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Photovoltaic Conversion by Reciprocity

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Photovoltaic Conversion by Reciprocity

Jean-François GUILLEMOLES

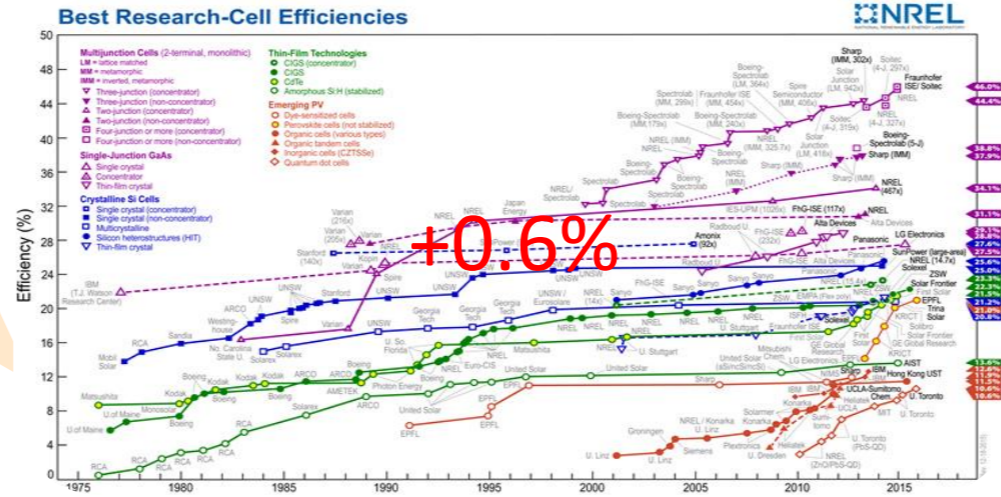
IPVF, UMR 9006, CNRS-X-ENSCP, Palaiseau, France

■ Nov. 2022



France : <45 €/MWh and >3% electricity production

25-45% Efficiency

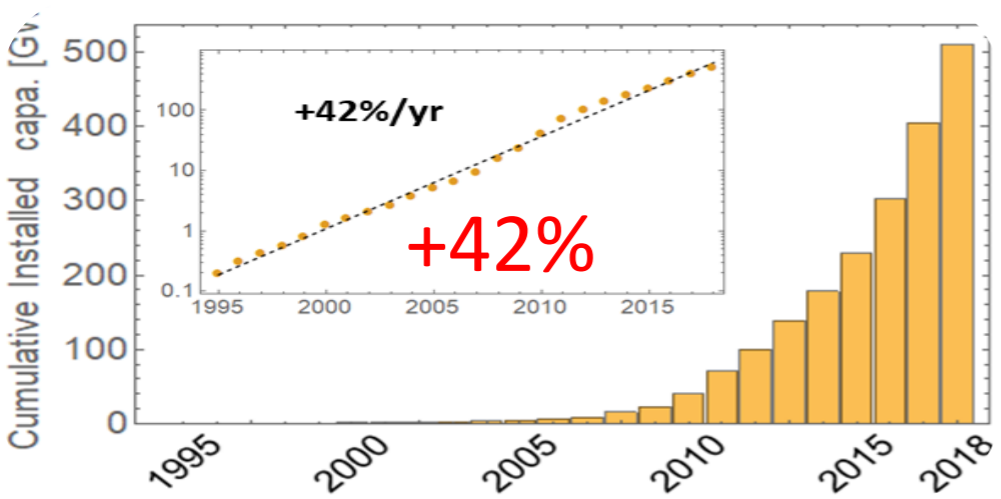


New challenges

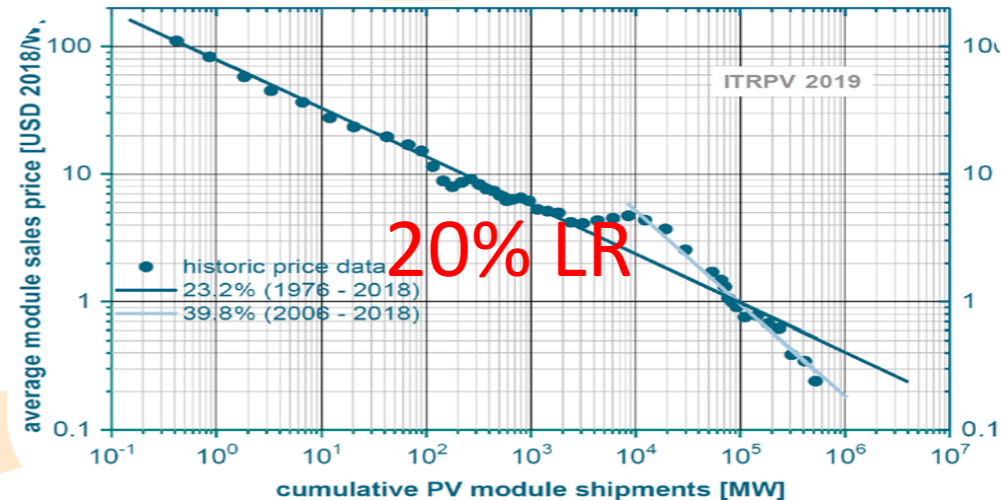
- TW scale
- Footprint and sustainability
- Reliability of the new technologies

A positive upward spiral worldwide

TW Volume

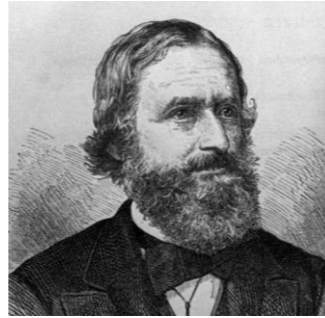
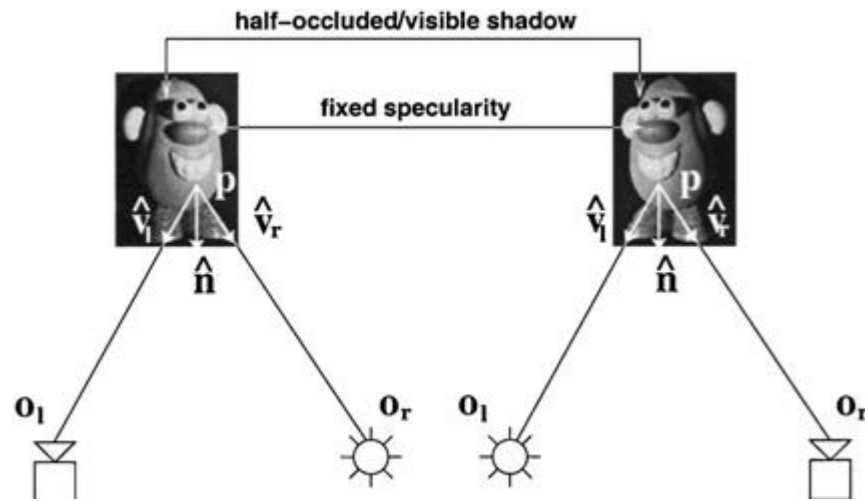


0.2 €/Wp Cost

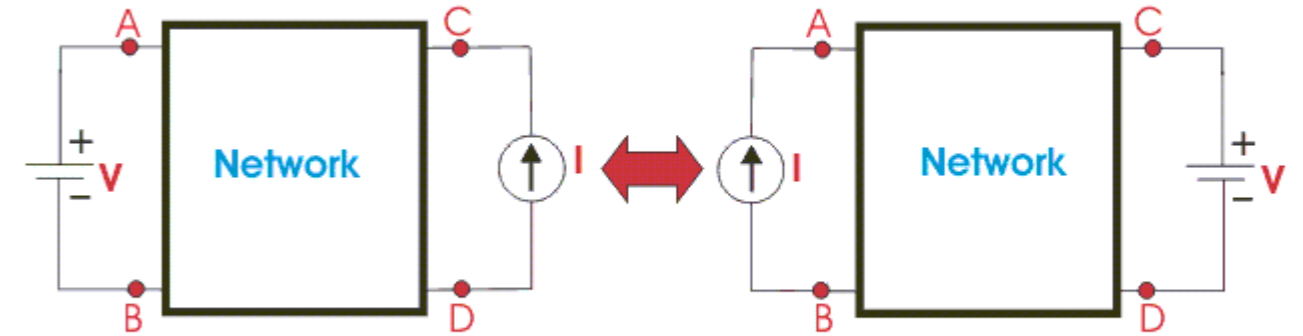


40% des modules sont installés depuis moins de 2 ans...

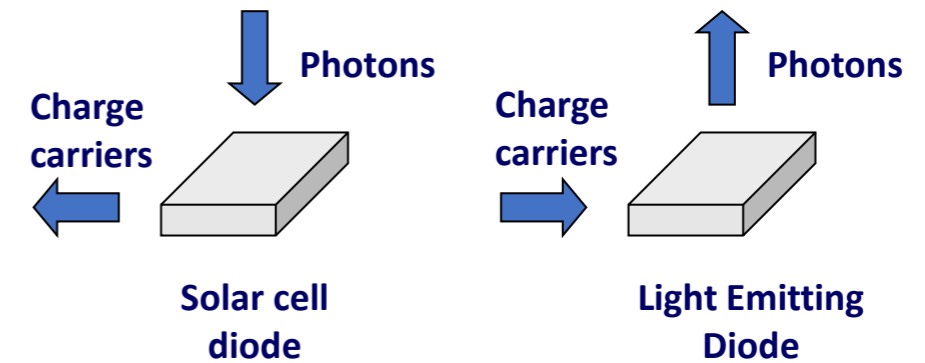
« What absorbs should emit »



Gustav Kirchhoff, 1859



- All related to exchange between causes and consequences
- All relevant to solar cell operation



