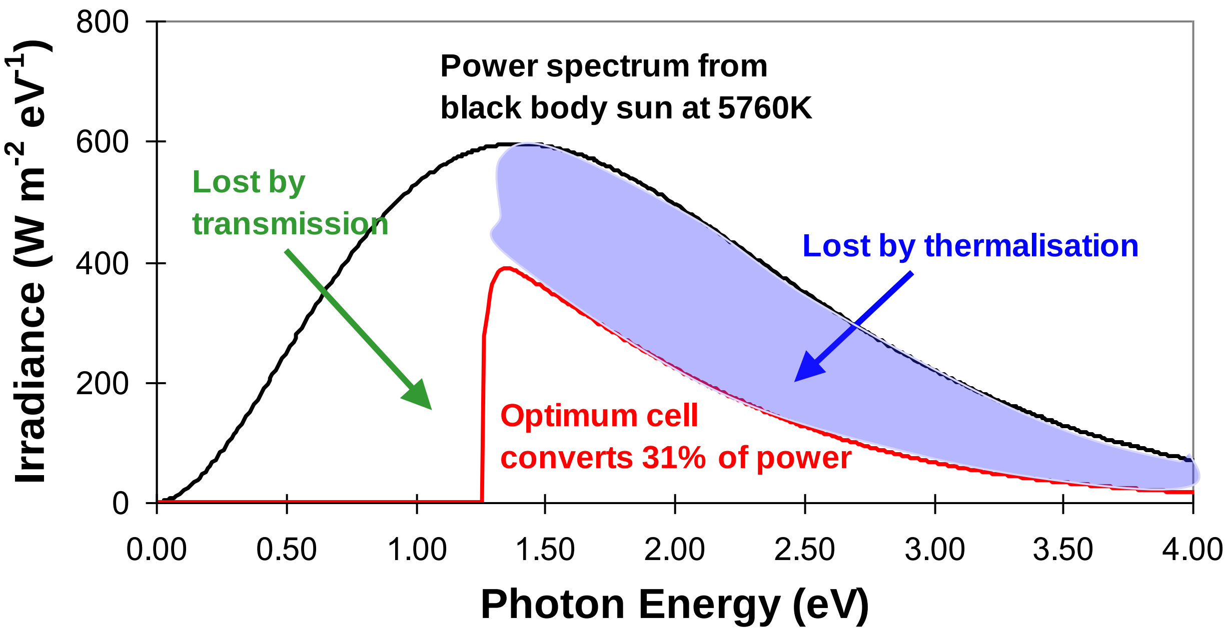


- Wide range of band gaps available but seek combinations with similar lattice constant
- Record of 43.5% by Solar Junction (April 2011) for a triple junction using dilute nitride (InGaP/GaAs/InGaAsN)

This works, but multijunction III-V structures are expensive to grow

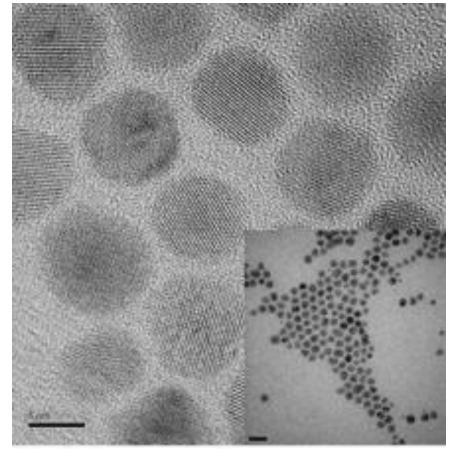
Route 2: More work per photon by slowed cooling

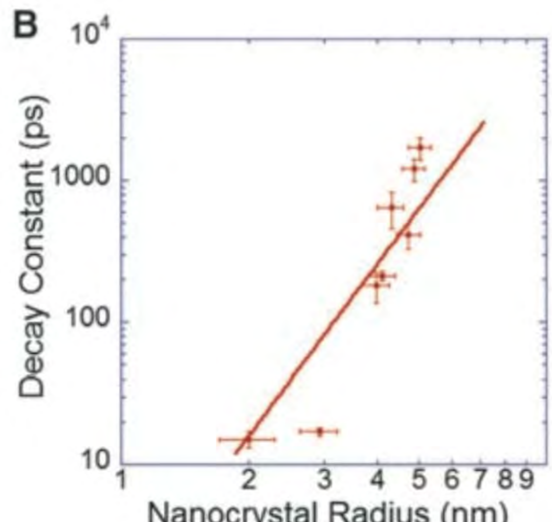


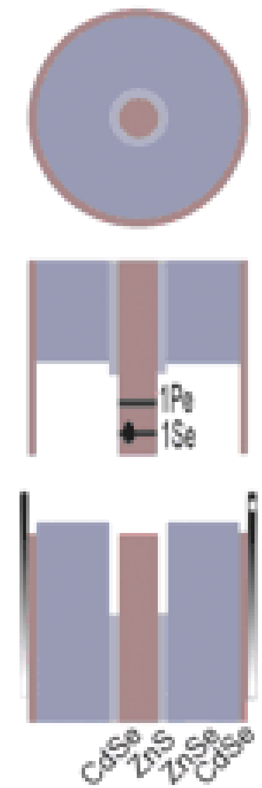


Strategies for slowing carrier cooling

- Exploit limited electronic and photon states in nano- or molecular systems
- Carrier cooling slowed down in quantum dots by 'phonon bottleneck' effect
- Enhance this with strategies to prevent recombination
    - Core-shell structure, interface passivation, ligands
    - Cooling slowed by 3 orders



