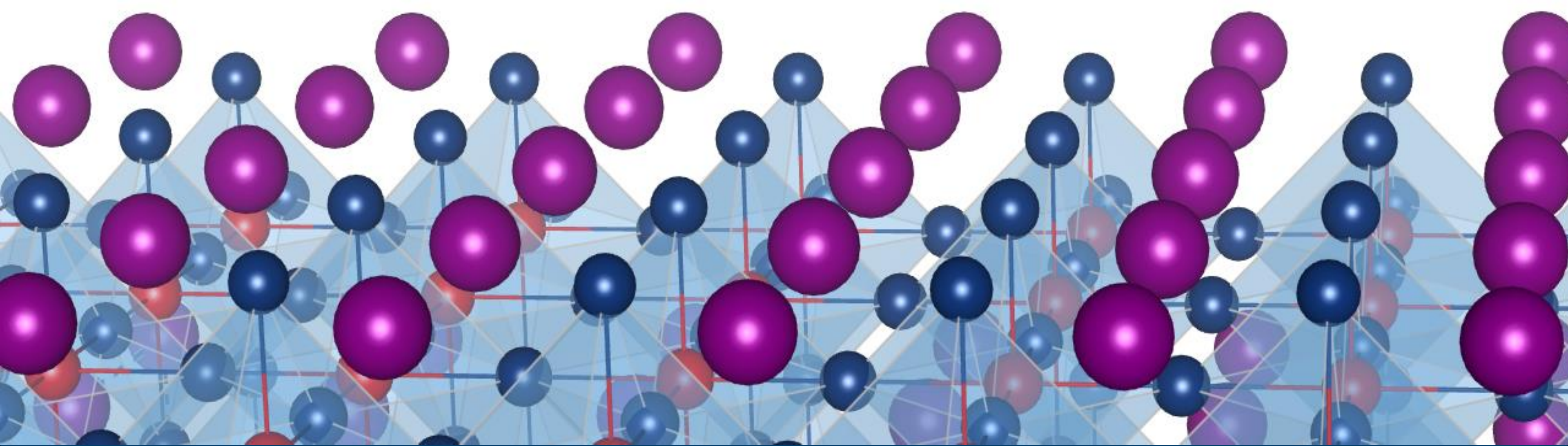


OPTOELECTRONIC DEVICE PHYSICS

QUANTIFYING RECOMBINATION LOSSES

Thomas Kirchartz, Lisa Krückemeier

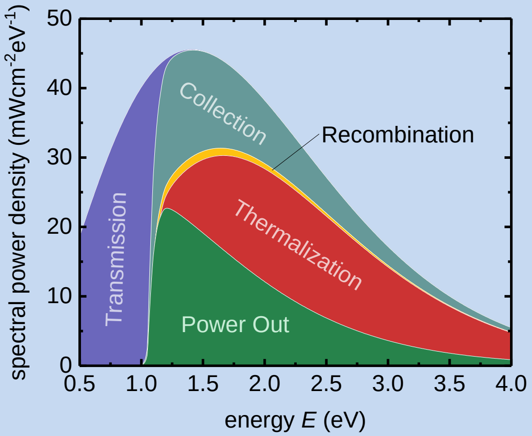
[1]IEK-5 Photovoltaik, Forschungszentrum Jülich,

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

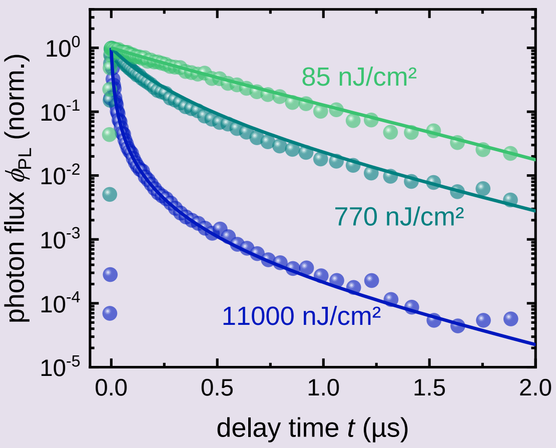
JÜLICH Forschungszentrum

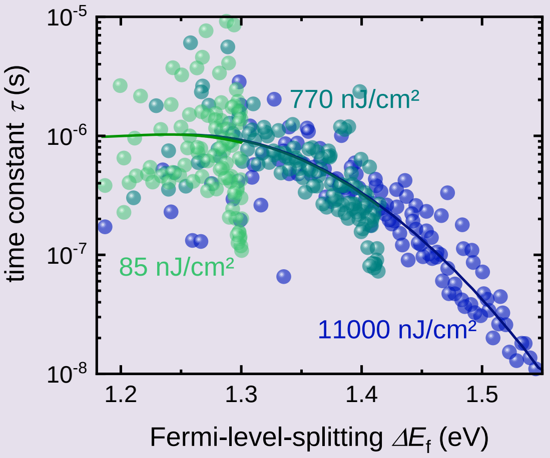
Outline

Functionality of Solar Cells – Main Losses

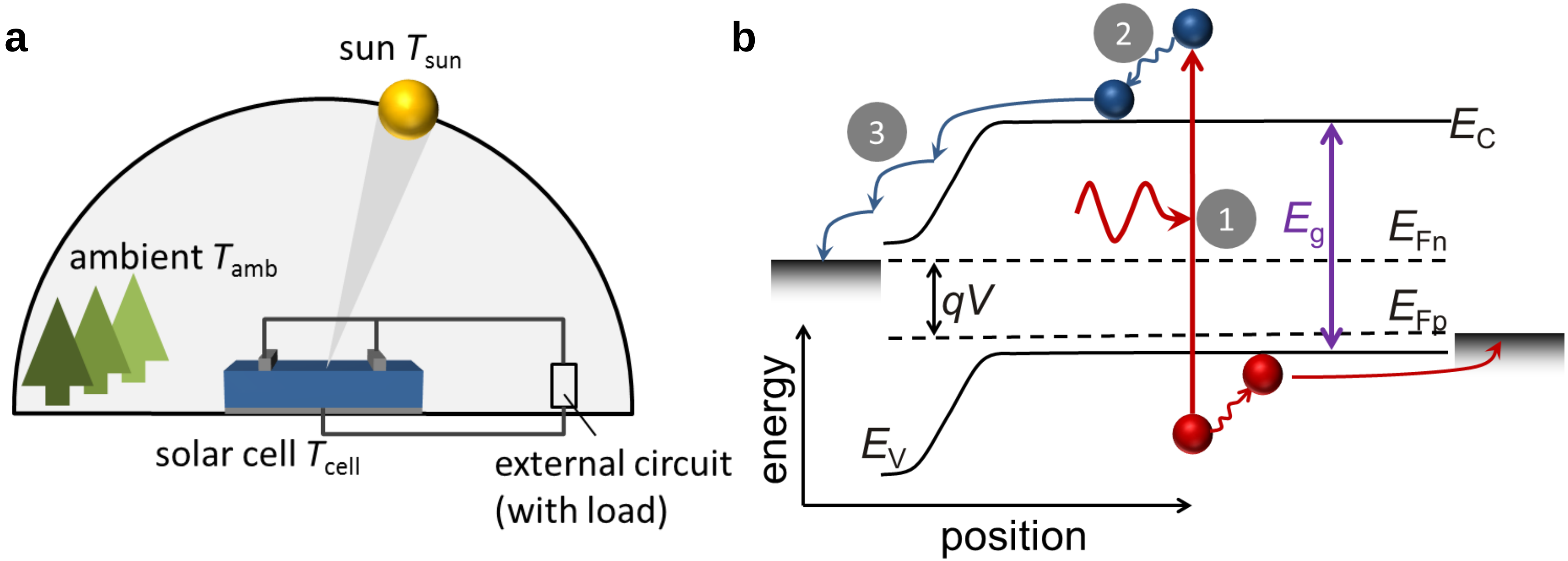


Characterizing Interface Losses by Photoluminescence





Photovoltaic Mechanism

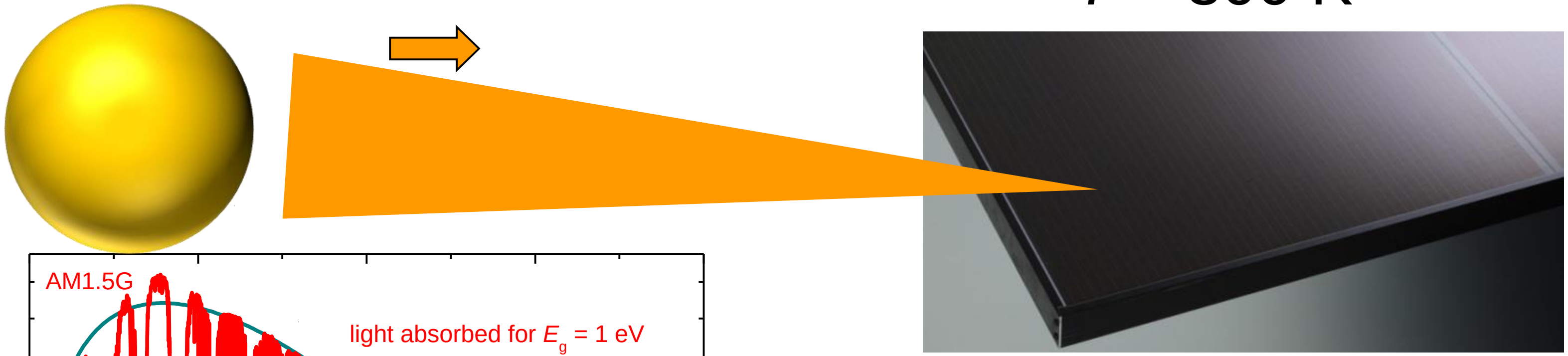


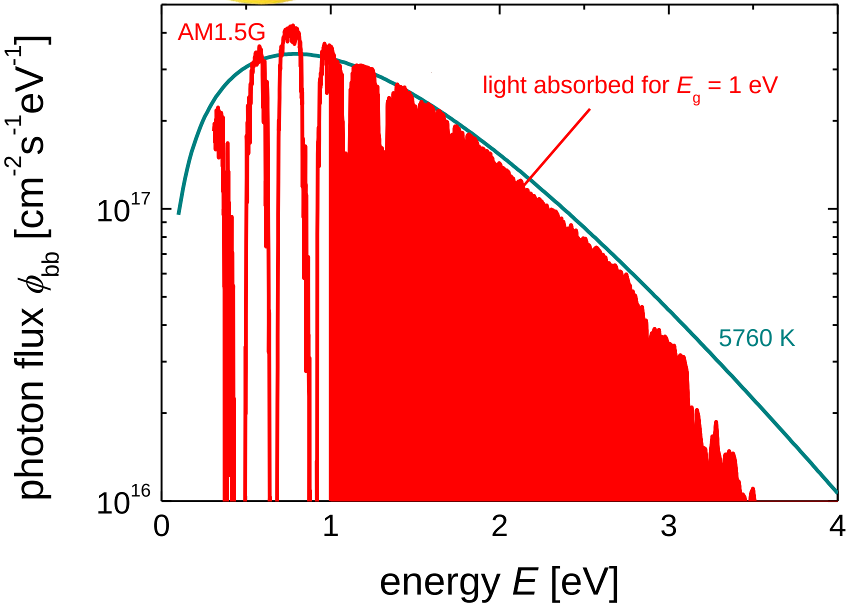
Guillemoles et al. Nat. Photonics (2019)

Step-Function Like Absorptance

$T = 5760$ K

$T = 300$ K





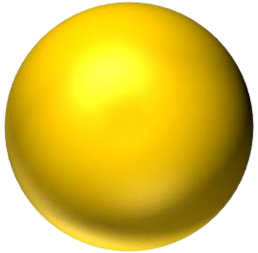
$$J_{sc} = q\int a(E)\phi_{sun}(E)dE$$

solar spectrum $\phi_{sun}(E)$

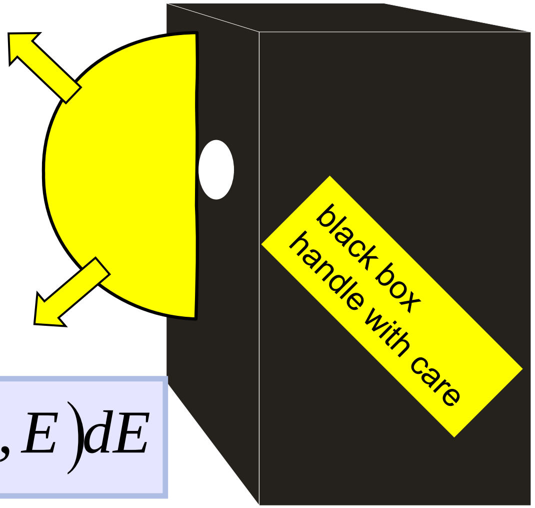
absorptance $a(E)$

Solar cell → Sun

$T = 5760$ K



$T = 300$ K



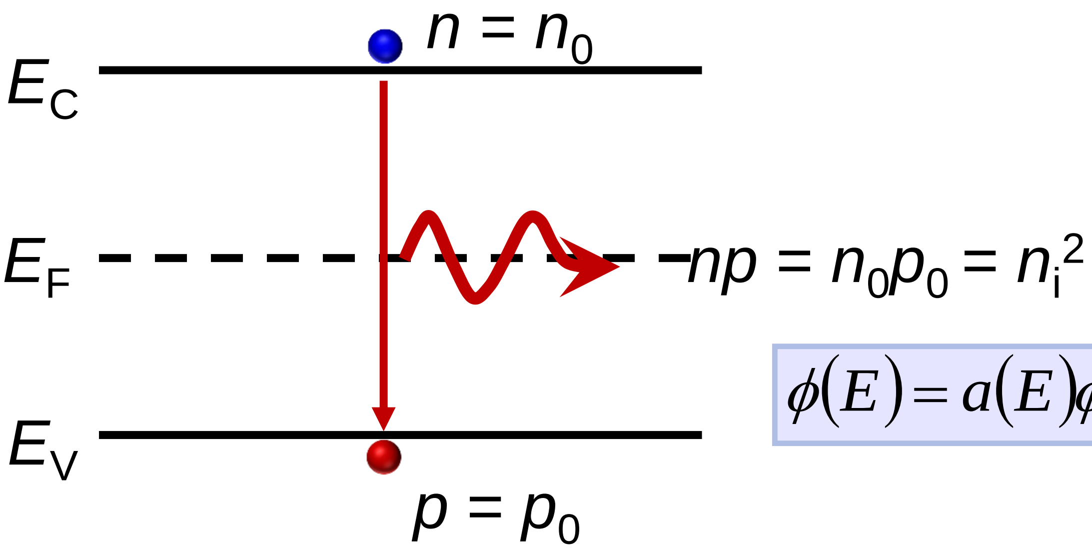
$$J_{0,\mathrm{em}} = q\int a(E)\,\phi_{\mathrm{bb}}(T_{\mathrm{sc}}, E)\,dE$$

Elementary charge q

Black body spectrum $\phi_{\mathrm{bb}}(E)$

absorptance $a(E)$ = emissivity $e(E)$

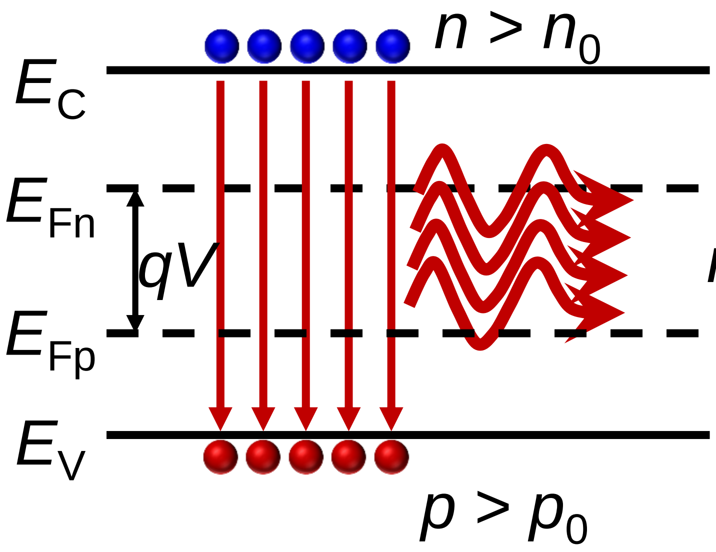
Radiative Recombination



$$\boxed{\phi(E) = a(E)\phi_{bb}(E)}$$

equilibrium

Radiative Recombination

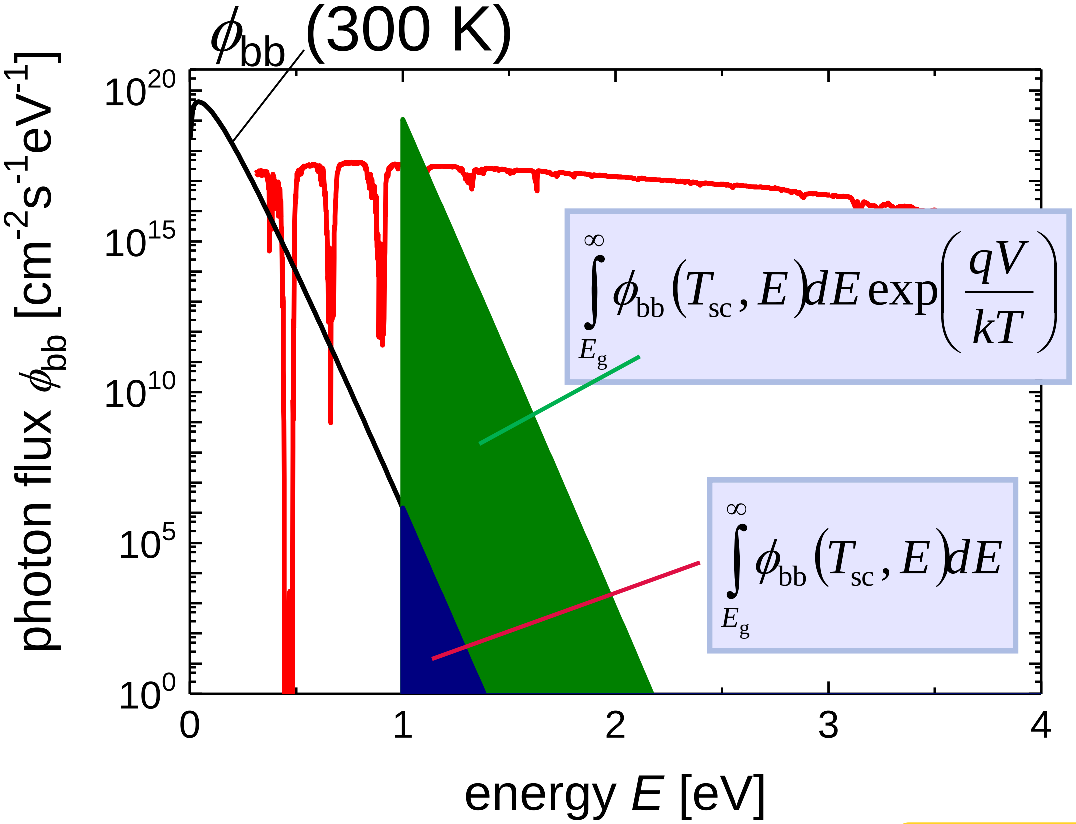


$$np = n_i^2 \exp(qV/kT)$$

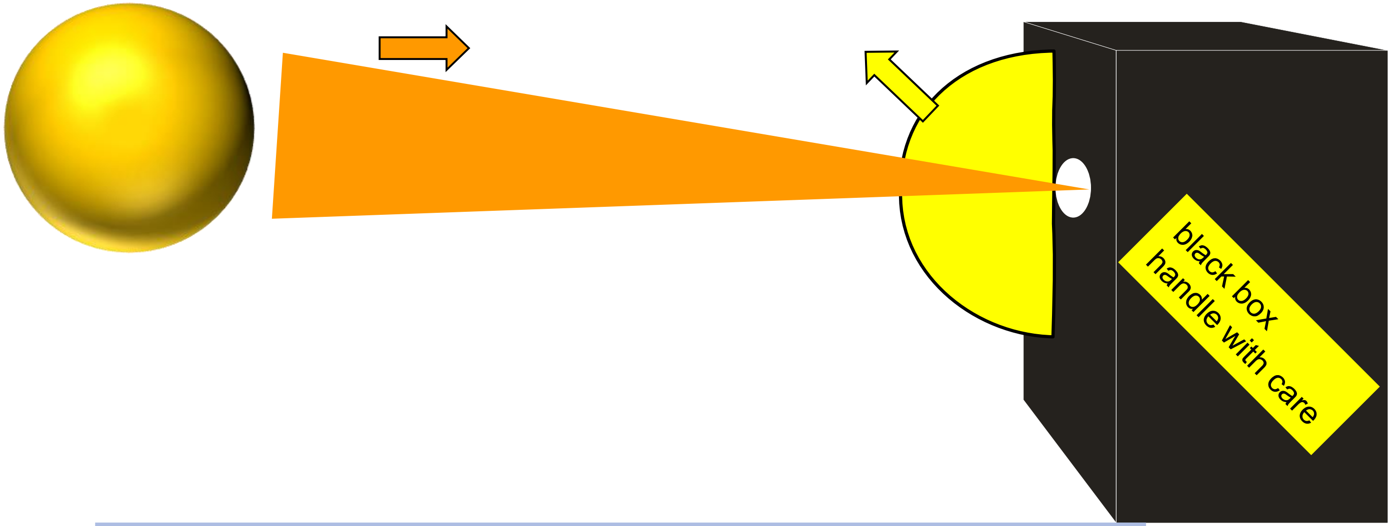
$$\boxed{\phi(E) = a(E)\phi_{bb}(E)e^{qV/kT}}$$

