Ultrafast Charge Transfer Processes in Dye-Sensitized Nanocrystalline Solar Cells

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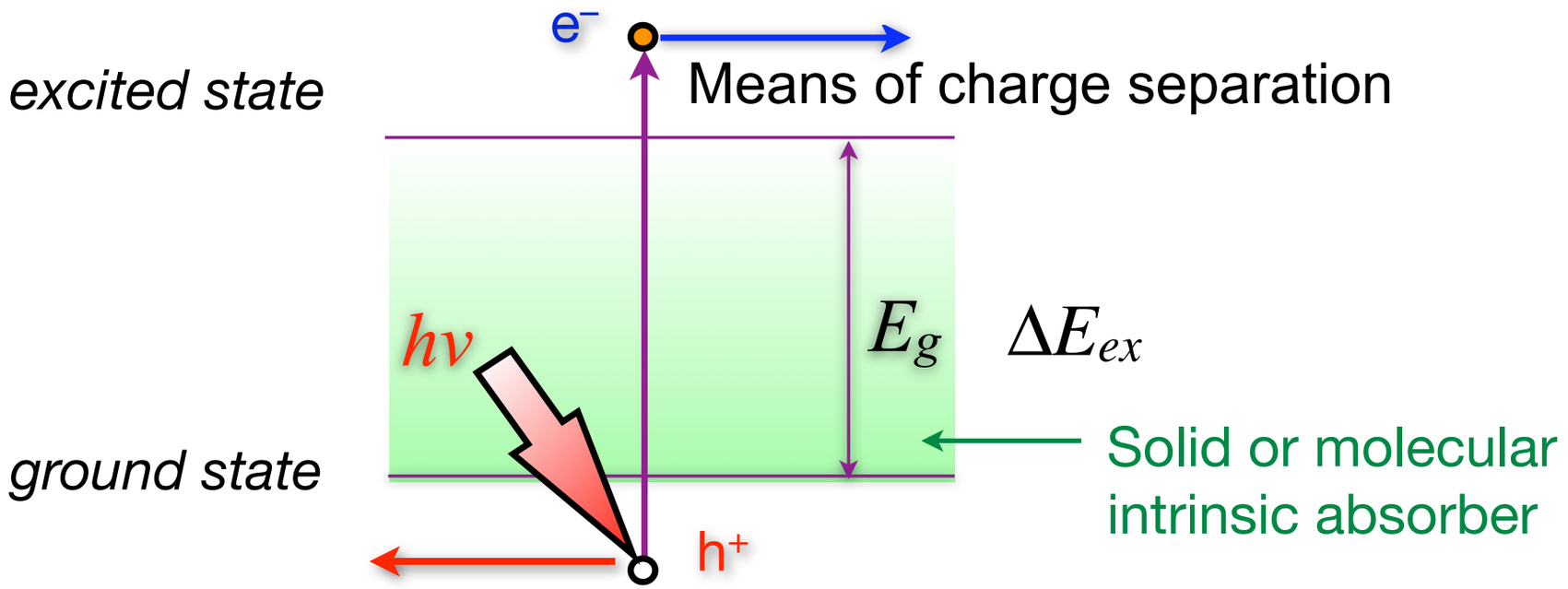
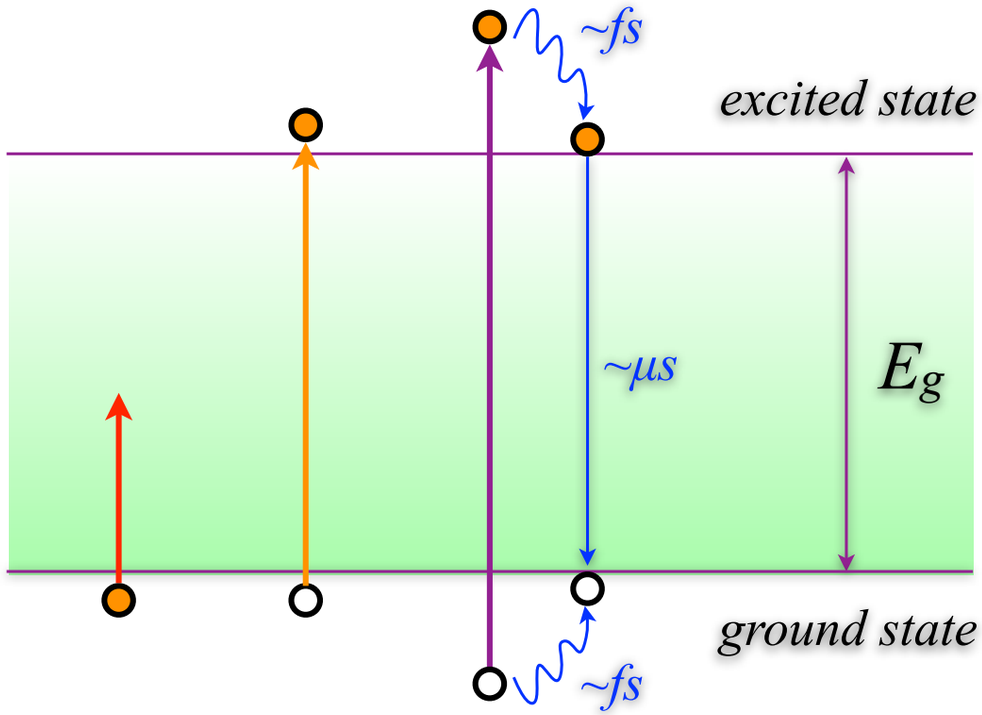
Principle of photovoltaic converters



1) Electronic transition leading to local charge separation (e^-...h^+)
2) Sustained charge separation through various possible mechanisms
3) Diffusion of charge carriers and collection in metal electrodes

Free energy waste under polychromatic irradiation



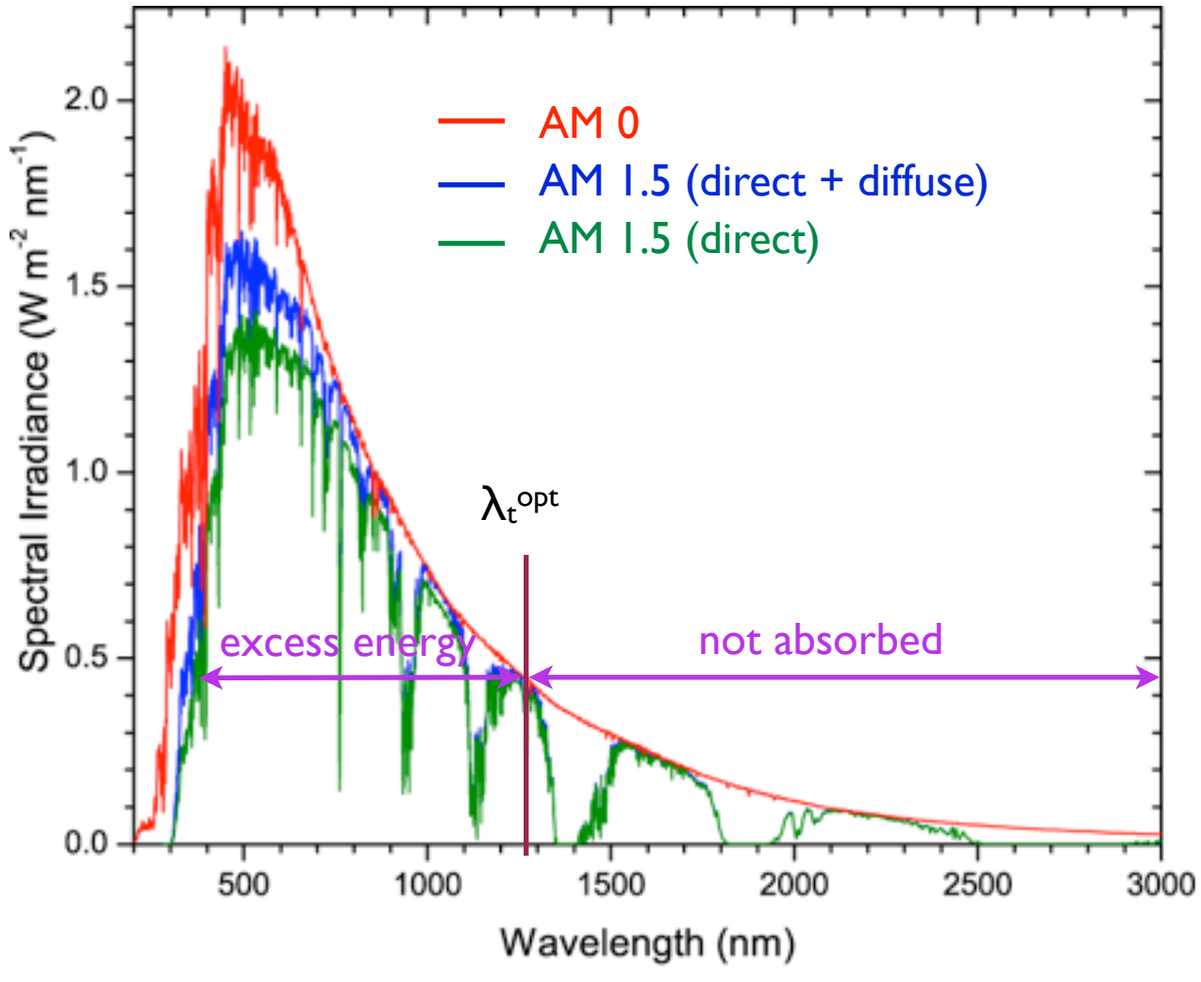
Available fraction of the energy absorbed from a polychromatic source

$$\theta = \frac{\int_0^{\lambda_t} F_\lambda \frac{\lambda}{\lambda_t} d\lambda}{\int_0^{\infty} F_\lambda \, d\lambda}$$

λ_{opt} = 1273 nm (0.97 eV) $\Rightarrow$ θ_{opt} = 0.44

At each wavelength $\lambda < \lambda_t$, the usable fraction of the absorbed photon energy is:

$$\theta = \frac{hc}{\lambda_t} \Big/ \frac{hc}{\lambda} = \frac{\lambda}{\lambda_t}$$



Power conversion efficiency limits

- **Non-reversible conditions at maximum power extraction**

  $\eta_p = 0.91$

- **Entropy of light (Carnot thermodynamic conversion limitation)**

  $T_R = 5500$ K $\Rightarrow$ $T_{R,a} = 1297$ K (without concentrator) $\Rightarrow$ $\eta_e = 1 - T_{R,a} / T_a = 0.77$

  With 1:10 light concentration $\Rightarrow$ $\eta_e = 0.80$

- **Polychromaticity of solar light**

  For monochromatic radiation:

  $\eta = \eta_p \times \eta_e = 0.91 \times 0.77 = 0.71$

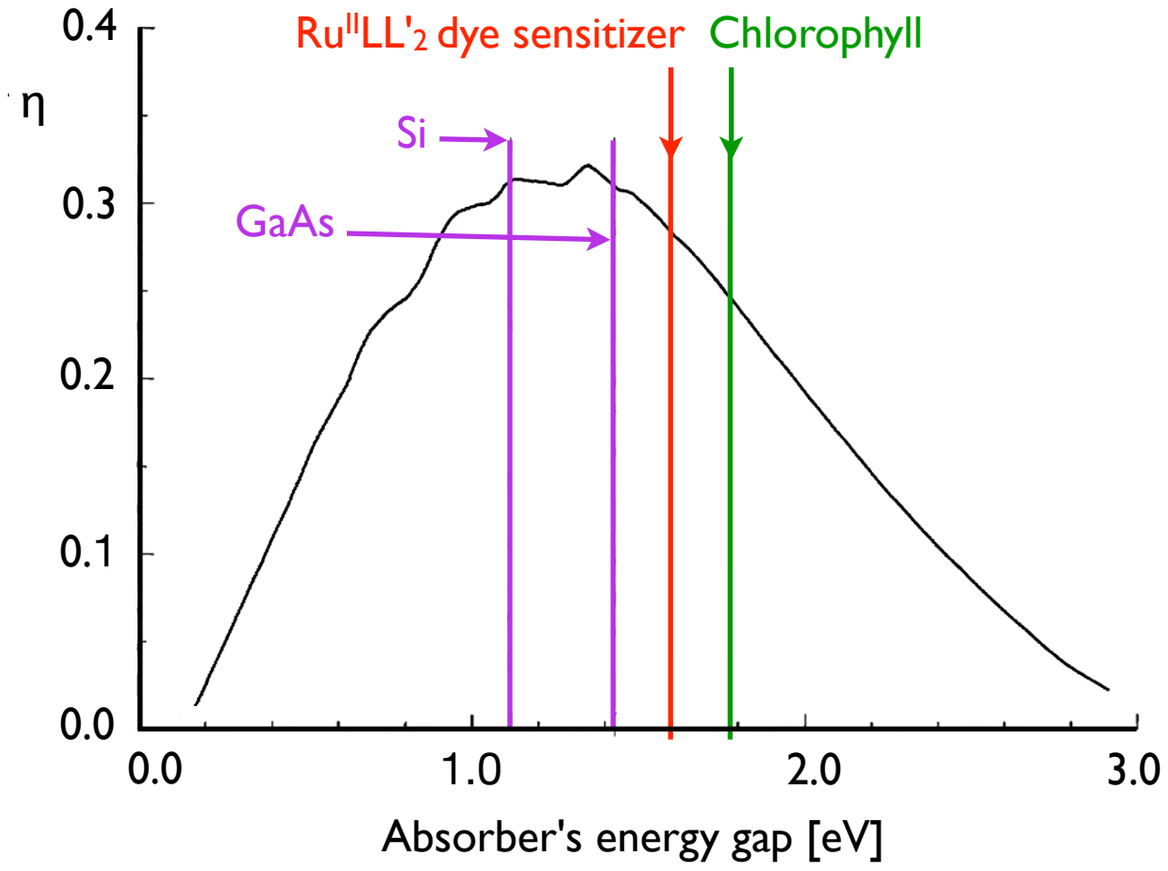
  For typical AM1.5 solar spectrum:

  $\lambda_{opt} = 1273$ nm (0.97 eV) $\Rightarrow$ $\theta_{opt} = 0.44$

  $\eta = \eta_p \times \eta_e \times \theta = 0.91 \times 0.77 \times 0.44$

  $\eta = 0.31$

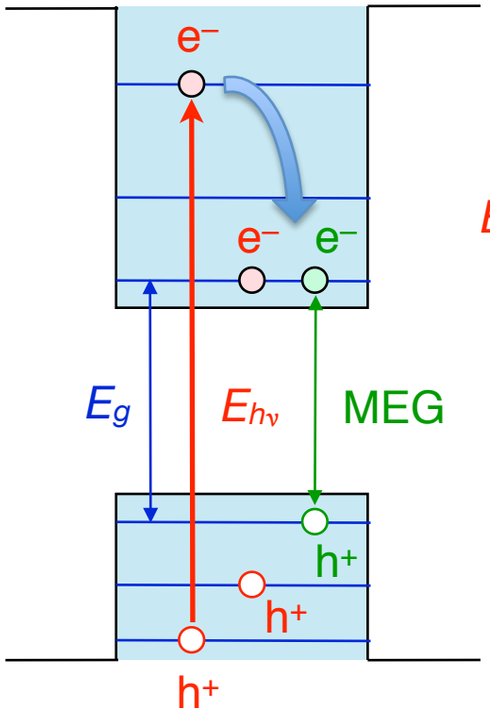
Shockley-Queisser limit
(single bandgap converter)



Beyond the Shockley-Queisser limit

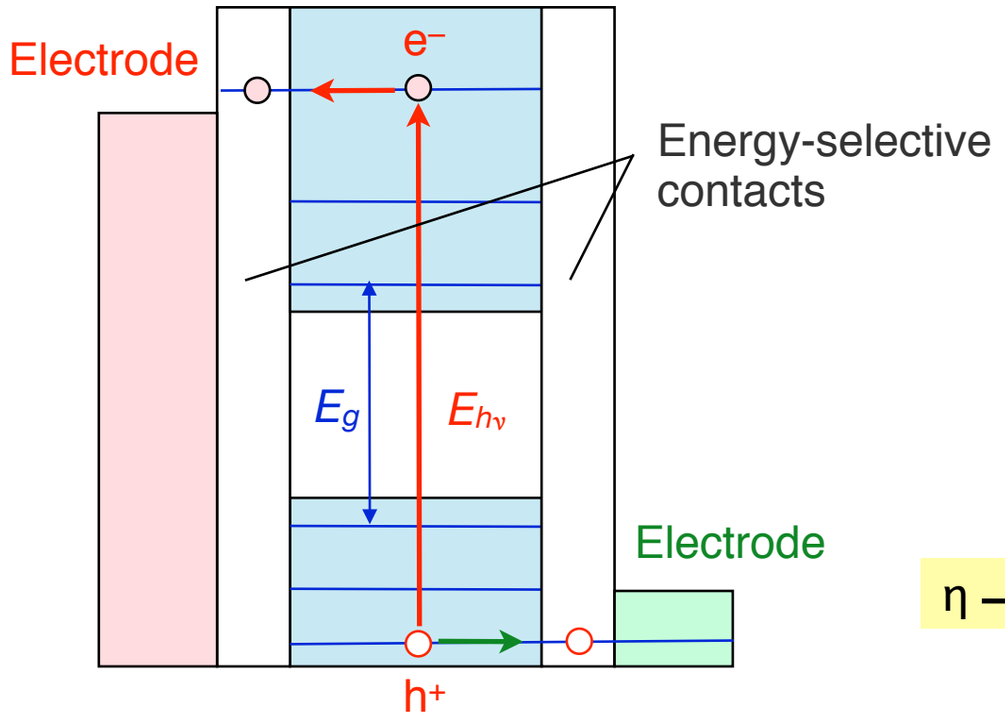
Strategies for extracting more work from the solar spectrum

- **Multiple junction cells**
  Tandem cells, intermediate bands, spectral splitting, **...**
- **Redistribution of photons**
  Spectral up- and down-conversion, **...**
- **More work per photon**
  Multiple exciton generation (MEG), hot carrier extraction