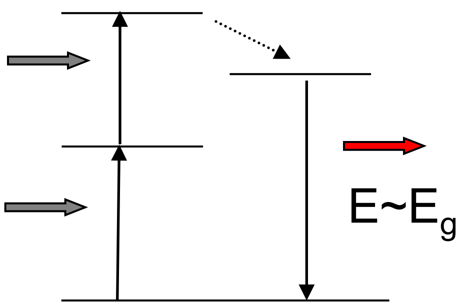


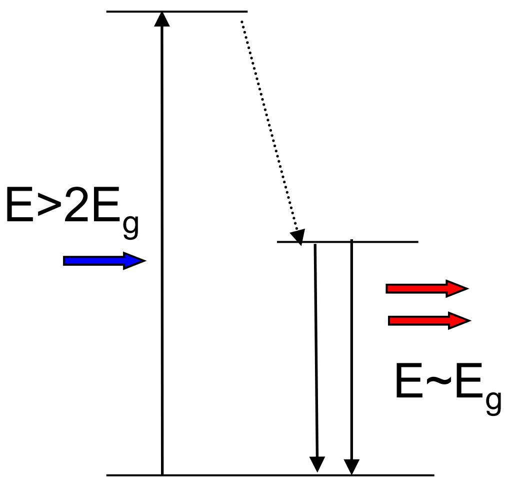


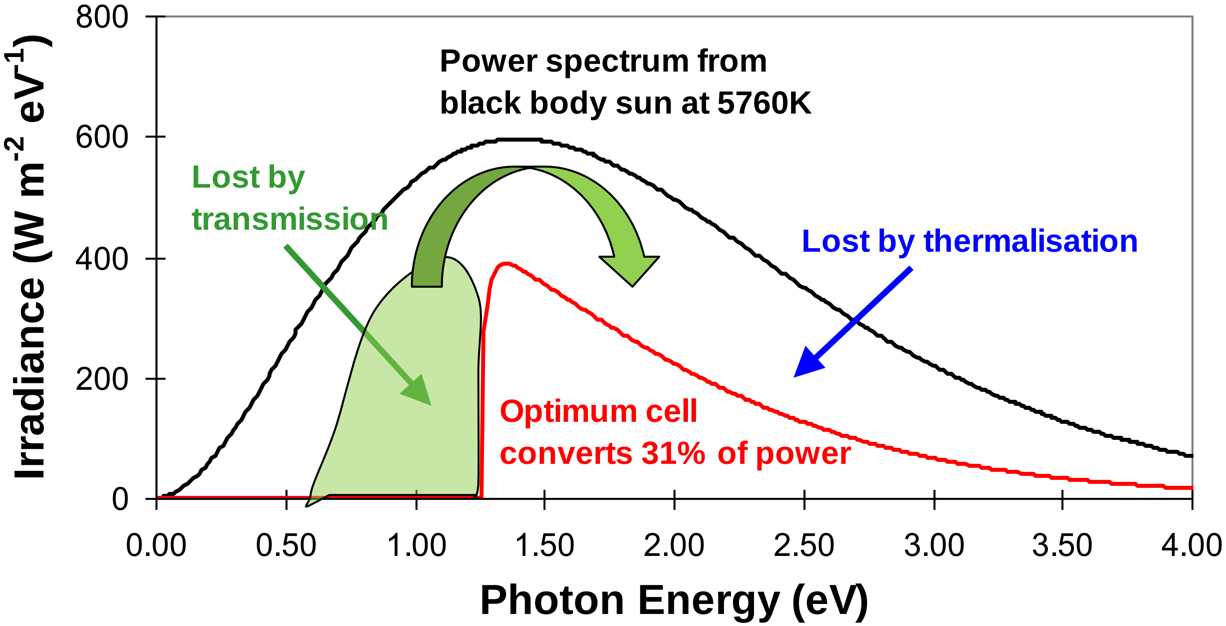
Evidence for slowed cooling but tiny effect at solar intensities

Pandey et al., Science 322, 929 (2009)

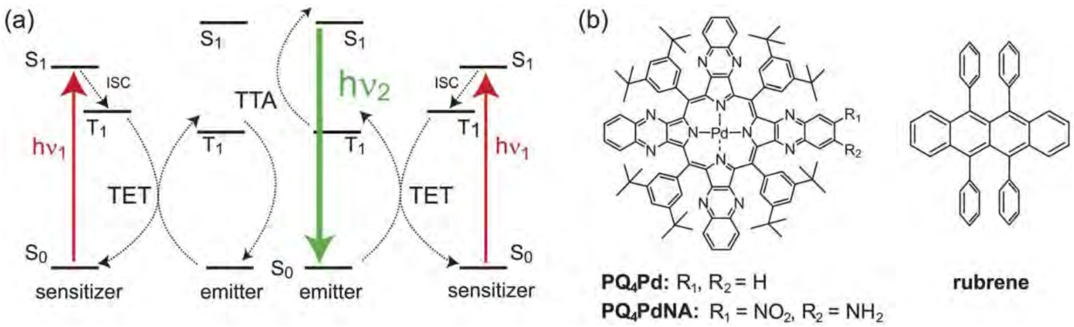
Route 3: Reshaping the spectrum by up and down-conversion