Non-equilibrium

Balance Between Generation and Recombination



The Current-Voltage Curve

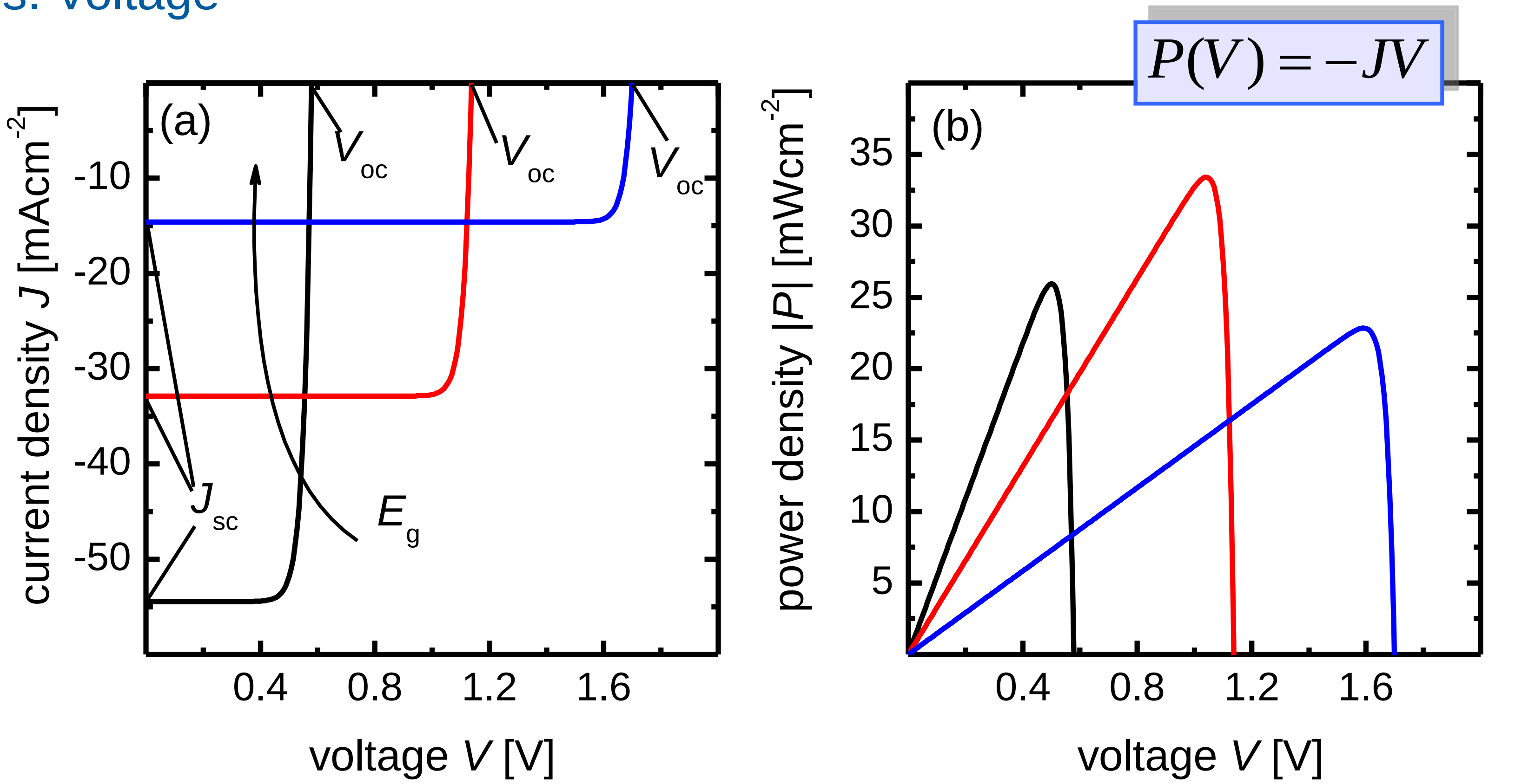


$$J = J_{\mathrm{d}} - J_{\mathrm{sc}}$$

$$= q\int a(E)\phi_{\mathrm{bb}}(T_{\mathrm{sc}}, E)dE\left[\exp\left(\frac{qV}{kT}\right) - 1\right] - J_{\mathrm{sc}}$$

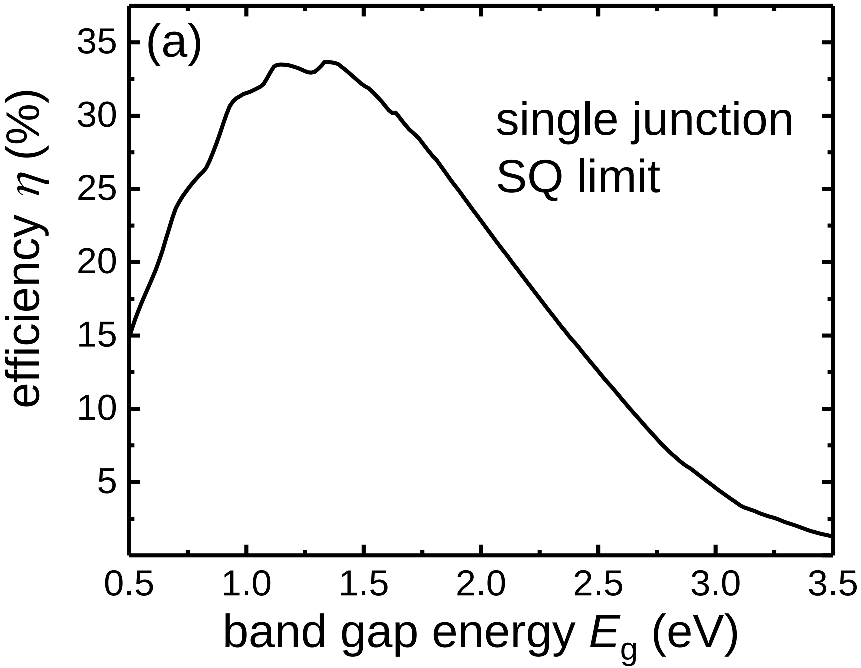
Current Density and Power Density

vs. Voltage



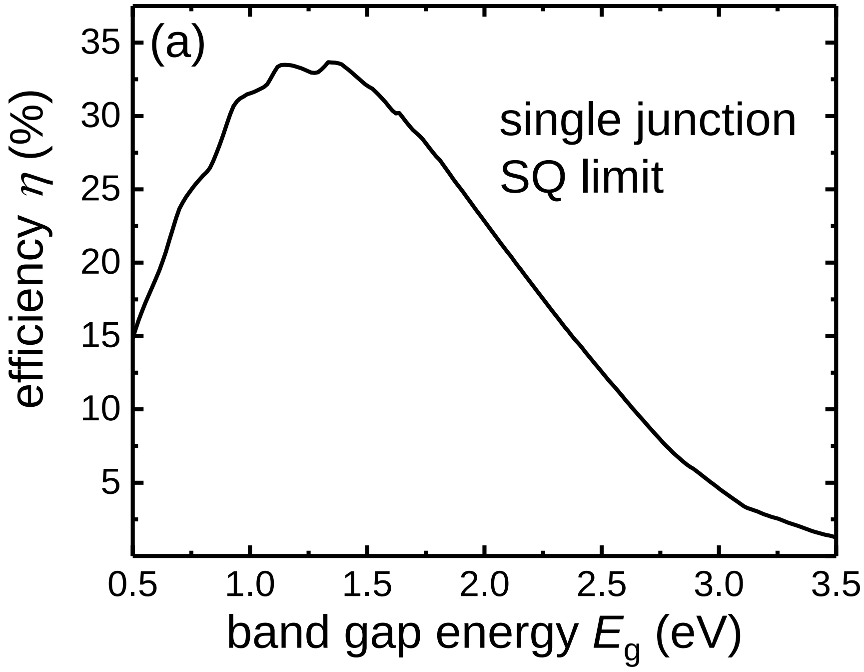
Shockley-Queisser Limit

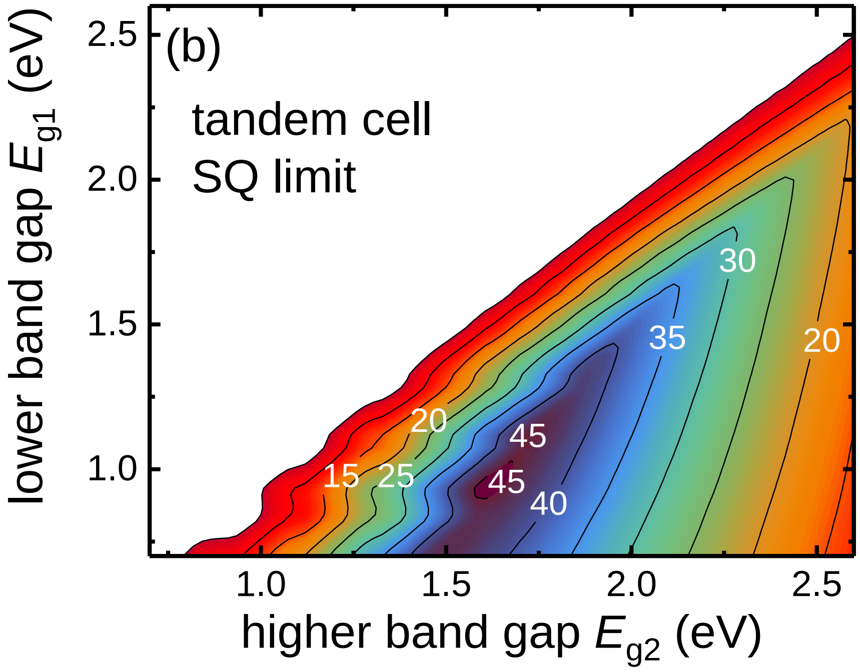
Shockley and Queisser, J. Appl. Phys. (1961)



Shockley-Queisser Limit

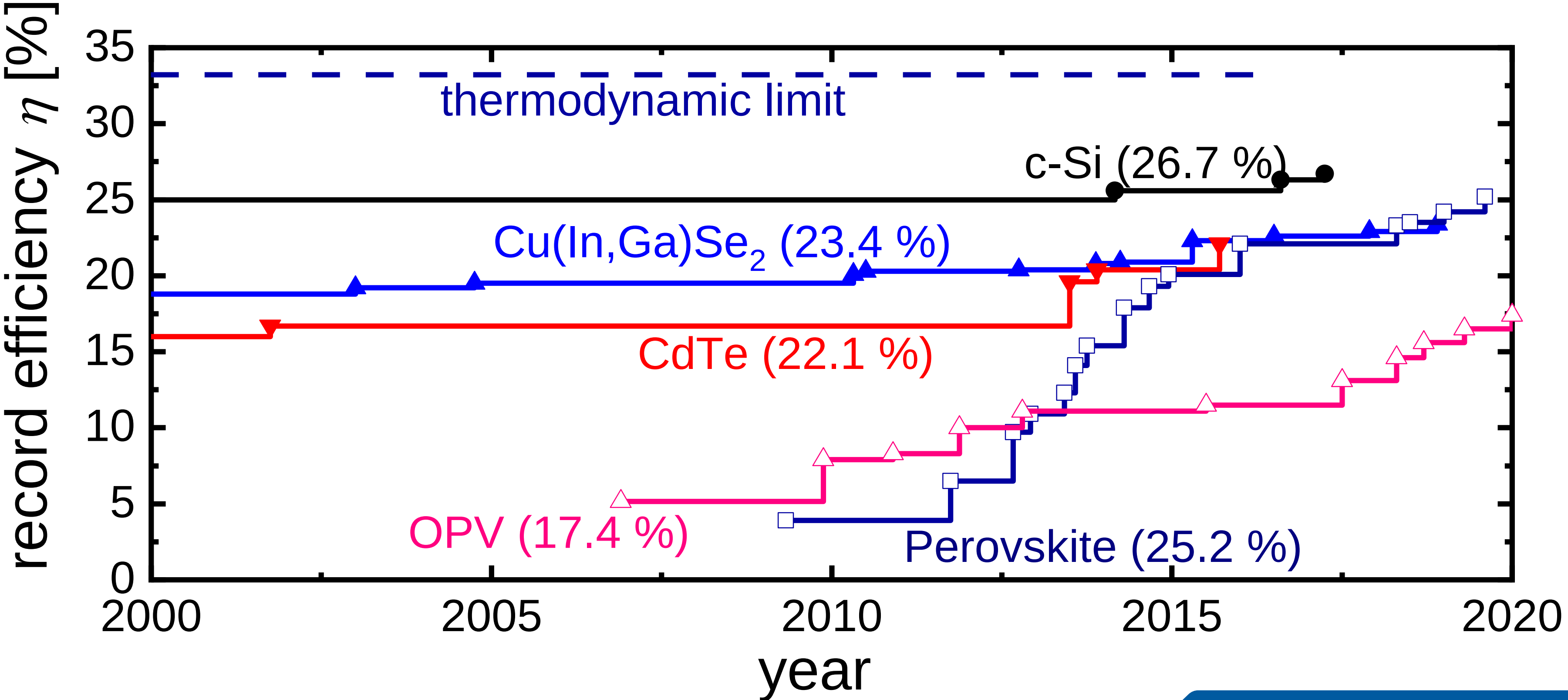
Shockley and Queisser, J. Appl. Phys. (1961)



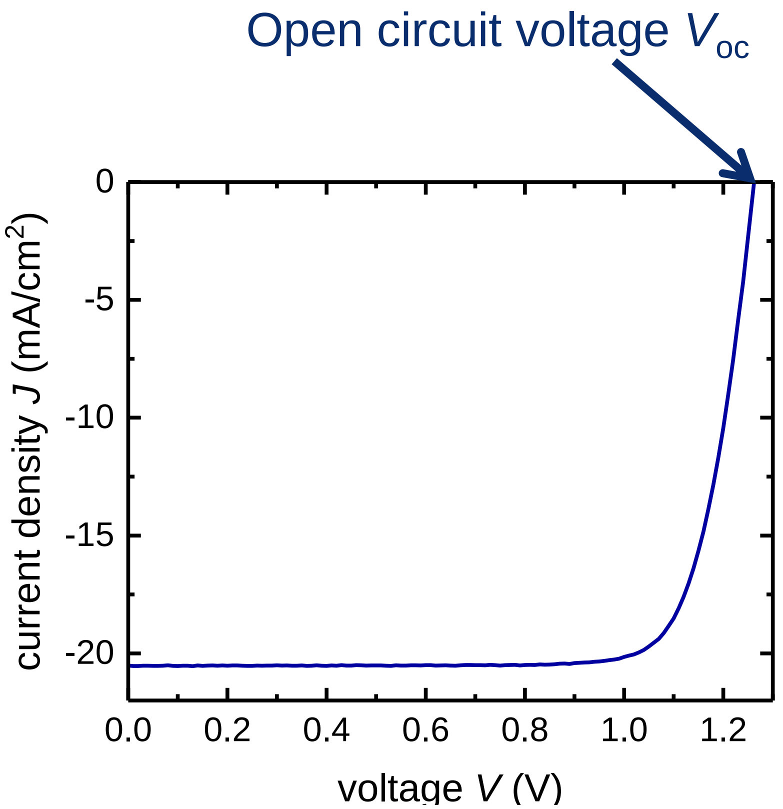


Kirchartz and Rau, Adv. Energy Mat. (2018)

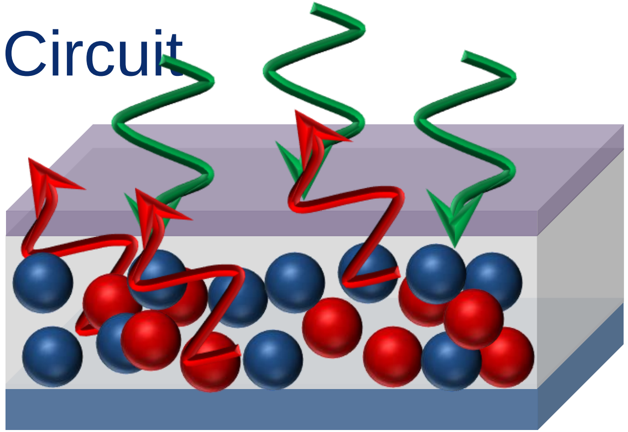
Efficiency trends for different PV technologies



Solar Cell Basics



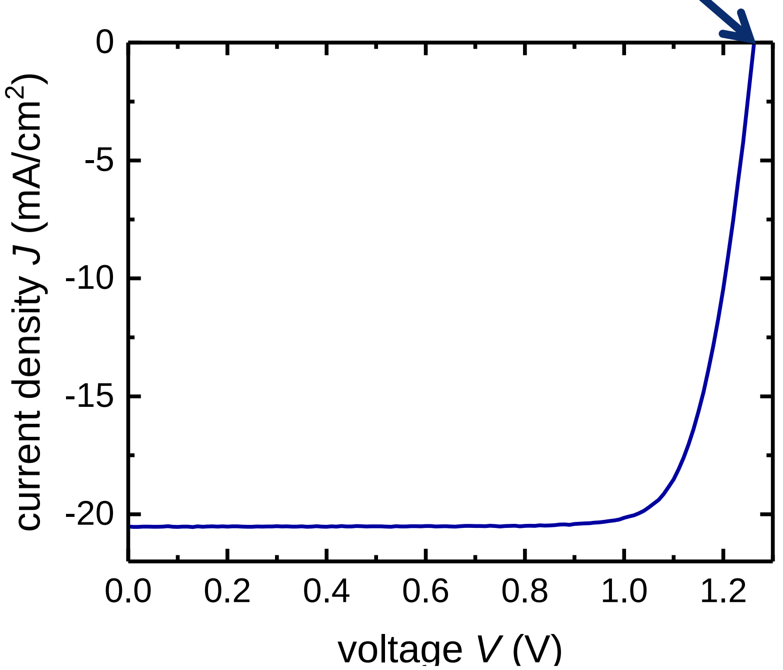
Open Circuit



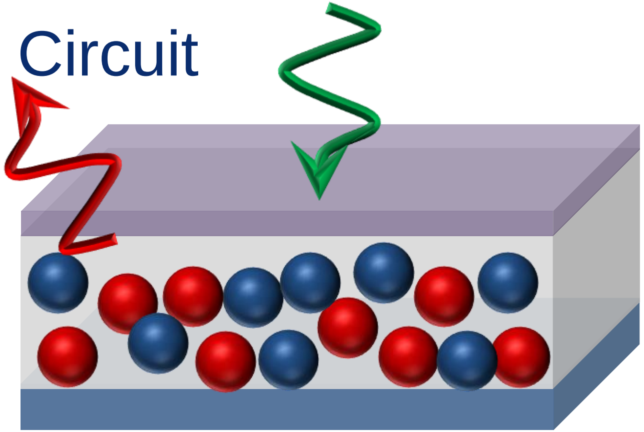
Open circuit voltage is controlled by recombination (radiative or non-radiative)