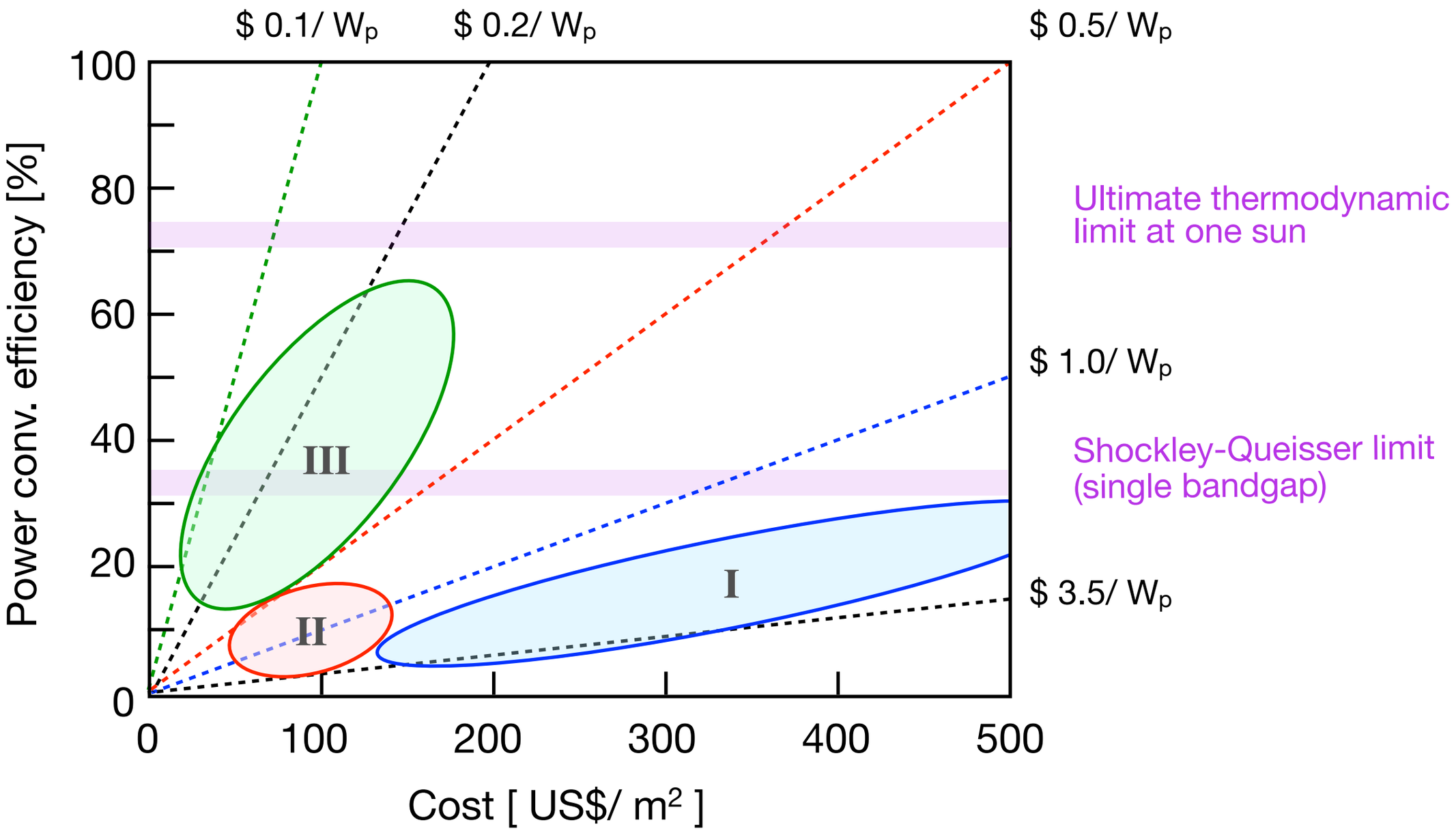
$E_{h\nu} > 2 \cdot E_g$

η ⟶ ~43%

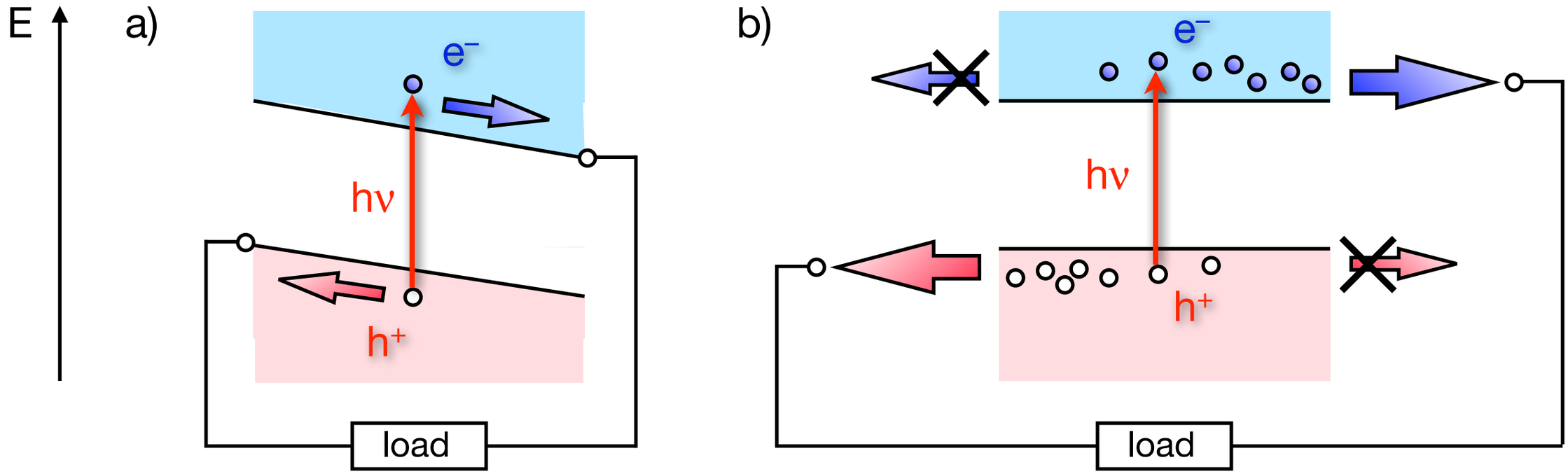


η ⟶ ~67%

Third generation solar cells



Mechanisms for sustained charge separation



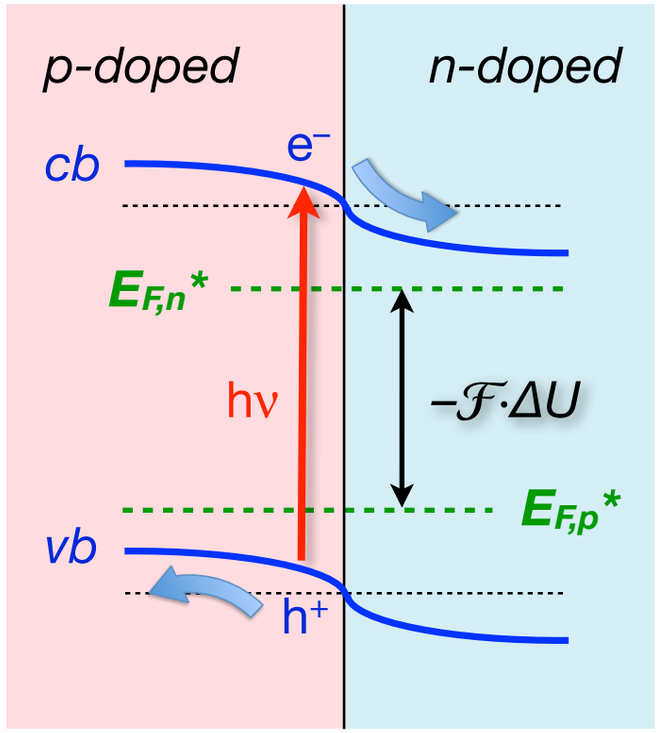
Sustained charge separation requires some built-in driving force

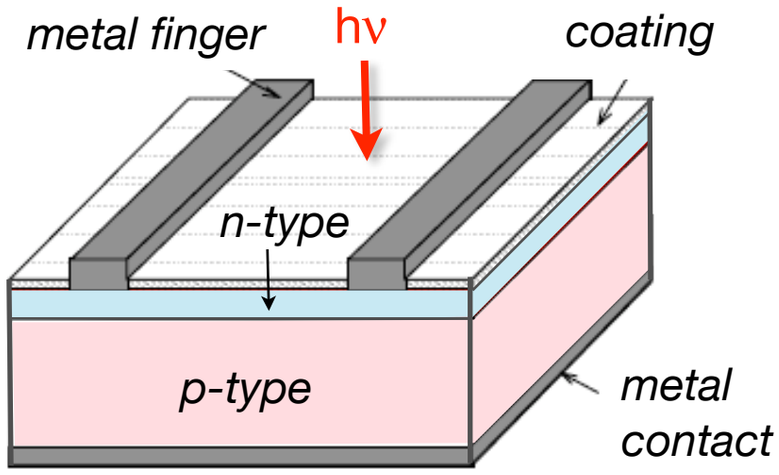
a) Light-induced spatial gradient of the quasi-Fermi levels of electrons and holes

b) Light absorbing material is connected by paths of different resistance. One has much lower resistance for electrons and the other for holes

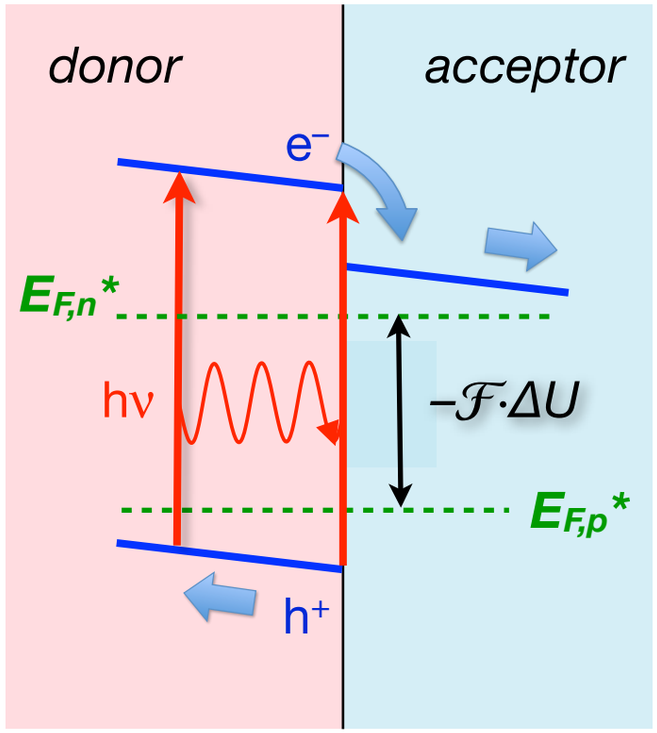
Conventional and emerging tehnologies

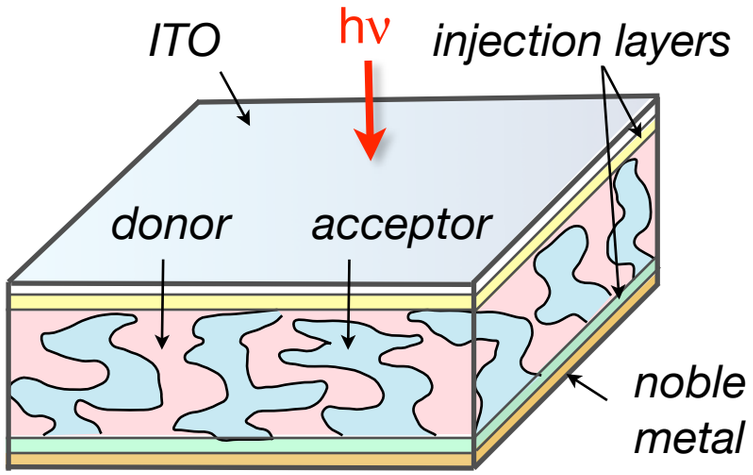
p-n junction: Si, GaAs(1G)
Thin-film CIGS, CdTe (2G)



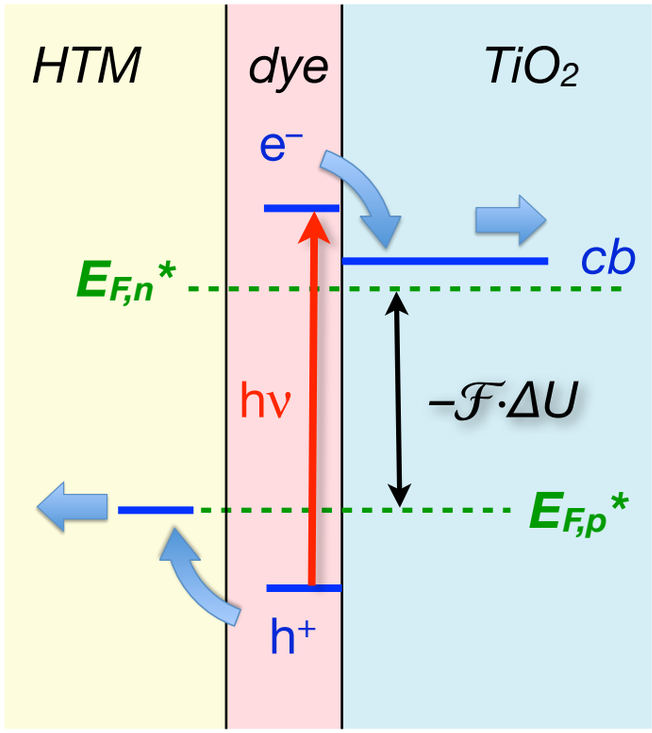


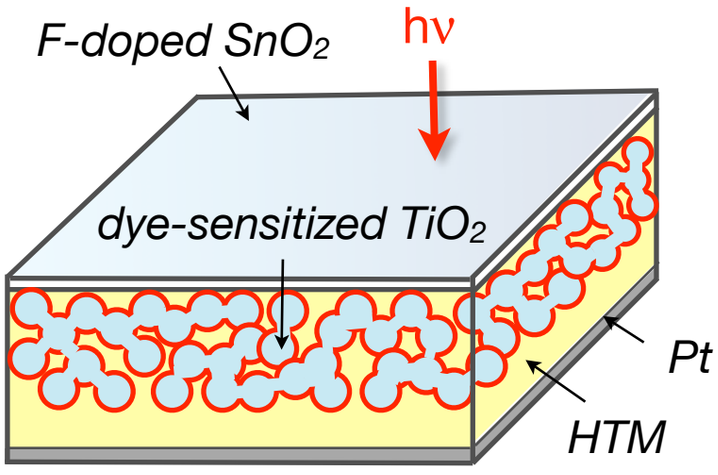
OPV : polymer,
small molecule-based (3G)