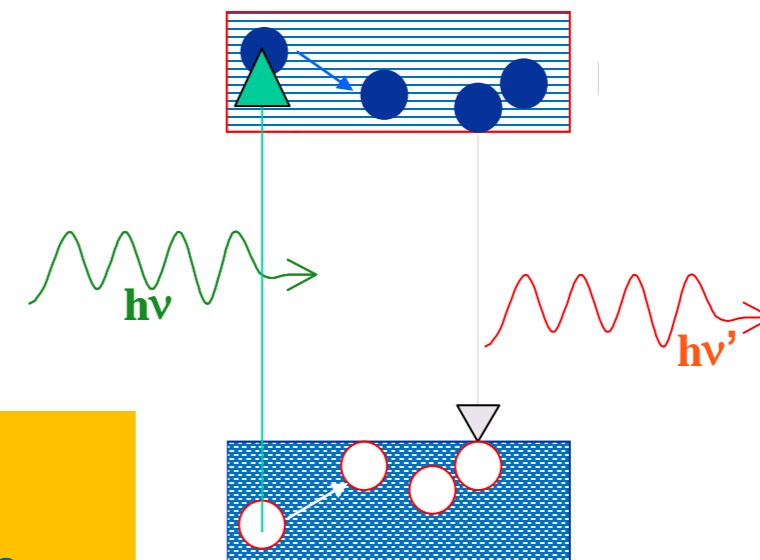
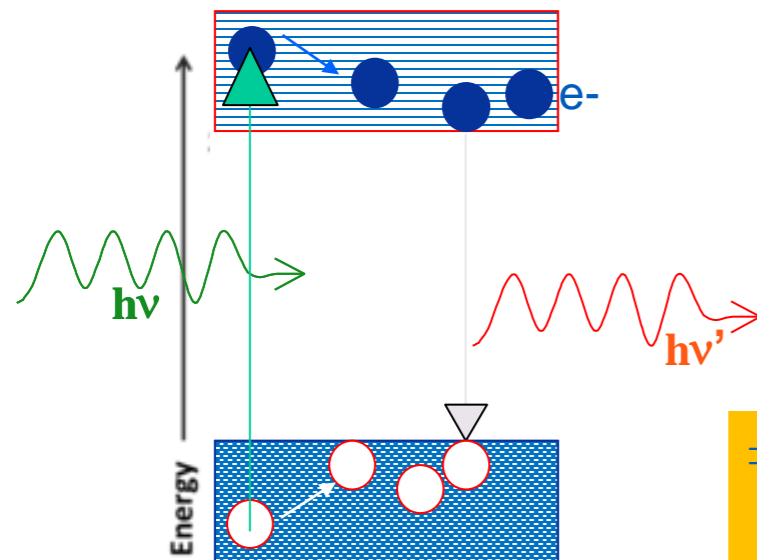
Why luminescence and Solar cells

Luminophore

- Light in: electrons promoted
- Excitations relax and wander around
- And disappear:
 - Radiatively => light out
 - Or not (heat)

Solar Cell

- Light in : electrons promoted
- Excitations relax and wander around
- And disappear:
 - Radiatively => light out
 - Or not (heat)
 - Or collected at electrodes/ Or not (Voc)



⇒ Both are energy conversion systems
⇒ Both are mostly described by the same physical phenomena

Reciprocity relationship and conversion of light

Exact relationships between related phenomena

Also:

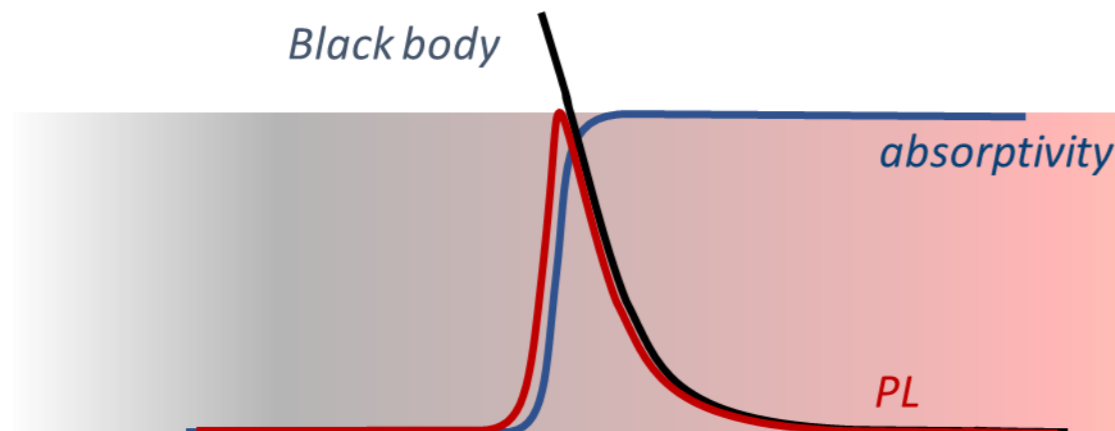
Stokes (1849) & Helmholtz (1856): optical reciprocity

Lorentz (1896): electromagnetic reciprocity

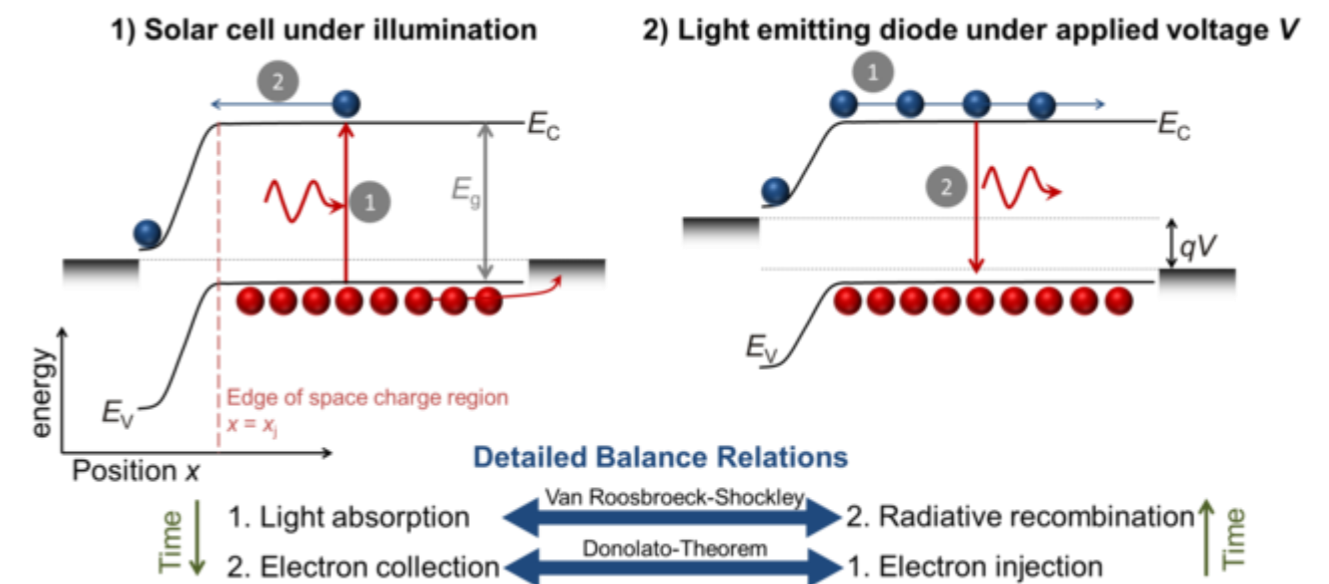
Max Planck (1900): Black Body radiation

Einstein (1917): Absorption, sp. & st. emission

Lars Onsager (1931) : microreversibility and reciprocity between fluxes and forces



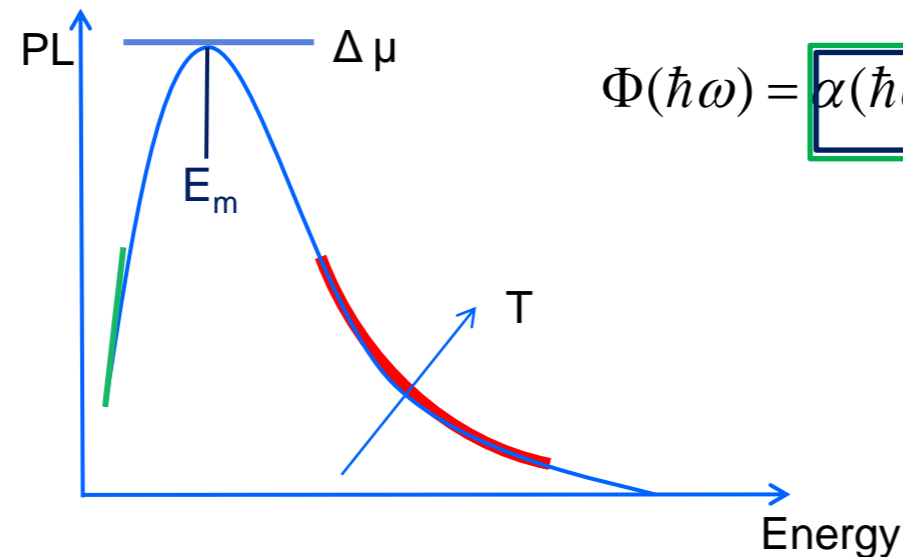
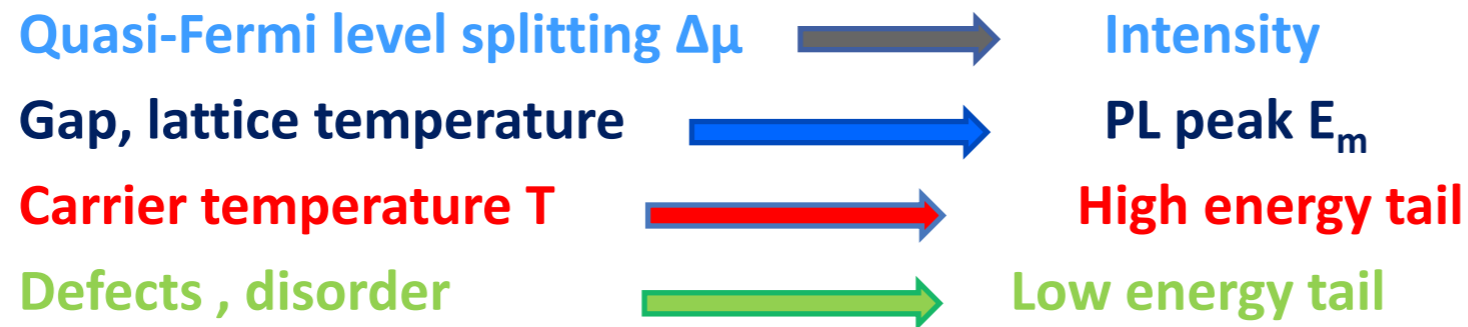
Absorption & Emission of photons, Injection & Collection of electrons: Reciprocity PV/LED



A long list of reciprocities in photovoltaics:
 Van Roesbroek 1954, Wurfel 1980, Donolato 1985,
 Araujo 1994, MA Green 1997,
 U. Rau 2007,
 Wong 2012, JJ. Greffet 2018

Use of quantitative light emission from solar cells

Exact relationships between phenomena



Generalized Planck law:

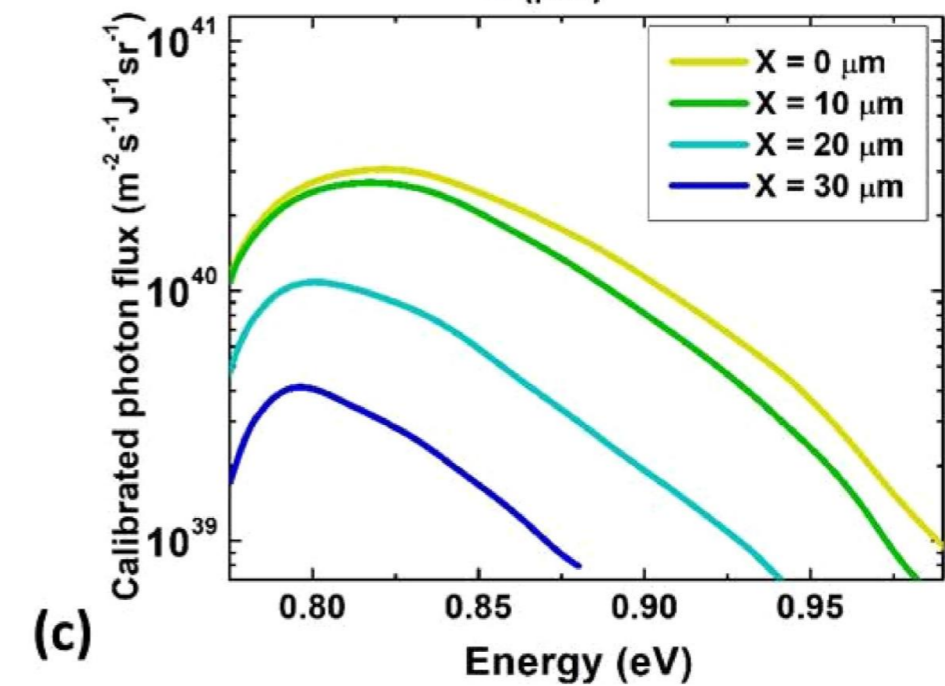
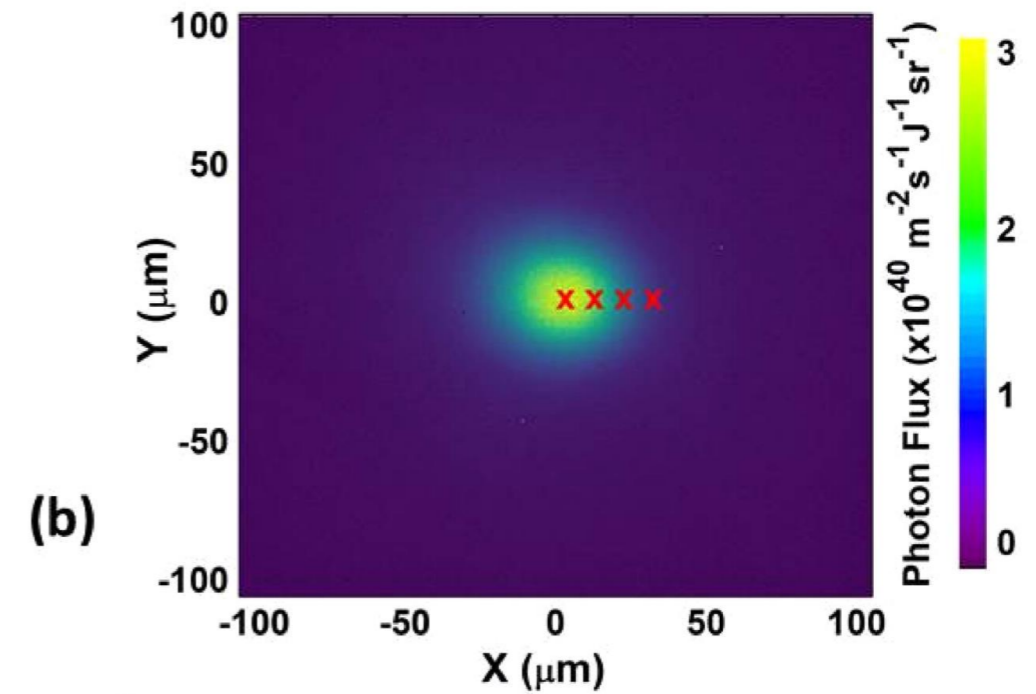
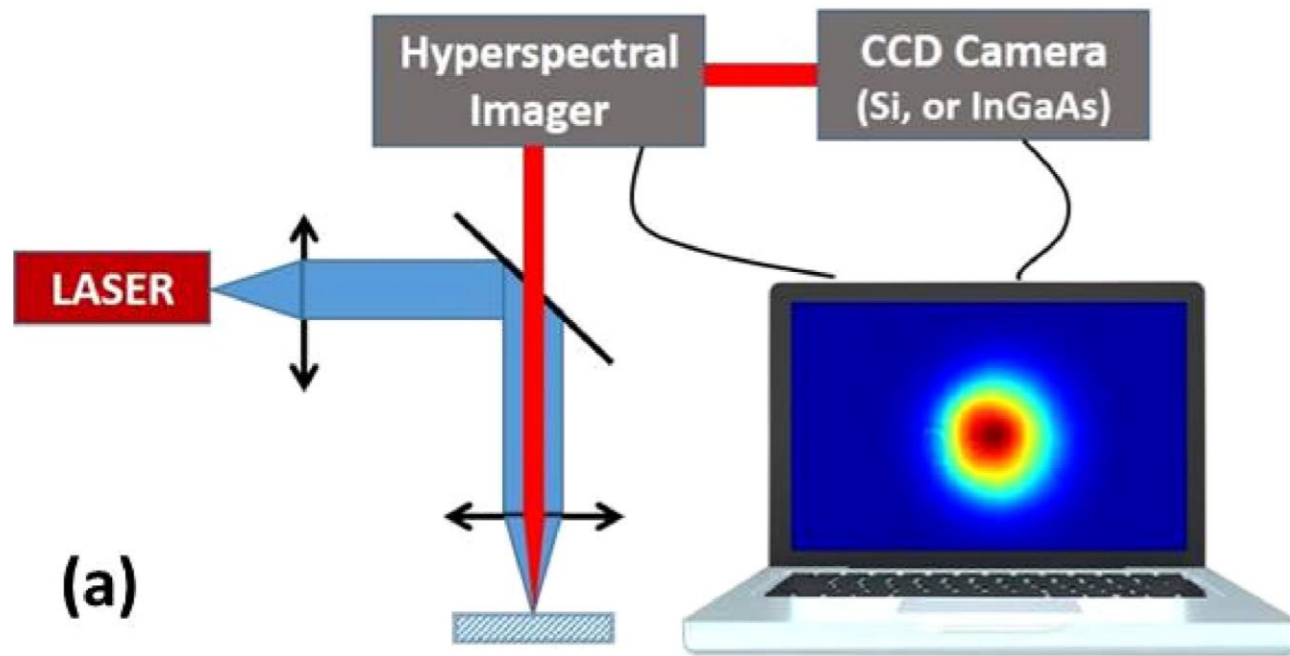
$$\Phi(\hbar\omega) = \alpha(\hbar\omega) \frac{\Omega}{4\pi^3 \hbar^3 c_0^2} (\hbar\omega)^2 \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{kT}\right) - 1}$$

$$\Delta\mu \approx qV$$

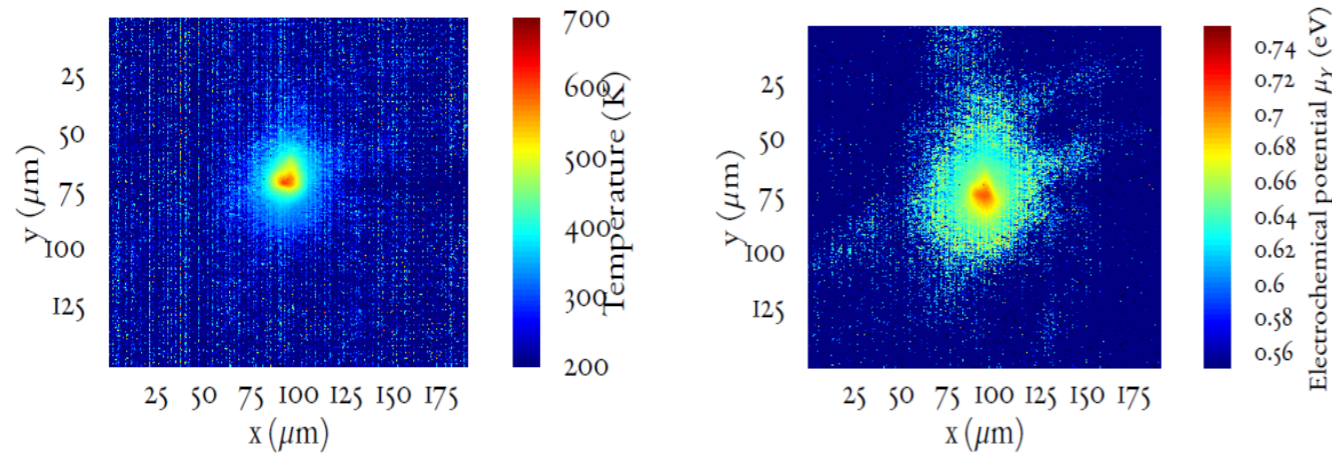
(free energy/particle)

T & $\Delta\mu$ are the thermodynamic variables for the energy conversion process

