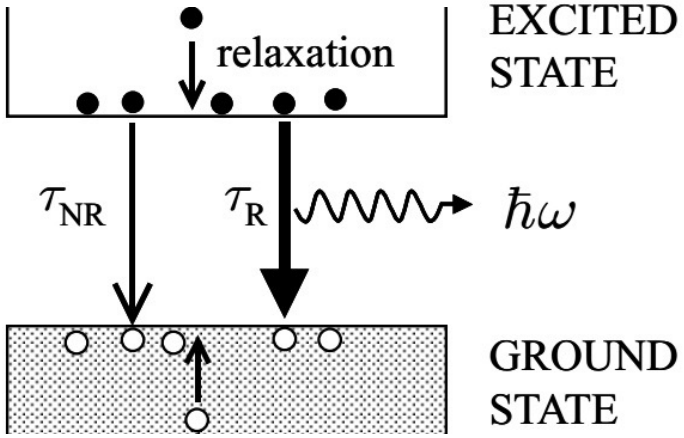
Examples and applications

Hybrid systems: Dye-sensitized solar cells and perovskite solar cells

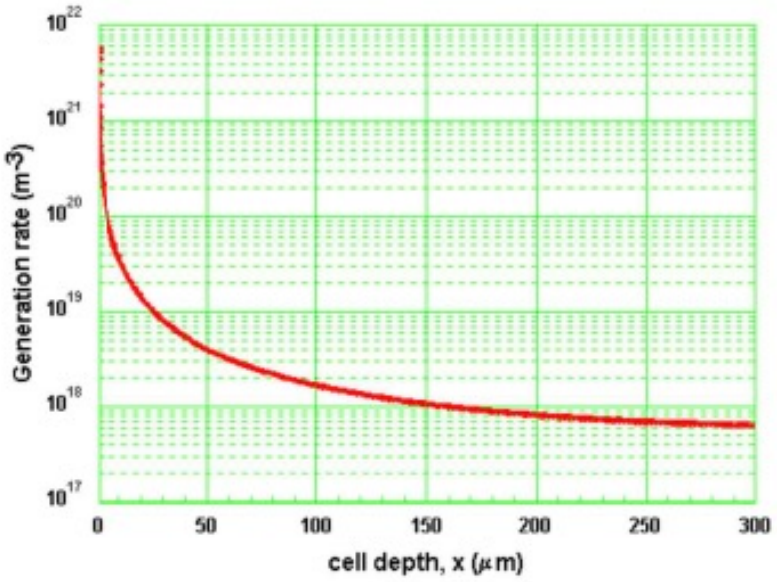
The quest for better solar cells: Charge separation vs. charge recombination



- Photoinduced e- and h^+ need to be separated and extracted at the respective electrodes before they can recombine

- Charges need to diffuse to a **p-n junction** or to an **interface** to be separated so need for long τ_R and τ_{NR}

The quest for better solar cells: Charge separation vs. charge recombination

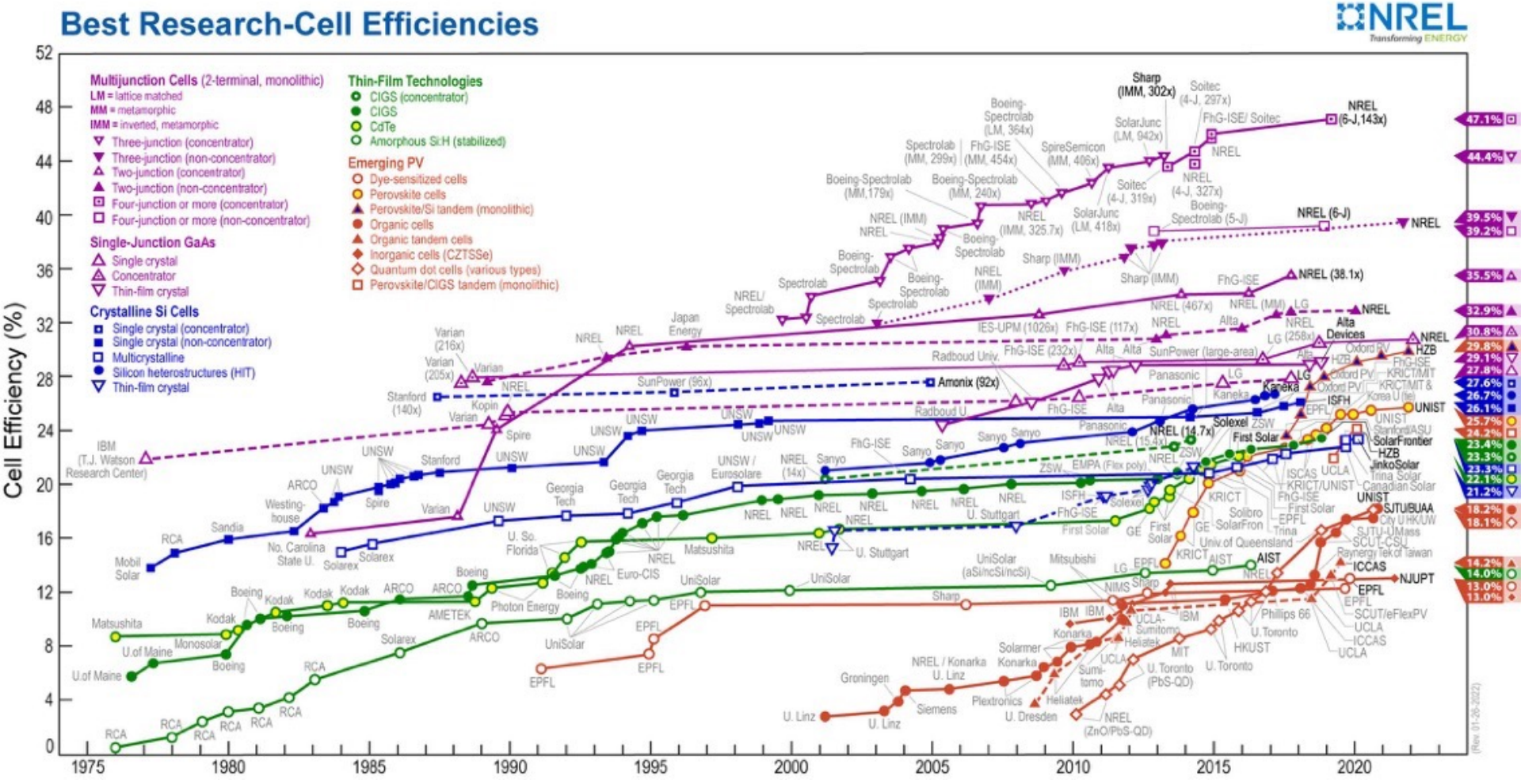


https://www.pveducation.org/pvcdrom/pn-junctions/absorption-coefficient

- More e-/h^+ pairs generated in the front of the cell and then need to travel
- Carrier diffusion length needs to be in the same range as the thickness/distance to the junction/to the electrodes for efficient solar cells!
- Purity/crystallinity plays a major role in conventional solar cells (Si: **99.9999(999)%**)
- What about hybrid, emerging photovoltaic technologies?

Different technologies for solar cells

Charges need to diffuse to a **p-n junction** or to an **interface** to be separated!



https://www.nrel.gov/pv/cell-efficiency.html

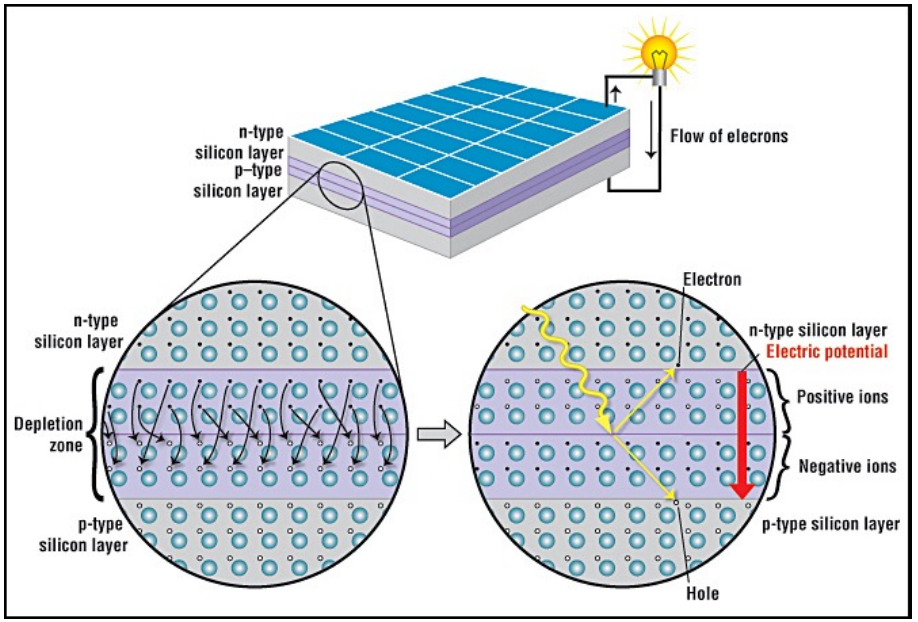
Separate charges: p-n junctions

https://www.acs.org/content/acs/en/education/resources/highschool/chemmatters/past-issues/archive-2013-2014/how-a-solar-cell-works.html