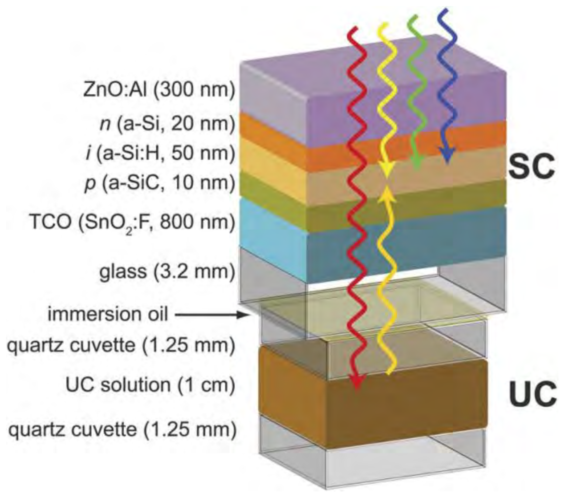


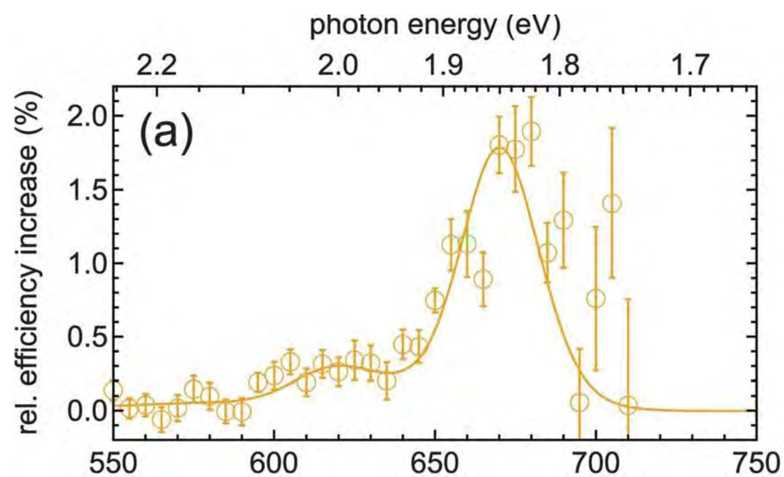




Molecular up-conversion: applied to a-Si solar cell







Cheng et al., Energy Env. Sci.2, 6593 (2012)

- Absorption in red absorbing molecules → triplet formation → triplet transfer to emitter → singlet regeneration → emis
- Applied to a-Si:H solar cell to increase EQI

Evidence for both up- and down-conversion, but small impact on total photocurrent

Outline

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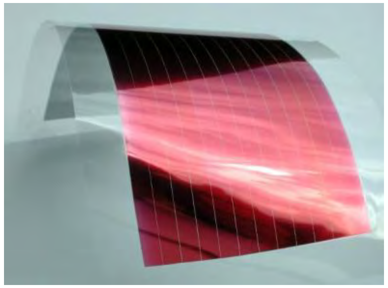
Thin films and emerging technologies

Amorphous Si
$CuInGaSe_2$
CdTe



Polymer:fullerene
Molecule:fullerene
Polymer:nanocrystal

Material	E_g (eV)	**Grain size (μm)**	**Max J_{sc} ($mAcm^{-2}$)**	**Actual J_{sc} ($mAcm^{-2}$)**	V_{oc} (V)	Efficiency (%)
Crystalline silicon	1.1	**>10^4**	**43**	**42.7**	0.706	25.0
Crystalline GaAs	1.4	**>10^4**	**32**	**29.7**	1.122	28.8
Polycrystallin e Silicon	1.1	**10-100**	**42**	**38.0**	0.664	20.4
$CuInGaSe_2$	> 1.0	**1**	**< 45**	**34.8**	0.713	19.6
Cd Te	1.4	**1**	**42**	**26.1**	0.845	16.7
Amorphous Si	~1.7	**<10^{-2}**	**~ 23**	**16.7**	0.886	10.1
Organic	~1.6	**<10^{-2}**	**~24**	**16.7**	0.899	10.0

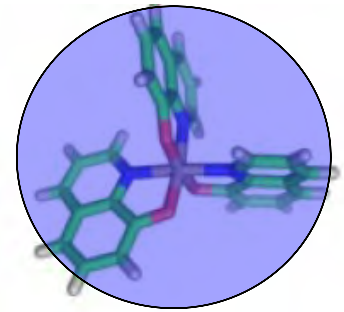
Single junction:
Limiting η as above

Practical η limited
by recombination:
small grains

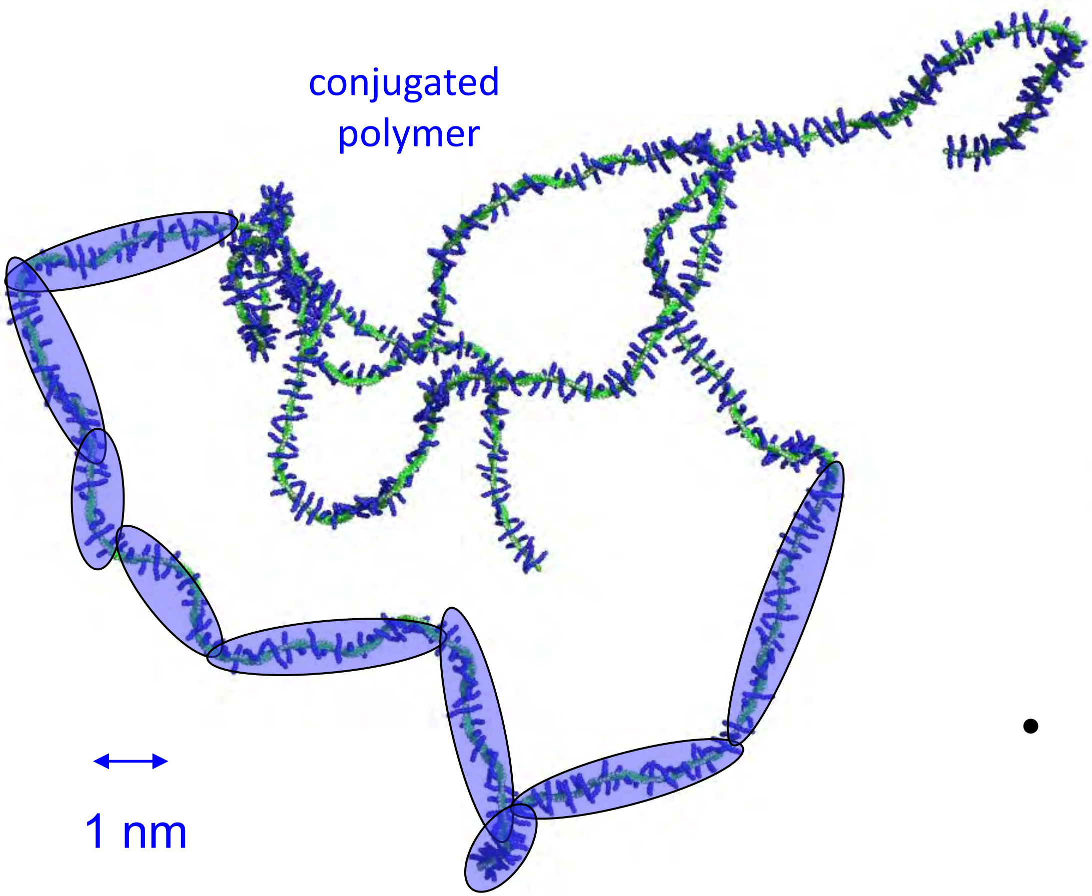
Heterojunction:
What limits η ?