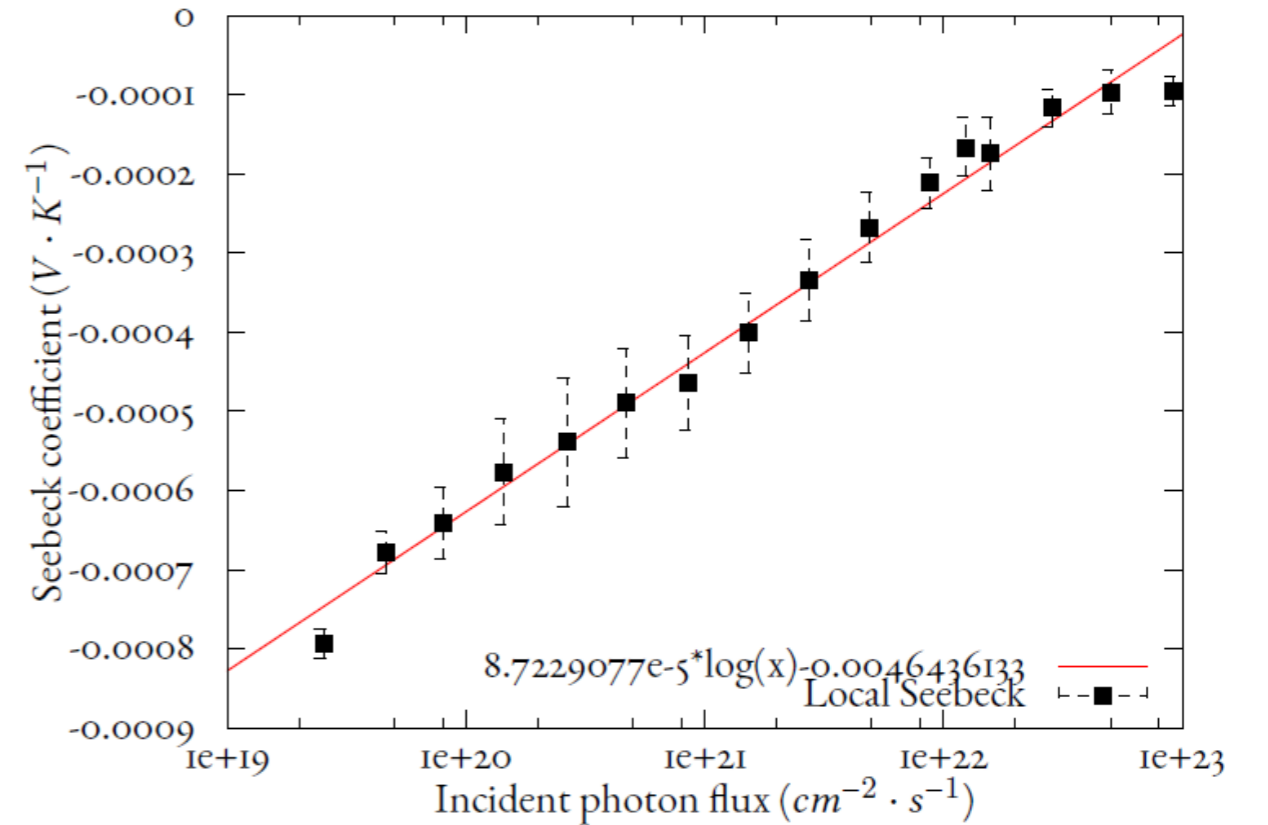
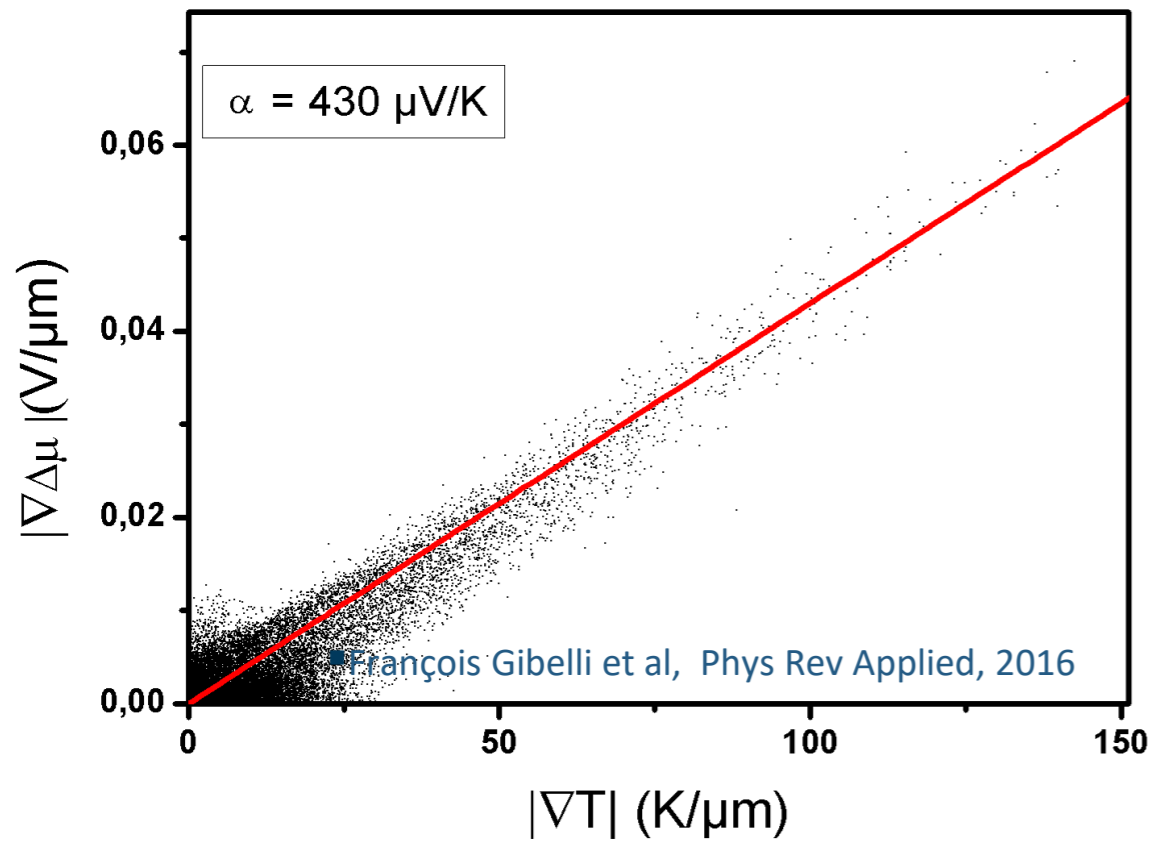
Transport properties measurement



Transport properties measurement



$$\mathcal{S} = \frac{\vec{\text{grad}}\mu_\gamma}{\vec{\text{grad}}T} \iff \vec{\text{grad}}\mu_\gamma = f(\vec{\text{grad}}T)$$



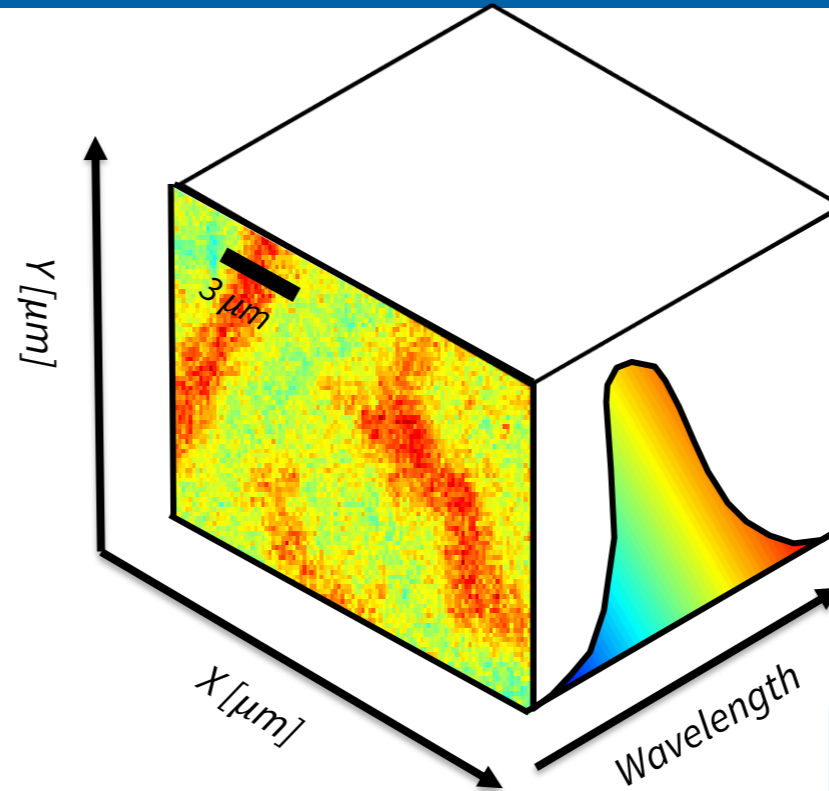
Ambipolar thermoelectric measurement, locally!

Device optimization at each fabrication step

- Contactless
- Non-destructive
- Local properties
- Method suitable for all PV absorbers

Imaging systems

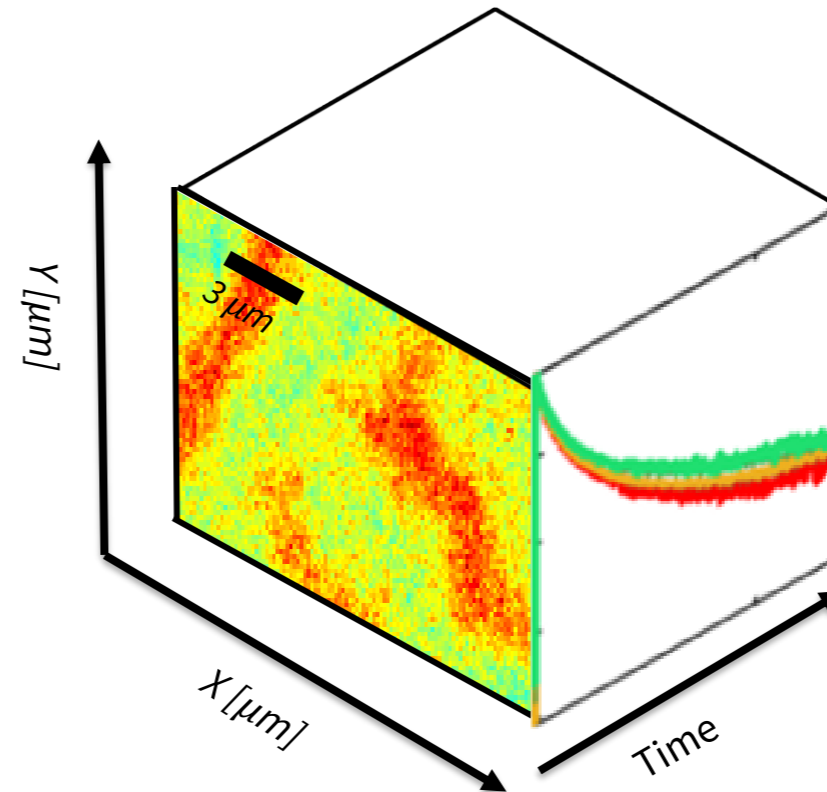
- Hyperspectral imager
 - Spectral & Spatial
- Time-resolved fluorescence imaging
 - Temporal & Spatial



Hyperspectral imager

- $I_{PL}(x,y,\lambda)$
- Spectral resolution : 2 nm
- Spatial resolution : 1 μm (mega pixel)

Studying device operation (CW, RT, ...)