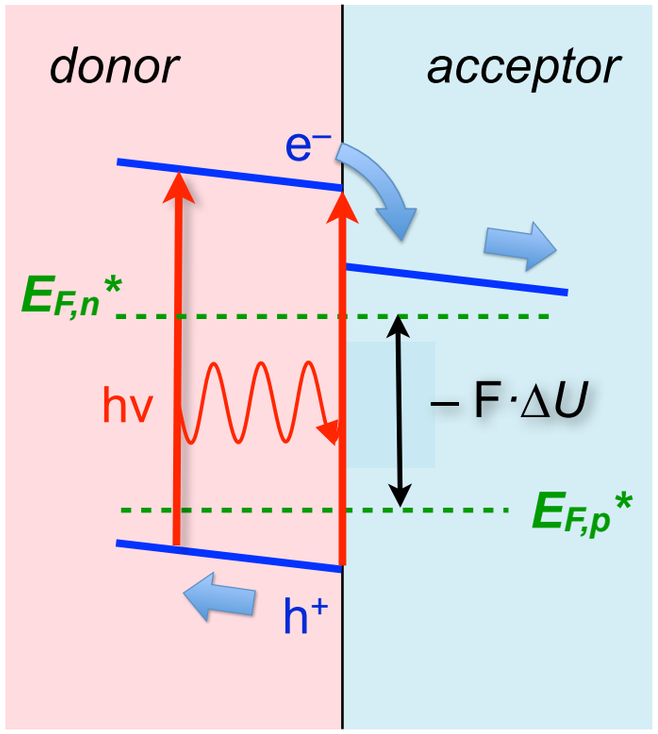
DSSC : liquid electrolyte,
solid HTM-based (3G)

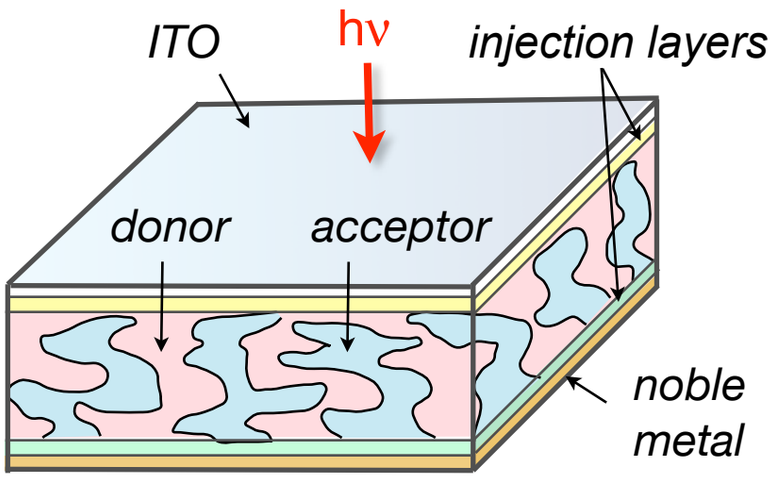


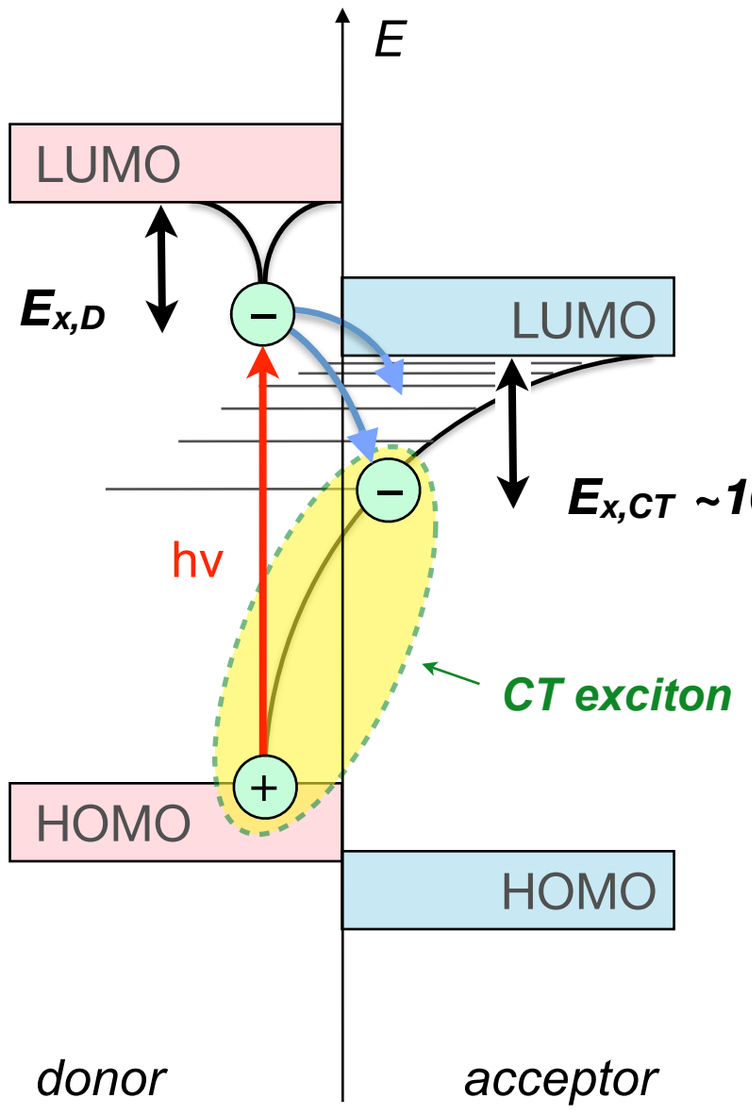


Charge transfer states in OPV systems

OPV







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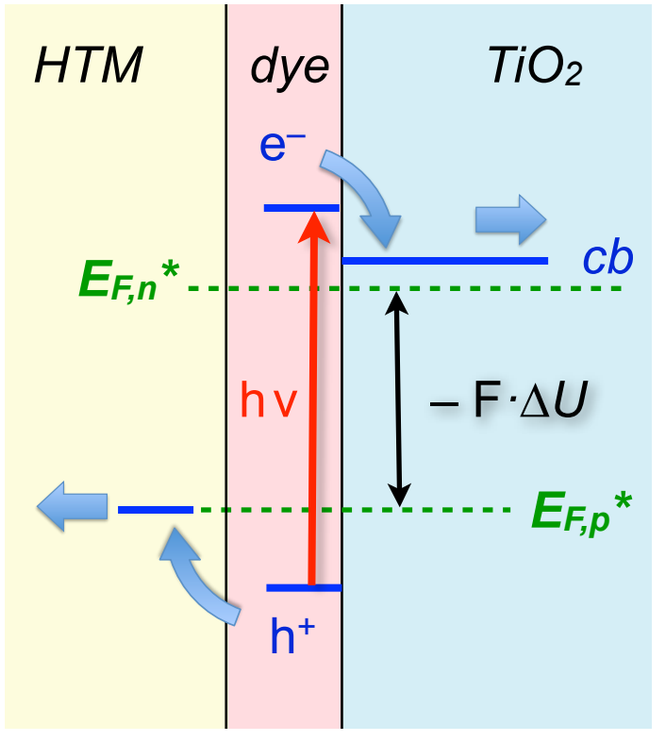
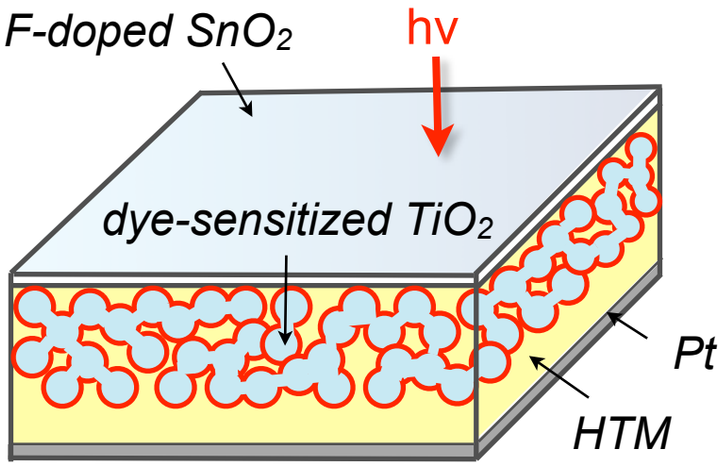
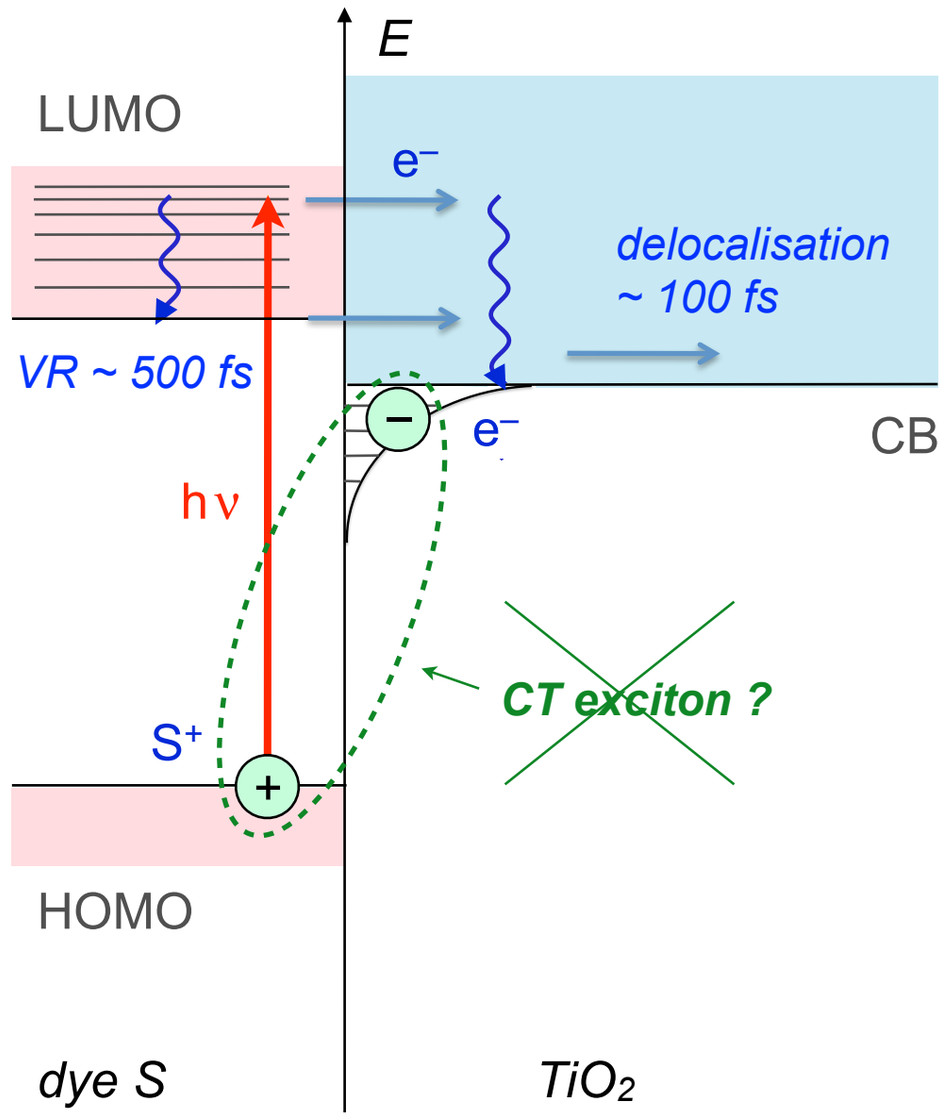
Charge transfer states in OPV systems