Solar Cell Basics

Open circuit voltage V_{oc}



Open Circuit

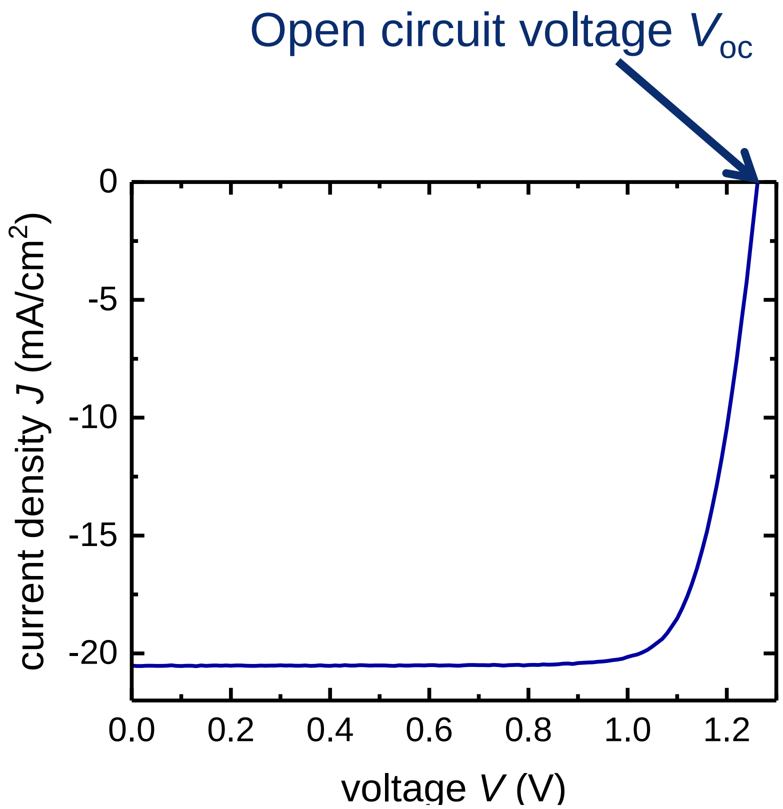


Ideal case: Only radiative recombination

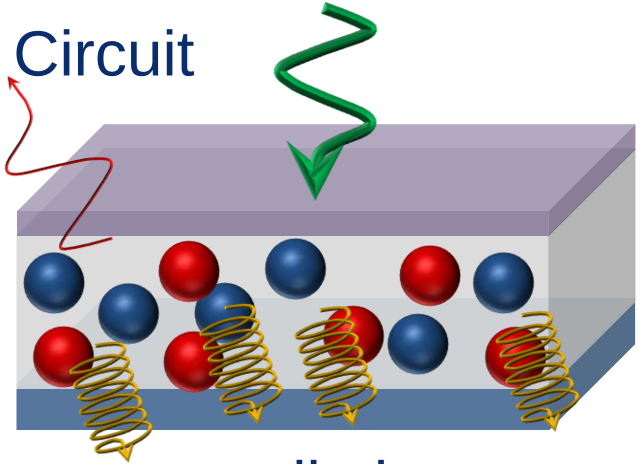
$$V_{oc} = V_{oc}^{rad}$$

$$Q_e^{lum} = 1$$

Luminescence and open-circuit voltage



Open Circuit

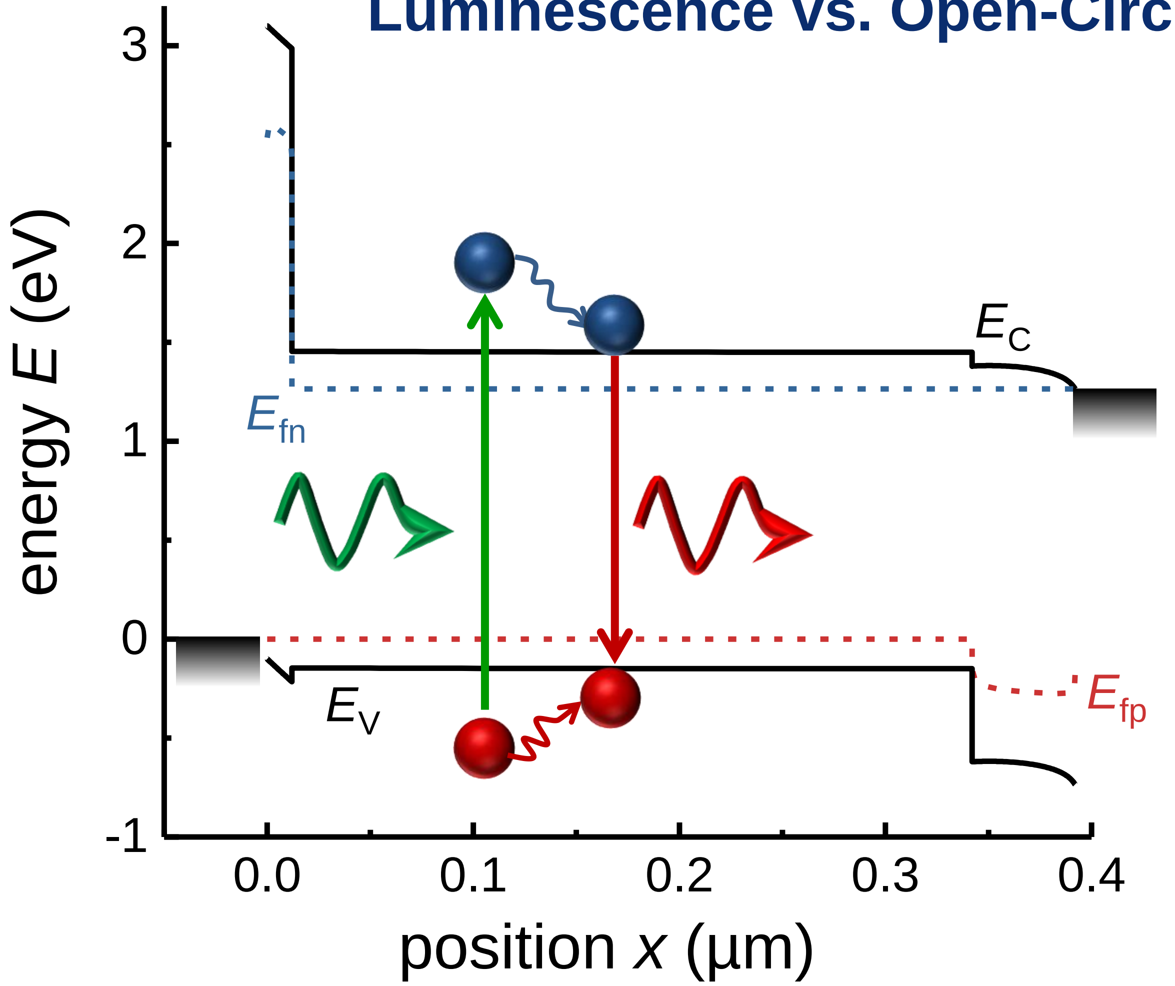


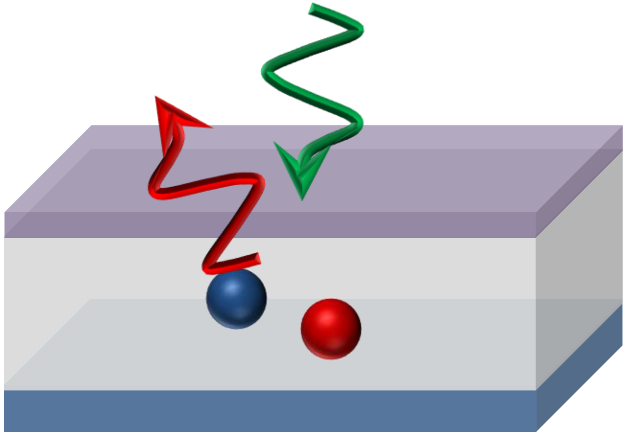
Real case: non-radiative recombination

$$V_{oc} = V_{oc}^{rad} - \frac{kT}{q}\left|\ln\left(Q_e^{lum}\right)\right|$$

$$Q_e^{lum} < 1$$

Luminescence vs. Open-Circuit Voltage



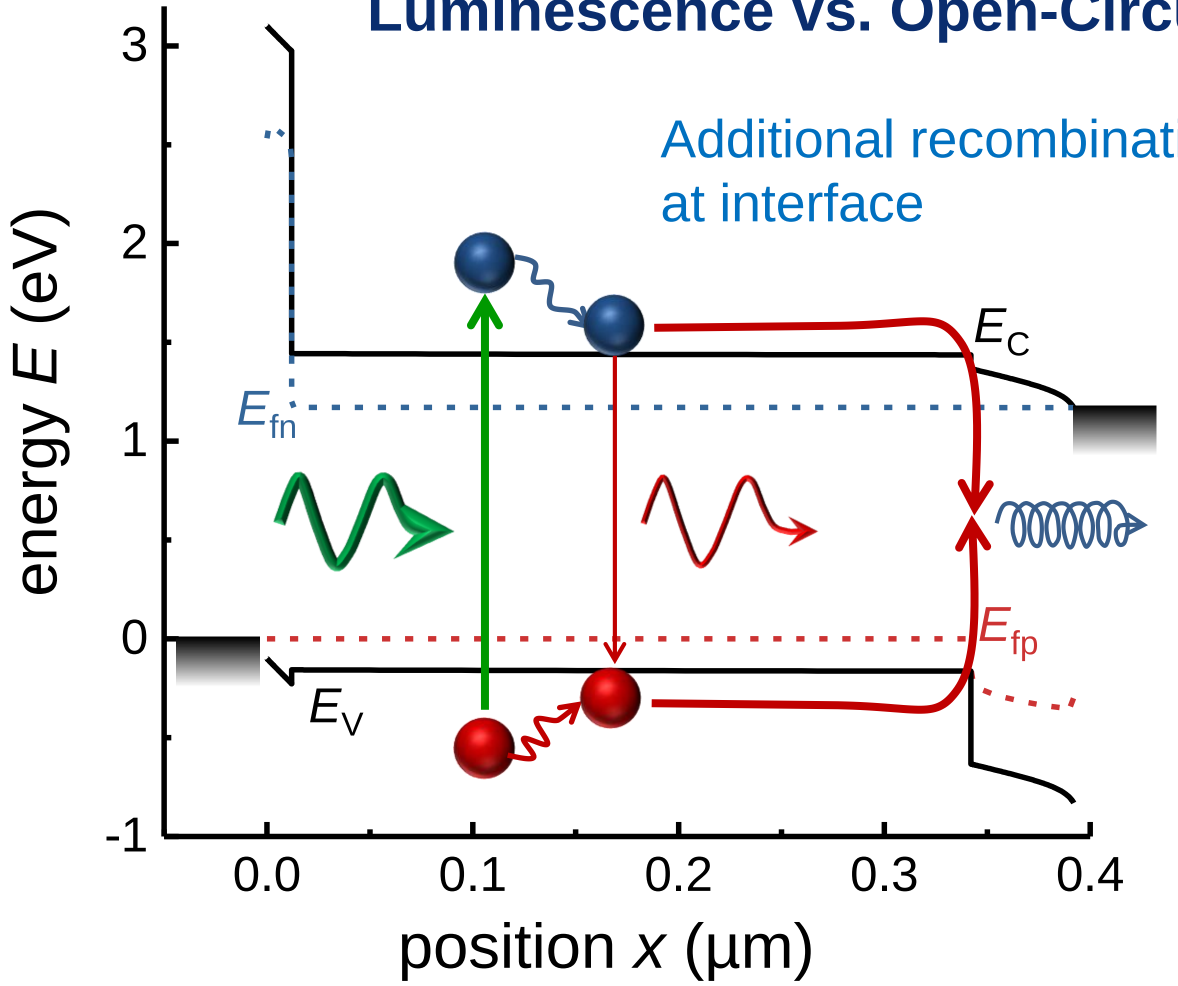


Radiative limit:

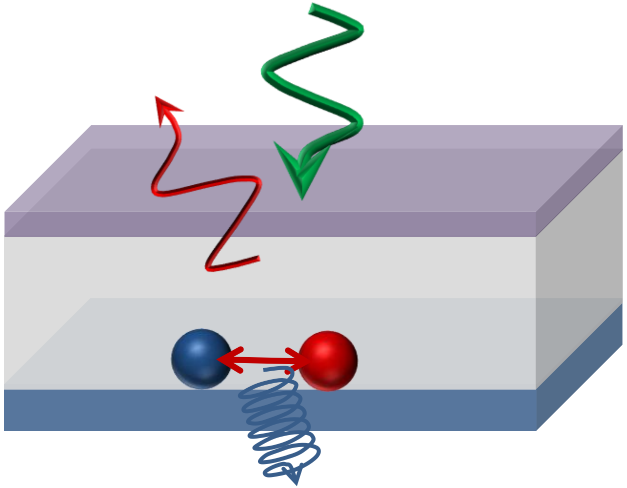
$$V_{oc} = V_{oc}^{rad}$$

$$Q_e^{lum} = 1$$

Luminescence vs. Open-Circuit Voltage



Additional recombination at interface



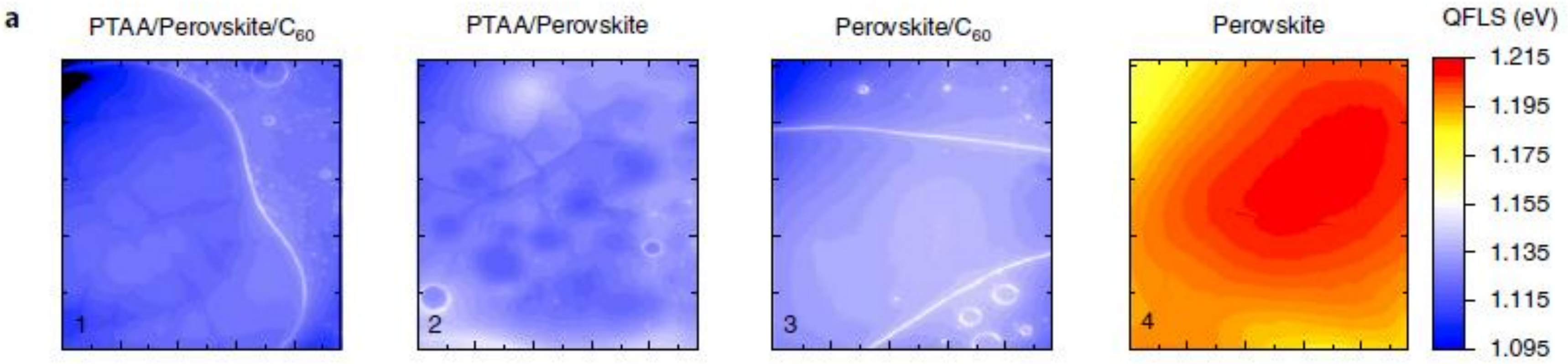
Non-radiative recombination:

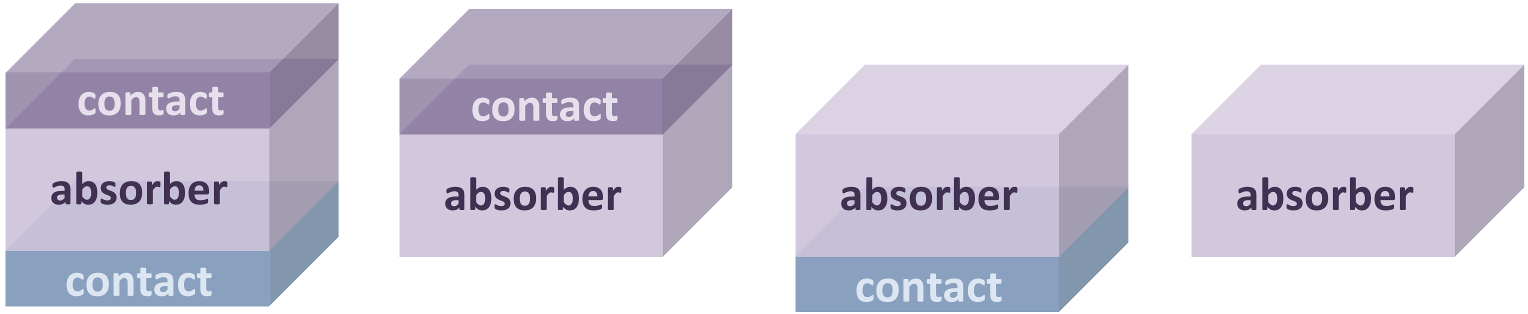
$$V_{oc} = V_{oc}^{rad} + \frac{kT}{q}\ln\left(Q_e^{lum}\right)$$

$$Q_e^{lum} \ll 1$$

Steady-State PL

Measuring indirectly the quasi-Fermi-level splitting

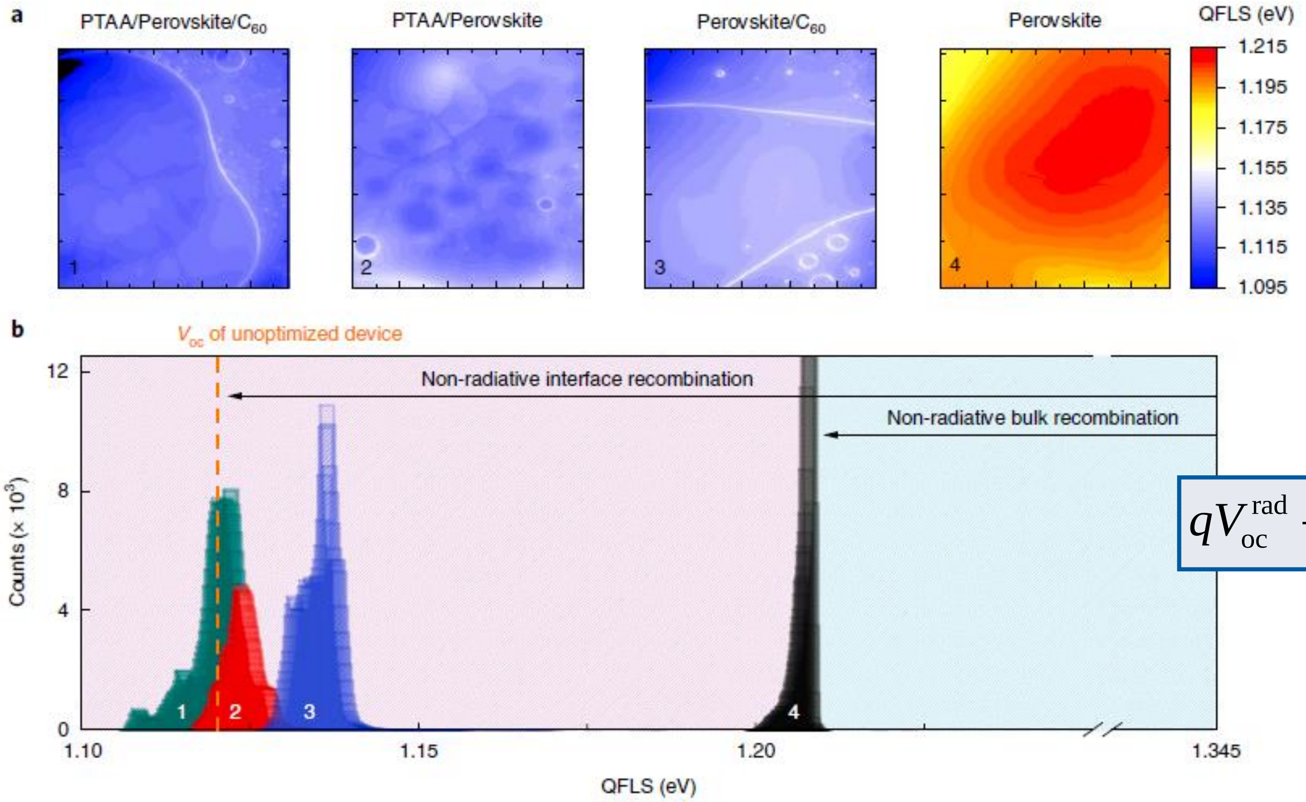




Stolterfoht et al. Nature Energy (2018)

Steady-State PL

Measuring indirectly the quasi-Fermi-level splitting



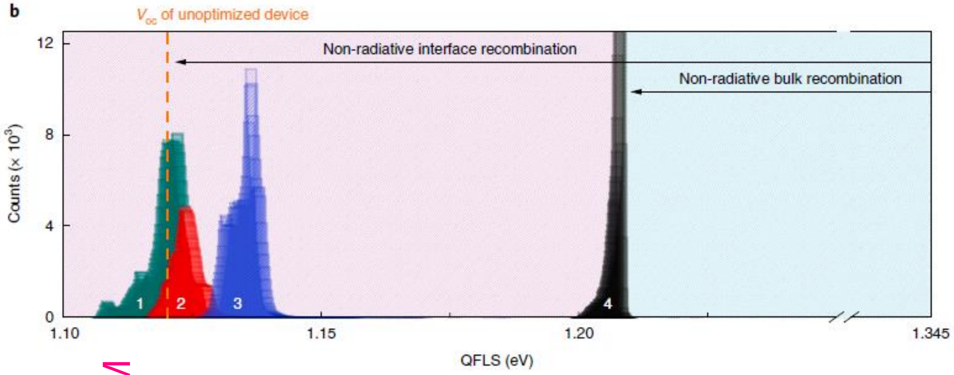
$$kT\ln(10) \approx 60\text{meV}$$

$$qV_{oc}^{rad} - qV_{oc} = -kT\ln\left(Q_e^{lum}\right) > 0$$

Stolterfoht et al. Nature Energy (2018)

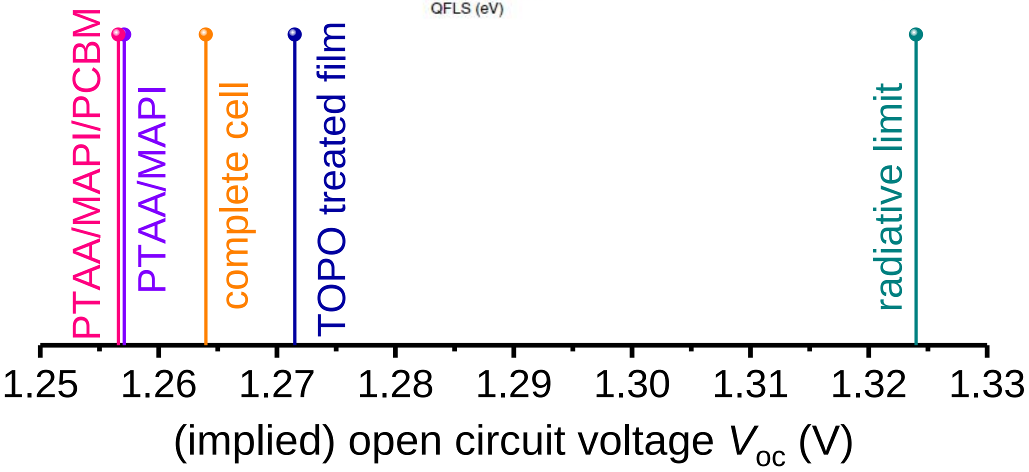
Steady-State PL

Measuring indirectly the quasi-Fermi-level splitting



$$kT\ln(10) \approx 60\text{meV}$$

Stolterfoht et al. Nature Energy (2018)