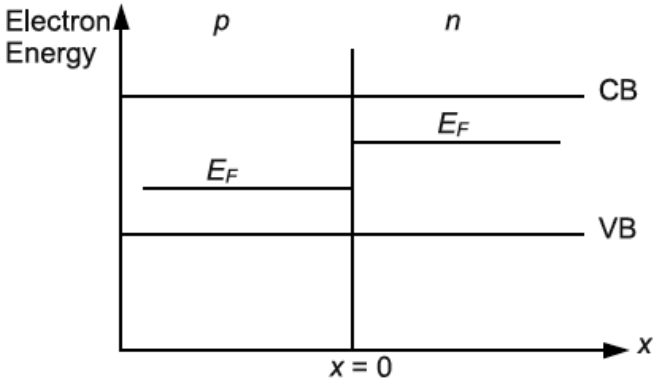
Conventional, first-generation solar cells

Crystalline Si

https://commons.wikimedia.org/w/index.php?curid=461648

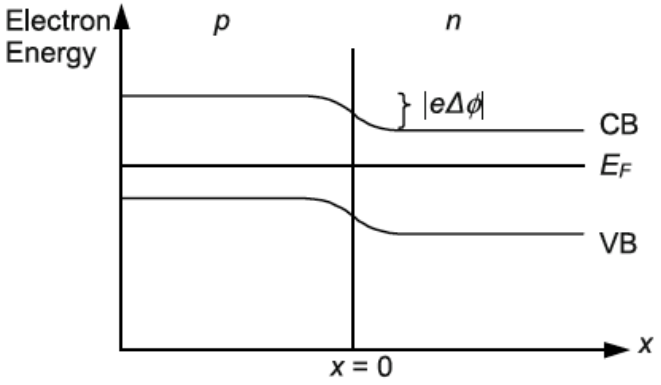


Patterson, Bailey, *Solid-state physics*



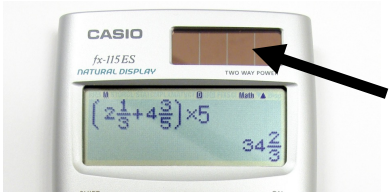
Fermi levels equilibrate

p-n junction forms

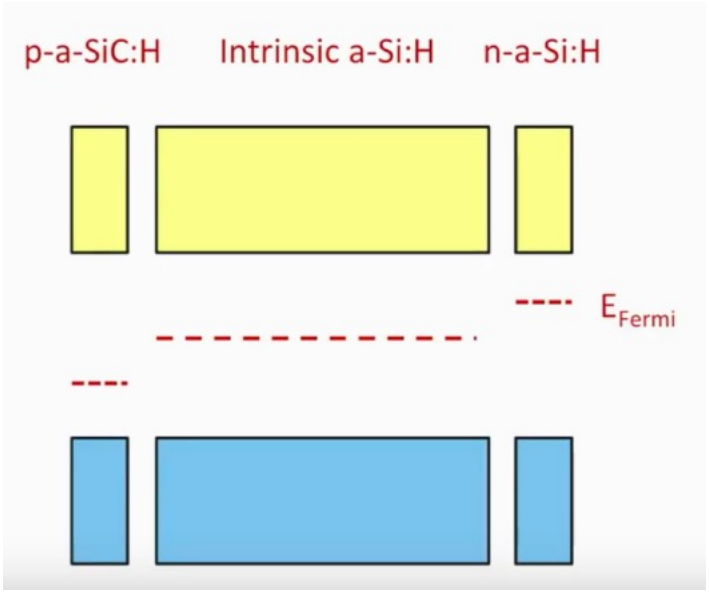


Separate charges: p-i-n junctions

Second-generation:
Thin film technologies (amorphous Si, CdTe, CIGS…)

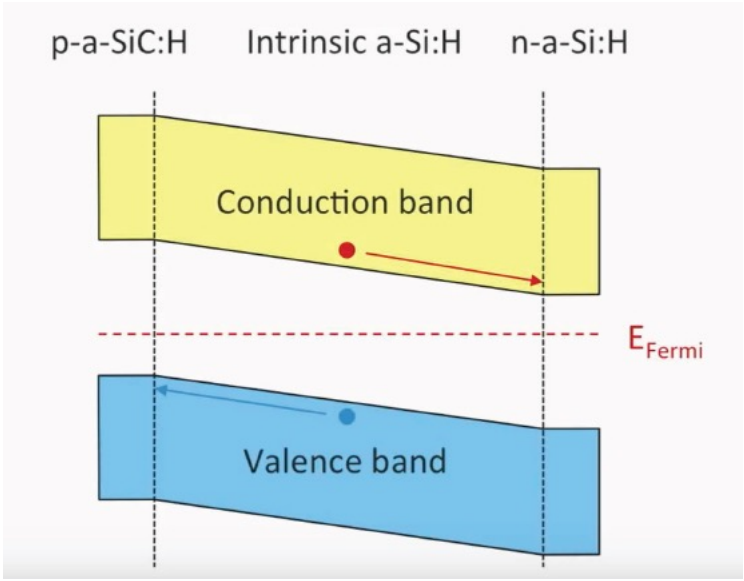


Cheap,
but low efficiency



Fermi levels equilibrate

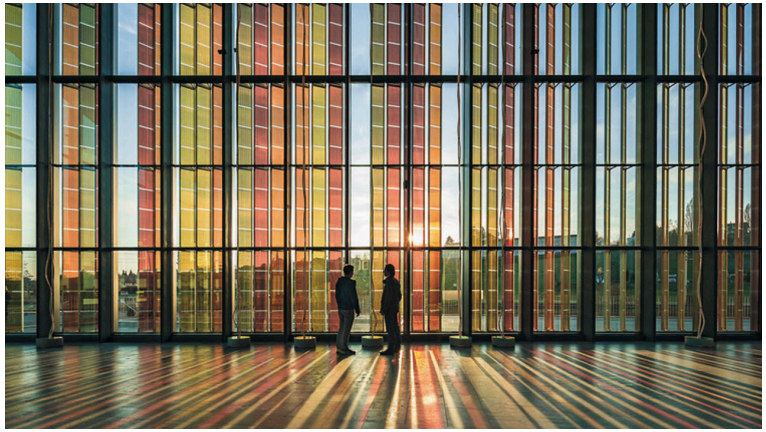
p-i-n junction forms



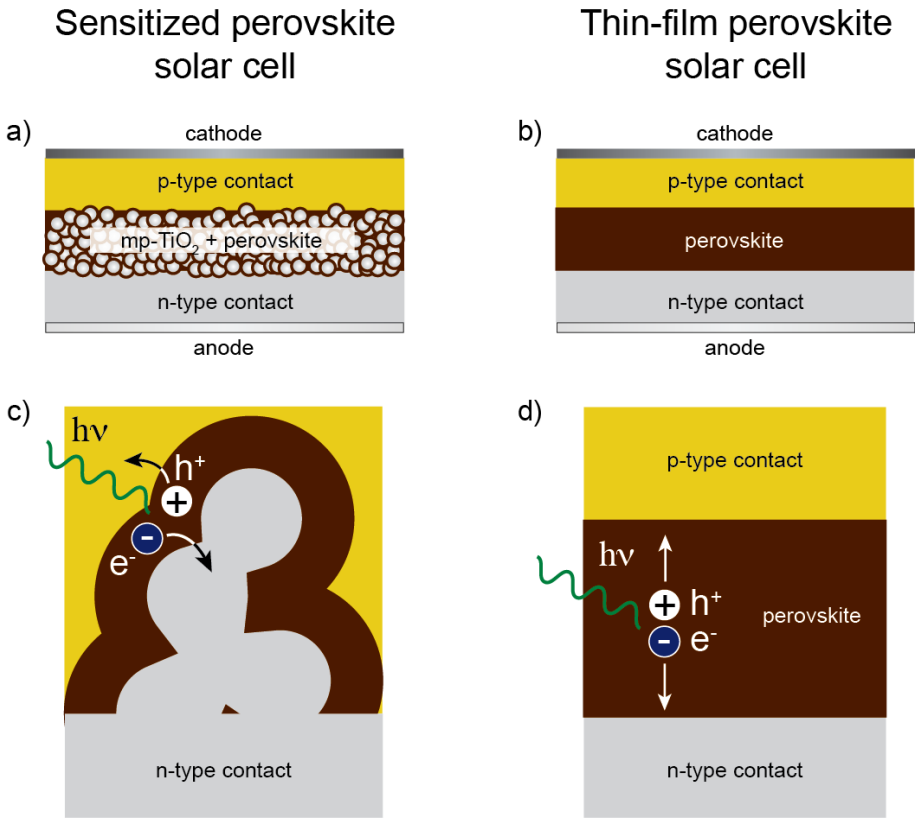
https://online-learning.tudelft.nl/courses/solar-energy-pv-technologies/