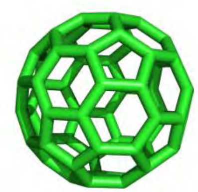
Molecular photovoltaic materials

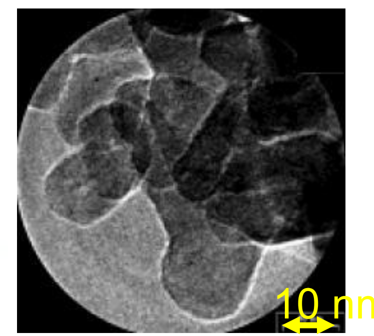
- Excited states are localised:
  - Photogenerated charge pairs don't separate
  - Separated charges move slowly



conjugated molecule



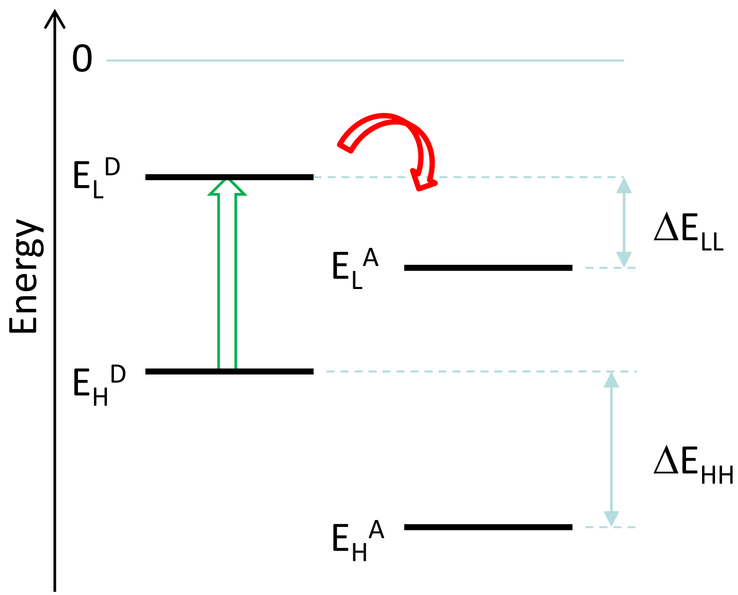


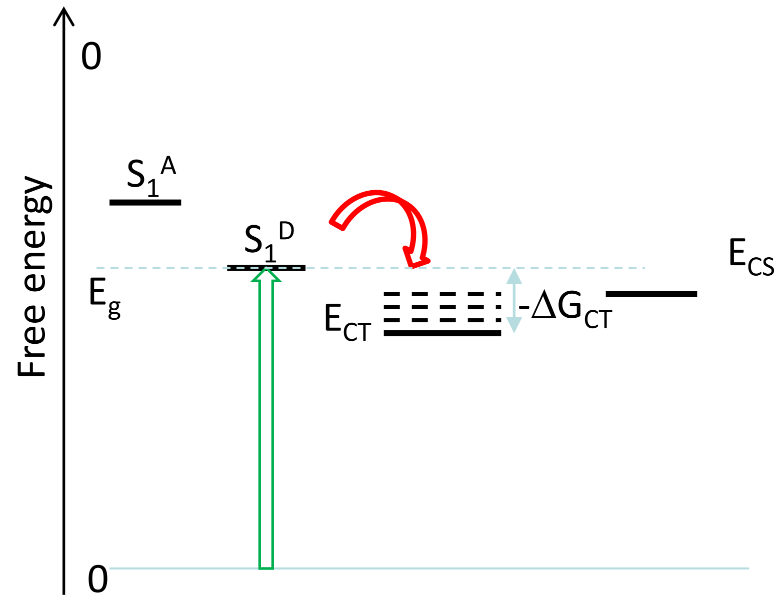


nanocrystal

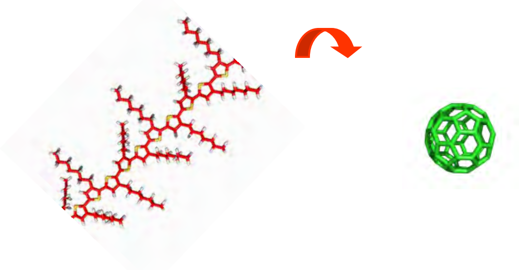
- Charge separation induced by doping with electron acceptors