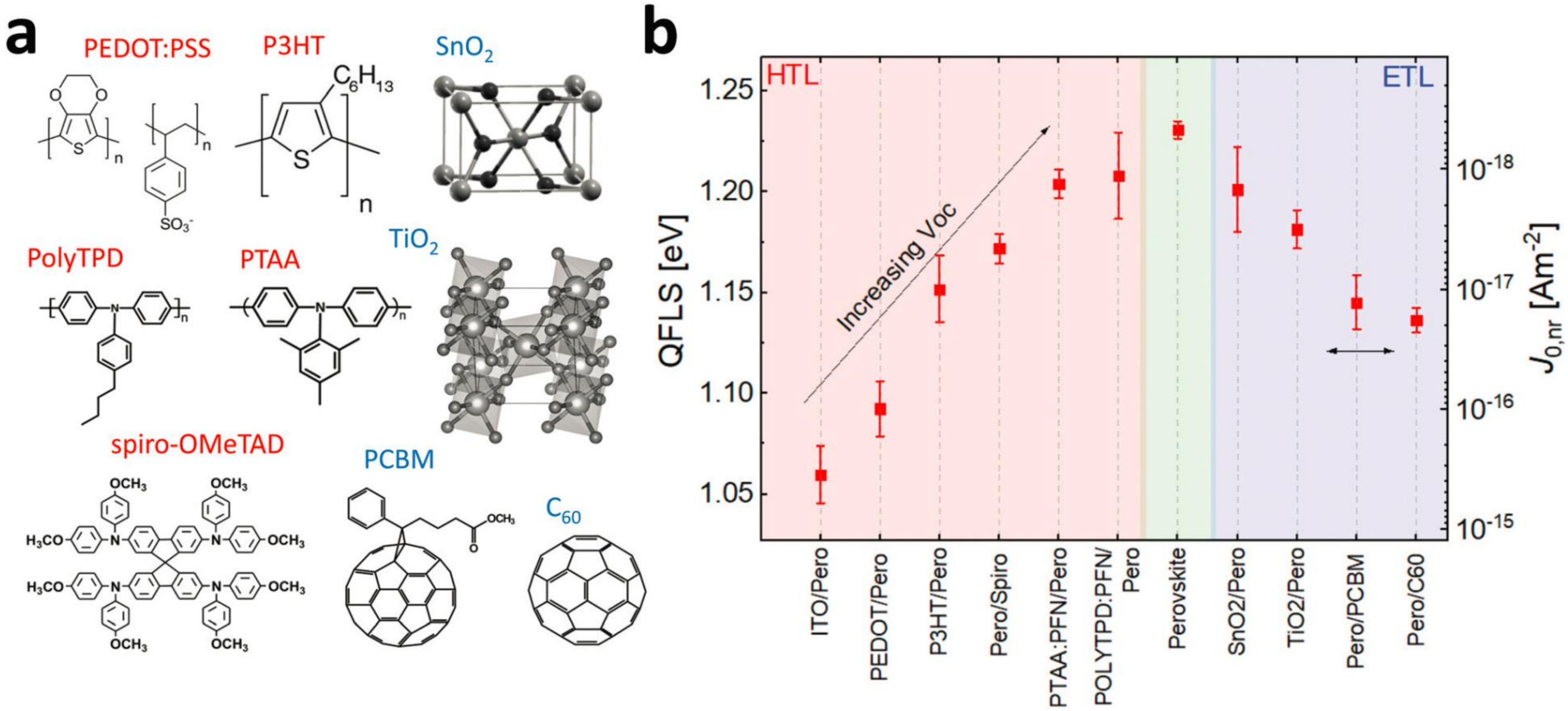


$$qV_{oc}^{rad} - qV_{oc} = -kT\ln\left(Q_e^{lum}\right) > 0$$

Liu et al., ACS Energy Lett. **4**, 110 (2019)

Screening of contact layers for high V_{oc}

Triple cation recipe from Potsdam University

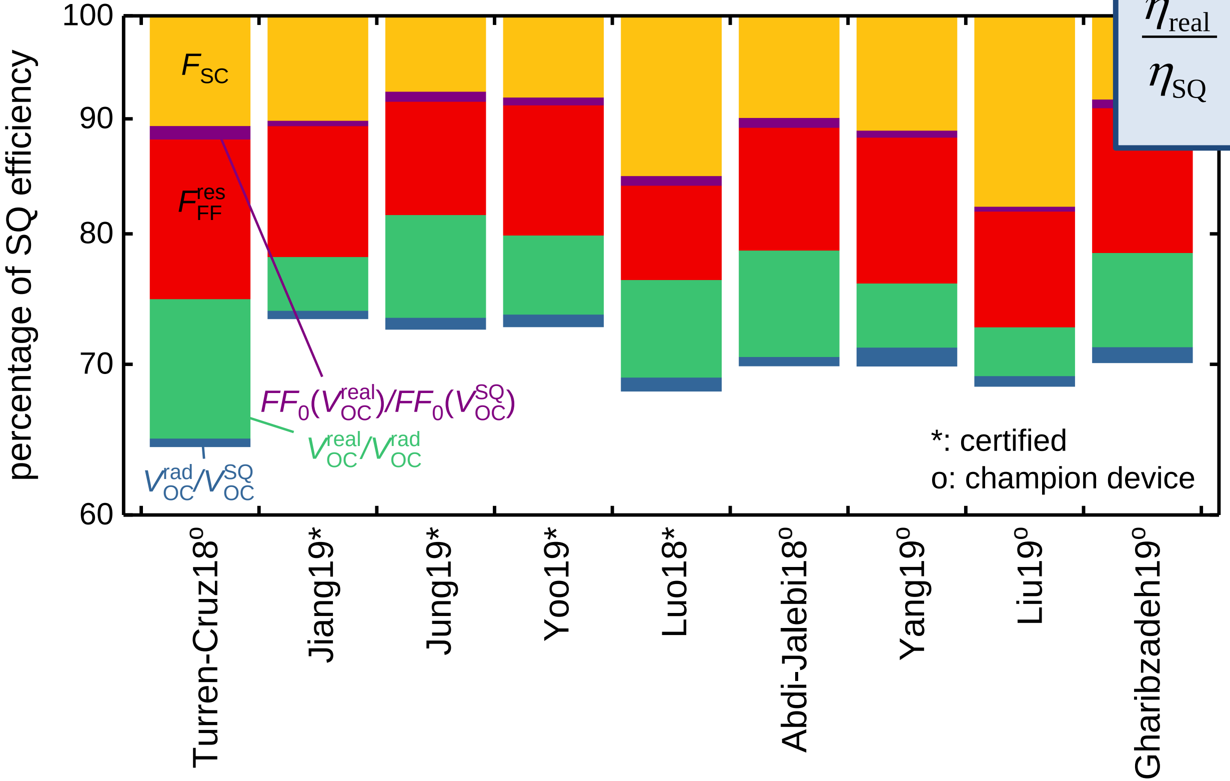


Stolterfoht et al. Energy Environ. Science (2019)

Development of perovskite solar cell efficiencies

…and associated losses

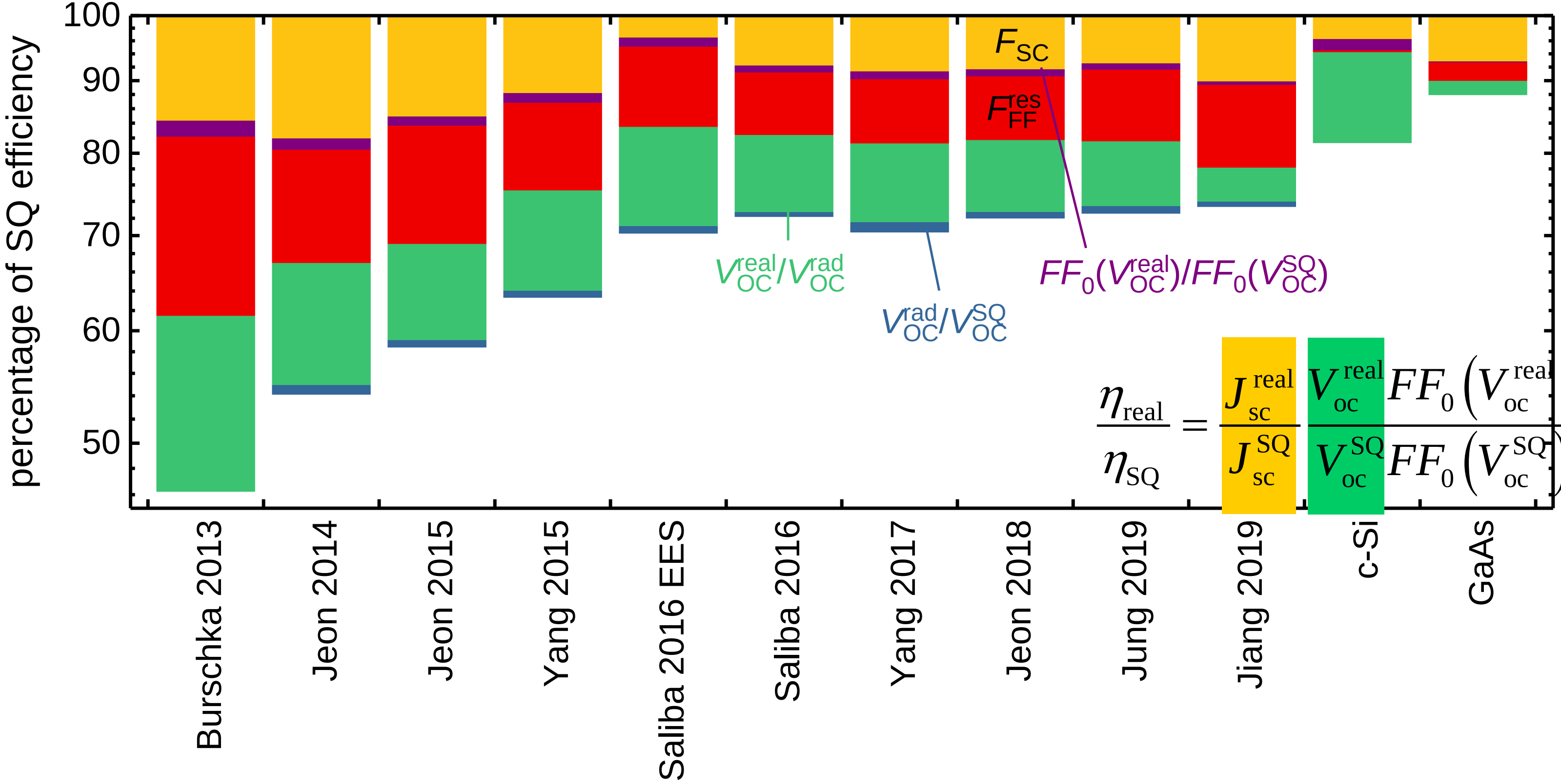
$$\frac{\eta_{\mathrm{real}}}{\eta_{\mathrm{SQ}}} = \frac{J_{\mathrm{sc}}^{\mathrm{real}}}{J_{\mathrm{sc}}^{\mathrm{SQ}}} \frac{V_{\mathrm{oc}}^{\mathrm{real}} FF_0\left(V_{\mathrm{oc}}^{\mathrm{real}}\right)}{V_{\mathrm{oc}}^{\mathrm{SQ}} FF_0\left(V_{\mathrm{oc}}^{\mathrm{SQ}}\right)} \frac{FF^{\mathrm{real}}}{FF_0\left(V_{\mathrm{oc}}^{\mathrm{real}}\right)}$$



Krückemeier et al. Adv. Energy Mater. 2020, Guillemoles et al. Nat. Photon. 2019

Development of perovskite solar cell efficiencies

…and associated losses



$$\frac{\eta_{real}}{\eta_{SQ}} = \frac{J_{sc}^{real}}{J_{sc}^{SQ}} \frac{V_{oc}^{real} FF_0\left(V_{oc}^{real}\right)}{V_{oc}^{SQ} FF_0\left(V_{oc}^{SQ}\right)} \frac{FF^{real}}{FF_0\left(V_{oc}^{real}\right)}$$

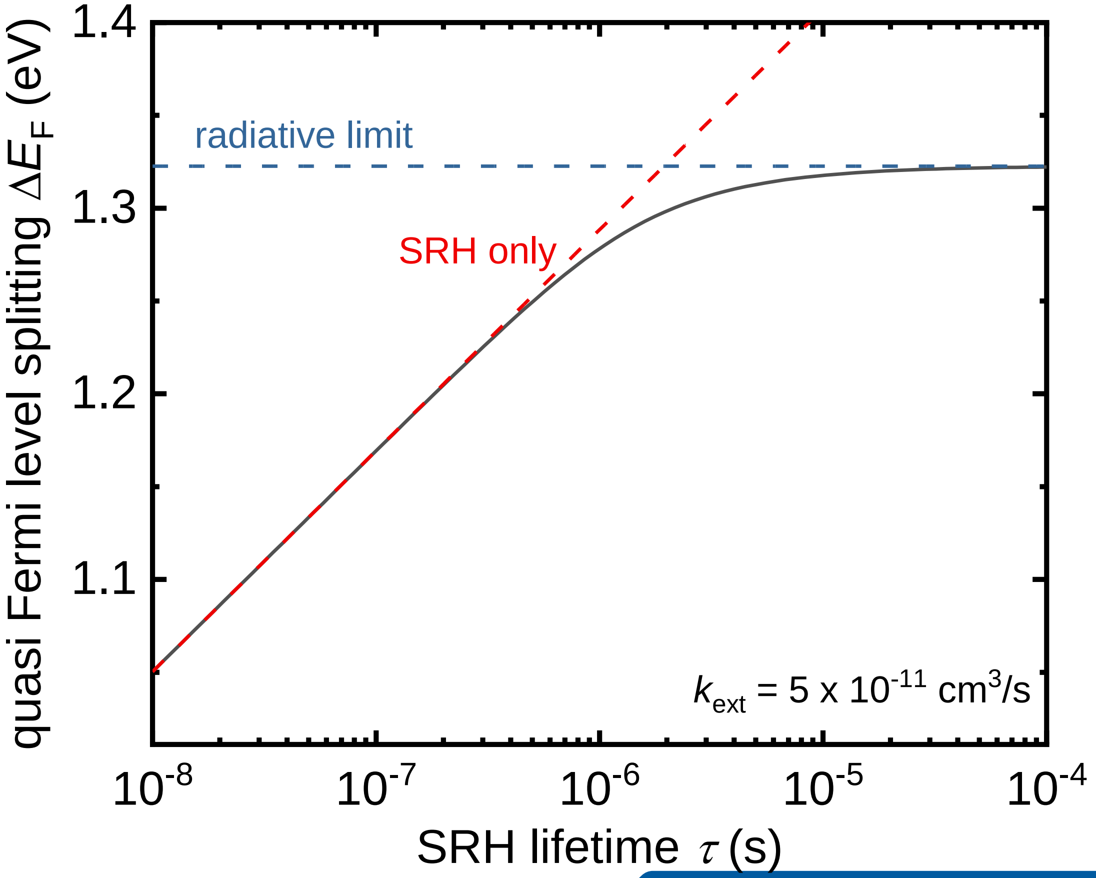
Krückemeier et al. Adv. Energy Mater. 2020, Guillemoles et al. Nat. Photon. 2019

Why are charge carrier lifetimes relevant?

@ open circuit

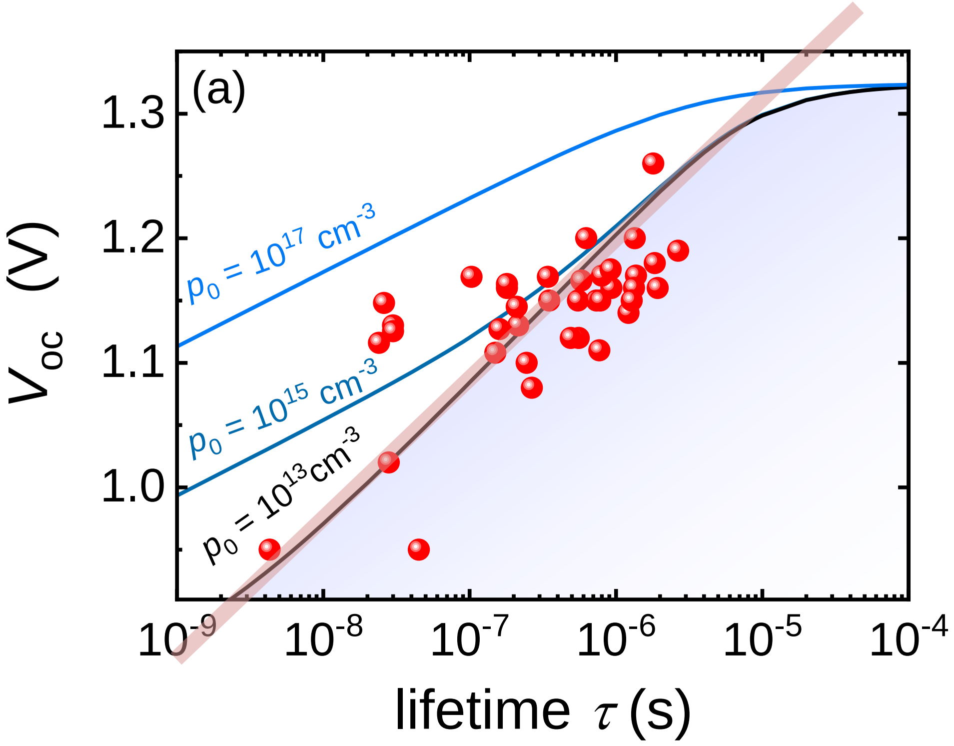
$$G = kn^2 + \frac{n}{\tau}$$

$$\Delta E_\mathrm{F} = kT \ln\left(\frac{n^2}{n_i^2}\right)$$



Kirchartz et al. Adv. Energy Mater. 2020

Why things are more difficult in reality than in theory?

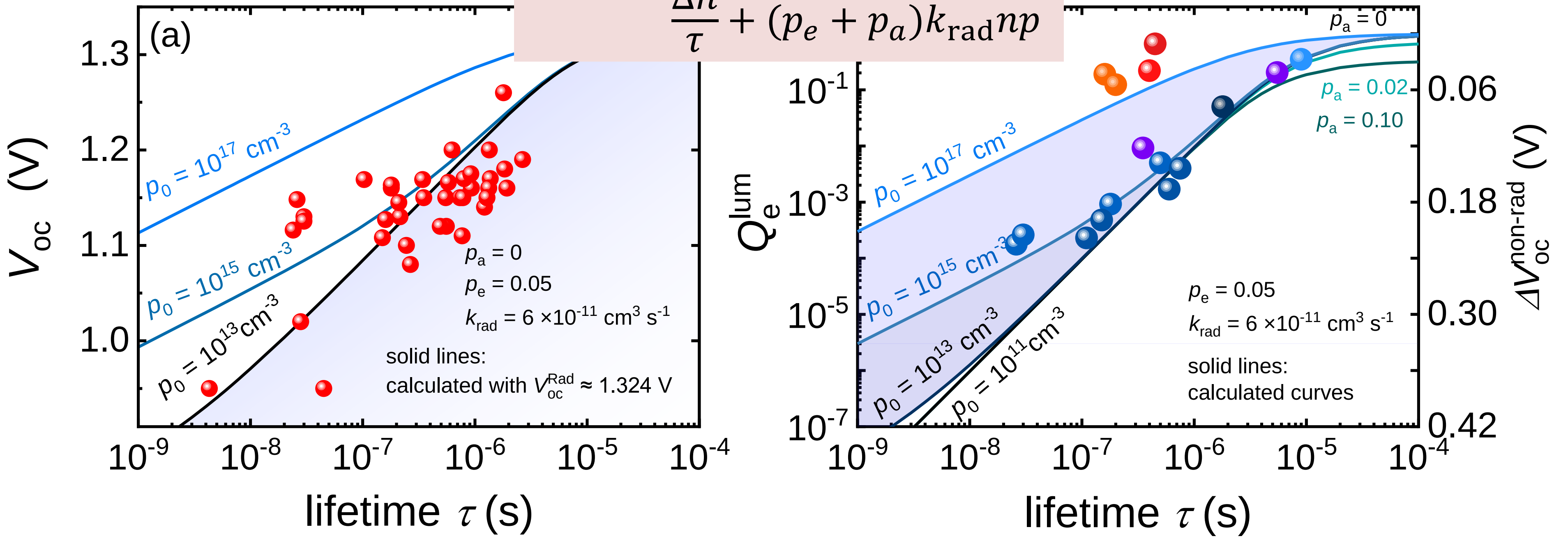


$$\Delta E_{\mathrm{F}} = 2kT \ln\left(\frac{G\tau}{n_{\mathrm{i}}}\right)$$

Kirchartz et al. Adv. Energy Mater. 2020

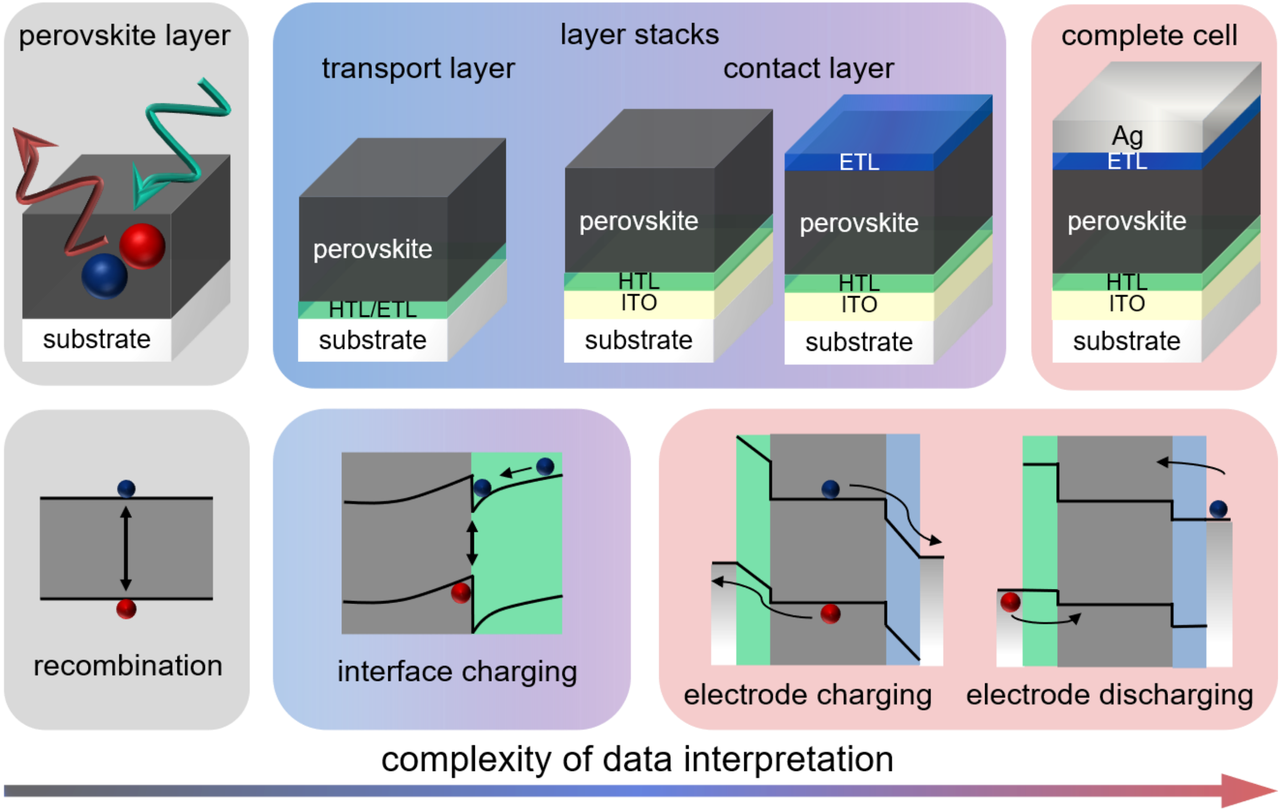
Why things are more difficult in reality than in theory?