Separate charges: Use interfacial charge transfer

Third-generation: Solution-processed solar cells



https://www.science.org/content/article/solar-cells-work-low-light-could-charge-devices-indoors

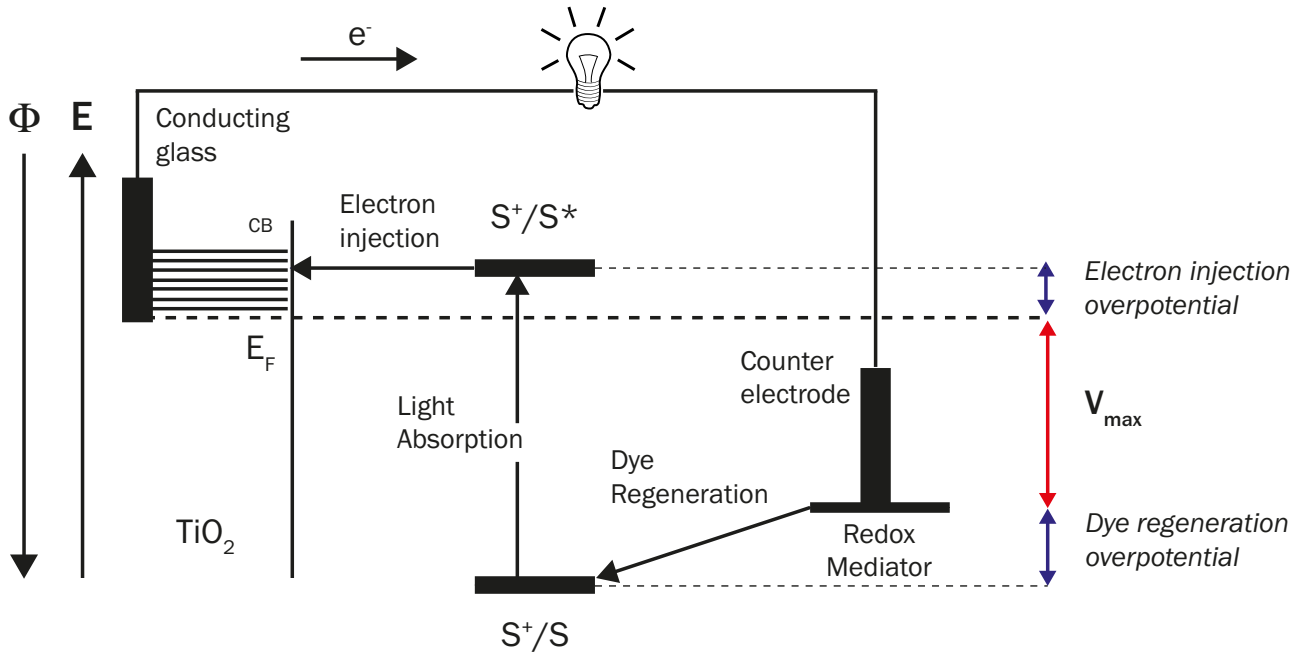


By Sevhab - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=35719179

Dye-sensitized solar cells

Perovskite cells: the best of both worlds!

Dye-sensitized solar cells



Kinetic competition between charge separation and recombination!

Electron injection $S^* \rightarrow S^+ + e^-_{CB}$	fs-ps
Dye regeneration $S^+ \rightarrow S + (Redox)^+$	µs

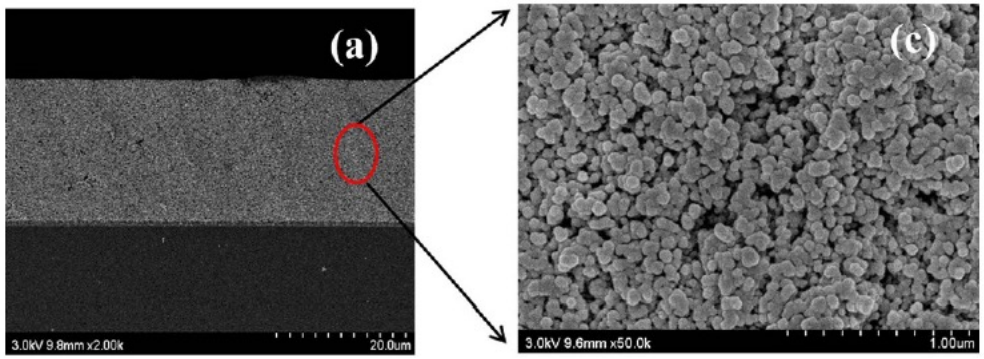
Recombination $e^-_{CB} + S^+ \rightarrow S$	µs-ms
Recombination $e^-_{CB} + (Redox)^+ \rightarrow Redox$	ms

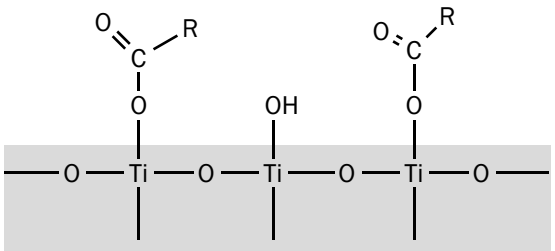
Electron acceptor/transporting material

- n-doped wide bandgap SC (usually > 3V): Does not absorb visible light (transparent)
- Anatase TiO_2, but can also use ZnO (possible to reverse the cell and use a p-doped SC)
- Nanoparticles of TiO_2 from a colloidal solution are deposited on a conductive glass

→ Mesoporous framework with large surface area

- Resulting film thickness can vary between 2 and 20 µm, with 10 to 30 nm diameter particles and porosity between 50 and 70%
- Surface Ti^{IV} sites are Lewis acids, offering a convenient way to attach dye molecules with electron-rich anchoring groups such as carboxylates





Cho et al., . Sci. Rep. 3, 1496; DOI:10.1038/srep01496 (2013).

Dye sensitizer

- Good molar extinction coefficient covering a broad wavelength range

→ ε in the range of 10^4 -10^5 M cm^{-1}

- Excited energy level should be as close as possible to the lower edge of the conduction band of TiO_2 in order to efficiently inject while minimizing energy losses by thermalisation of the carriers in the semiconductor oxide

- Oxidized energy level should be well matched so that it can be regenerated via electron donation from the redox electrolyte

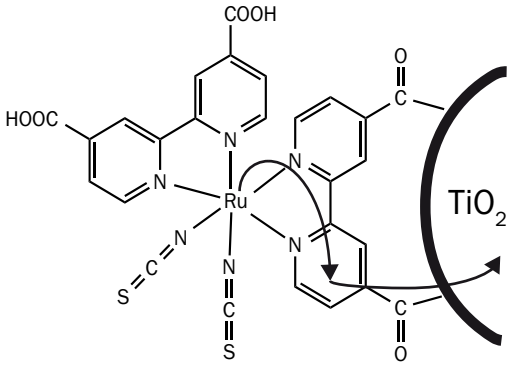
- Should be stable enough to sustain about 20 years of exposure to natural sunlight (10^8 turnover cycles!)

- Grafted onto the TiO_2 surface through suitable anchoring groups, e.g. carboxylate or phosphonate groups – ideally as a monolayer

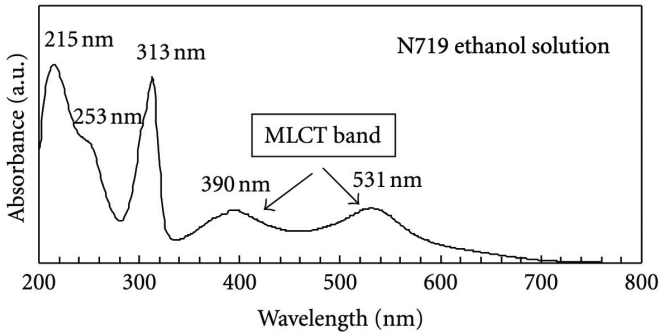
- Design: separate charges spatially as much as possible!