DSC







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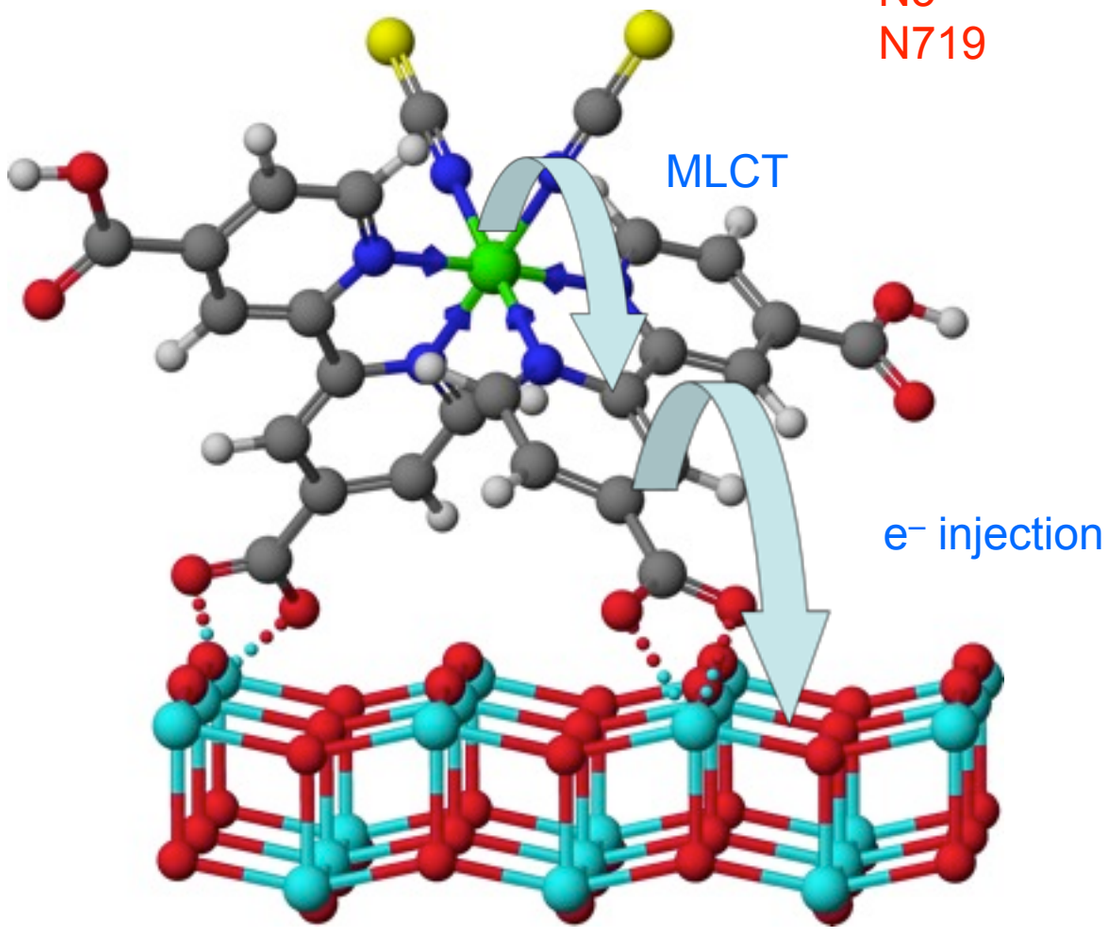
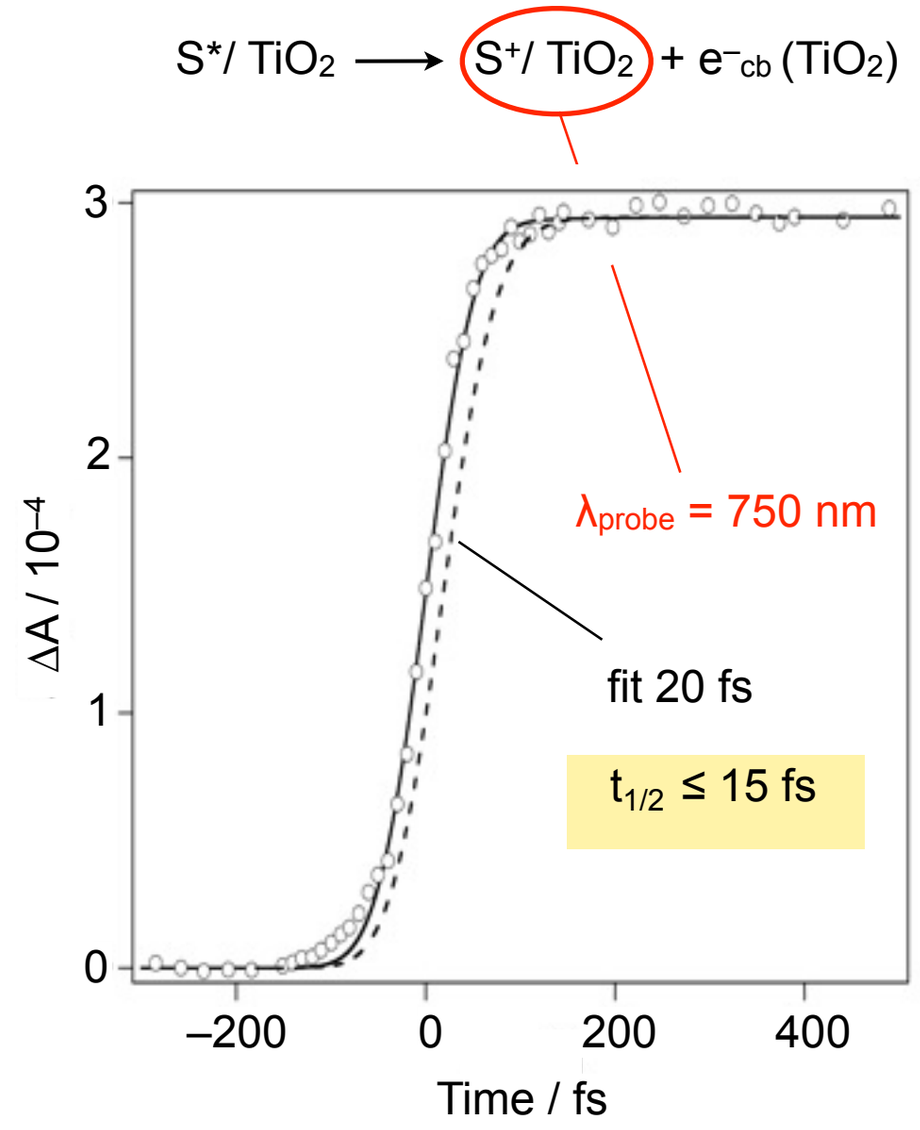
Prog. Surf. Sci. **2009**, *84,* 39