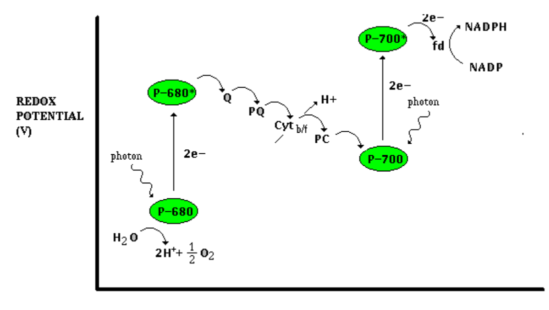
Molecular photovoltaic conversion



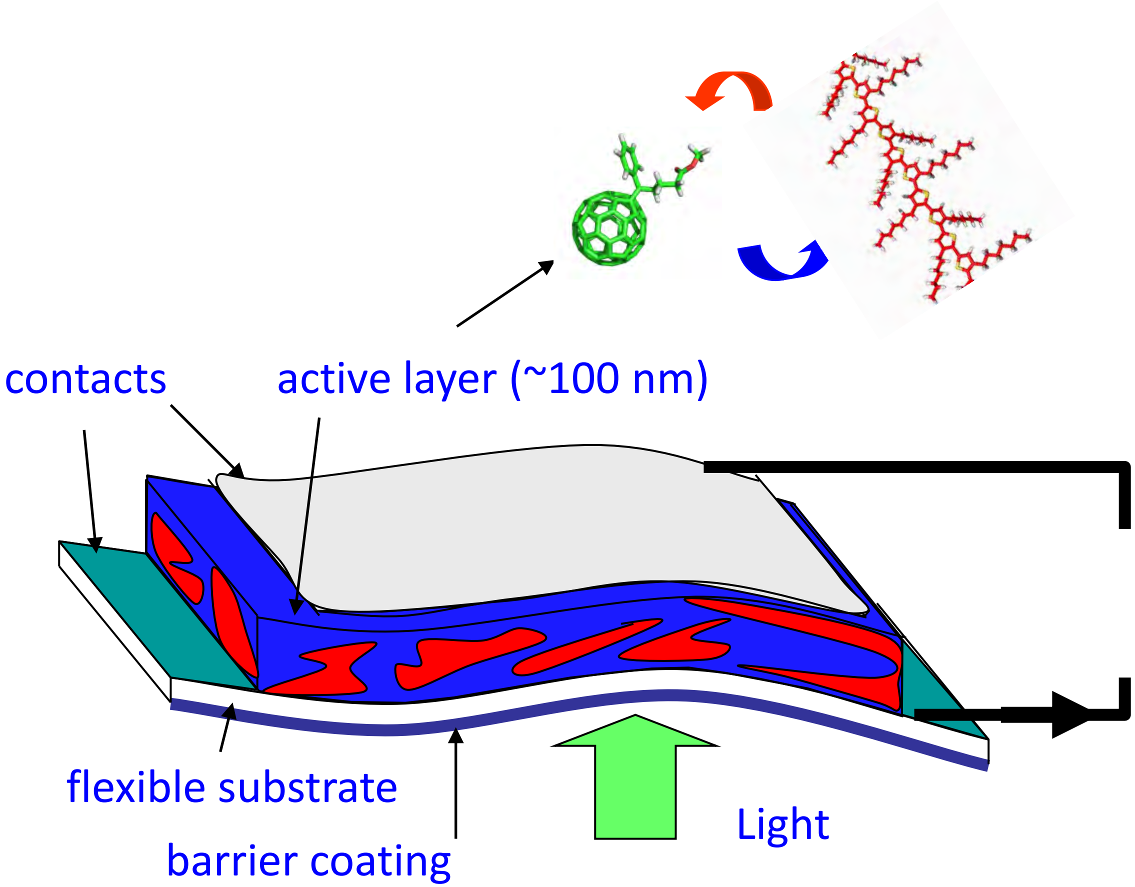


donor **acceptor**





State of the Art in Molecular Photovoltaics



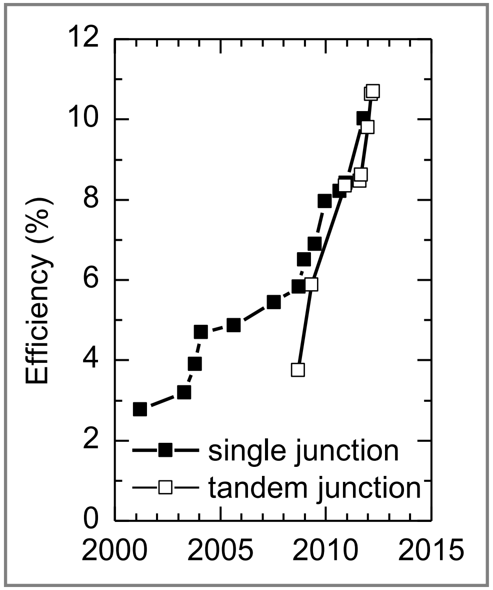
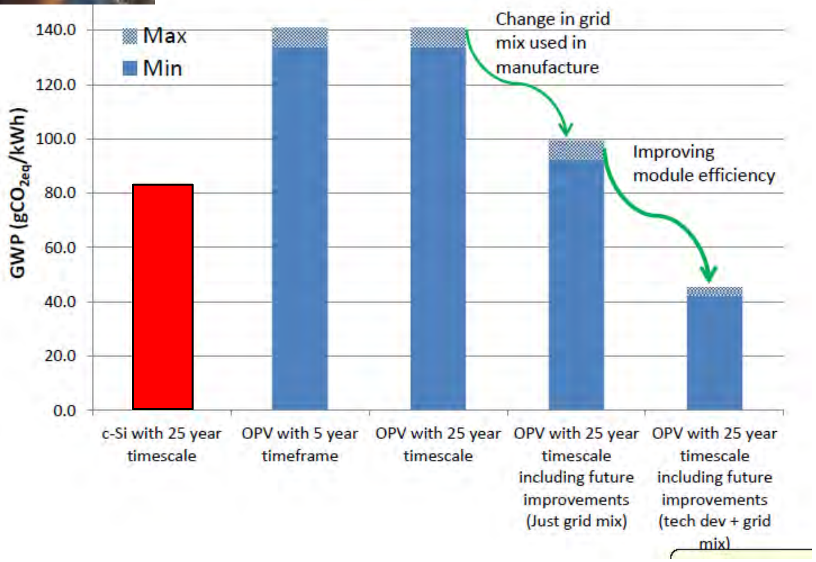