Optimize the dye for faster electron transfer…and slower back electron transfer!

Example a): Ruthenium-based dyes



- Absorption in the visible involves an MLCT transition that places the excited e- on the diimine (directly attached to the TiO_2)
- Results in ultrafast charge injection
- The positive charge density that remains on the dye is distributed over the metal, and to some extent over the NCS ligands

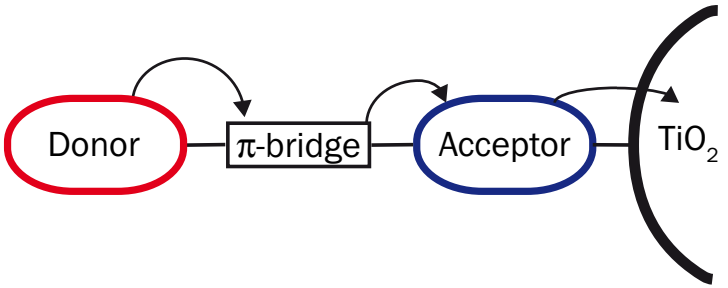


→ The resulting spatial separation of the positive charge density on the dye and the injected electrons retards the rate of charge recombination

→ The charge-recombination dynamics is closely dependent on this separation (Marcus inverted region: distance dependence becomes important)

Optimize the dye for faster electron transfer…and slower back electron transfer!

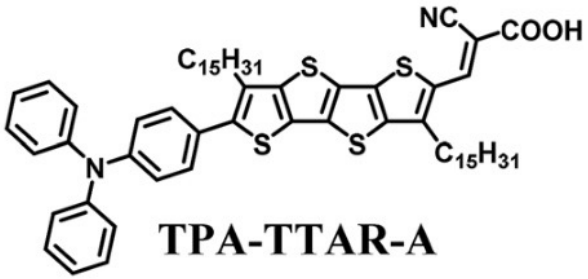
Example b): D-π-A organic dyes



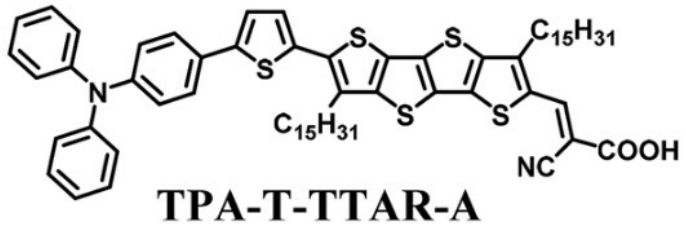
- Panchromatic absorption and high molar ε can be achieved by modifying the dye structure with different moieties

- HOMO and LUMO can be adjusted to energetically favorable levels

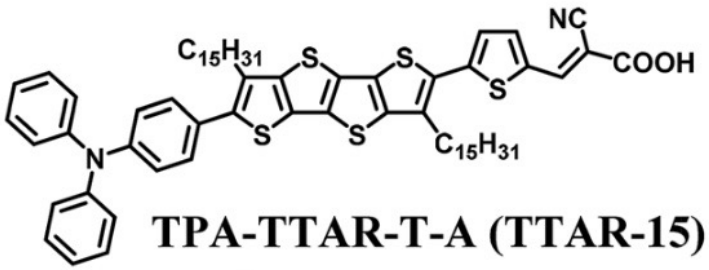
HOMO mainly localized on D and π-bridge
LUMO localized over A



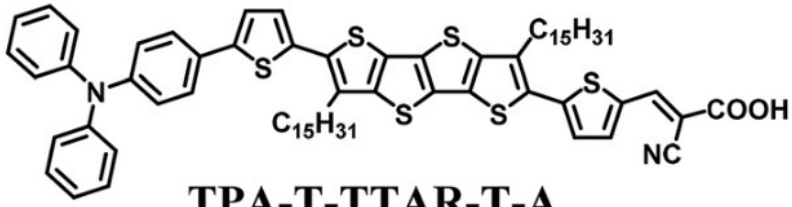
TPA-TTAR-A



TPA-T-TTAR-A



TPA-TTAR-T-A (TTAR-15)



TPA-T-TTAR-T-A

Ji et al., *J. Mater. Chem. A*, **2018**, *6*, 14518–14545

Dye regeneration

Liquid redox mediator

- Triiodide/iodide redox couple (I_3^-/I^-) has a suitable redox potential allowing for efficient dye regeneration, works well with ruthenium-based dyes
- The reduction of the triiodide species by photoinjected electrons on the surface of TiO_2 is very slow so not many losses there

Drawbacks:

- **Slow regeneration reaction due to the complex chemistry**
- (I_3^-/I^-) mixture absorbs slightly in the visible region – *we would like no parasitic absorption*
- LIQUID!!!

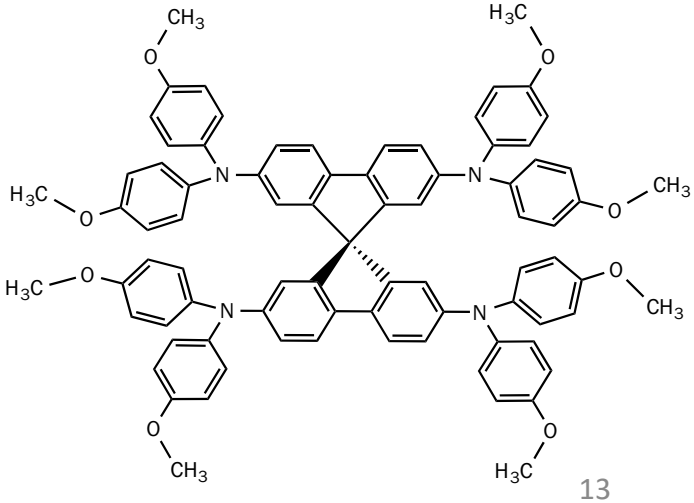
Hole transport material

- Circumvent leakage and corrosion
- Solution processable, cheap
- Hole injection can potentially be faster!

Drawbacks:

- Mobility is generally low
- Partial or incomplete pore filling of the mesoscopic structure

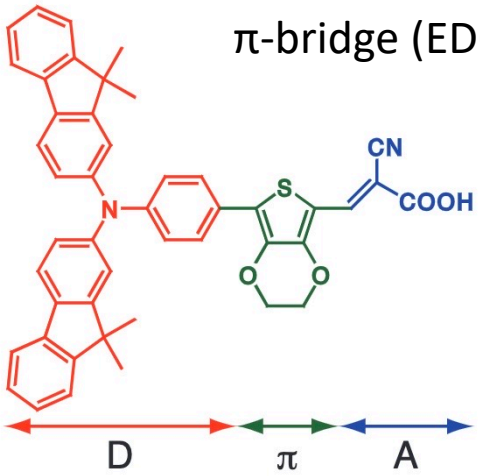
Spiro-OMeTAD



A step-by-step case study using absorption spectroscopy, PIA and TA

A step-by-step case study: C204 D-π-A dye

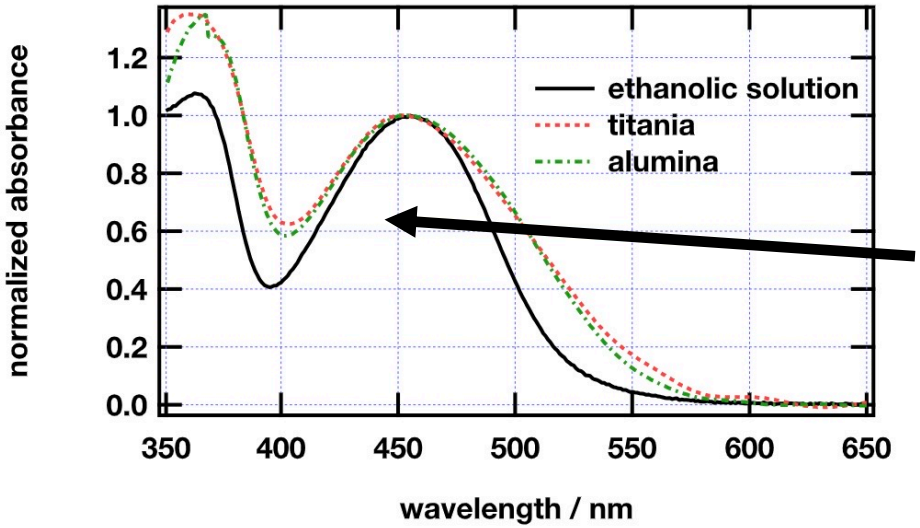
Electron-rich
π-bridge (EDOT moiety)