Sub-20 fs electron injection



$Ru^{II}(dcbpy)_2(NCS)_2$ / TiO_2 anatase <001>



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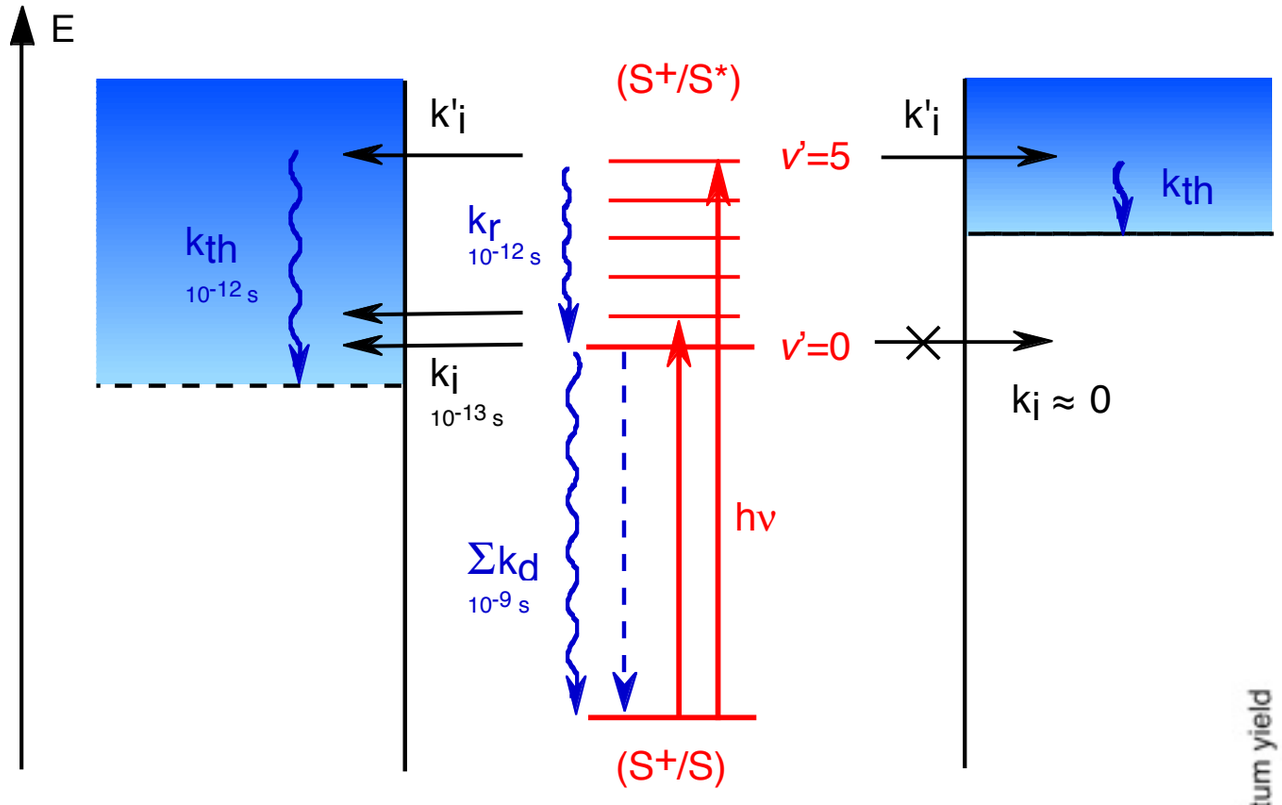
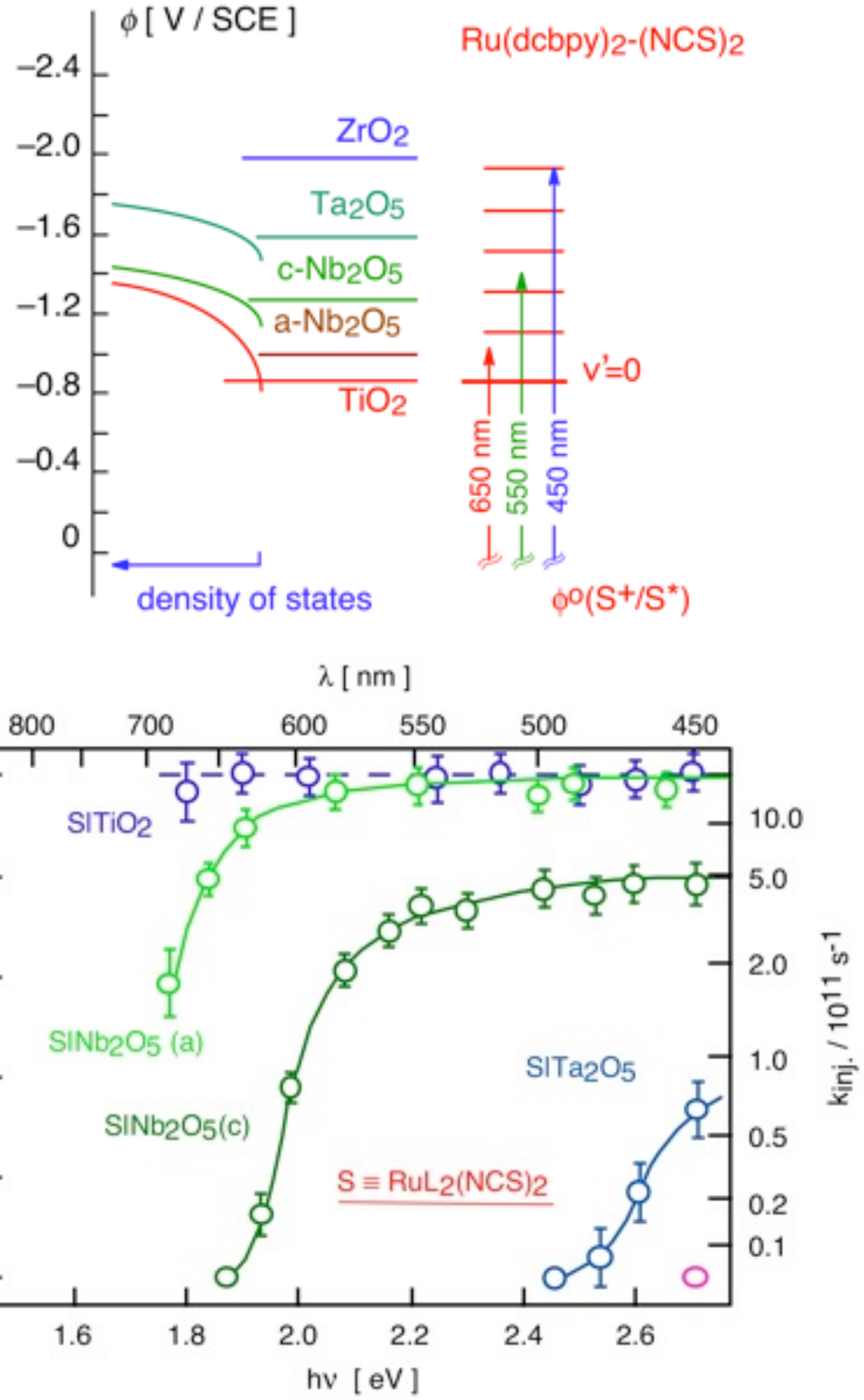
O. Bräm, A. Cannizzo, M. Chergui
Phys. Chem. Chem. Phys. 2012,
DOI:10.1039/c2cp40590c

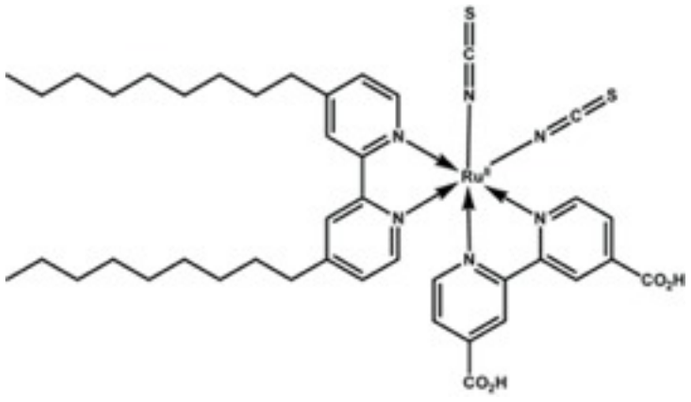
Ultrafast injection from hot excited states





- Wavelength dependence of injection rate and yield

Electron and hole injection dynamics



S = *Z-907*

$S^*/TiO_2 \longrightarrow S^+/TiO_2 + e^-_{cb}$

e^- injection

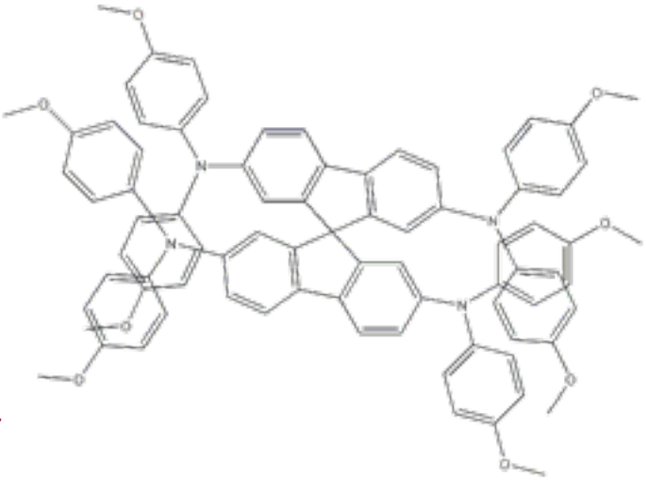
$\tau_{inj.1}$ (e^-, TiO_2) < 100 fs (80-90 %)
$\tau_{inj.\,2}$ (e^-, TiO_2) = 59 ps (10-20 %)