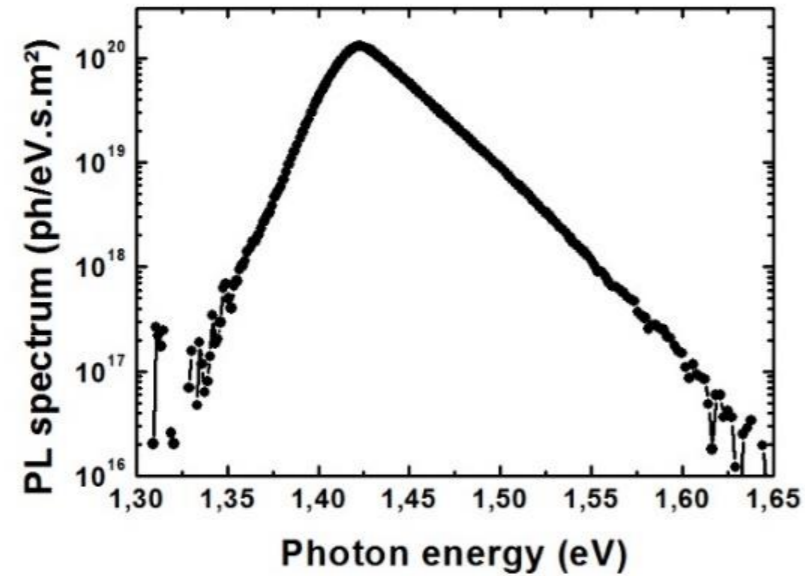
Time-resolved fluorescence Imaging

- $I_{PL}(x,y,t)$
- Time resolution : 250 ps
- Spatial resolution : 1 μm (mega pixel)

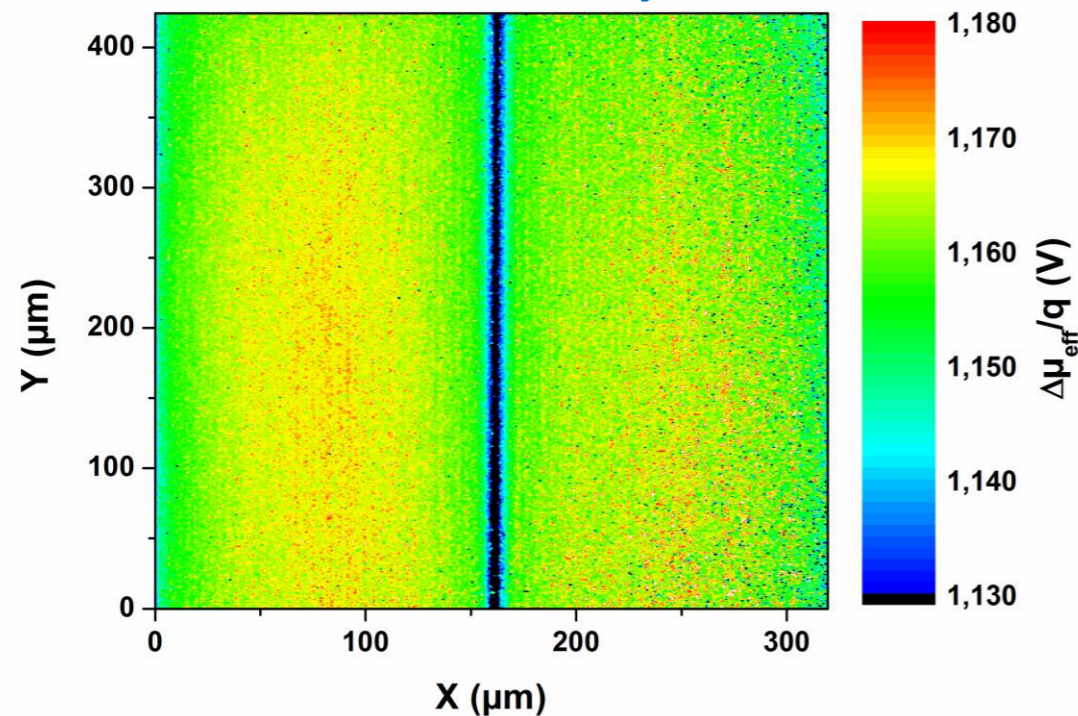
Studying Kinetic parameters

Proof of concept

Spectral information



Extracting $\Delta\mu$



$$\Phi_{\text{PL}}(E) = \frac{A(E)E^2}{4\pi^2 \hbar^3 c_0^2} \frac{1}{\exp\left(\frac{E - \Delta\mu}{kT}\right) - 1}$$

$$\Delta\mu_{\text{eff}} / q \approx V_{\text{OC}}$$

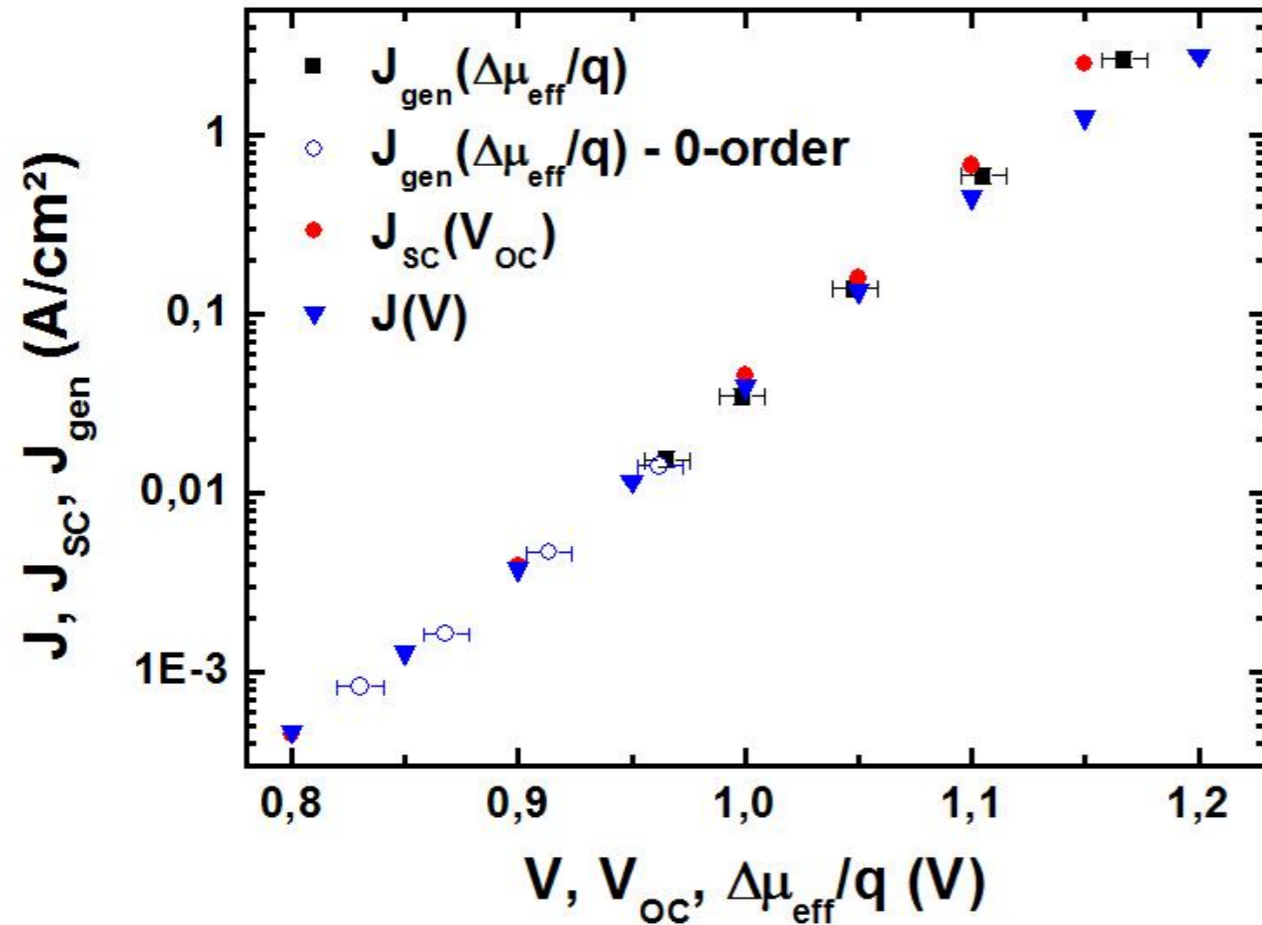
	Optical $\Delta\mu_{\text{eff}}/q$	Electric V_{OC}
GaAs	1,164 V	1,149 V
CIGS	0,808 V	0,801 V
Halide Perovskite	1,030 V	1,017 V

Delamarre et al. Appl. Phys. Lett. 100, 131108 (2012)

A. Delamarre et al., JAP 2014

Gilbert El-Hajje, et al., Energy & Environmental Science, 2016, 9, 2286 - 2294

Measuring non radiative recombination by PL



Proof of concept: Optical measurements of $I_{sc}(V_{oc})$ curve on GaAs cell

$$j_{rec} = j_{01} \exp\left(\frac{qV}{kT}\right) + j_{02} \exp\left(\frac{qV}{2kT}\right)$$

Measurement method	j_{01} (A/m ²)	j_{02} (A/m ²)
PL with HI	$(1.8 \pm 0.6) \times 10^{-16}$	$(8.9 \pm 1.5) \times 10^{-7}$
j(V)	$(7.4 \pm 0.1) \times 10^{-16}$	$(5.6 \pm 0.7) \times 10^{-7}$