Triarylamine donor moiety

Cyanoacrylate anchoring group

First:
Characterization of the ground state

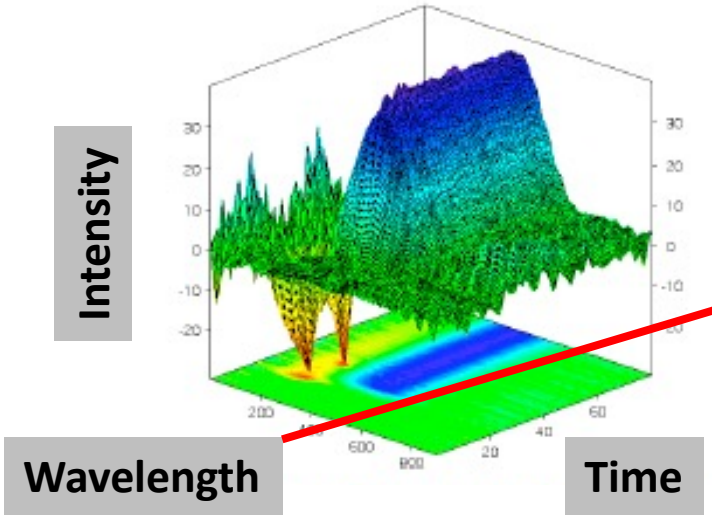


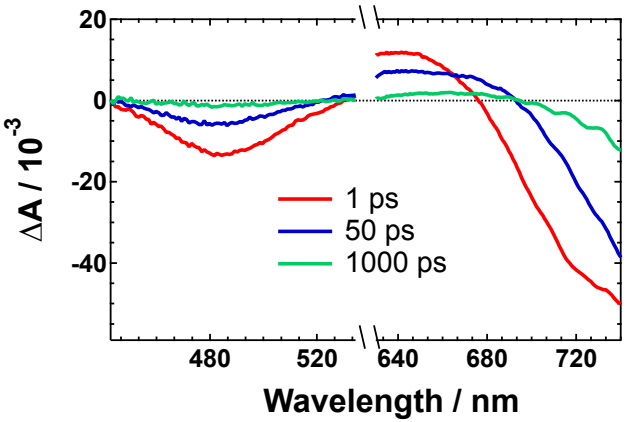
Intramolecular charge transfer

Joël Teuscher, EPFL Thesis

Figure 5.2: Normalized UV-Vis absorption spectra of C204 in ethanolic solution (–), C204/TiO_2 (···) and C204/Al_2O_3 (-·-).

Reminder of TA data analysis





Absorption changes at different times after light excitation

NEGATIVE SIGNALS

$$\Delta A = -log\left(\frac{I_{T*}}{I_T}\right) < 0$$

$$I_{T*} > I_T$$

Ground state loss (=“bleaching”) or stimulated emission

POSITIVE SIGNALS

$$\Delta A = -log\left(\frac{I_{T*}}{I_T}\right) > 0$$

$$I_T > I_{T*}$$

Absorption from photoinduced species

Case study: C204 D-π-A dye

Second:
General characterization of the excited state

Energy diagram
on alumina/titania:

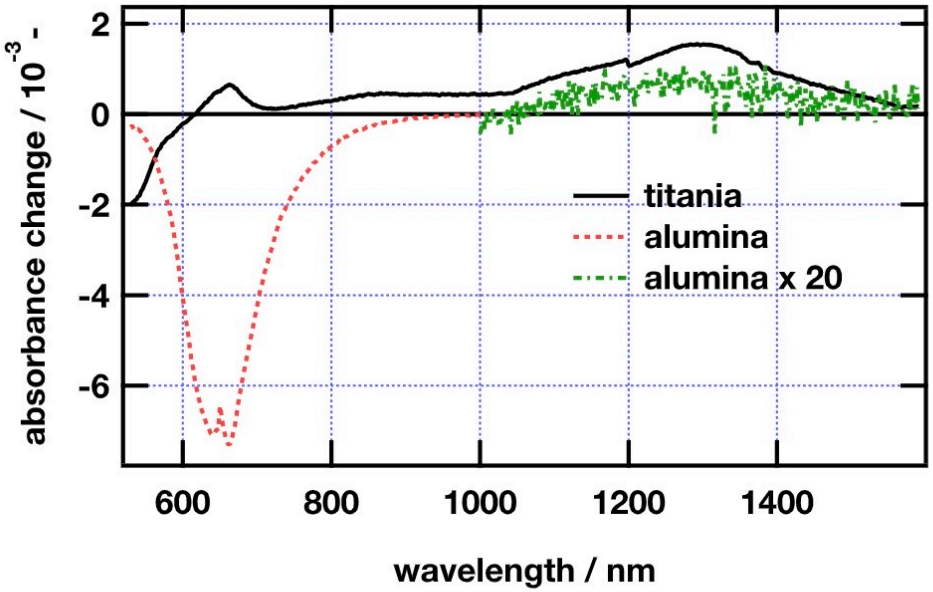


Figure 5.4: PIA spectrum of C204/TiO_2 4.8 μm (–), C204/Al_2O_3 5 μm (···), C204/Al_2O_3 expanded 20x (-·-), λ_{ex} = 470 nm at 9 Hz in air.

Case study: C204 D-π-A dye

Electron transfer
(or lack thereof)

Probe: Hole on the triarylamine at 1100 nm (and e- as well)

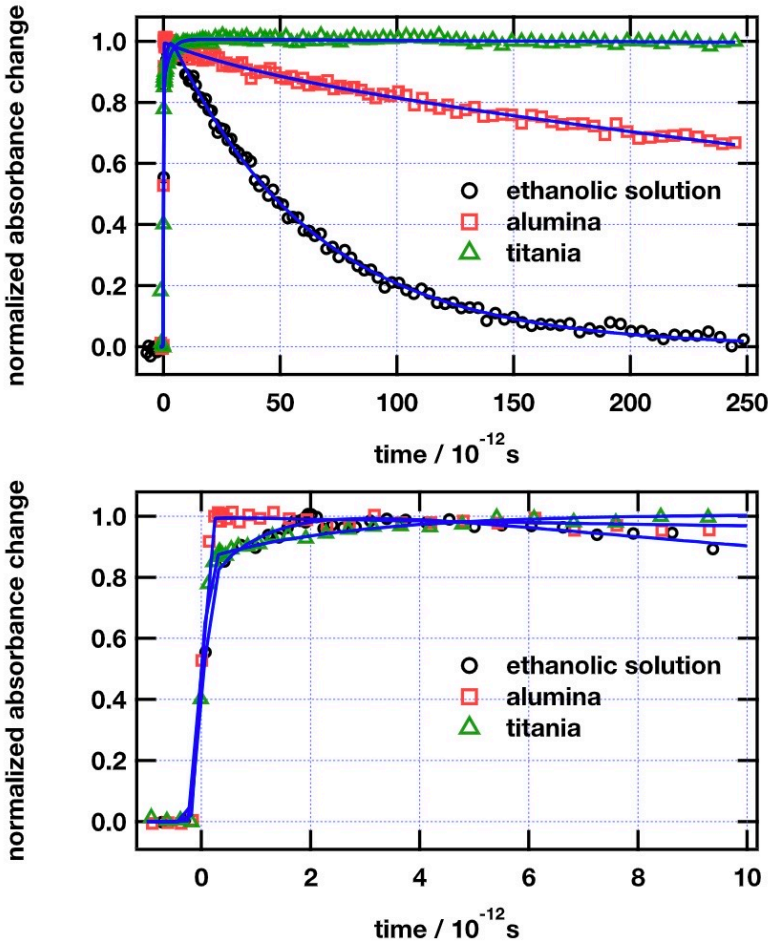


Figure 5.7: Top: Femtosecond transient absorbance, λ_{obs} = 1100 nm, λ_{ex} = 530 nm, C204 in ethanolic solution (○), C204/Al_2O_3 in MPN (□) and C204/TiO_2 in MPN, solid lines are fits results for a convolution of a gaussian and two exponentials. Ethanolic solution: σ = 132 fs, τ_1 = 1.1 ps (rise), τ_2 = 61 ps (decay). C204/Al_2O_3: σ = 88 fs, τ_1 = 37 ps (decay), τ_2 = 711 ps (decay). C204/TiO_2: σ = 93 fs, τ_1 = 2.7 ps (rise), τ_2 = 2400 ps (dec
the parameters of equation 2.10. Bottom: zoom of the first ten