$S^+/TiO_2 + HTM \longrightarrow S/TiO_2 + HTM^+$

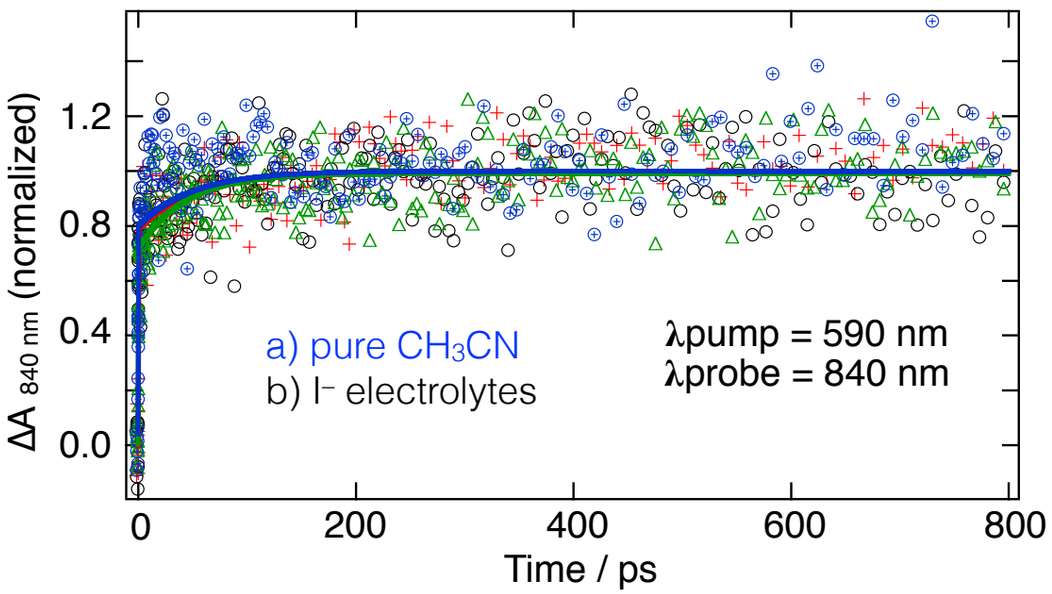
h^+ injection

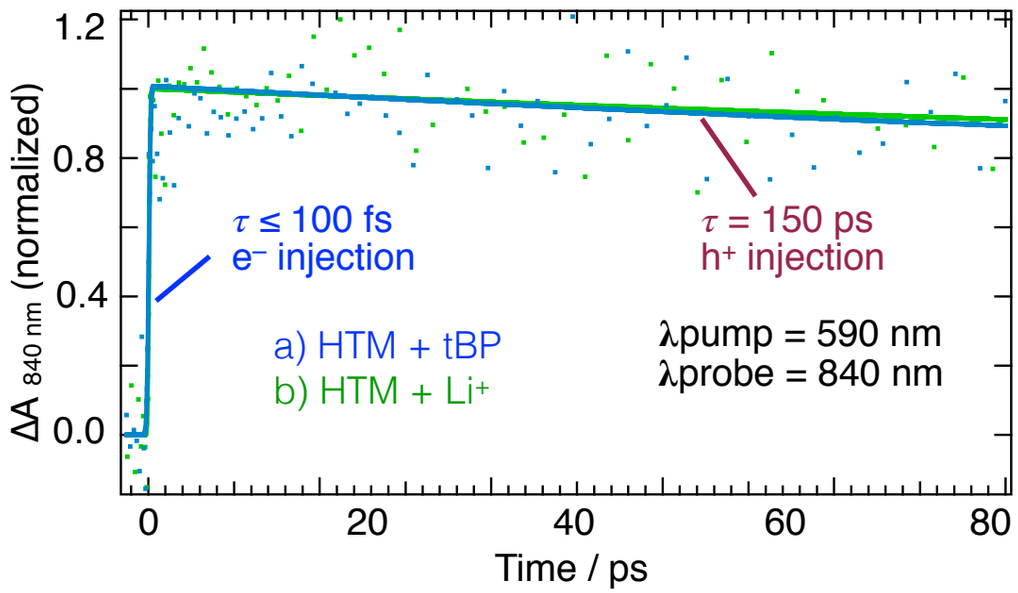
NIR

$\tau_{inj.}$ (h^+, HTM) = 150 ps

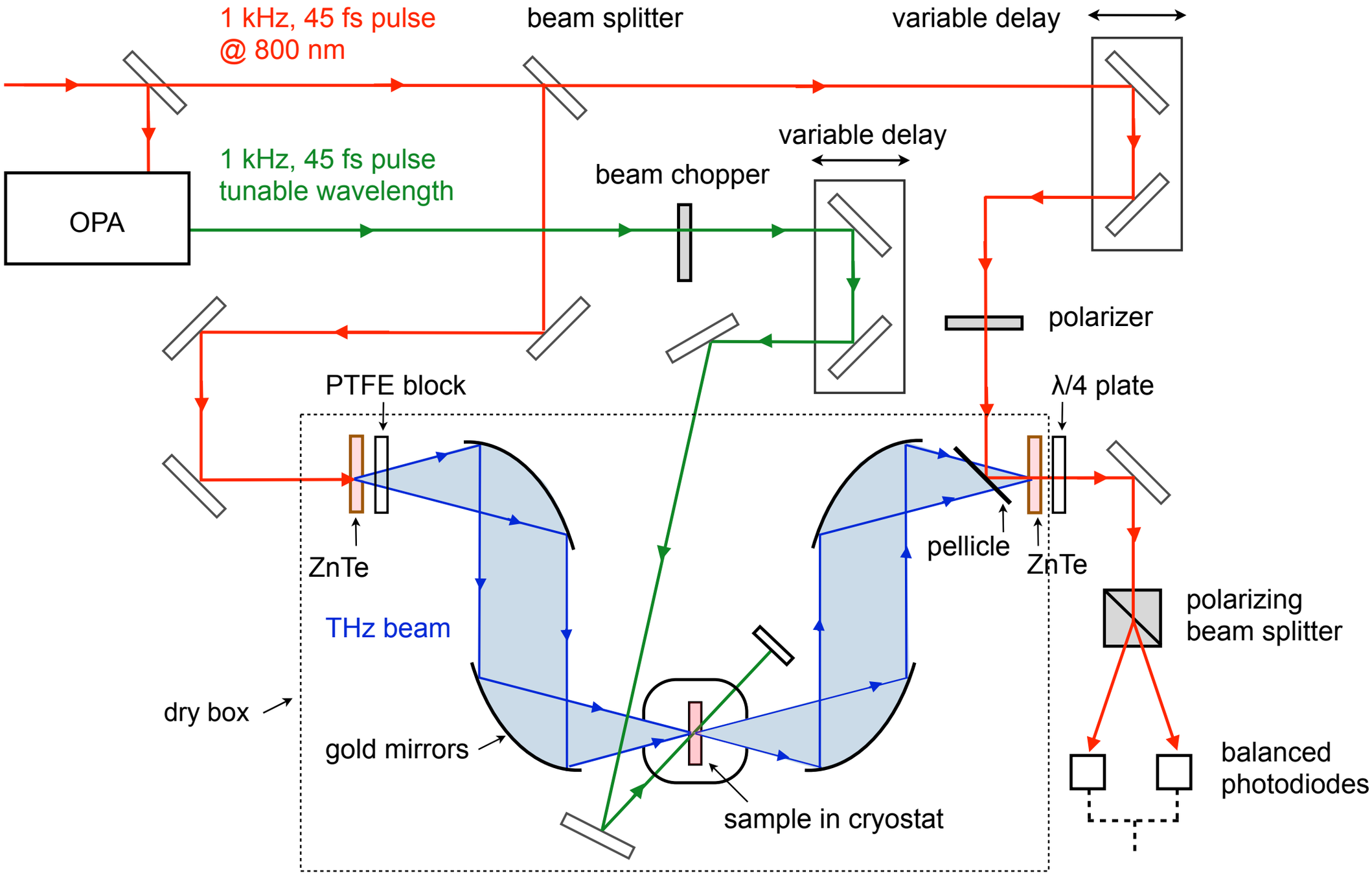


HTM = *spiro*-OMeTAD

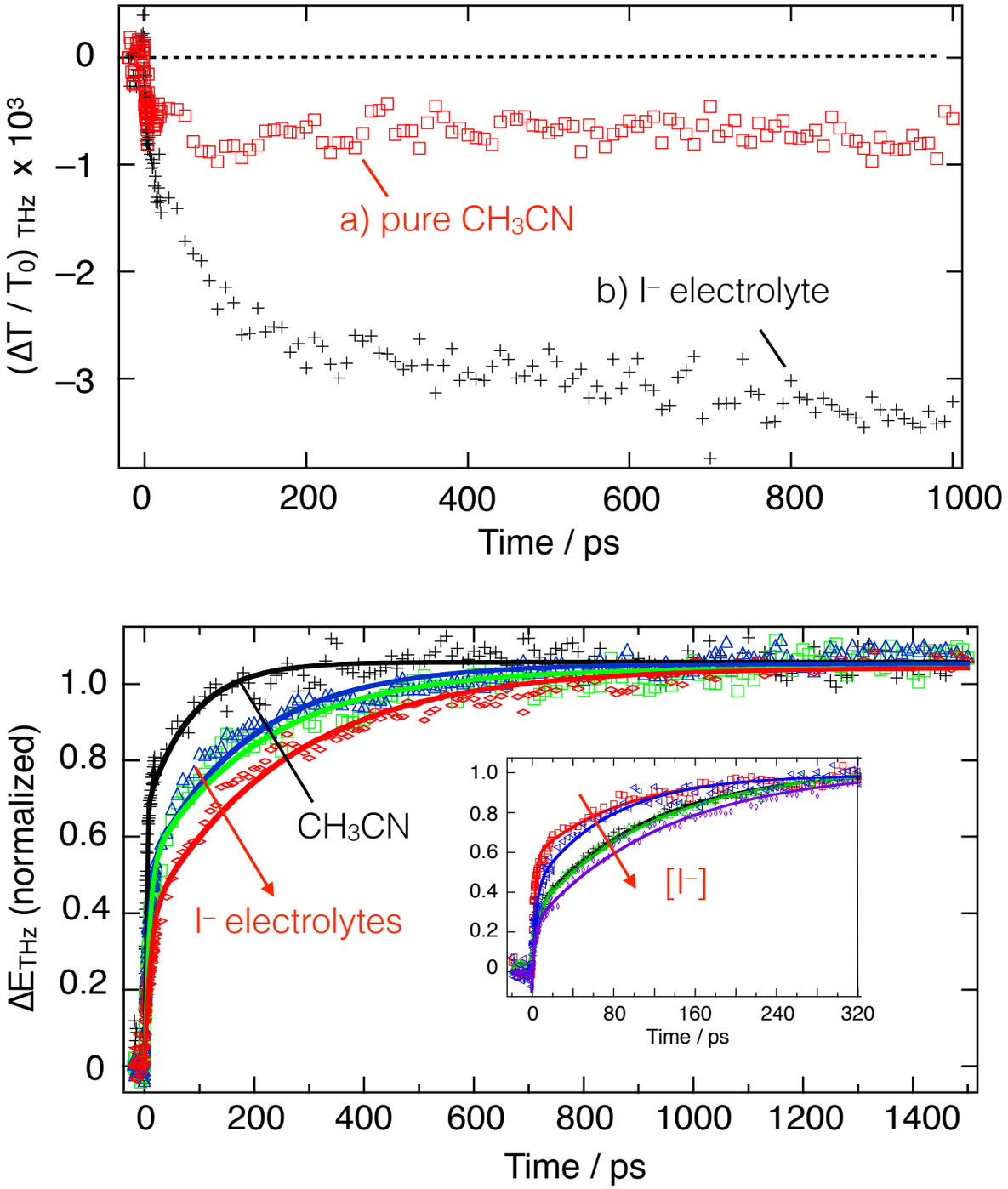


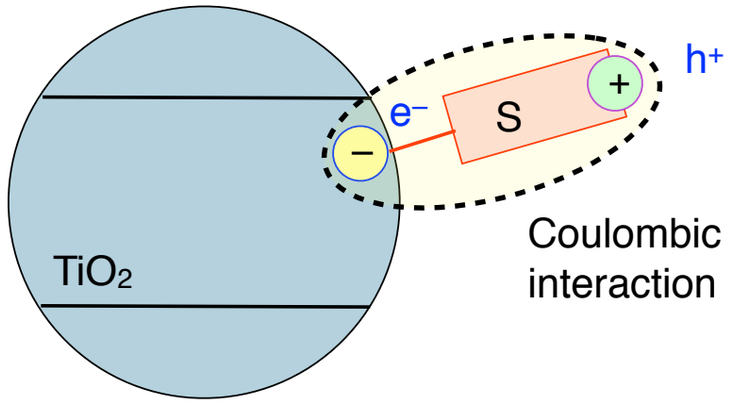


Time-resolved terahertz spectroscopy

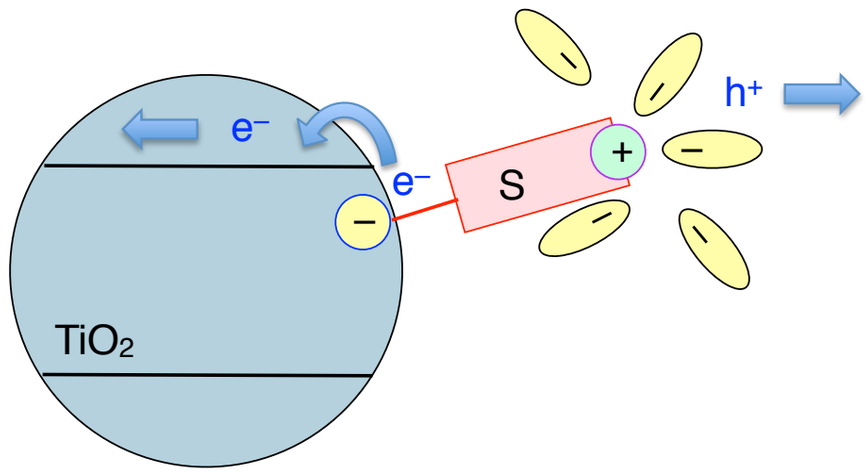


Evidence for CT exciton formation and splitting