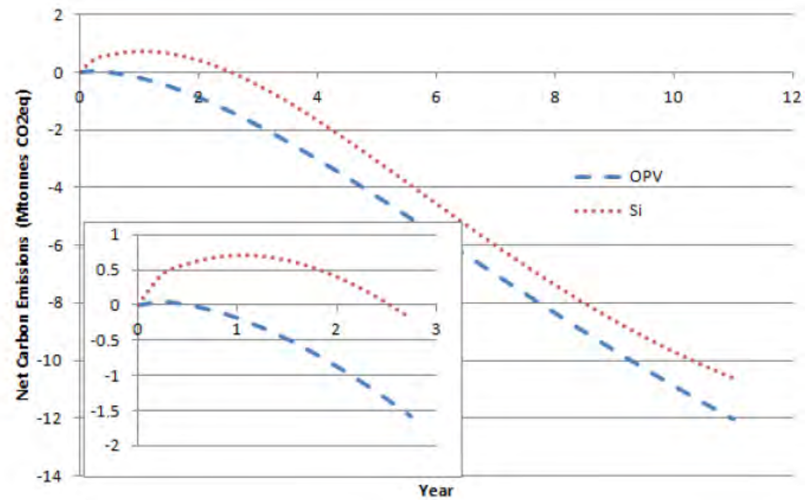
Figure: courtesy Rene Janssen, 2012

- Successive layers deposited from solution

- Cell efficiency > 10%
- Modules follow slowly..

Molecular Photovoltaics: Energy efficiency

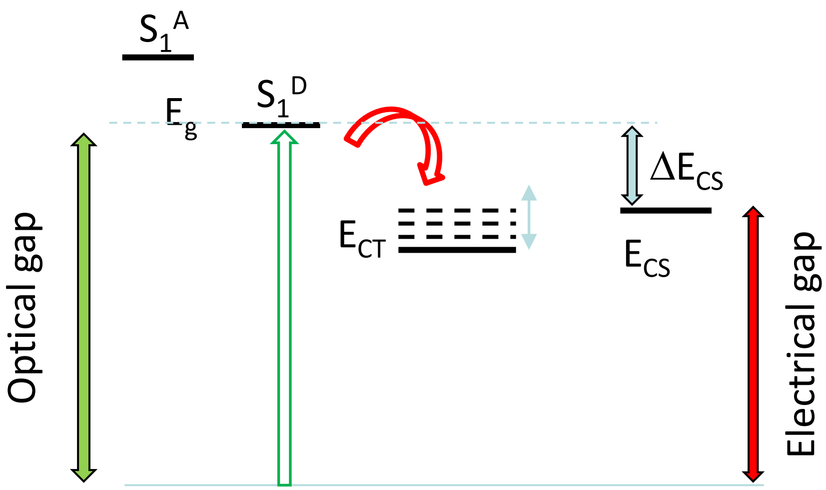




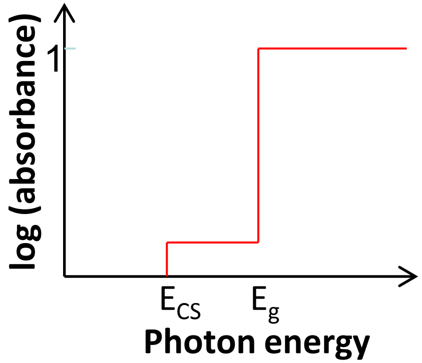
Chris Emmott, (PhD research), 2012

- Motivation is lower manufacture cost, but also lower energy intensity
- Enable larger impact on CO_2 emissions in short term, especially if lower cost stimulates faster uptake
- In long term, higher power conversion efficiency is key

Limiting efficiency in molecular heterojunction

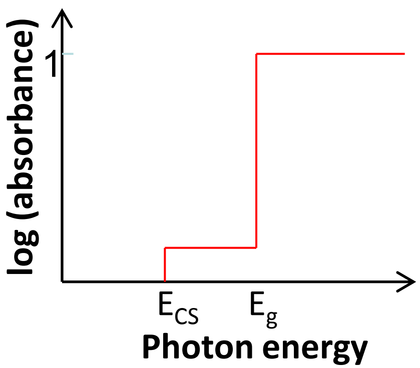


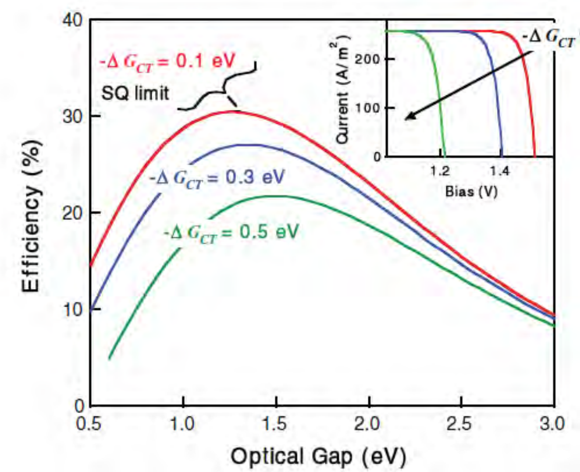
- Optical gap > electrical gap
- In detailed balance limit, charges recombine radiatively across electrical gap