$$Q_e^{lum} = \frac{p_e k_{rad} np}{\frac{\Delta n}{\tau} + (p_e + p_a) k_{rad} np}$$



Kirchartz et al. Adv. Energy Mater. 2020

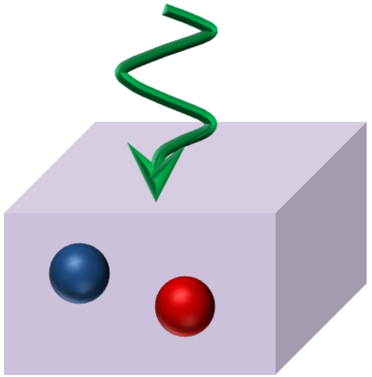
Transient Photoluminescence in Lead-Halide Perovskite Layer Stacks and Solar Cells

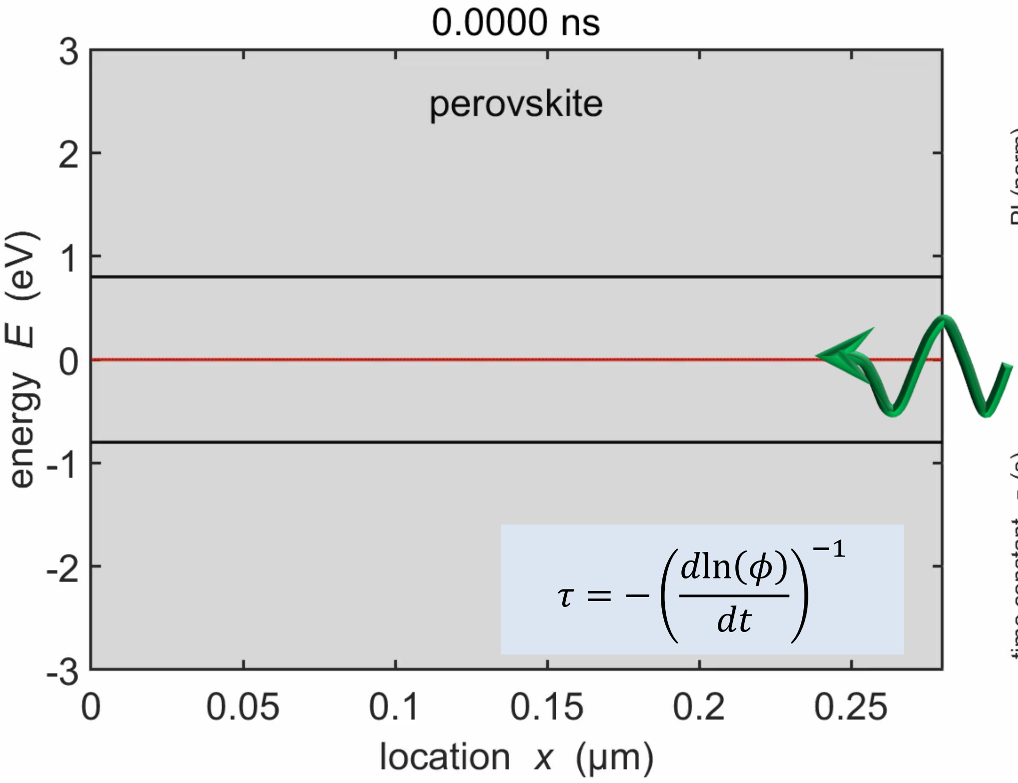


Krückemeier et al. (submitted)

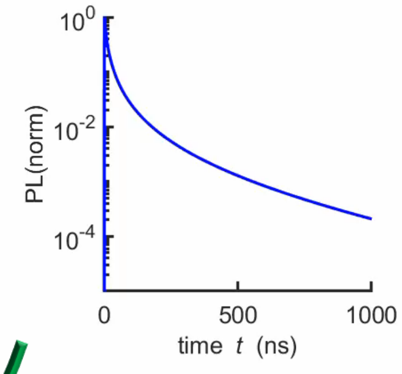
Transient Photoluminescence

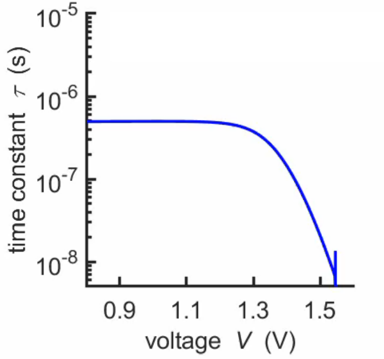
Layer on glass - Video





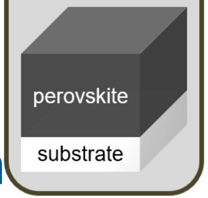
$$\tau = -\left(\frac{d\ln(\phi)}{dt}\right)^{-1}$$

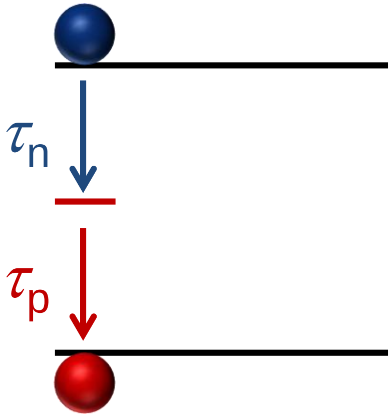


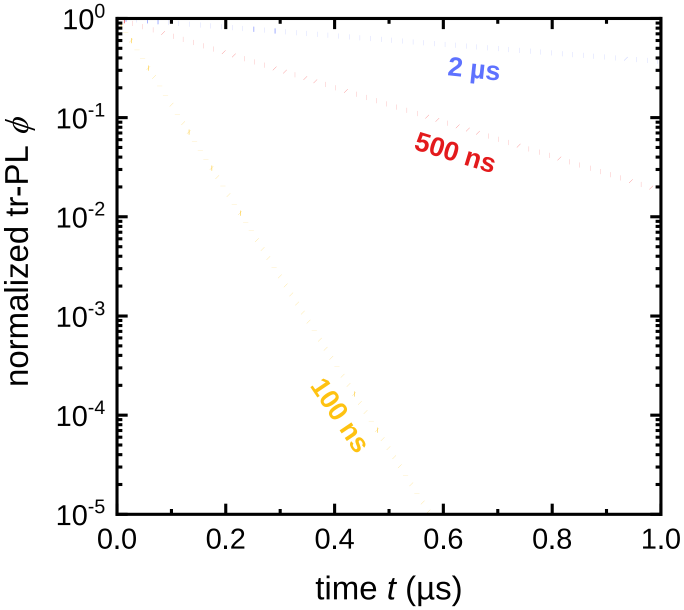


Transient Photoluminescence

Layer on Glass – SRH Recombination





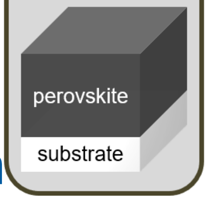


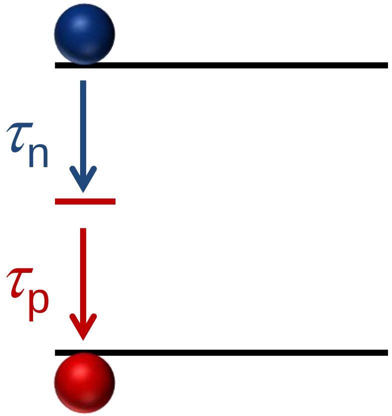
$$\frac{dn}{dt} = -\frac{np}{\tau_p n + \tau_n p}$$

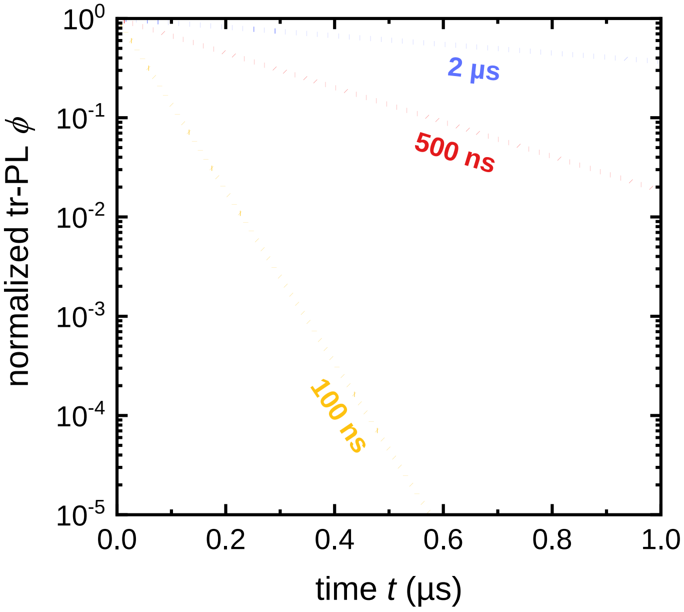
Shockley-Read-Hall (SRH) recombination only

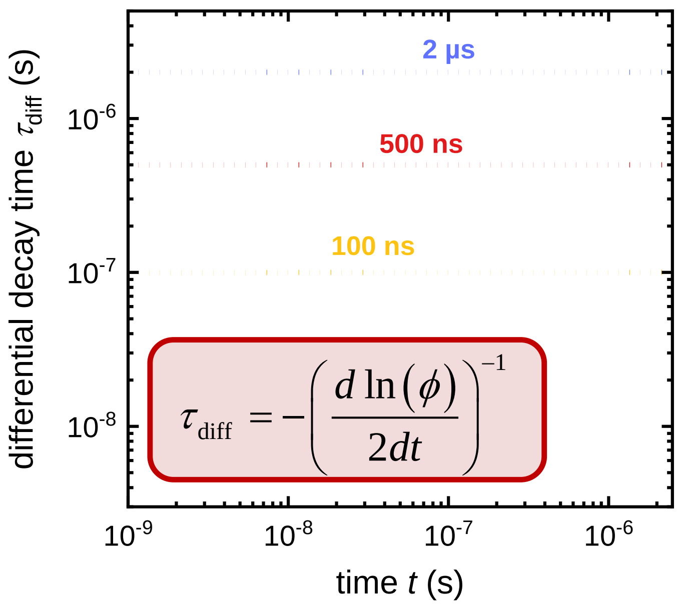
Transient Photoluminescence

Layer on Glass – SRH Recombination







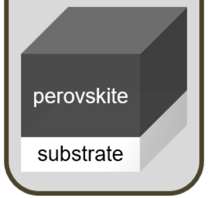


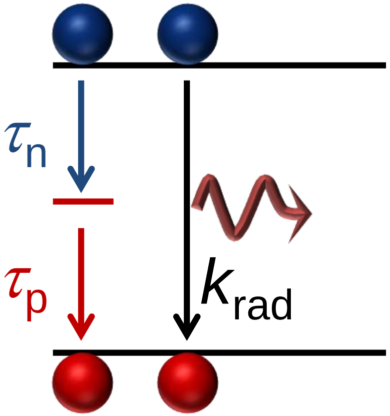
$$\frac{dn}{dt} = -\frac{np}{\tau_p n + \tau_n p}$$

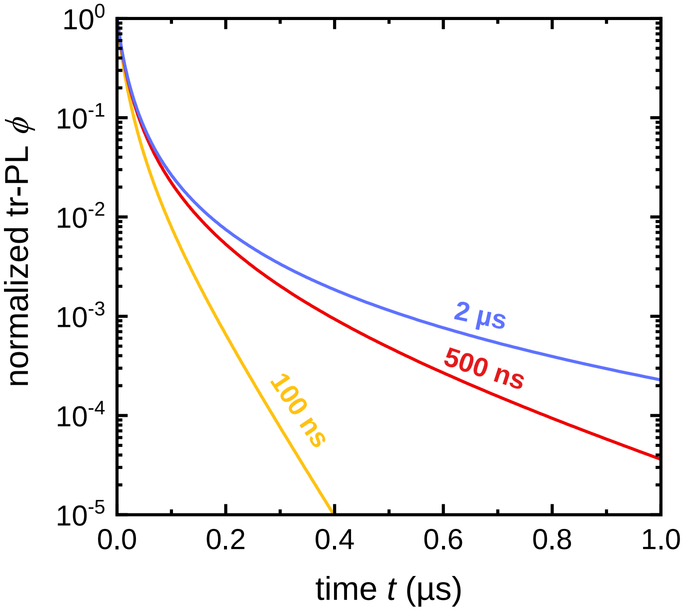
Shockley-Read-Hall (SRH) recombination only

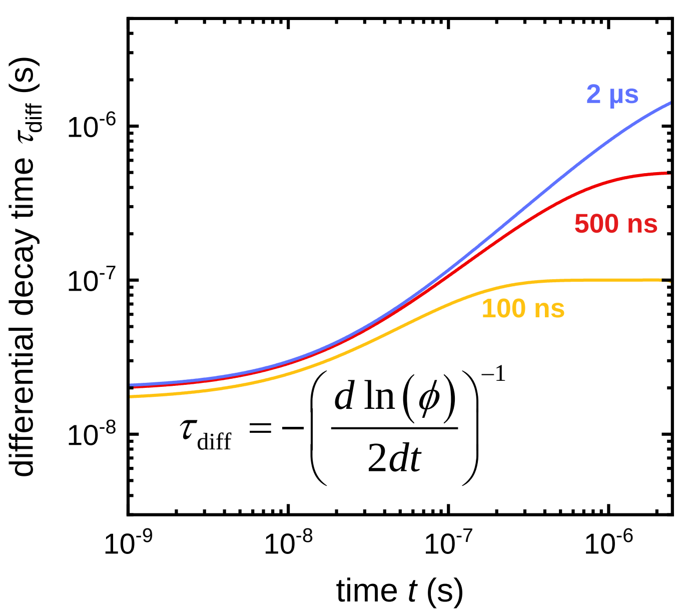
Transient Photoluminescence

Layer on Glass – Bulk Recombination







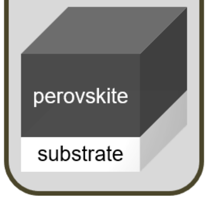


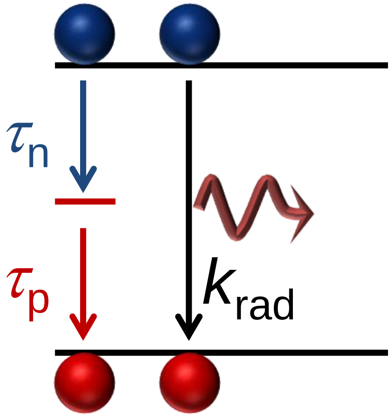
$$\frac{dn}{dt} = -k_{rad} np - \frac{np}{\tau_p n + \tau_n p}$$

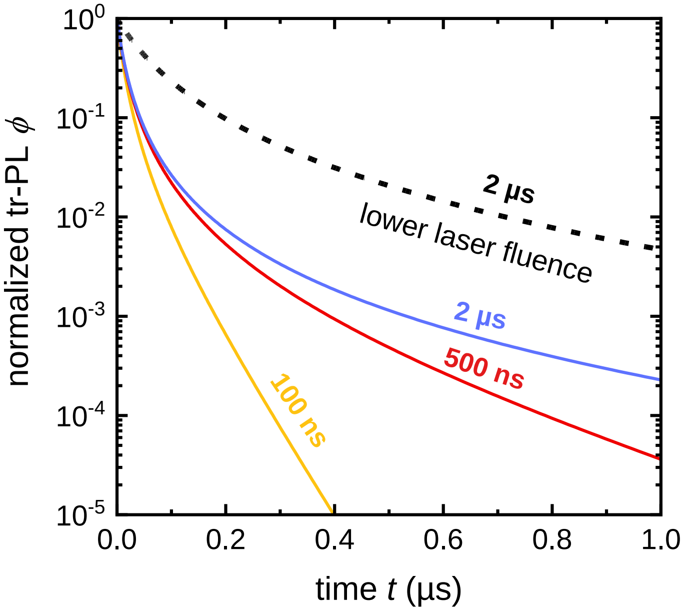
SRH + radiative recombination

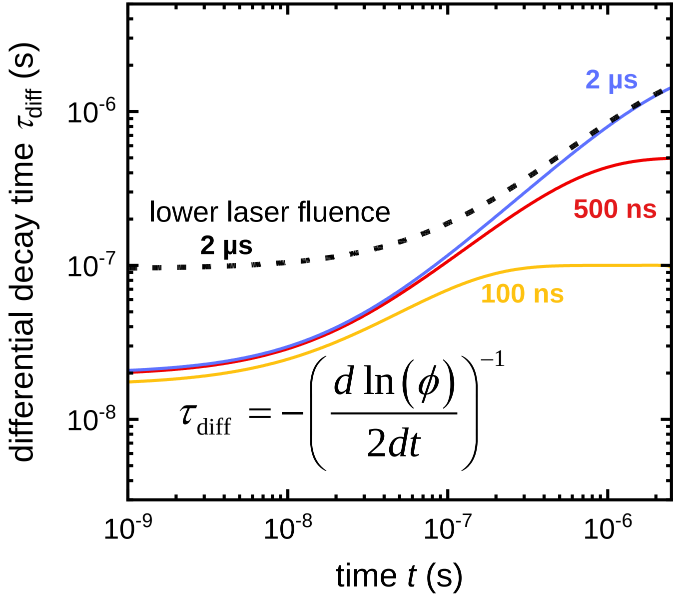
Transient Photoluminescence

Layer on Glass – Bulk Recombination







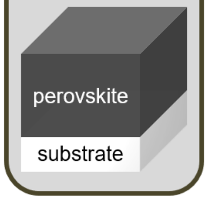


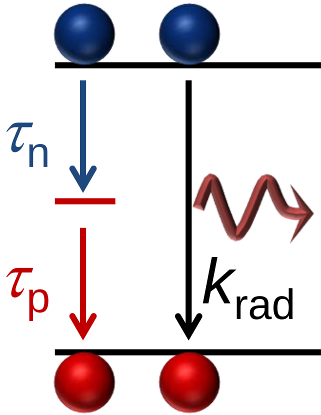
$$\frac{dn}{dt} = -k_{rad}np - \frac{np}{\tau_p n + \tau_n p}$$

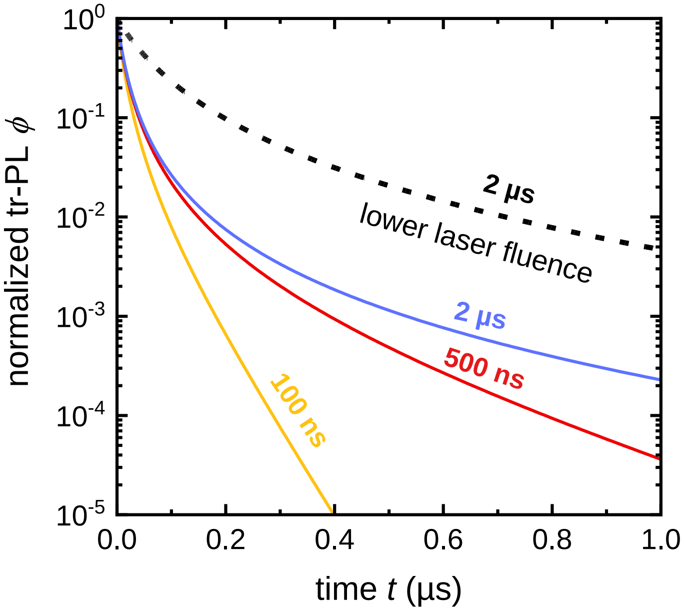
SRH + radiative recombination

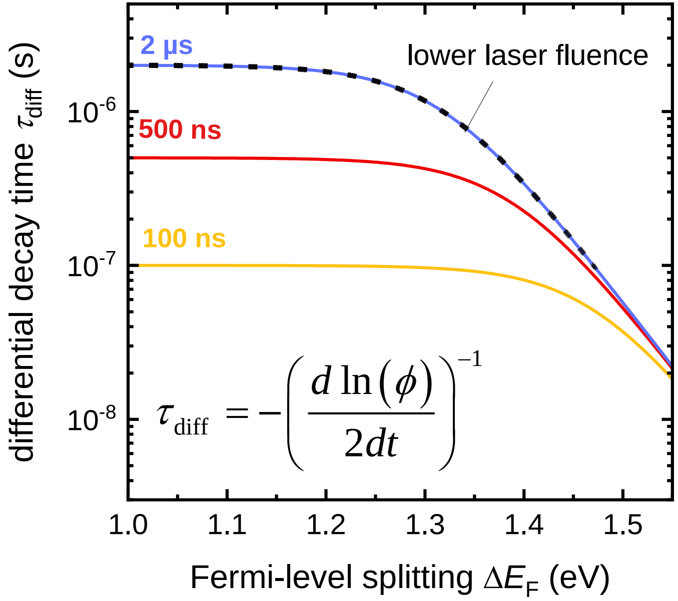
Transient Photoluminescence

Layer on Glass – Bulk Recombination









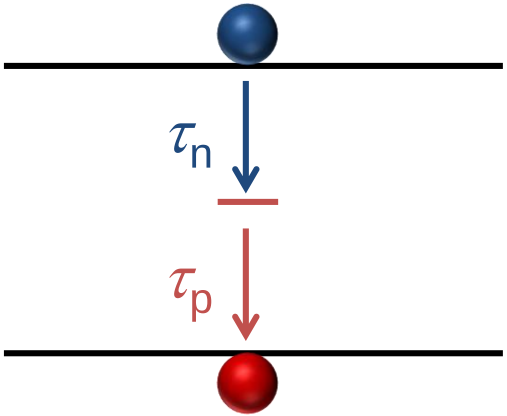
$$\frac{dn}{dt} = -k_{\mathrm{rad}}np - \frac{np}{\tau_p n + \tau_n p}$$