Case study: C204 D-π-A dye

We know look at how long it takes to recover the dye in the presence of a solvent (no redox reaction possible)…

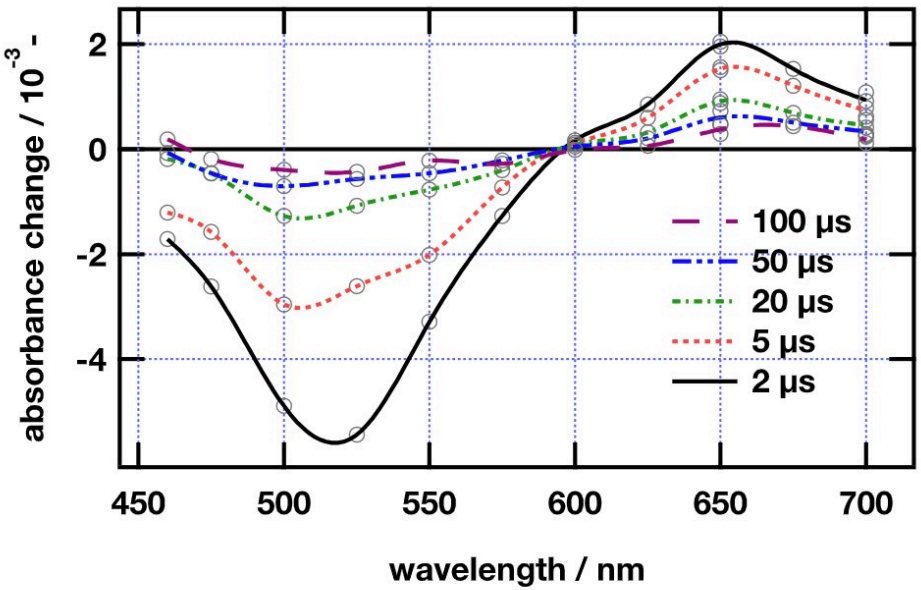


Figure 5.5: Nanosecond transient spectra of C204/TiO_2 at 2 (–), 5 (· · ·), 20 (-·-), 50 (-··-) and 100 μs (– –) after the excitation pulse, $\lambda_{ex} = 530$ nm in MPN.

Case study: C204 D-π-A dye

…and how long it takes to recover the dye ground state in the presence of a redox couple (donor Z952)

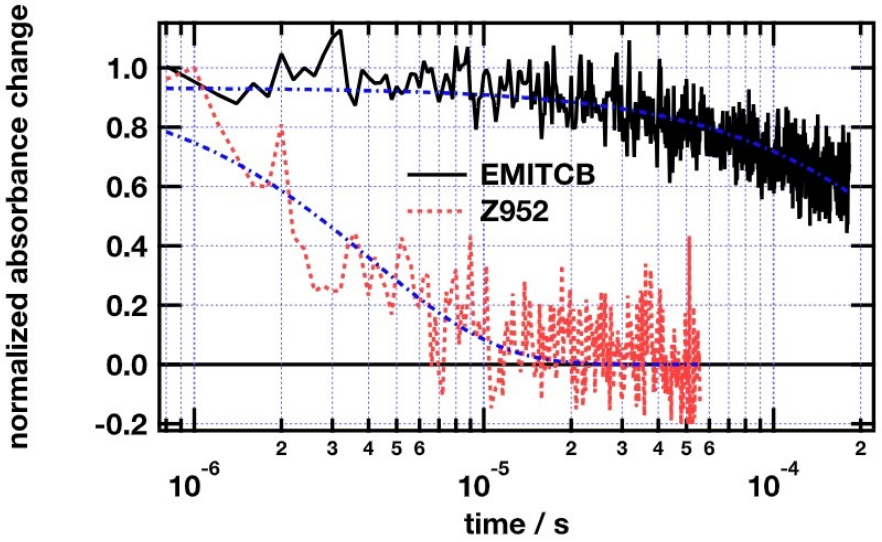
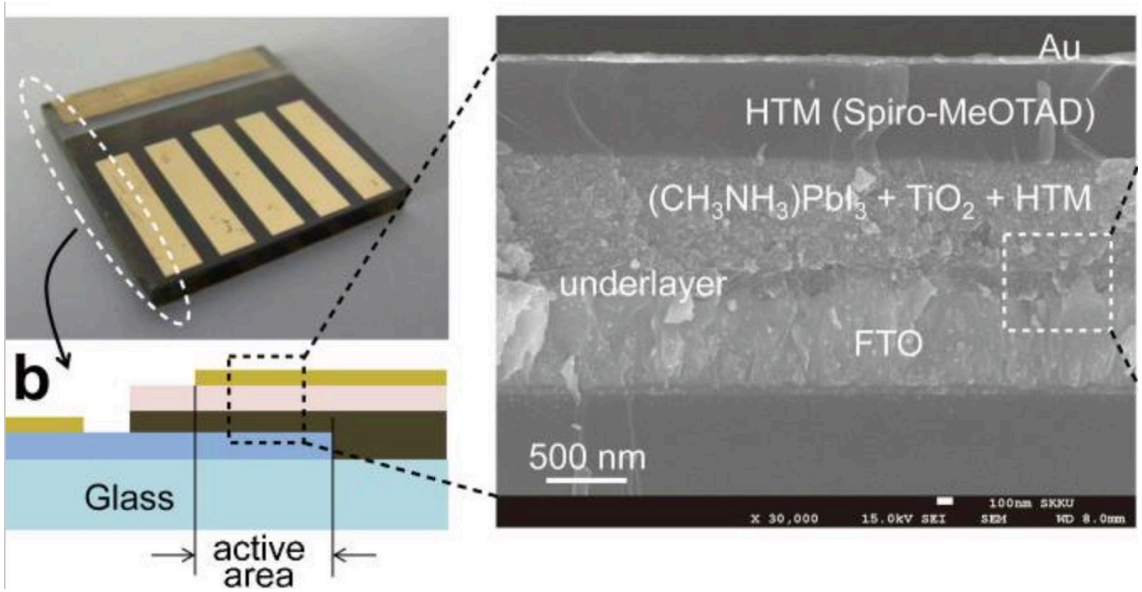


Figure 5.6: Nanosecond transient of C204/TiO_2 in EMITCB (–), Z952 electrolyte (···) and monoexponential fits (-·-), $\lambda_{ex} = 530$ nm, $\lambda_{obs} = 650$ nm.

Joël Teuscher, EPFL Thesis

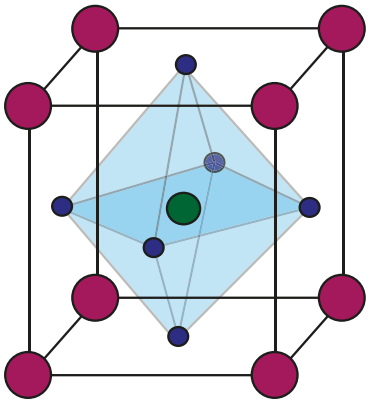
Conclusion: Engineer fast electron transfer, design for slow electron recombination, and use a donor that can transfer an electron to the oxidized species as soon as possible to avoid back electron transfer!!!

Perovskite-based solar cells



Kim et al., *Sci. Rep.*, **2012**, 2, 591

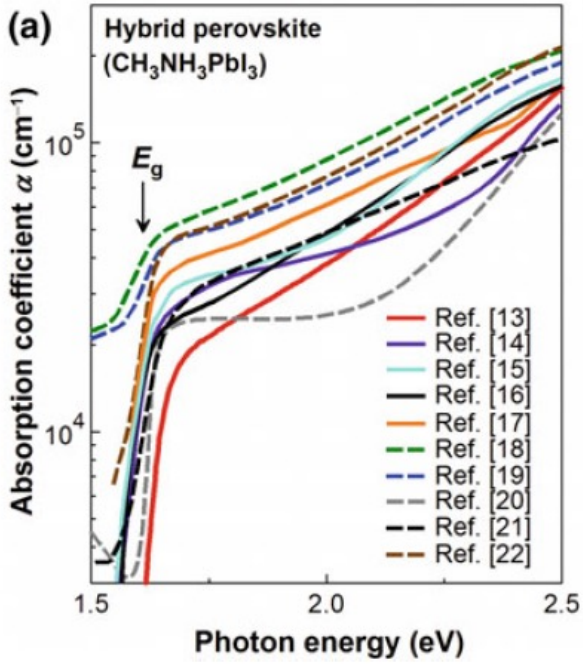
"Sensitized" version!