- Efficiency with 5% rel. error
- Measuring all recombination mechanisms with PL

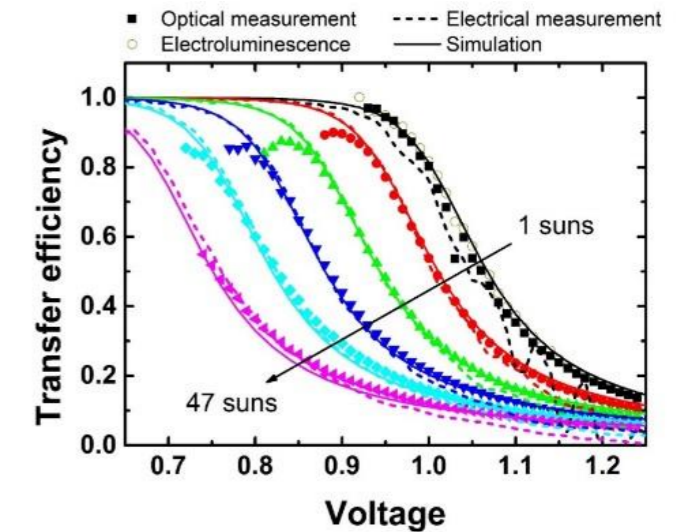
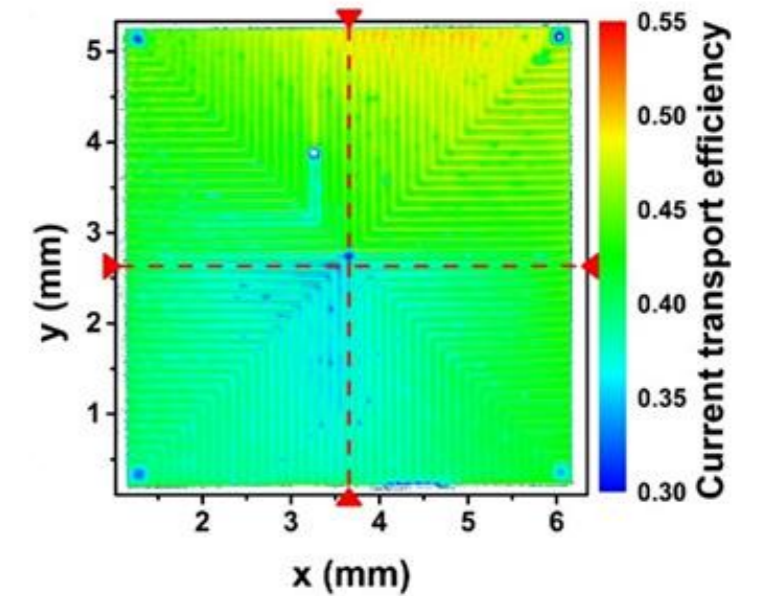
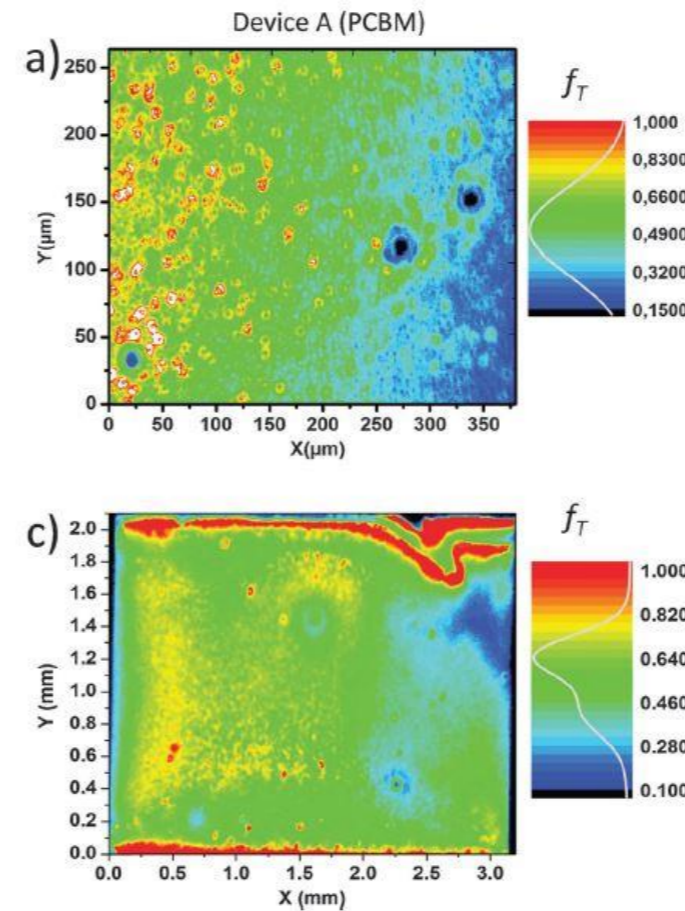
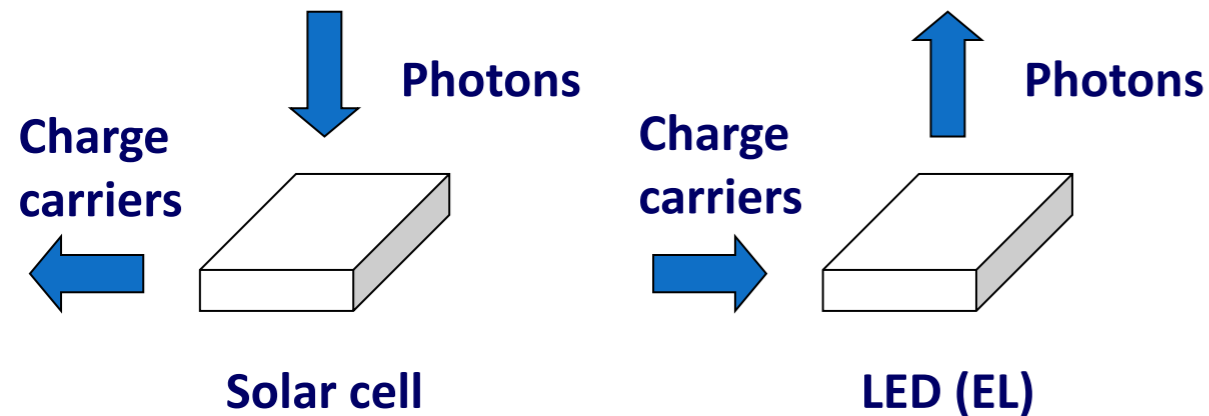
HI on full stack : optically extracting electric parameters

Collection efficiency f_T determined from EL images at incremental voltages

$$f_T(x, y) \approx \frac{kT}{q} \frac{\partial \ln \Phi_{EL}(E, V, x, y)}{\partial V}$$

J. Wong and M. Green, Phys. Rev. B 85, (2012)

- Microscopic and macroscopic inhomogeneities revealed on evaporated perovskite solar cells



El-Hajje et al., Energ. Env. Sci. (2016).

Amaury Delamarre, et al. IEEE Journal of Photovoltaics 2016, 6 (2), 528-531

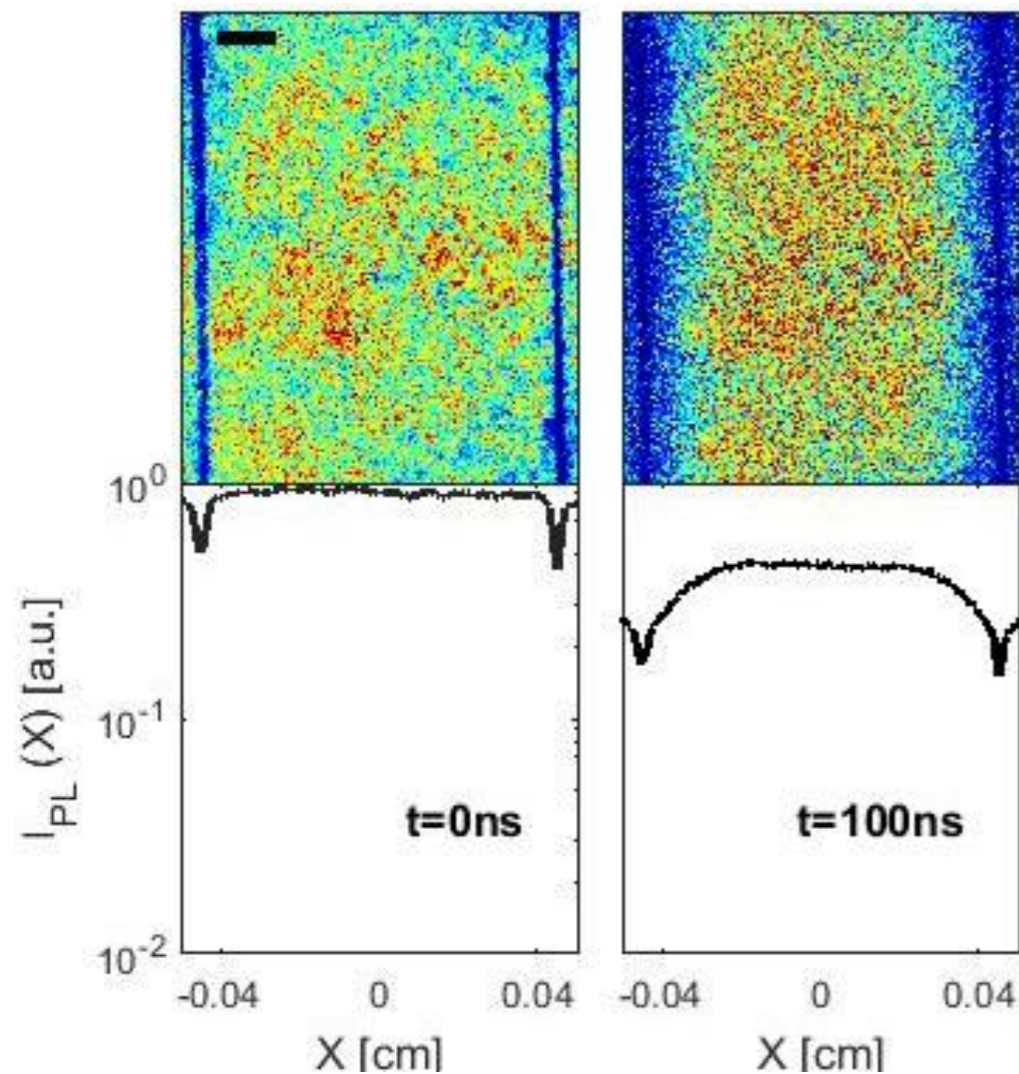
Access to transport efficiency and superposition assumption