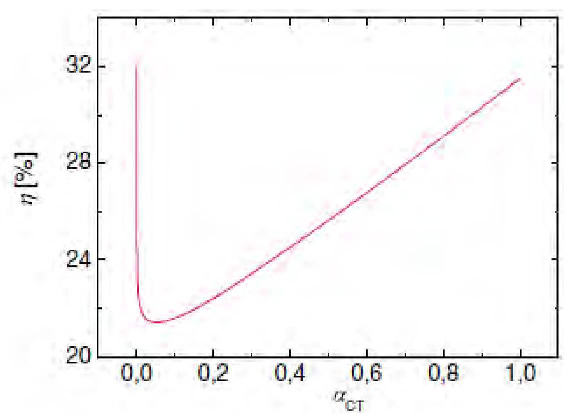
- Introduce sub-gap states of finite oscillator strength

Limiting efficiency in molecular heterojunction





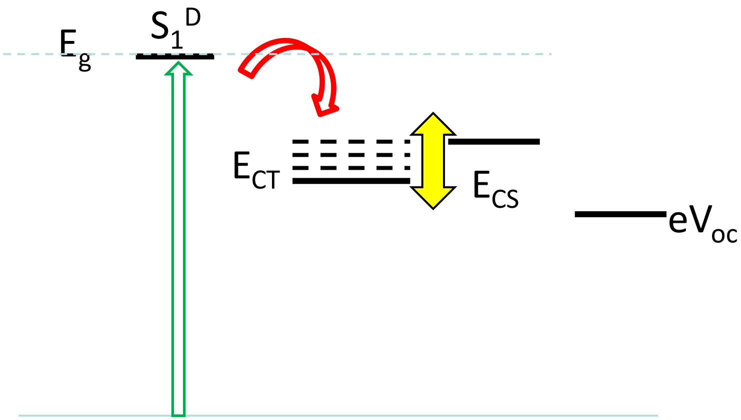
N. Giebink et al. Phys Rev B 83, 195326 (2011)

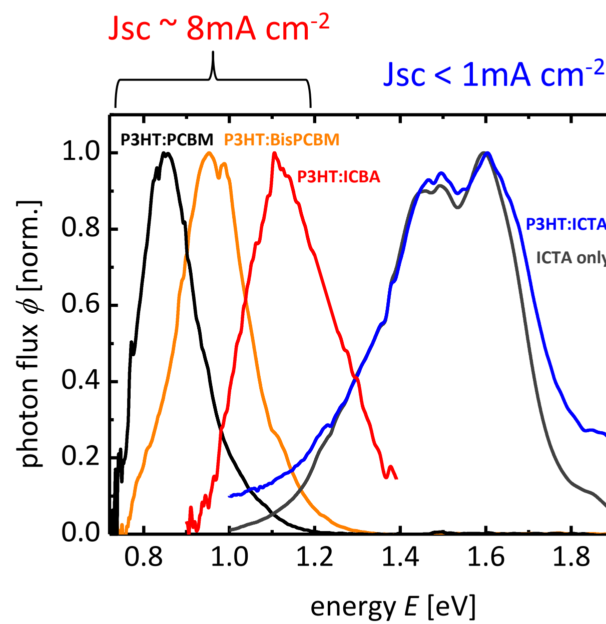


L. J. A. Koster et al., Adv. Energy. Mat. (2012)

- Limiting η is lower and optimum E_g larger than for single junction
- Most models predict 20%, practical best is 10%
- **Where are losses?**
- How large must ($E_g - E_{CS}$) be?

Size of energetic losses in molecular heterojunction



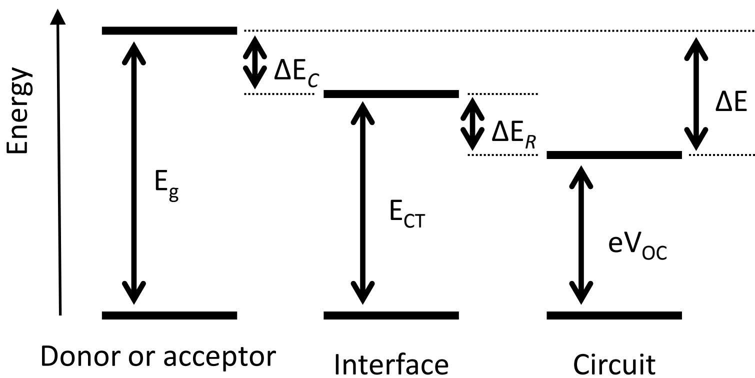


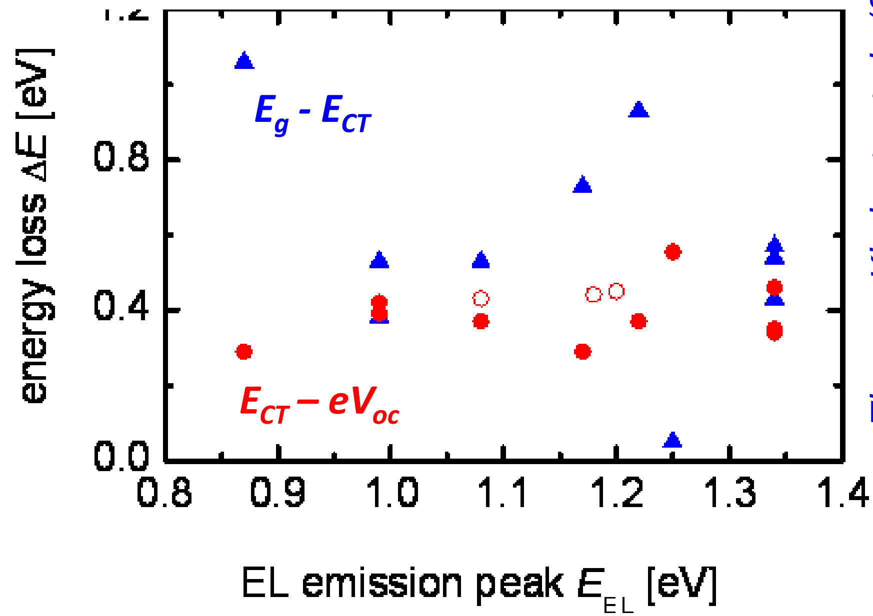
- Probe energy of charge pair at interface, E_{CT} with electroluminescence
- Modulate E_{CT} for same E_g by varying fullerene acceptor
- Find
  - photocurrent is generated only when $(E_g - E_{CT}) > 0.35$ eV (with exceptions)
  - eV_{oc} is smaller than E_{CT} (and E_{CS}) by ~ 0.4 eV