$A = CH_3NH_3^+$

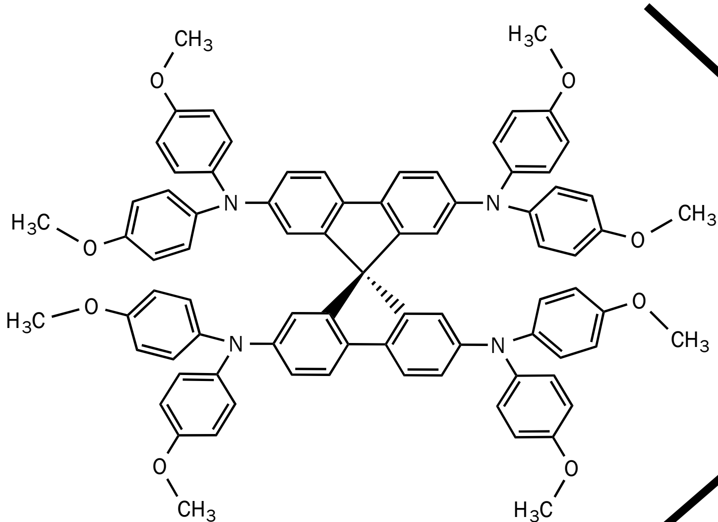
$M = Pb^{2+}$

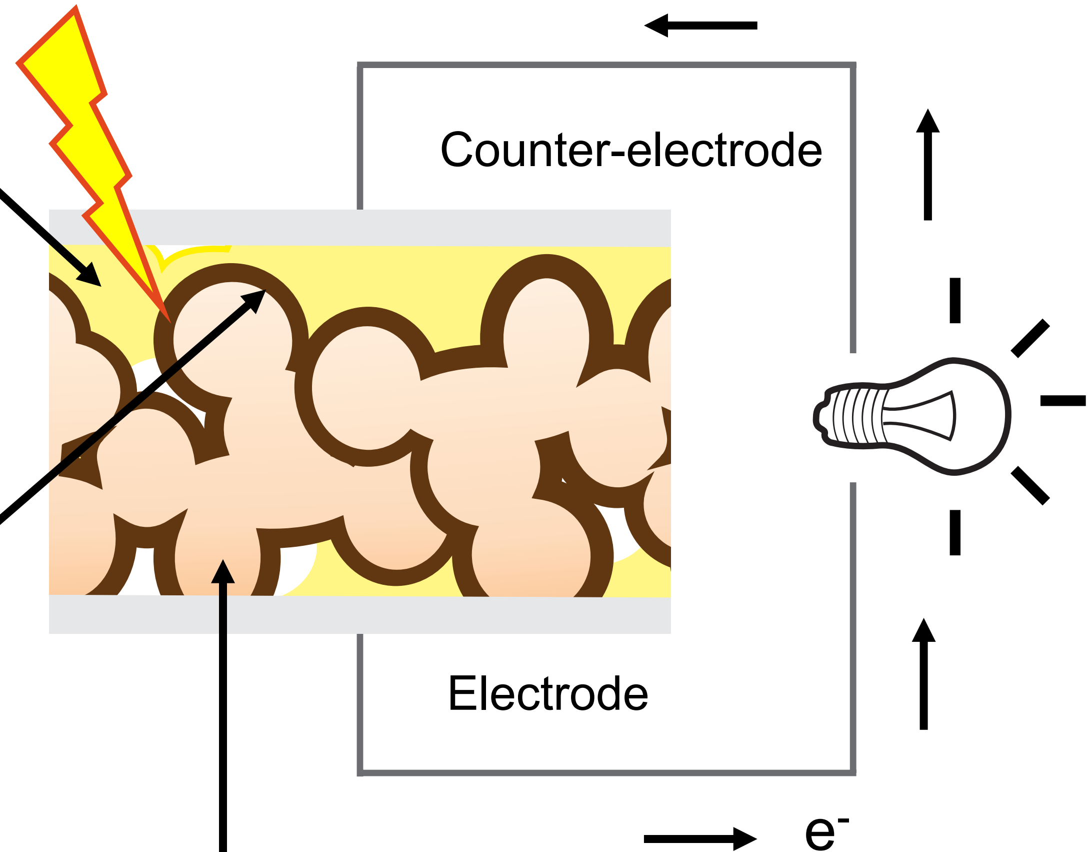
$X = I^-$



Operation

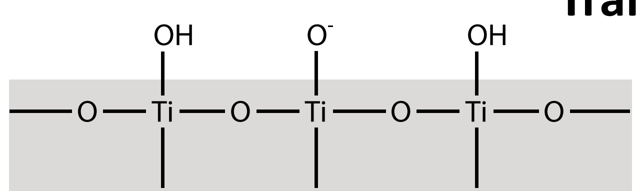
Transports holes h^+



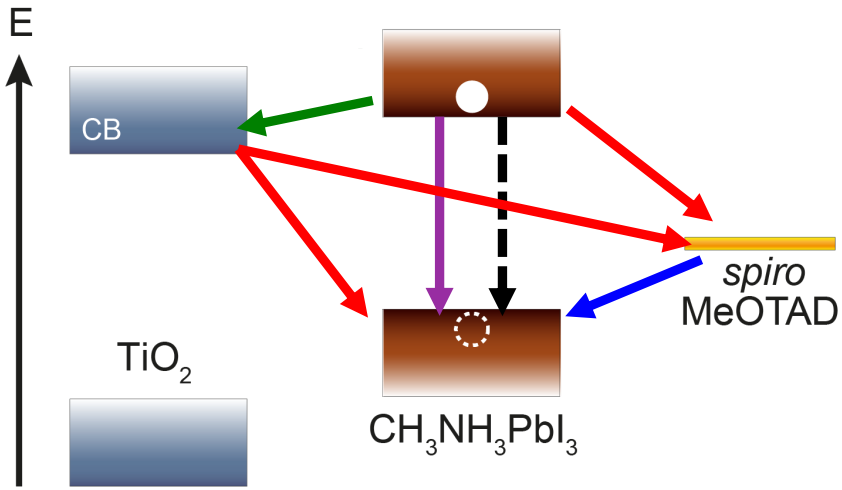


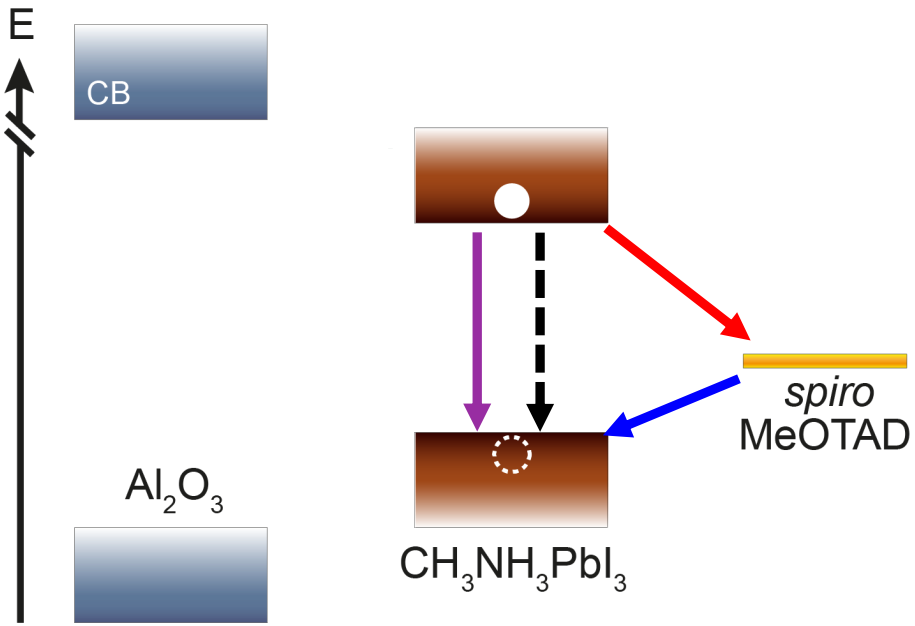
Perovskite
Broad absorption in the visible
Also e^- and h^+ transport!