SRH + radiative recombination

time

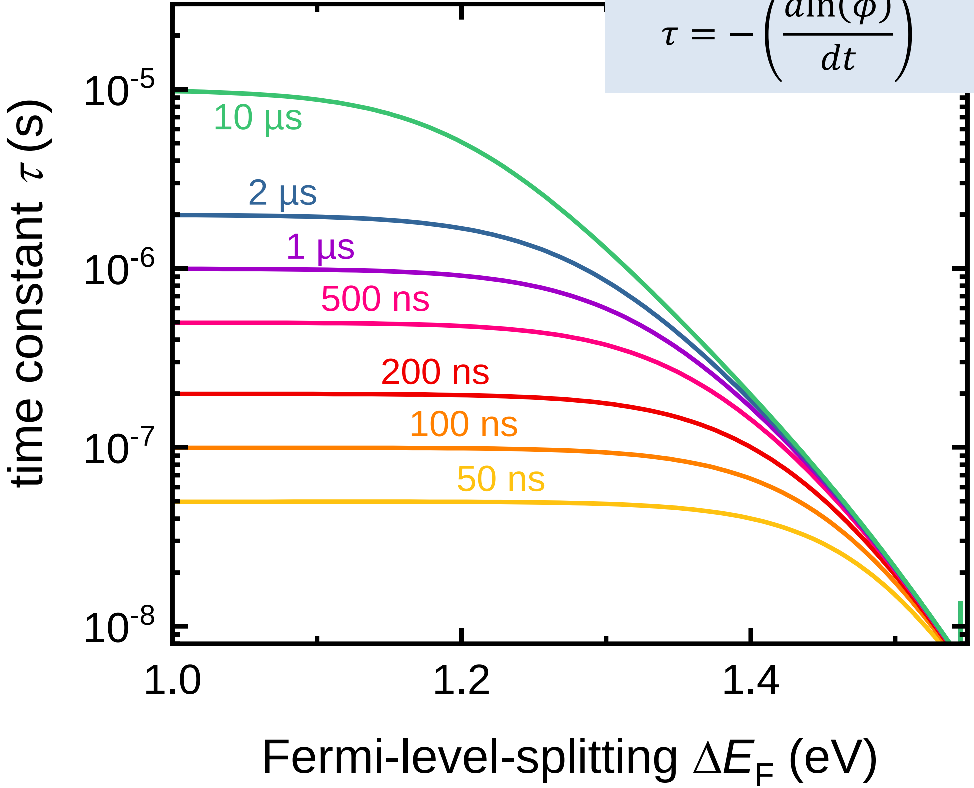
Transient Photoluminescence

Layer on glass – Bulk recombination



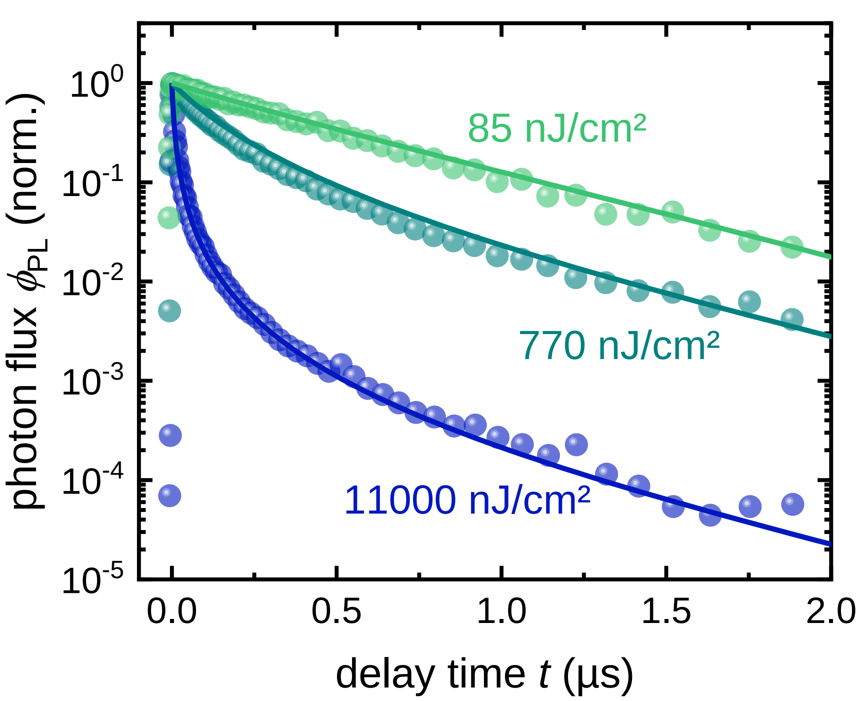
$$\frac{\mathrm{d}n}{\mathrm{d}t} = -knp - \frac{np}{\tau_p n + \tau_n p} - C(np^2 + n^2 p)$$

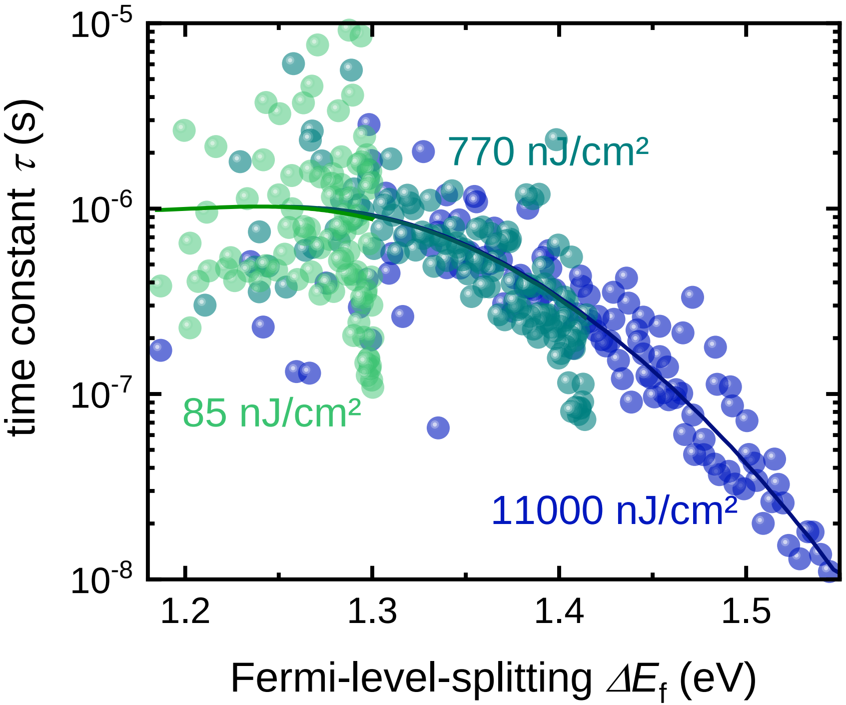
$$\tau = -\left(\frac{d\ln(\phi)}{dt}\right)^{-1}$$



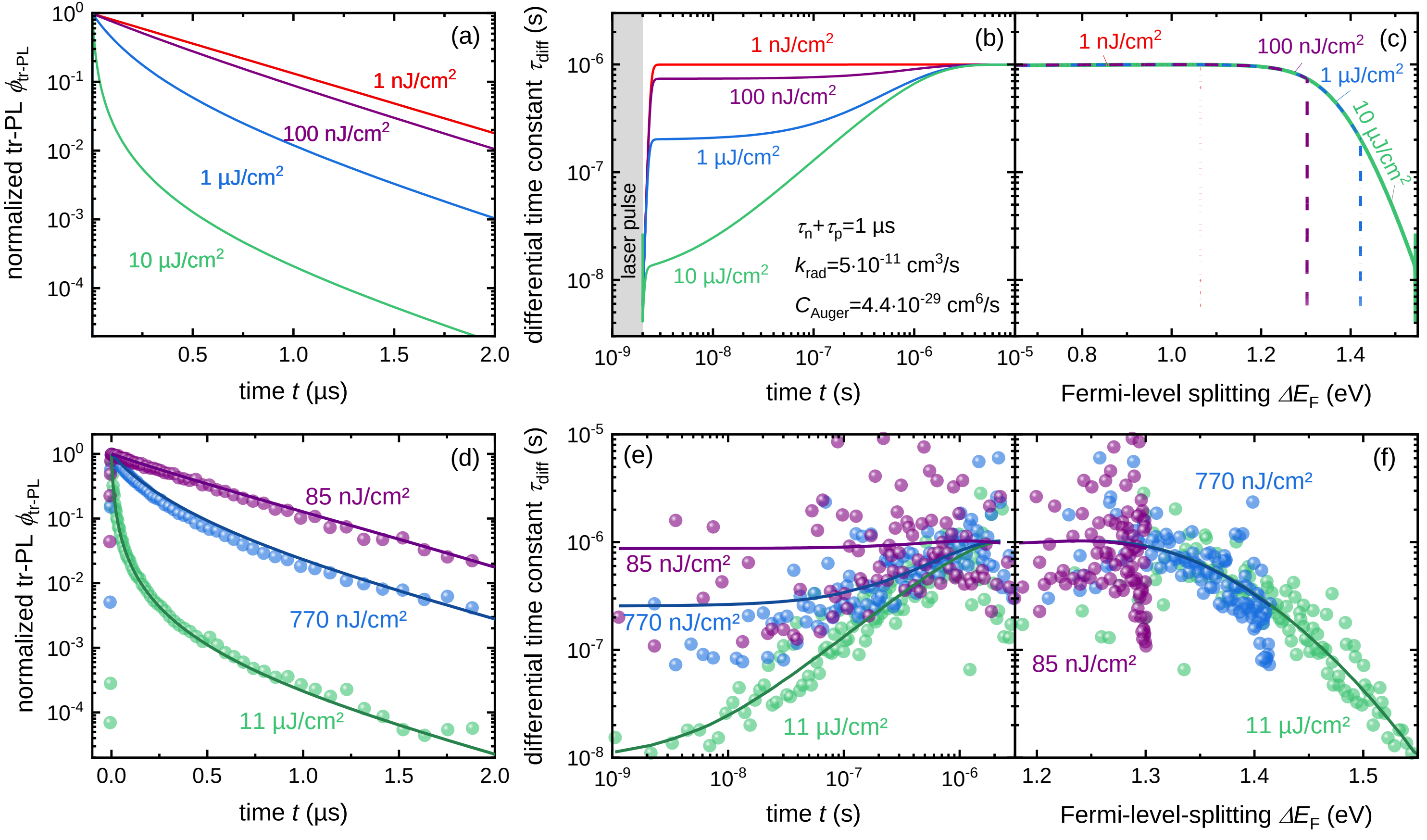
Layer on Glass

Experimental data





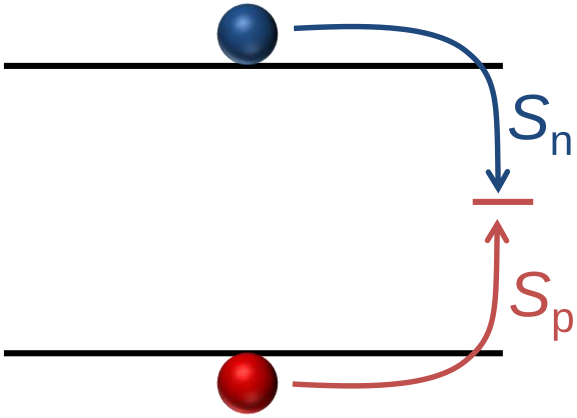
From time axis to QFLS axis

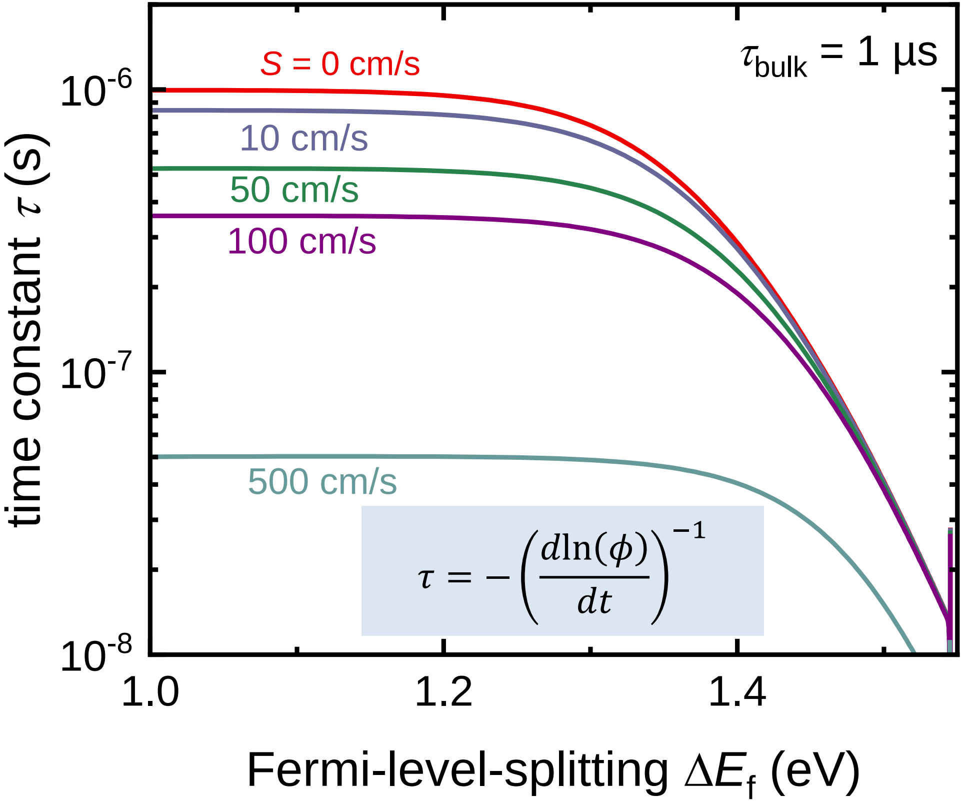


Krückemeier et al. (submitted)

Transient Photoluminescence

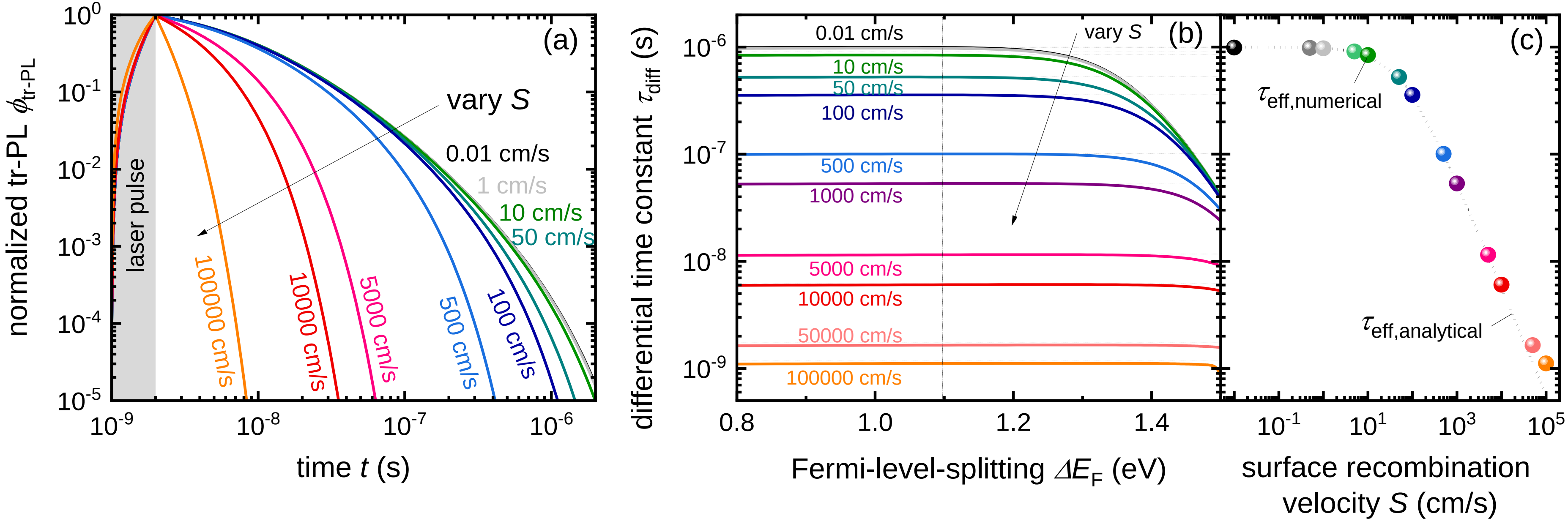
Layer on glass – Surface recombination





Transient Photoluminescence

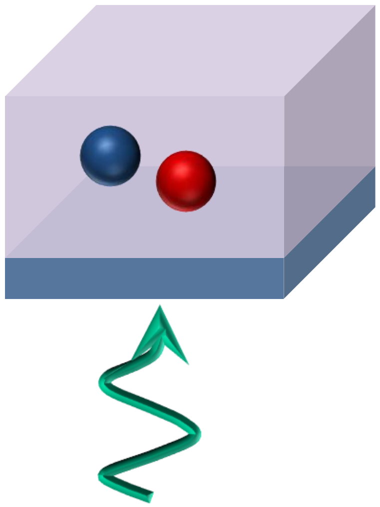
Layer on glass – Surface recombination

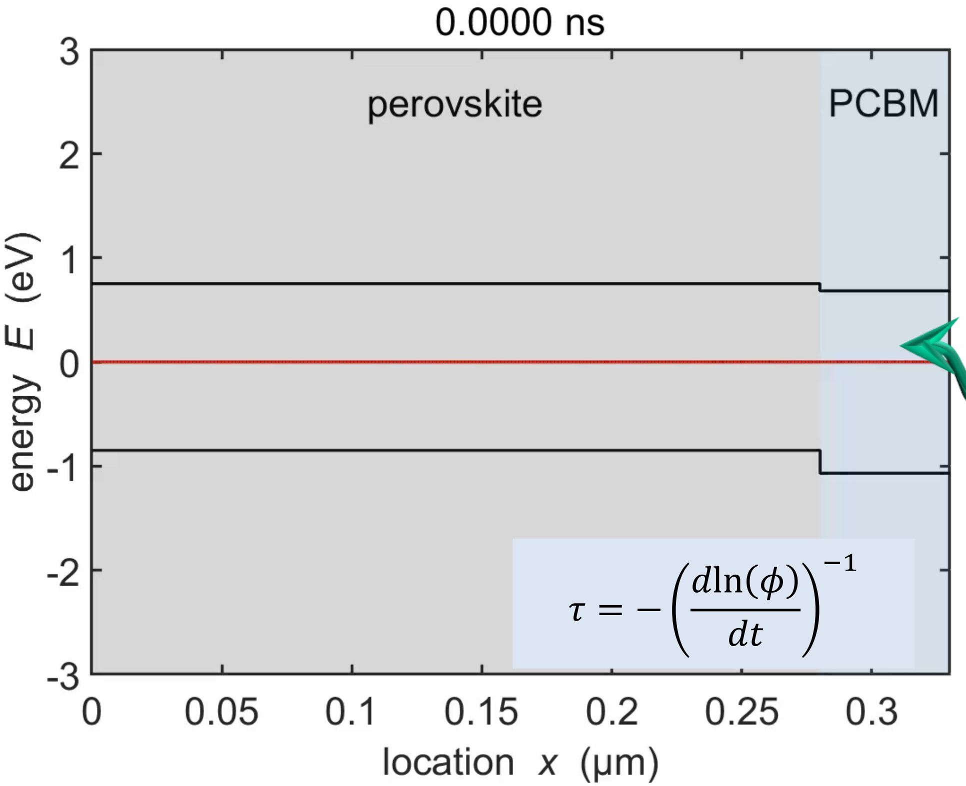


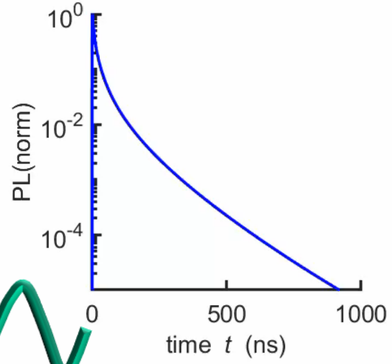
Krückemeier et al. (submitted)