Mark Faist et al., J Am Chem Soc 134, 685 (2012)

Size of energetic losses in molecular heterojunction

- Resolve energy loss $\Delta E = E_g - eV_{OC}$ into two components:





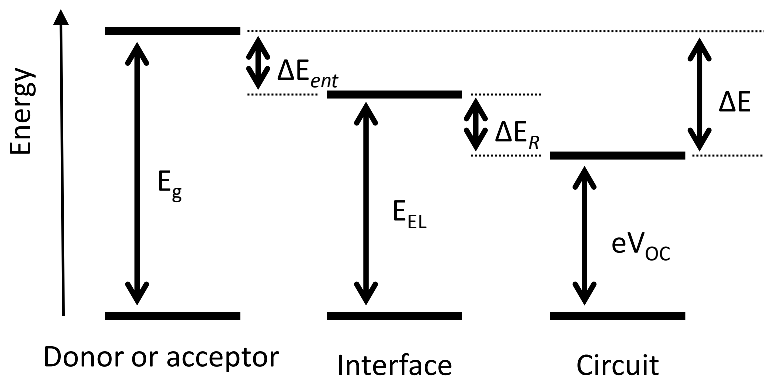
Thomas Kirchartz et al., (2012)

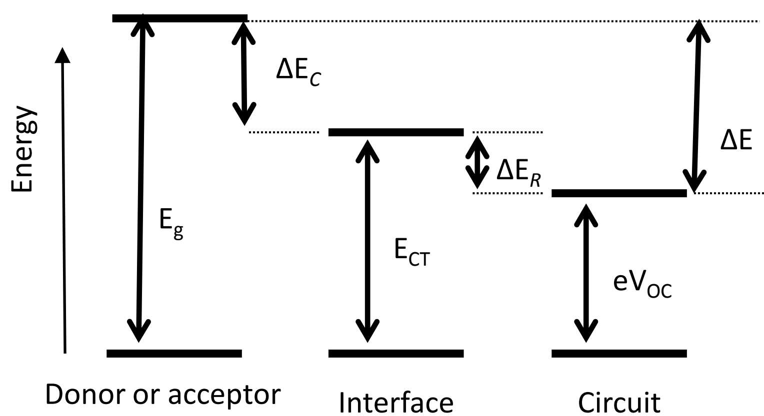
- **Charge separation loss** ΔE_C normally > 0.3 eV. Absent in inorganics.

- Non-geminate **recombination loss** ΔE_R ~ 0.4 eV, similar to inorganics

- Net $E_g - eV_{oc}$ > 0.6 eV, c.f 0.4 eV for inorganic single junctions

Size of energetic losses in molecular heterojunction

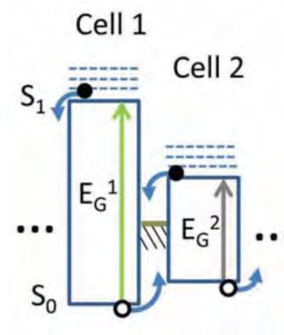




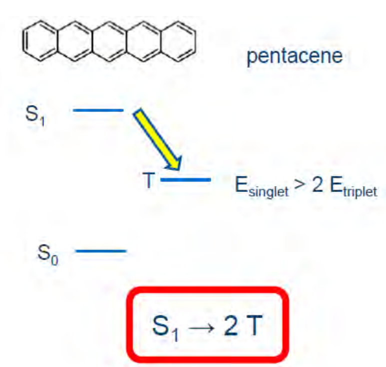
- **Inorganic junctions:**
  $E_g - eV_{oc} \sim 0.4$ eV in best cases.
  Efficiency within ~5% of DB limit
- **Molecular heterojunctions**
  $E_g - eV_{oc} > 0.6$ eV
- Can we reduce ΔE_C ?
- Yes – in some cases, ΔE_C as low as 0.1 eV
  - Function of chemical structure
  - But compensated by high ΔE_R
  - Need to understand why!

Molecular higher efficiency approaches?

- **Multi junctions**:
  - Tandems demonstrated.
    Easy to manufacture

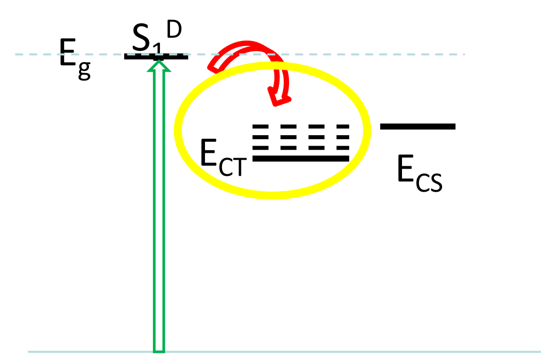


- **Spectral conversion**:
  - Singlet exciton fission for downconversion
  - Triplet-triplet annihilation for upconversion



A. Rao et al*J. Am. Chem. Soc.* **2010**, 132, 12698-12703.

- **Slow carrier thermalisation**?
  - Helps to reduce losses to trapping at interfaces and in transport
  - *Might* give access to hot carrier effects if energy selective contacts possible



Where do we go from here?

- Solar electricity is abundant, sustainable, versatile and available
- Existing technologies operate within a factor of 2 of the physical limit of 30%
- Goal is to reach similar or higher efficiencies with low energy technologies that can grow quickly.
- Challenges remain for physicists, chemists and materials scientists – but none of them known to be insurmountable

Thank you for your attention!