Transports electrons e^-



Mechanism



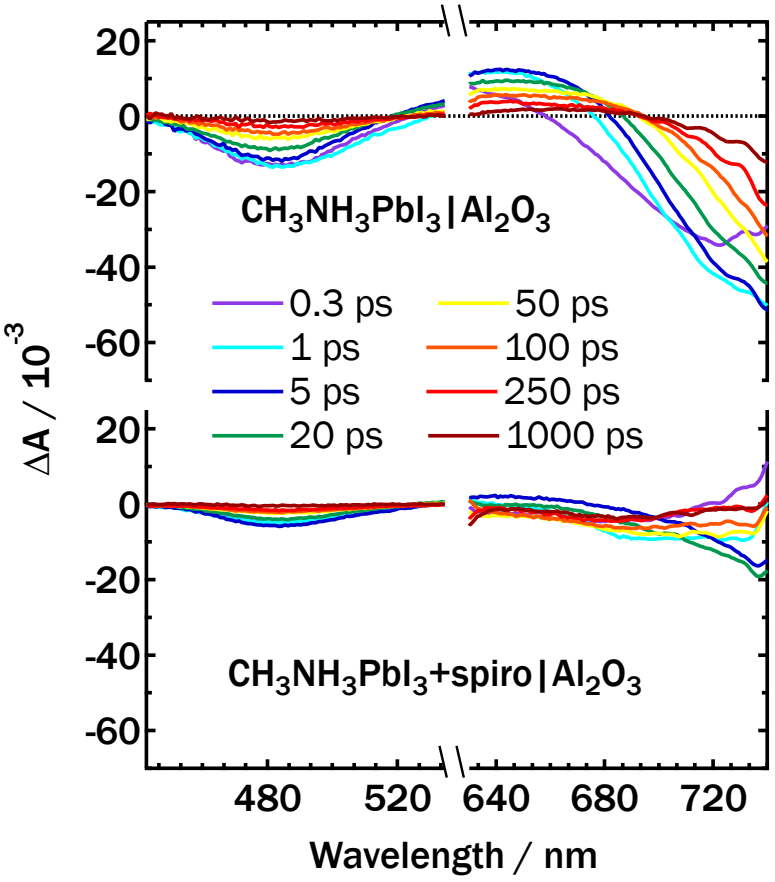


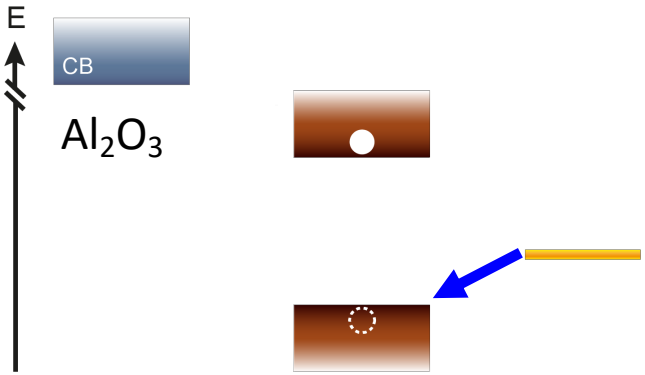
Charge separation	**Electron Injection** **Hole injection**
Charge recombination	**Luminescence** **With oxidized species** **Non-radiative**

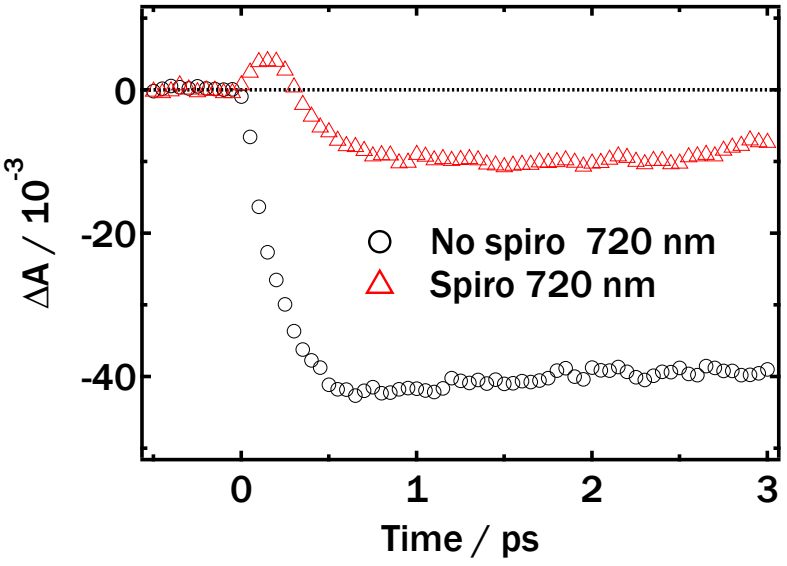
Charge separation	**Hole injection**
Charge recombination	**Luminescence** **With oxidized species** **Non-radiative**

Example of hole transfer

Pump 580 nm





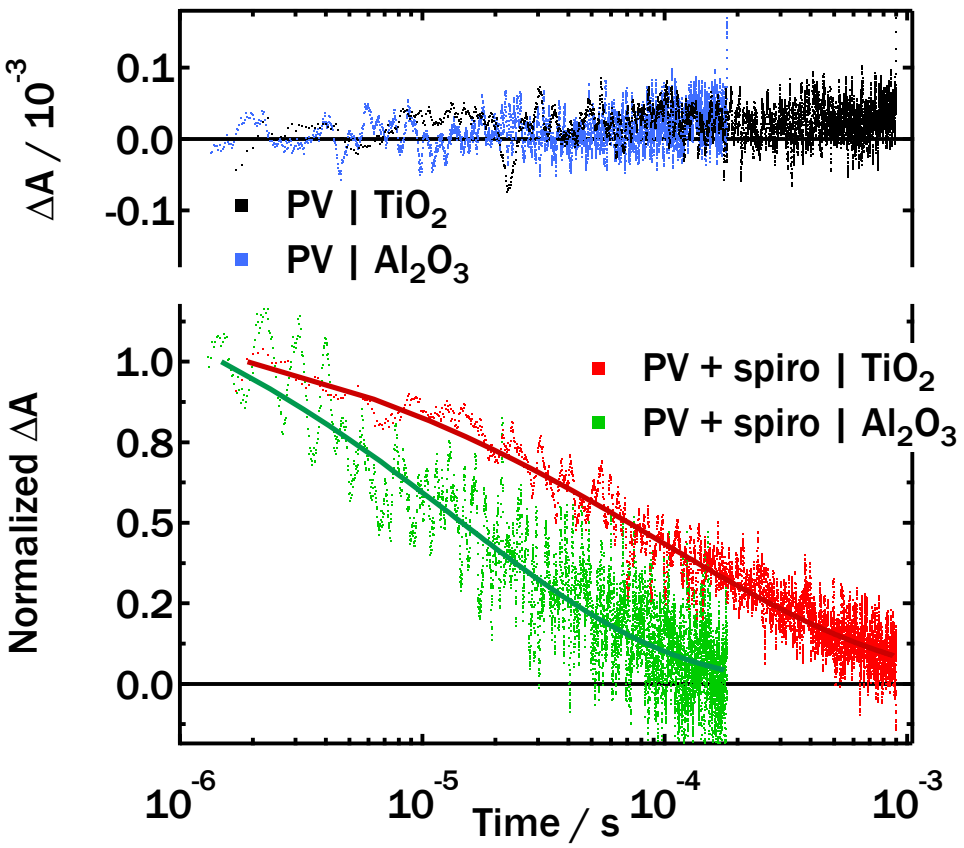


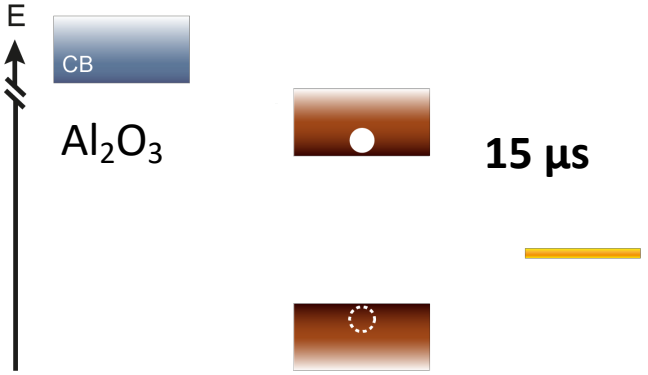
Hole transfer is very fast

(electron transfer as well, but more complicated…)!

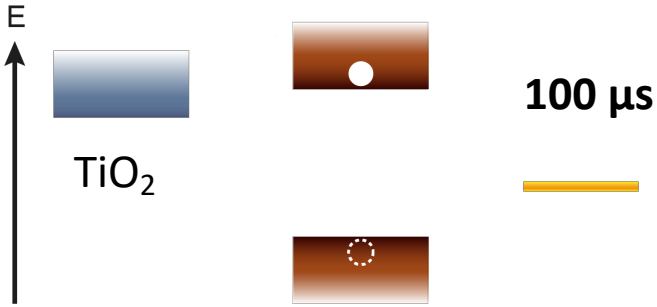
Example of charge recombination

Pump 580 nm
Probe 1400 nm: oxidized spiro





Stretched exponential
Broad distribution of distances between charges



Two heterojunctions help to separate the charges!