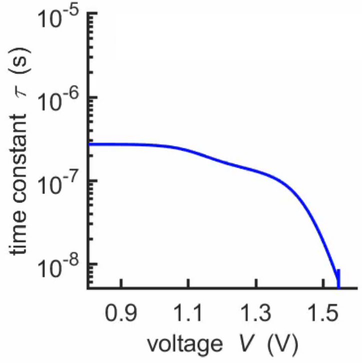
Charge transfer and recombination

General idea



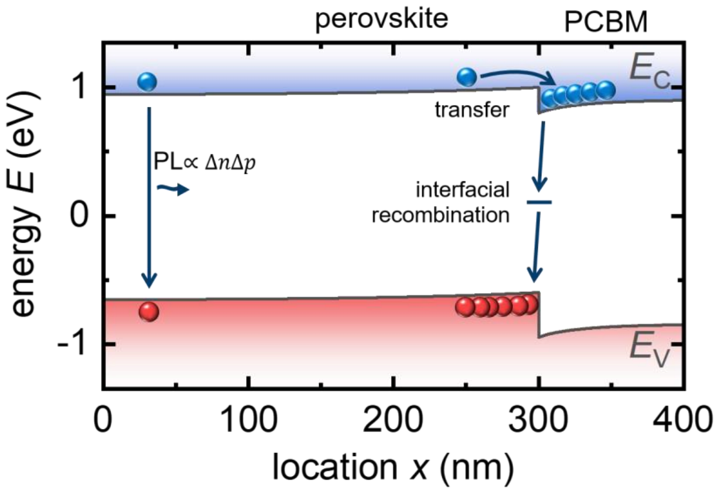




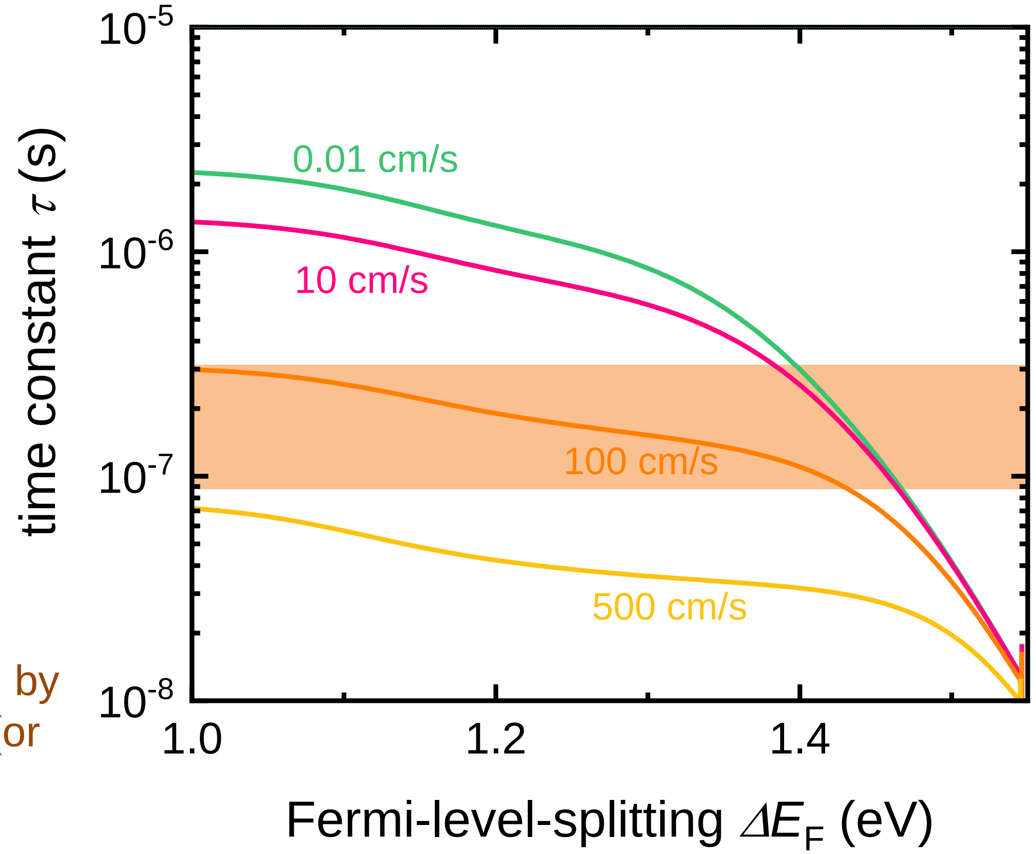


Charge transfer and recombination

Data

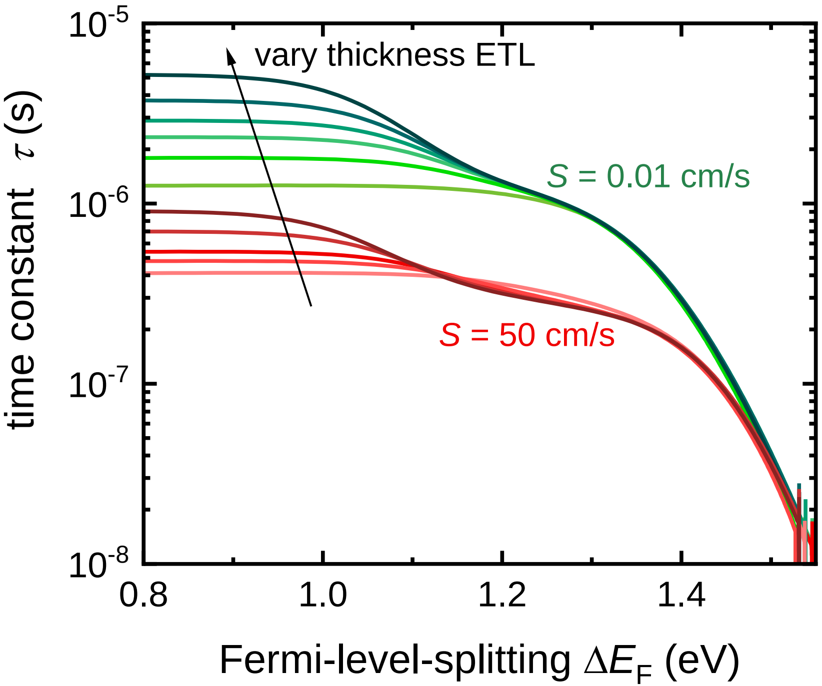


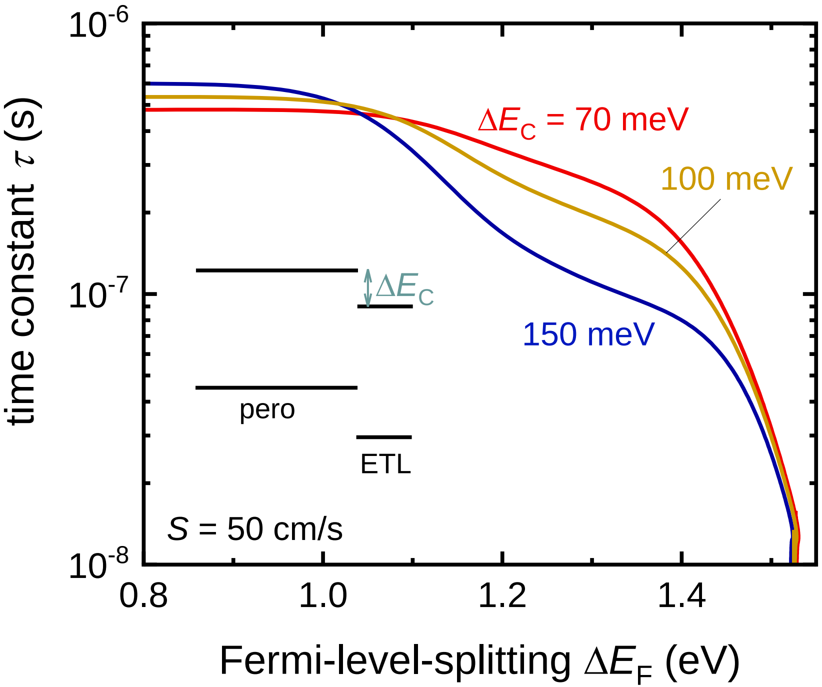
Time constant affected by band offsets and ETL (or HTL) thickness



Charge transfer and recombination

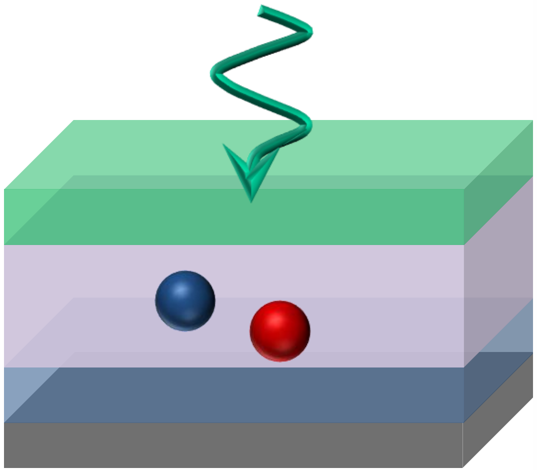
Effect of ETL thickness and band offsets



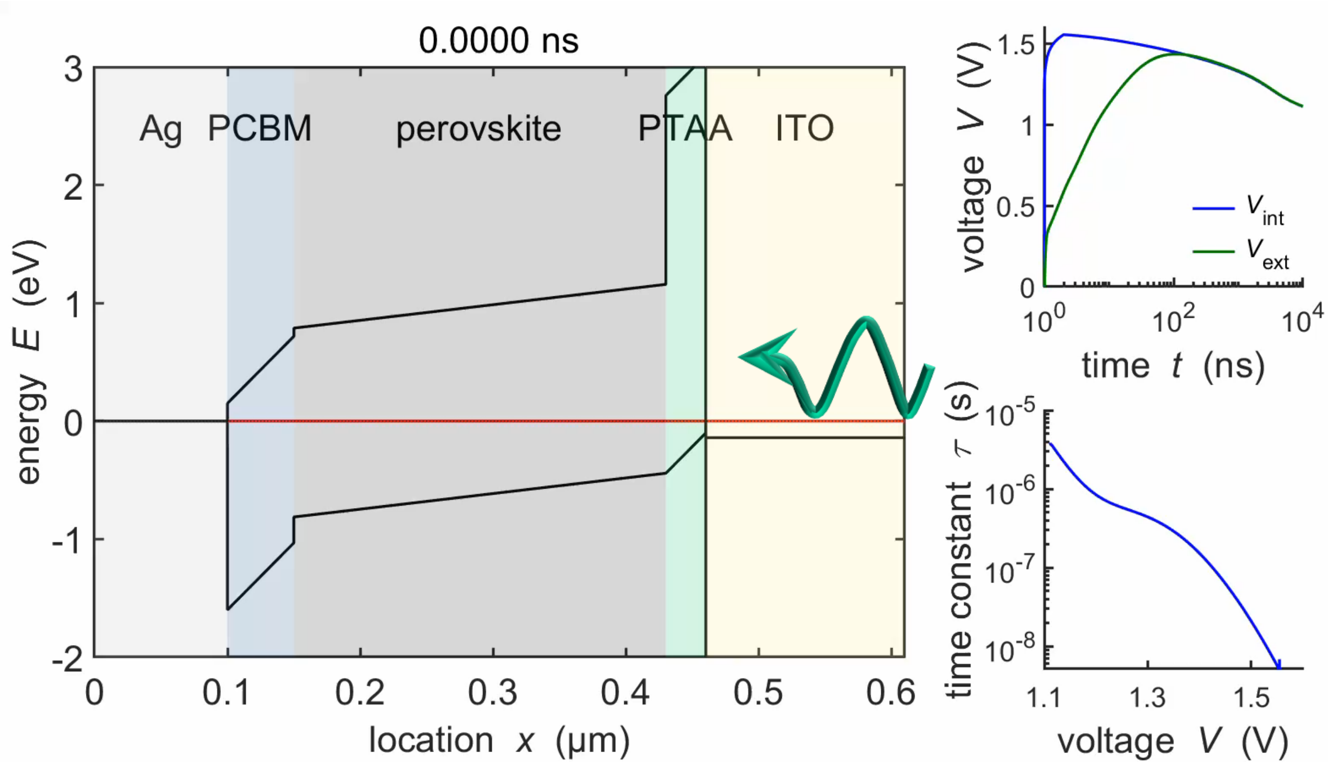


Transient Photoluminescence – Solar Cell

Video

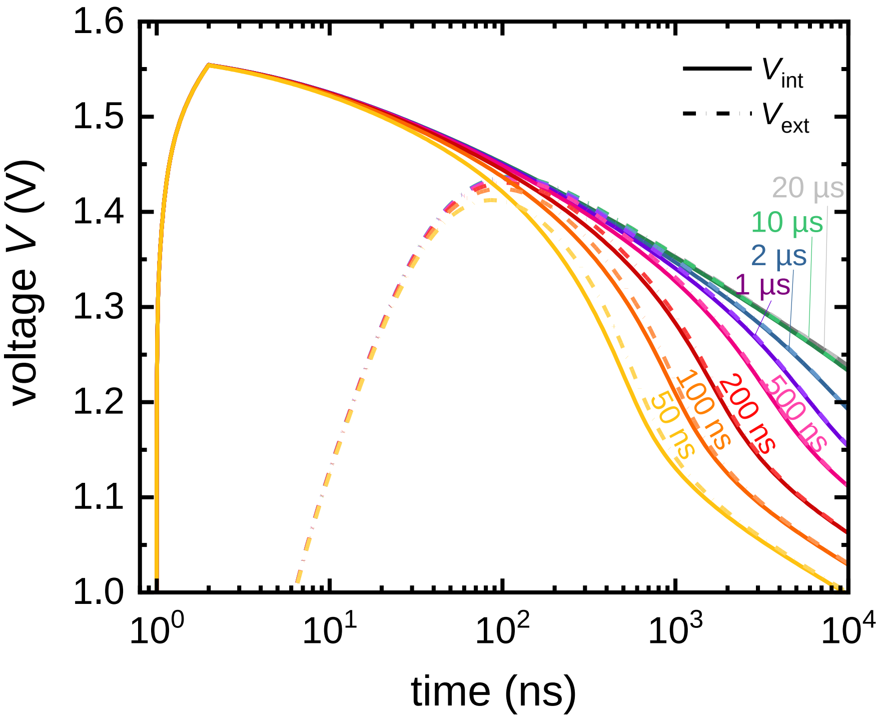


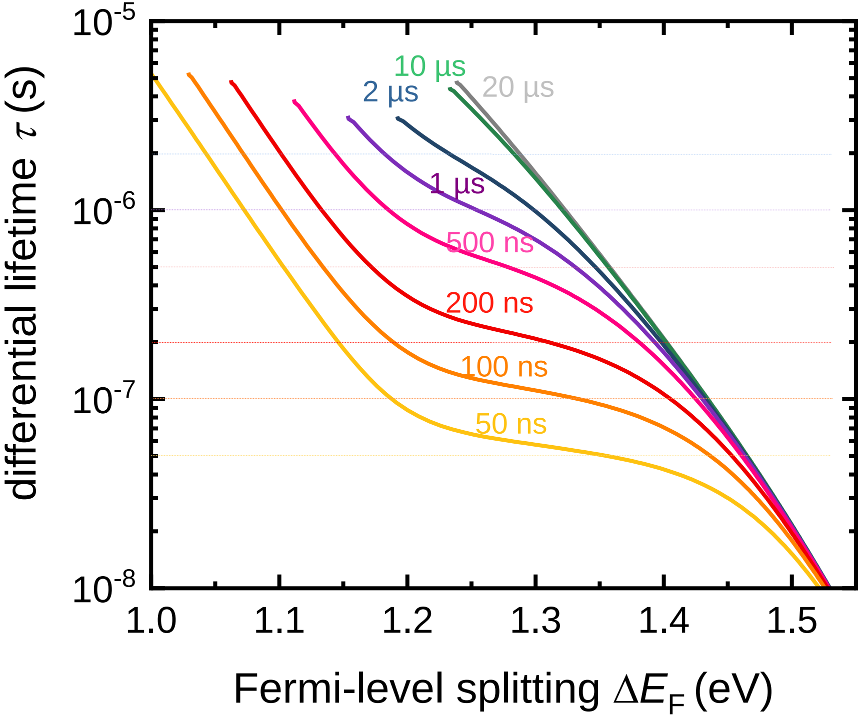
$$-\frac{dn}{dt} = kn^2 + \frac{n}{\tau} + \frac{C}{qd}\frac{dV}{dt}$$



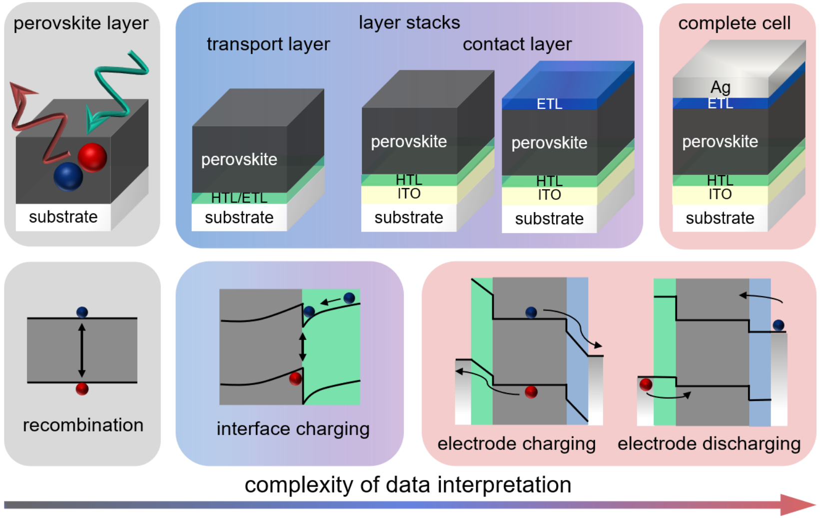
Large signal lifetime from TPL (wo bias)

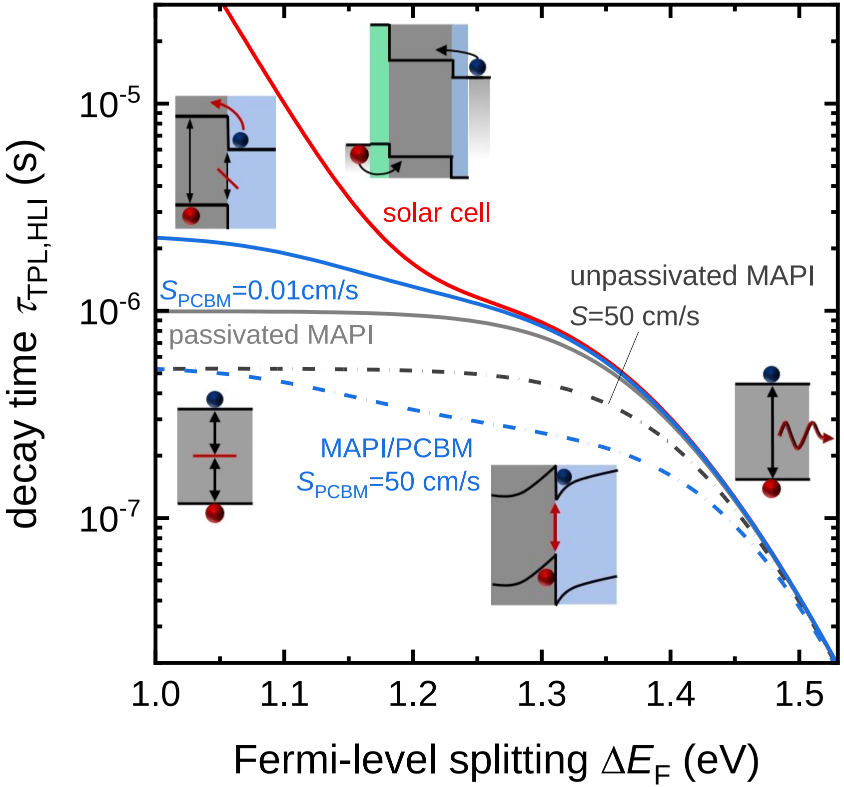
Bulk lifetime variation, S=0.1 cm/s, laser fluence 10 µJ/cm^2