TR-FLIM : Proof of concept

Output : time-resolved PL maps

- 1D symmetry → Time-resolved PL profiles

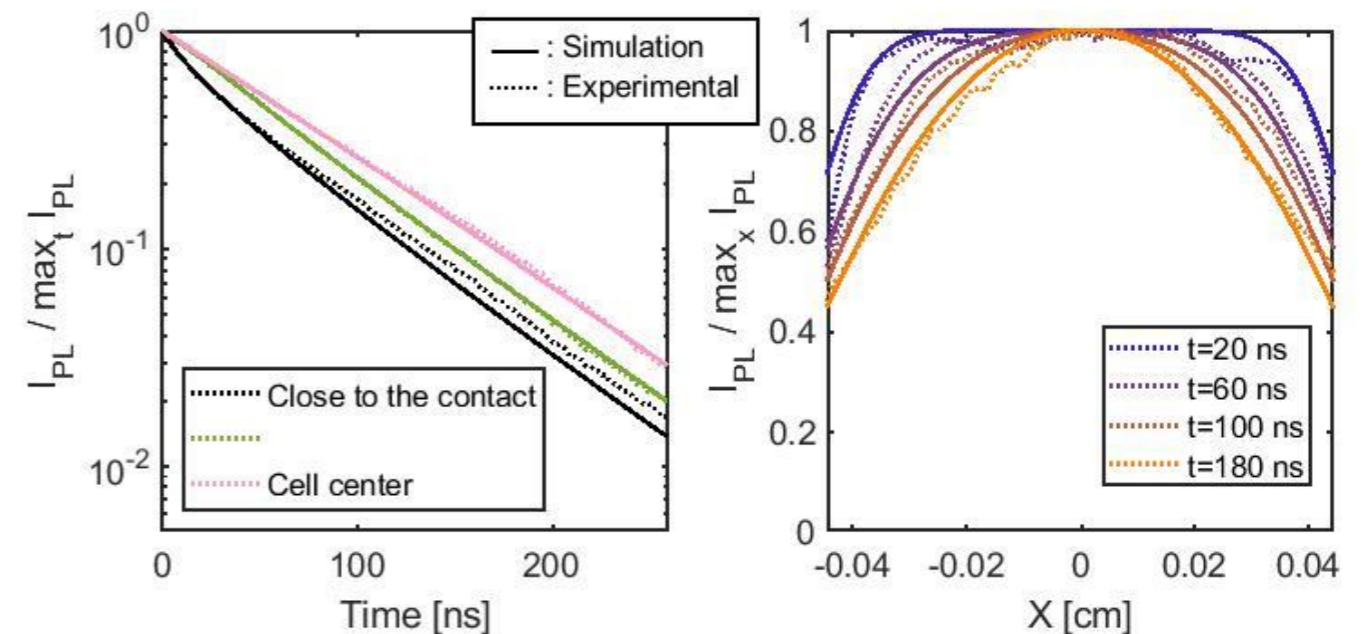
GaAs



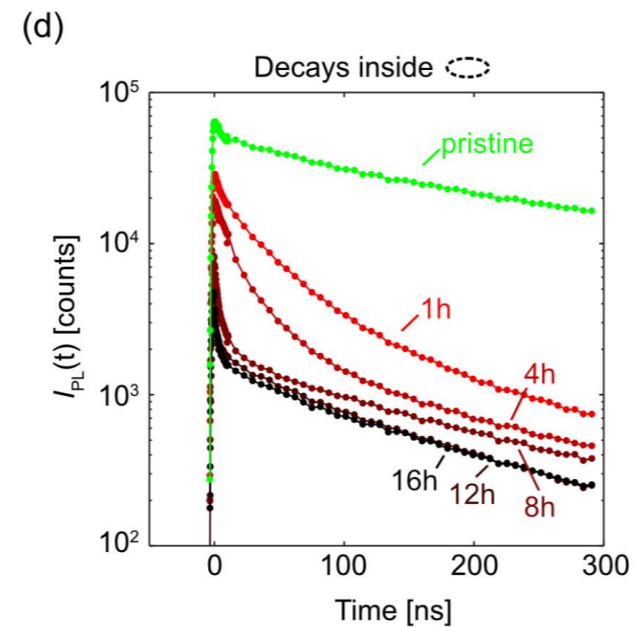
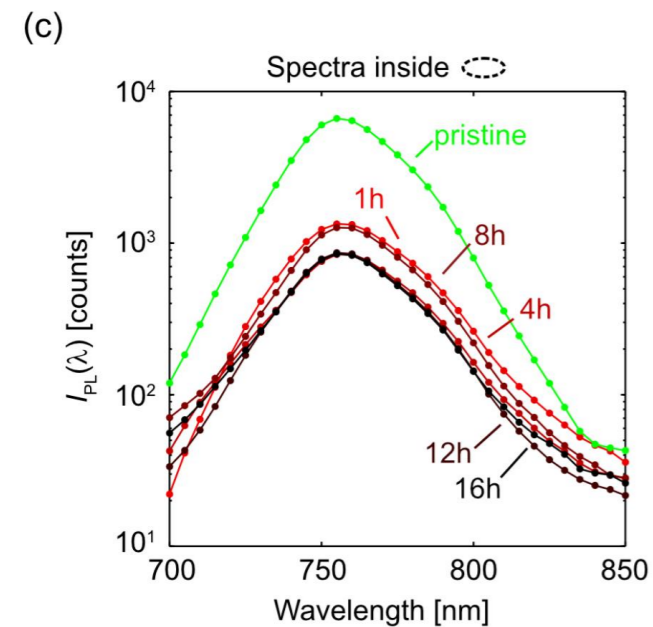
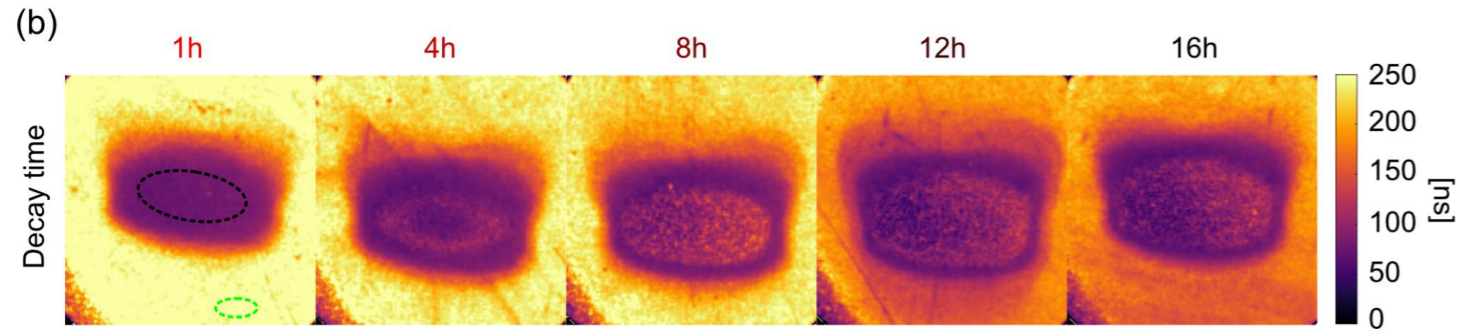
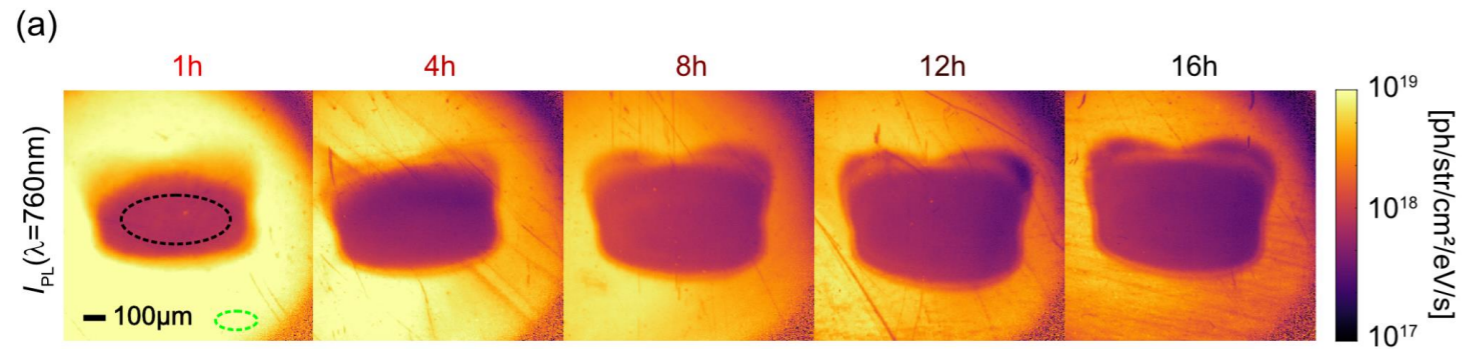
Access to transport parameters

- Bulk lifetime $\tau_n = 75 \pm 1\text{ ns}$
- Lateral rec. $S_n = (1 \pm 0.1) \times 10^5\text{ cm/s}$
- Lateral diff. $L_{\text{eff}} = 200 \pm 10\ \mu\text{m}$
- Photon recycling

... With a single experiment



Degradation studies



Degradation of the perovskite opto-electronic properties at different X-ray exposure times.

(a) PL intensity maps at 760 nm from the steady-state experiment

(b) Decay time fitted between $t=100\text{ns}$ and $t=300\text{ns}$ after the laser pulse in the pulsed experiment. The exact same regions are imaged on the two setups. The dotted ellipses represent the regions of interest used for the computation of the averaged spectra and decays.

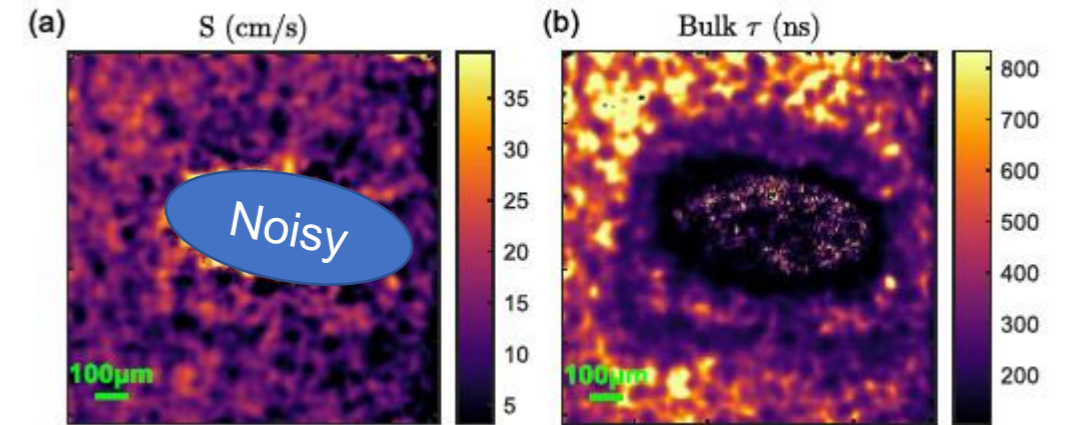
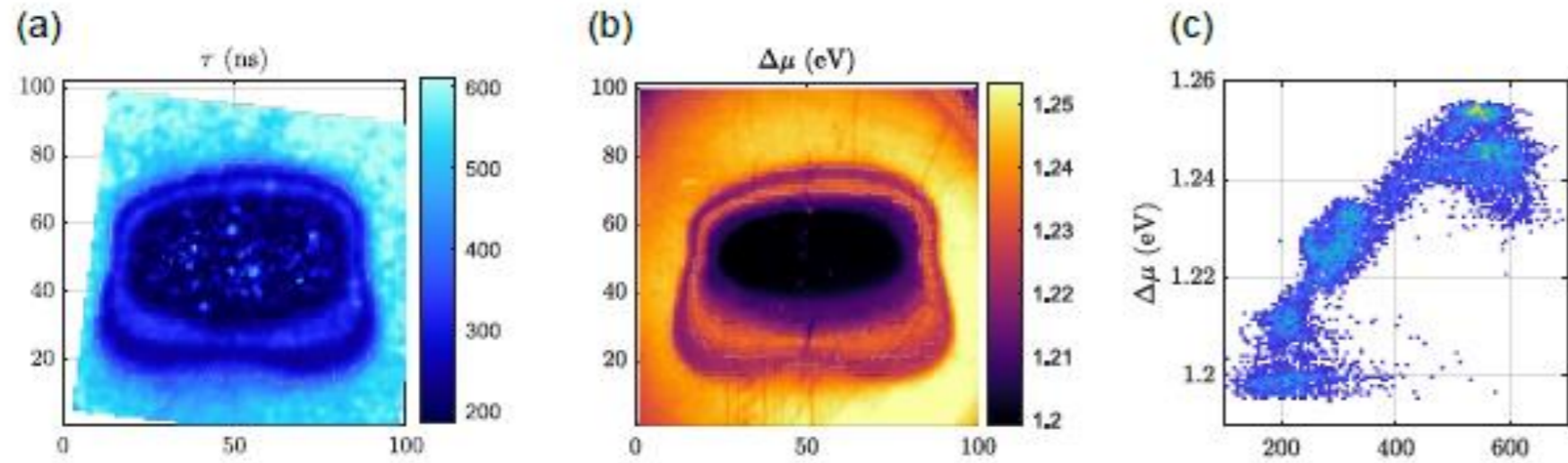
(c) PL spectra inside the damaged area (black ellipse in (a)) and pristine sample (green ellipse in (a)) for different exposure times.

(d) Decays inside the damaged area (black ellipse in (b)) and pristine sample (green ellipse in (b)) for different exposure times.