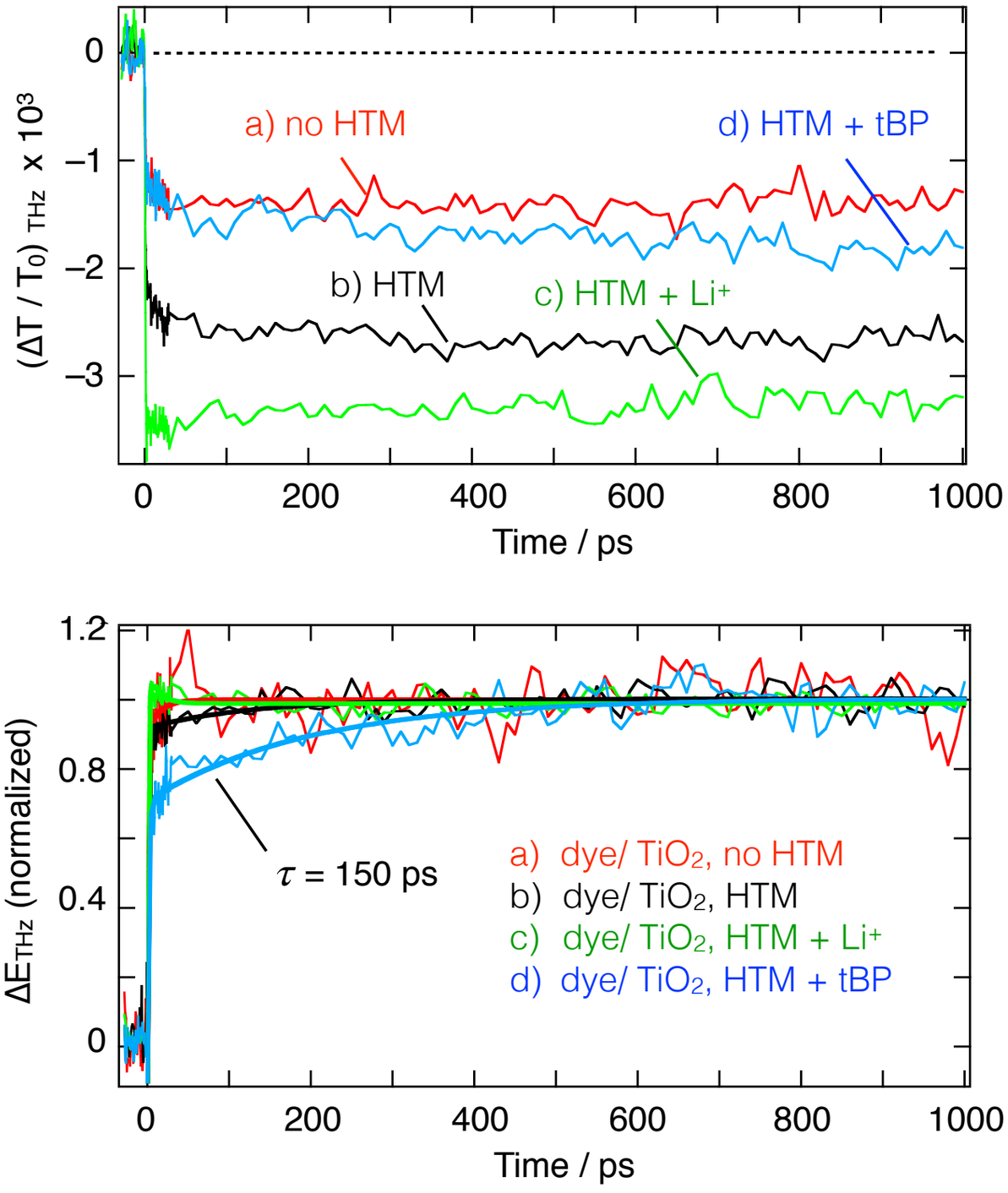


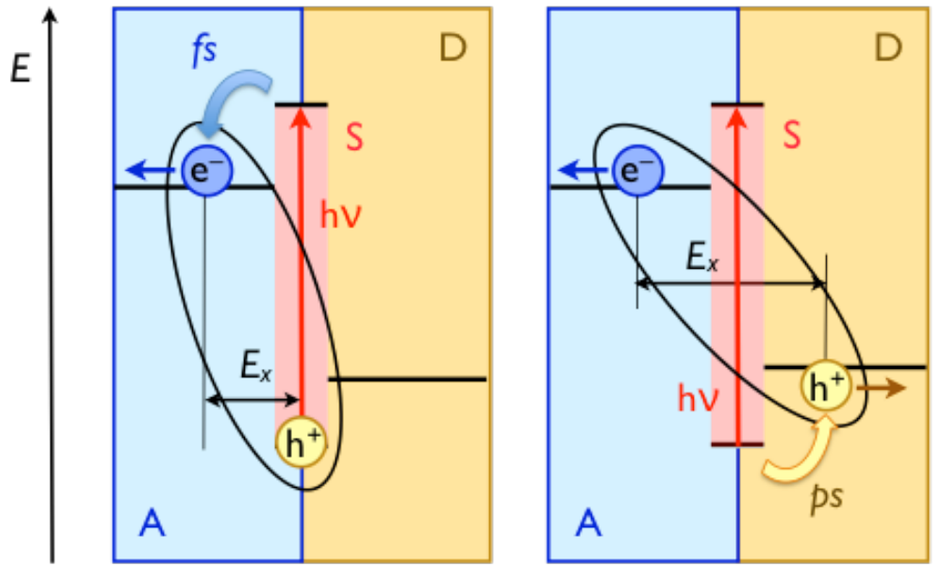


Polarization
reorganization

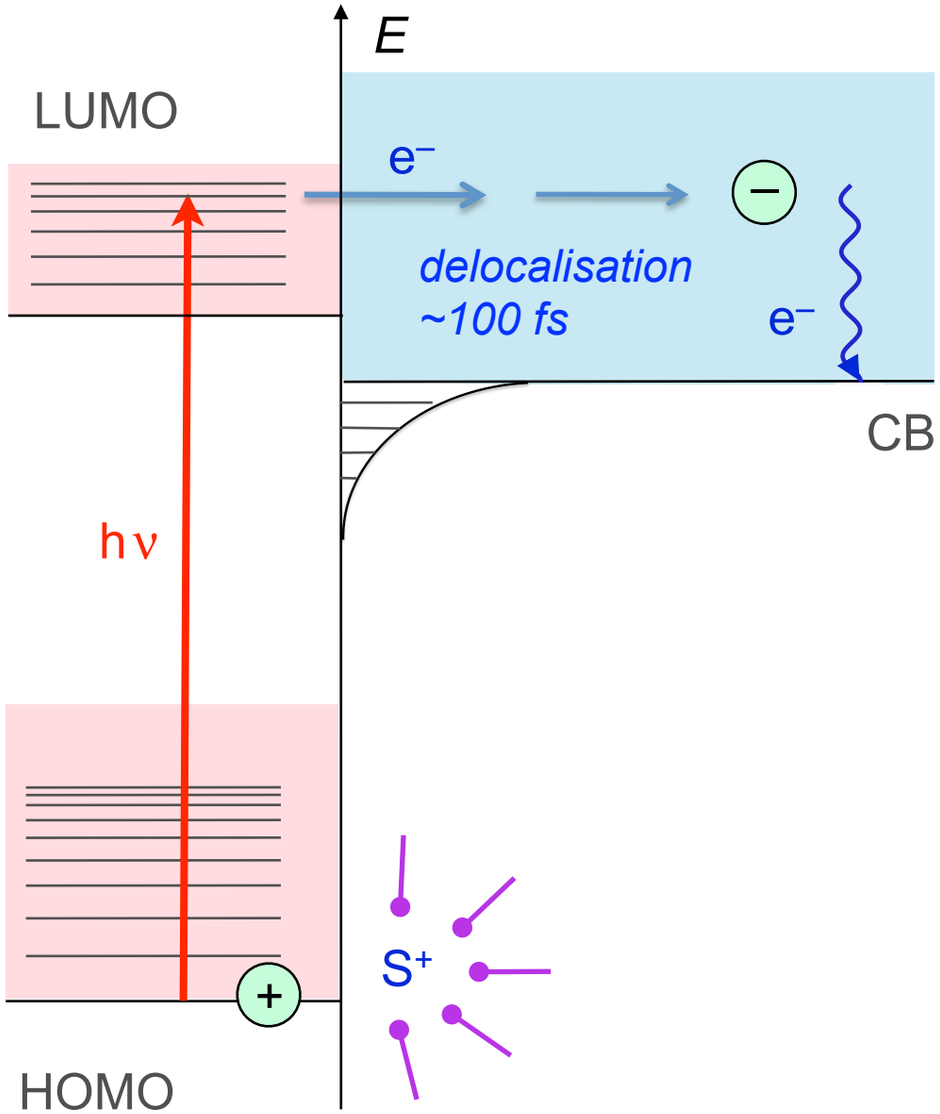


CT exciton splitting upon hole injection in HTM

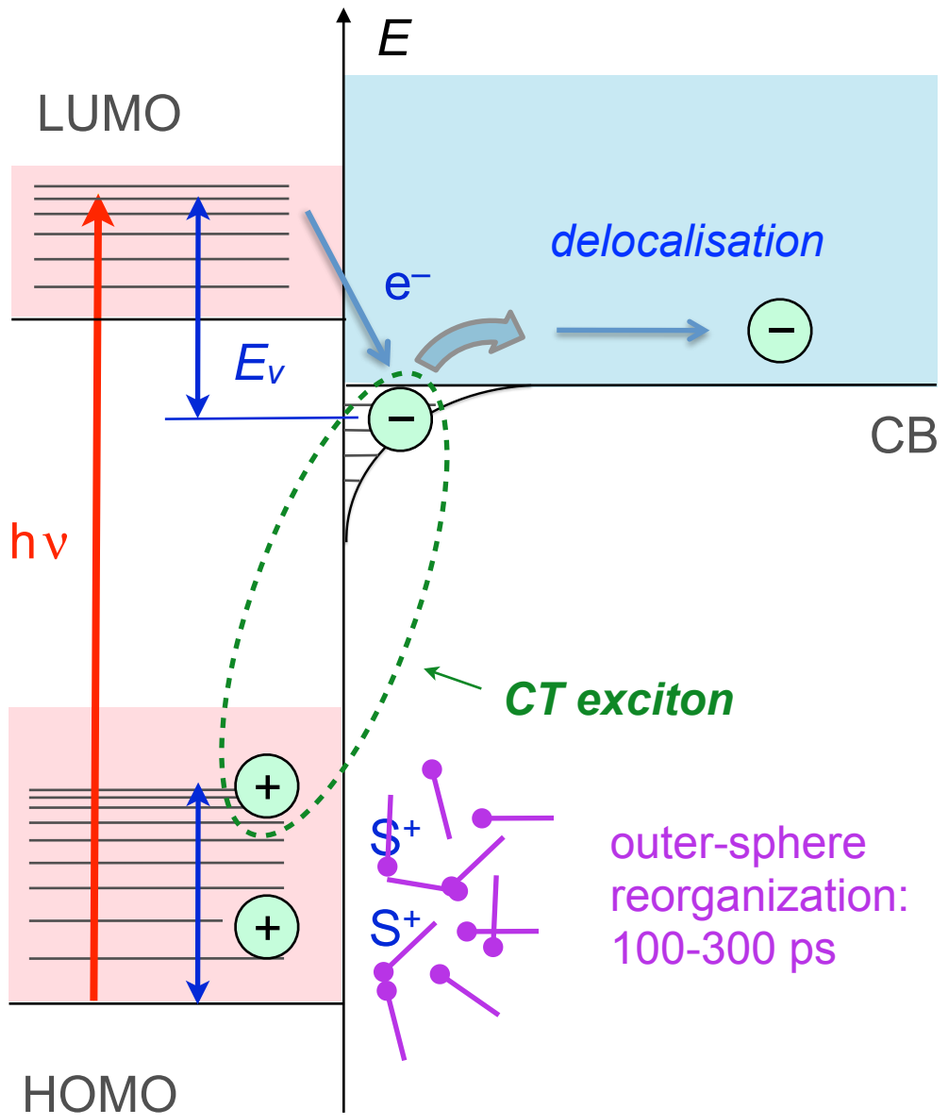




Mechanism of e⁻ photoinjection: A new paradigm



Path 1



Path 2

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Thank you

Best research cell power conversion efficiencies