Correlation lifetime and Voc

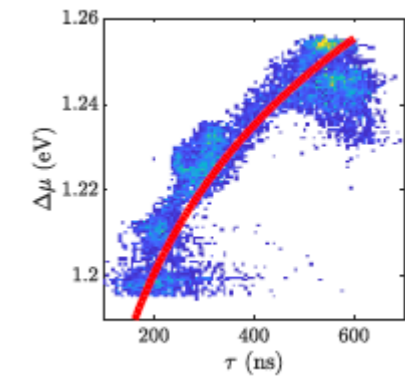
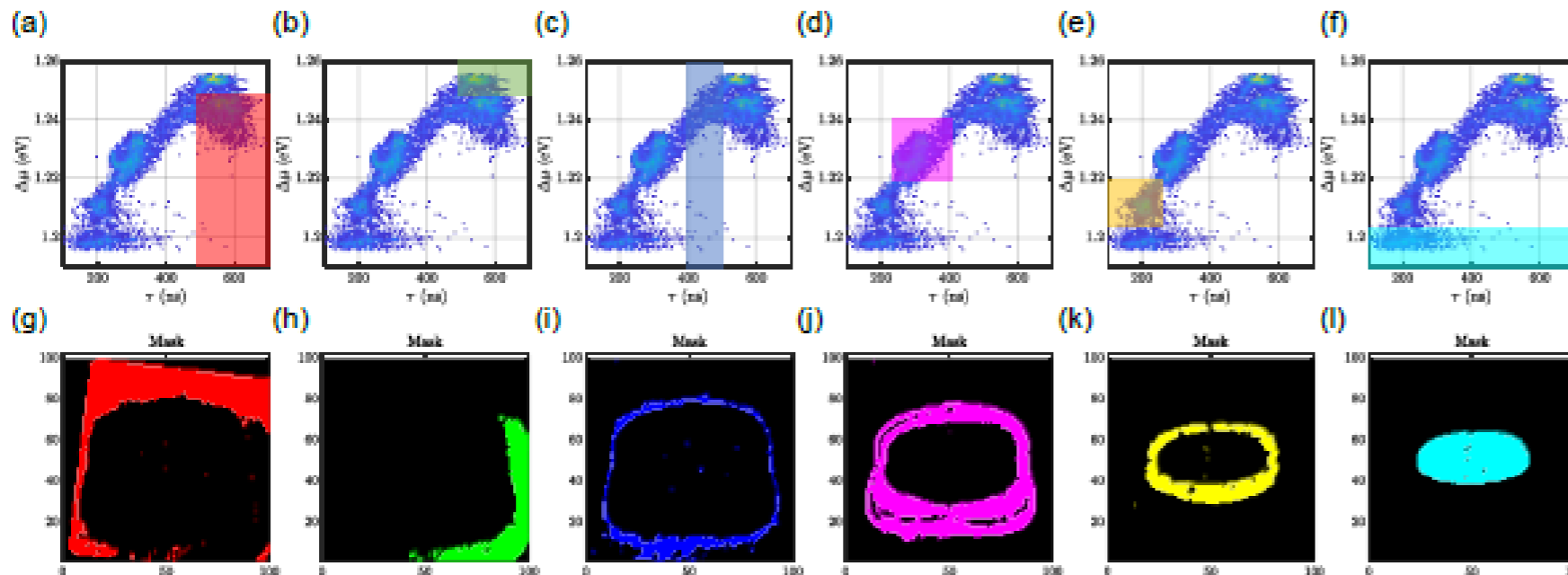
X-Ray damage => CW and TRPL image correlations

Bulk recombinations increases



$$\Delta\mu = 2kT \ln\left(\frac{G}{n_1} \tau_{tr}\right)$$

$$n_1 \approx 3 \times 10^3 \text{ cm}^{-3}$$



Local correlation
No free parameter

Absorption: required for photoluminescence interpretation

Classical techniques

- Not always relevant to our experimental conditions
- Rarely provides imaging



Generalized Planck's law

$$I_{PL}(z, E_{emit}) = A(E_{emit}) * \frac{2\pi}{\hbar^3 c_0^2} * \frac{E^2}{\exp\left(\frac{E - \Delta\mu(z)}{k_B T}\right) - 1}$$

Absorptivity

[1]

Grey body radiation

$$\Delta\mu(z) = f(A(E_{excit}))$$

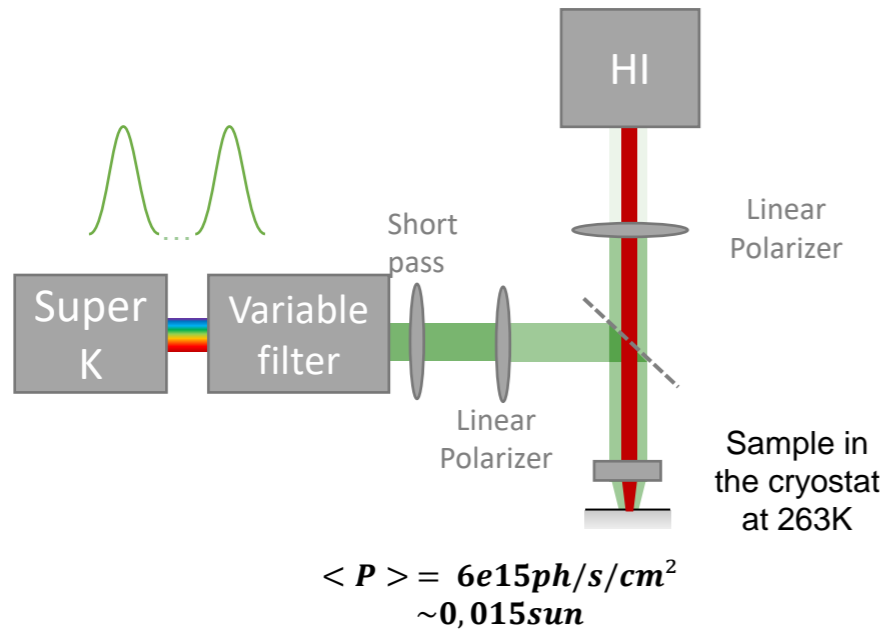
Photoluminescence
Excitation (PLE)

Challenges

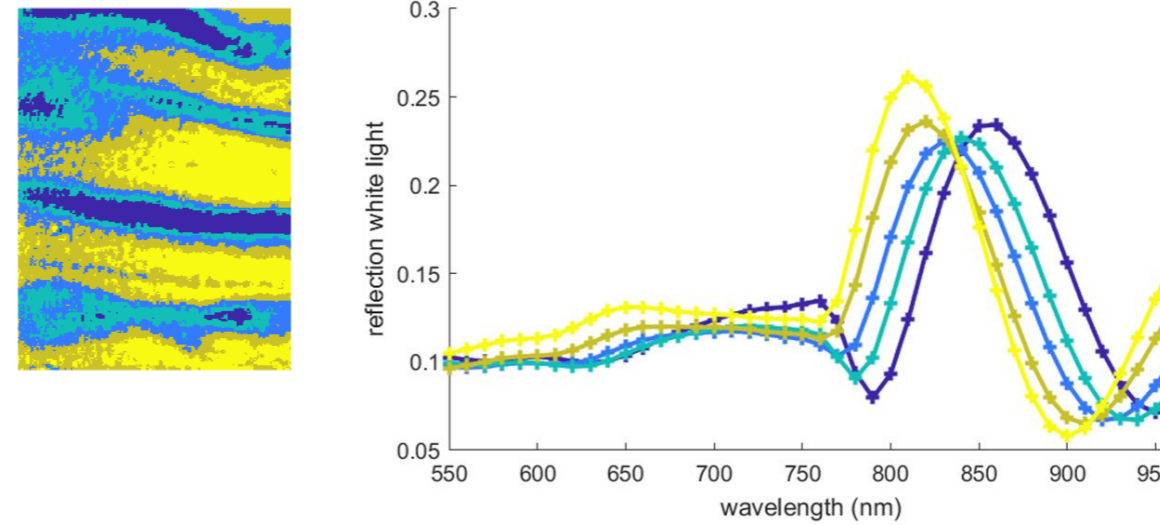
- Small absorption values both critical and hard to measure
- Disentangle influences of layers and texturing

[1] Daub, E. & Würfel, P. Ultralow Values of the Absorption Coefficient of Si Obtained from Luminescence. *Phys. Rev. Lett.* **74**, 1020–1023 (1995).

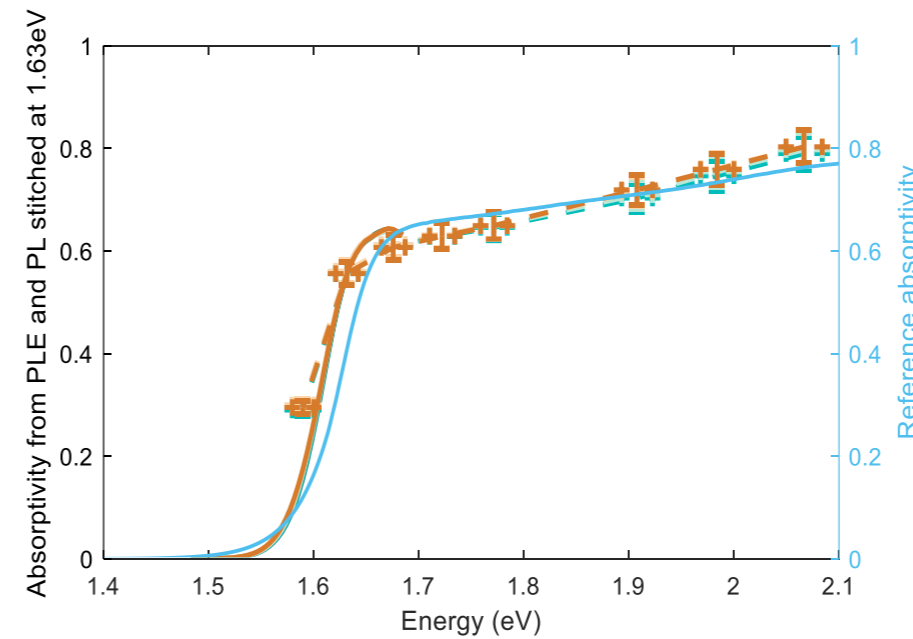
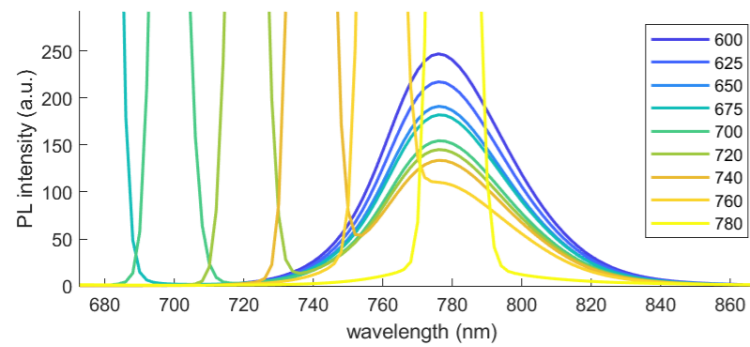
Experimental results on halide perovskite



PLE spectra & Reflectivity maps



PL spectra for different excitation wavelengths



Acknowledgements

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