Summary of the different effects

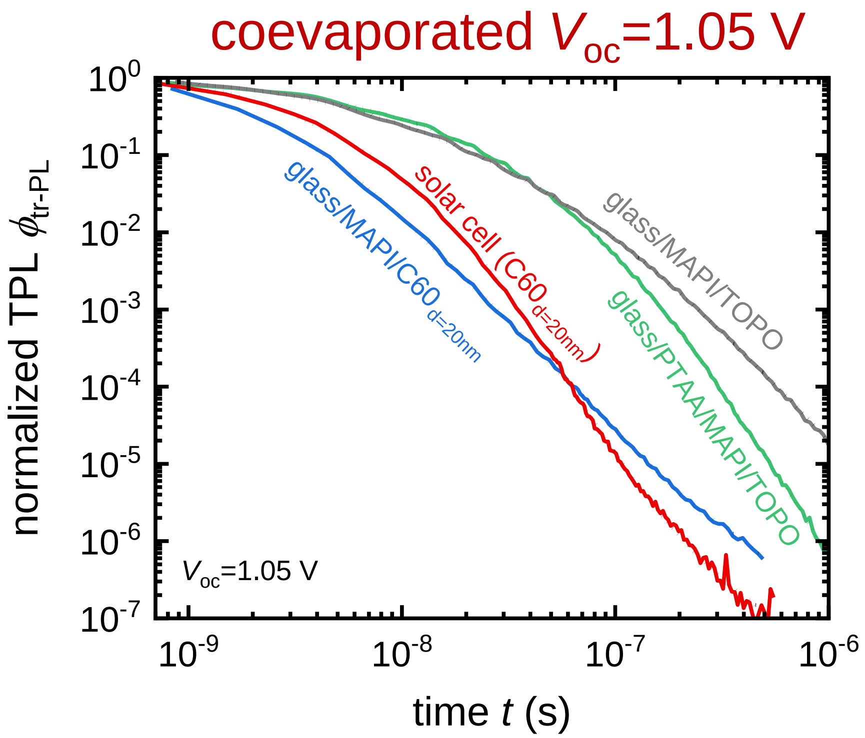


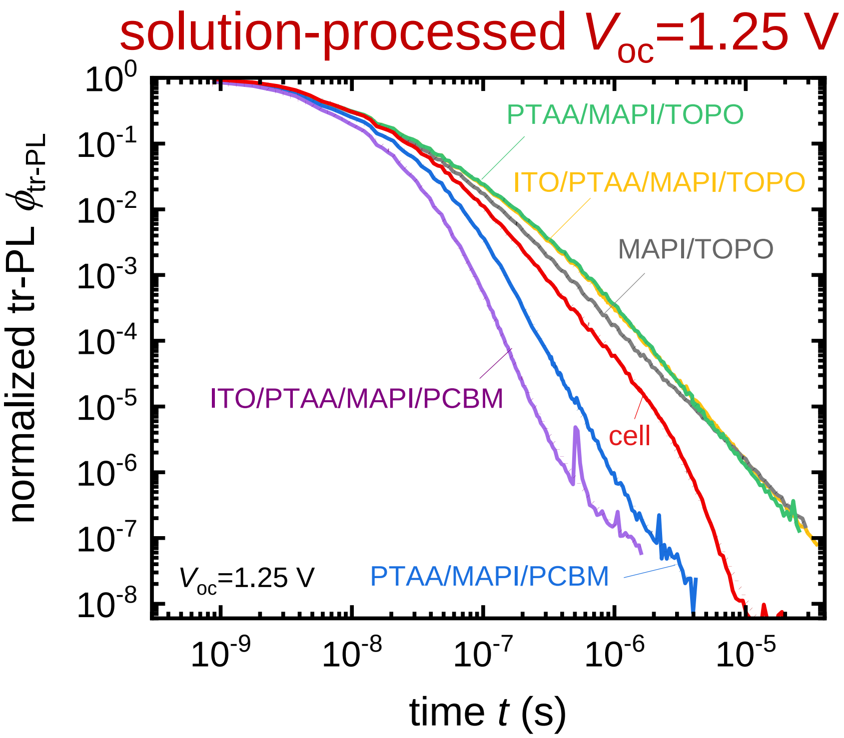


Krückemeier et al. (submitted)

Coevaporated vs. Solution-processed MAPI Solar Cells

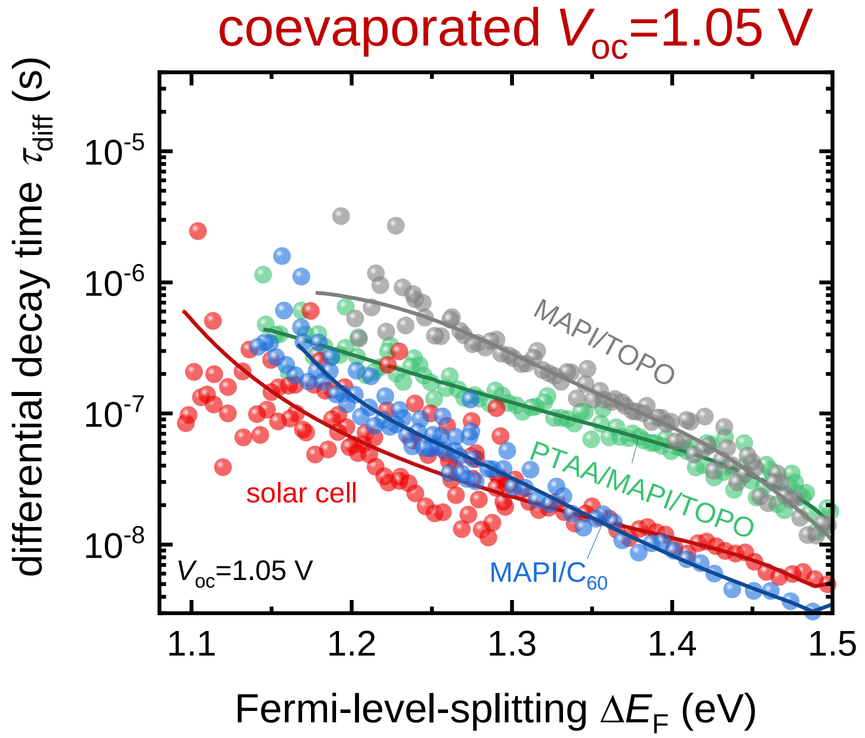
Experimental Data – Transient PL

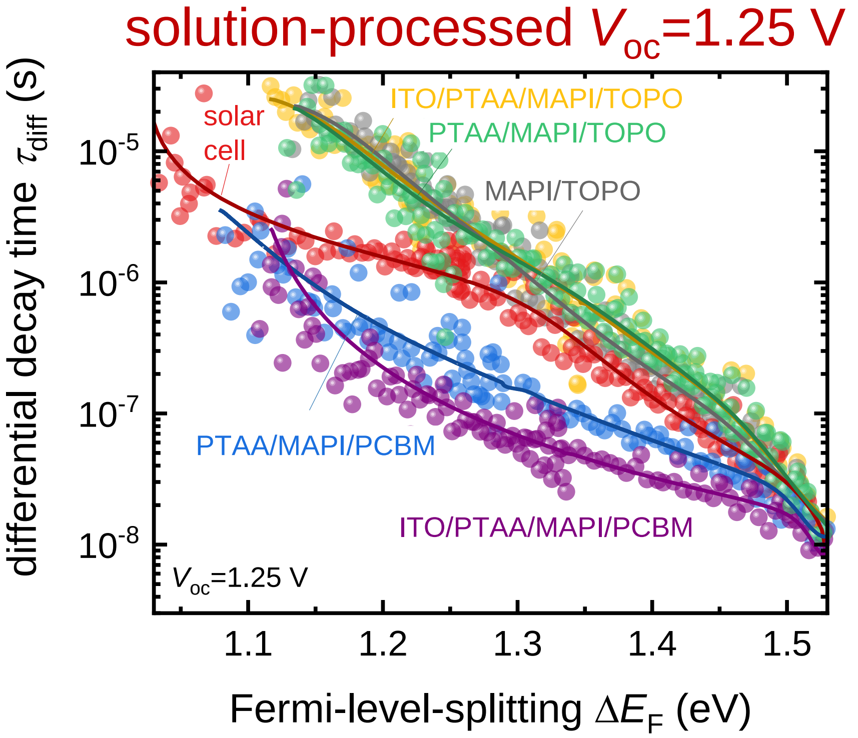




Coevaporated vs. Solution-processed MAPI Solar Cells

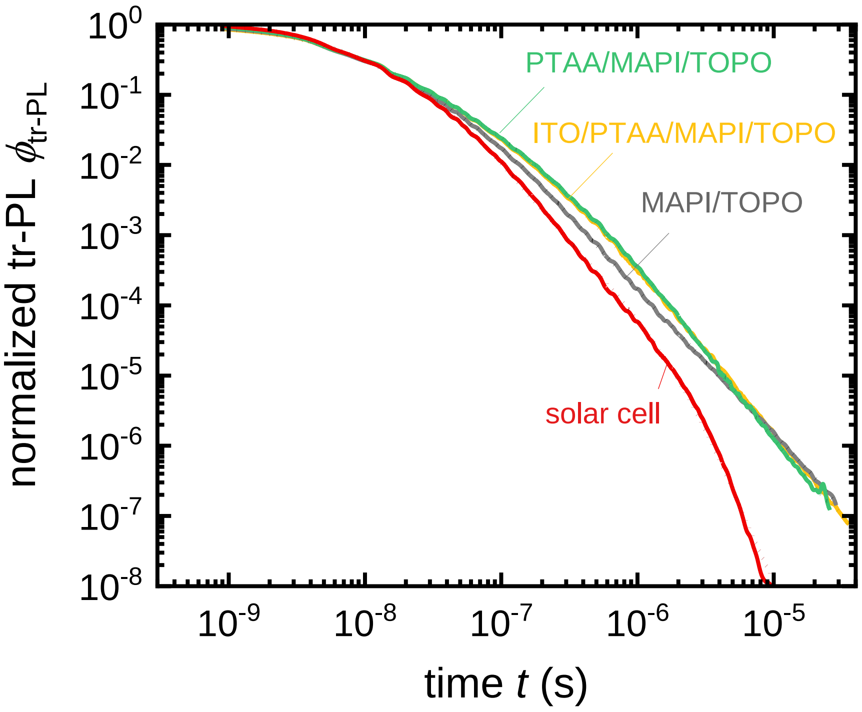
Experimental Data – Transient PL

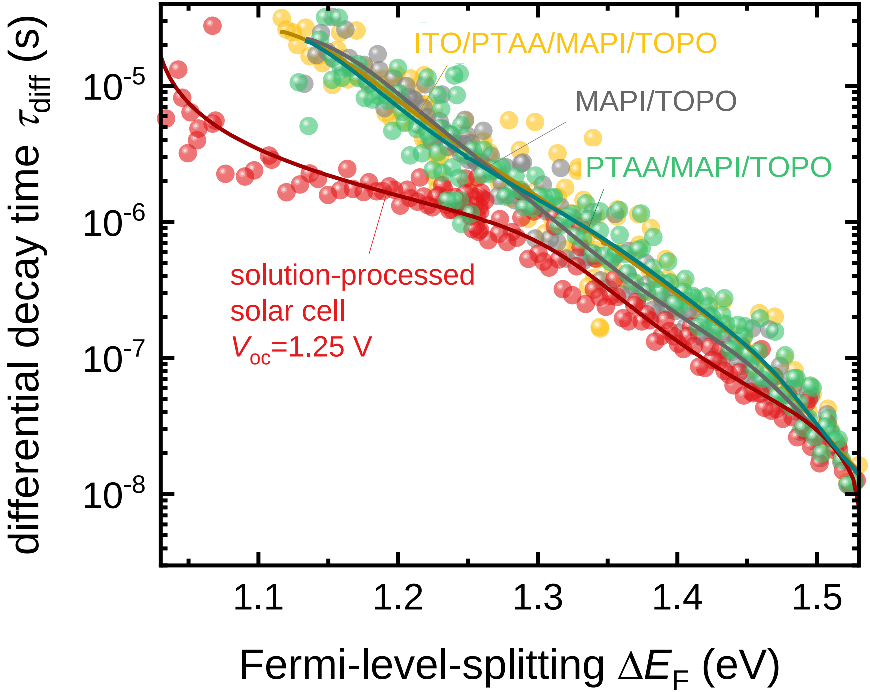




Sample series of solution-processed MAPI

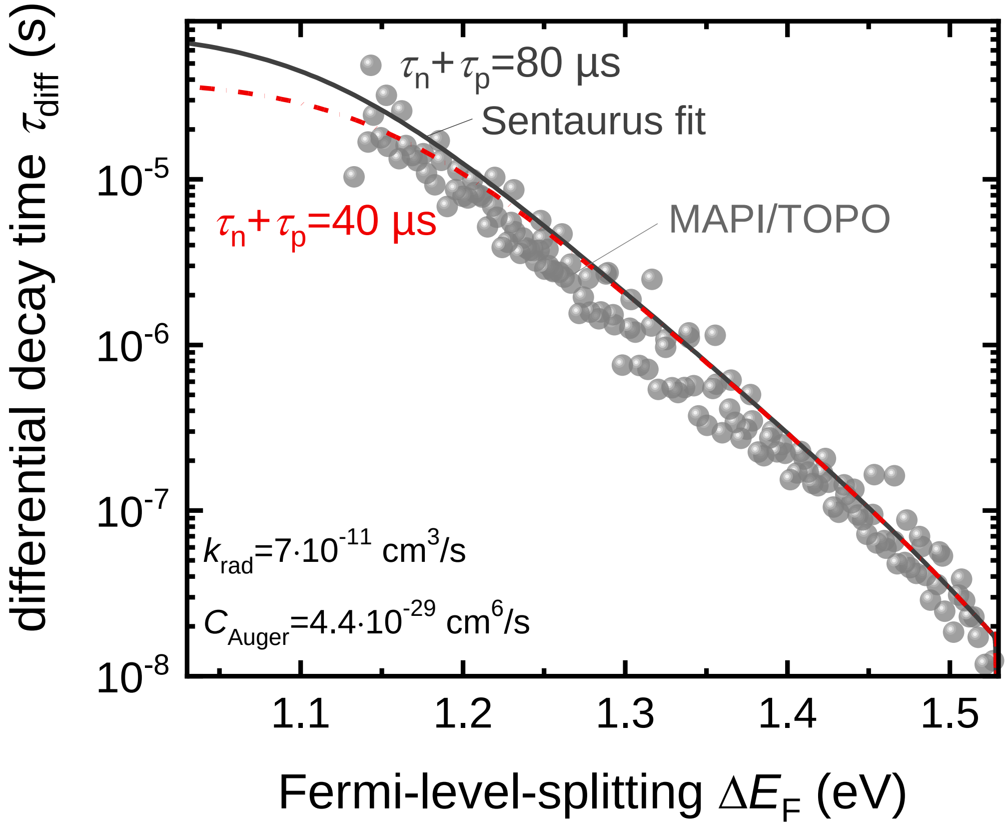
Experimental Data – Transient PL





Solution-processed MAPI – V_{oc}=1.25 V in cell

Explain experimental Data with Sentaurus Simulations



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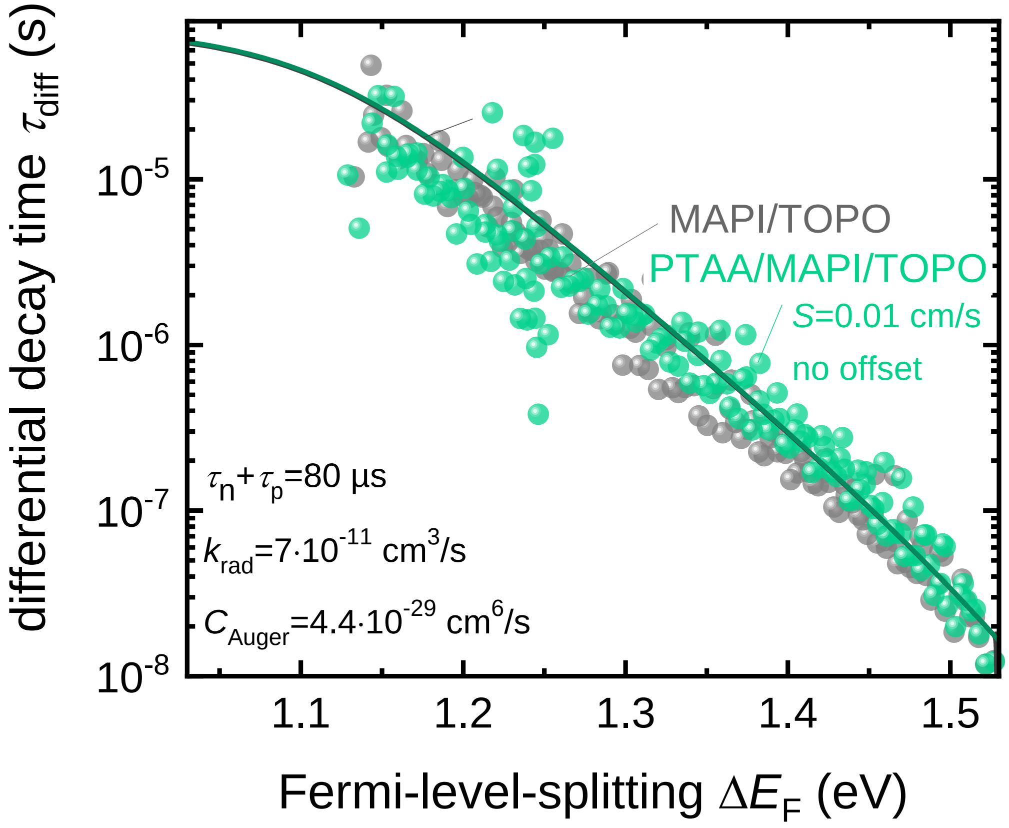

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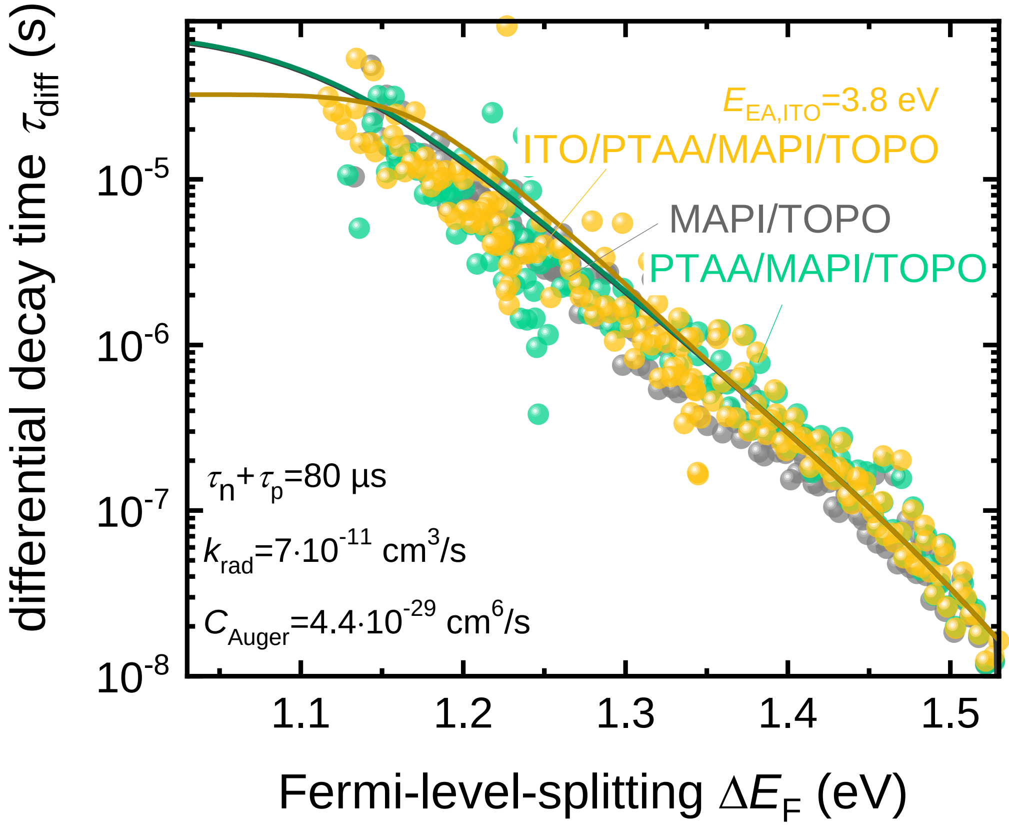

Solution-processed MAPI – V_{oc}=1.25 V in cell

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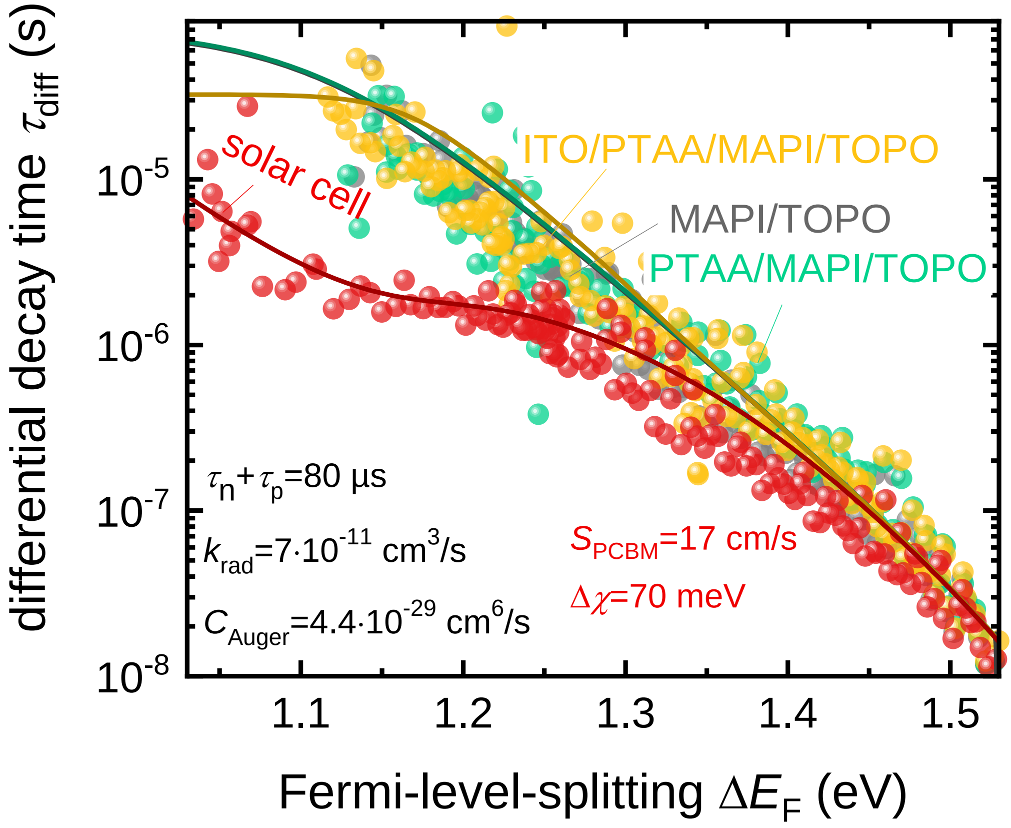
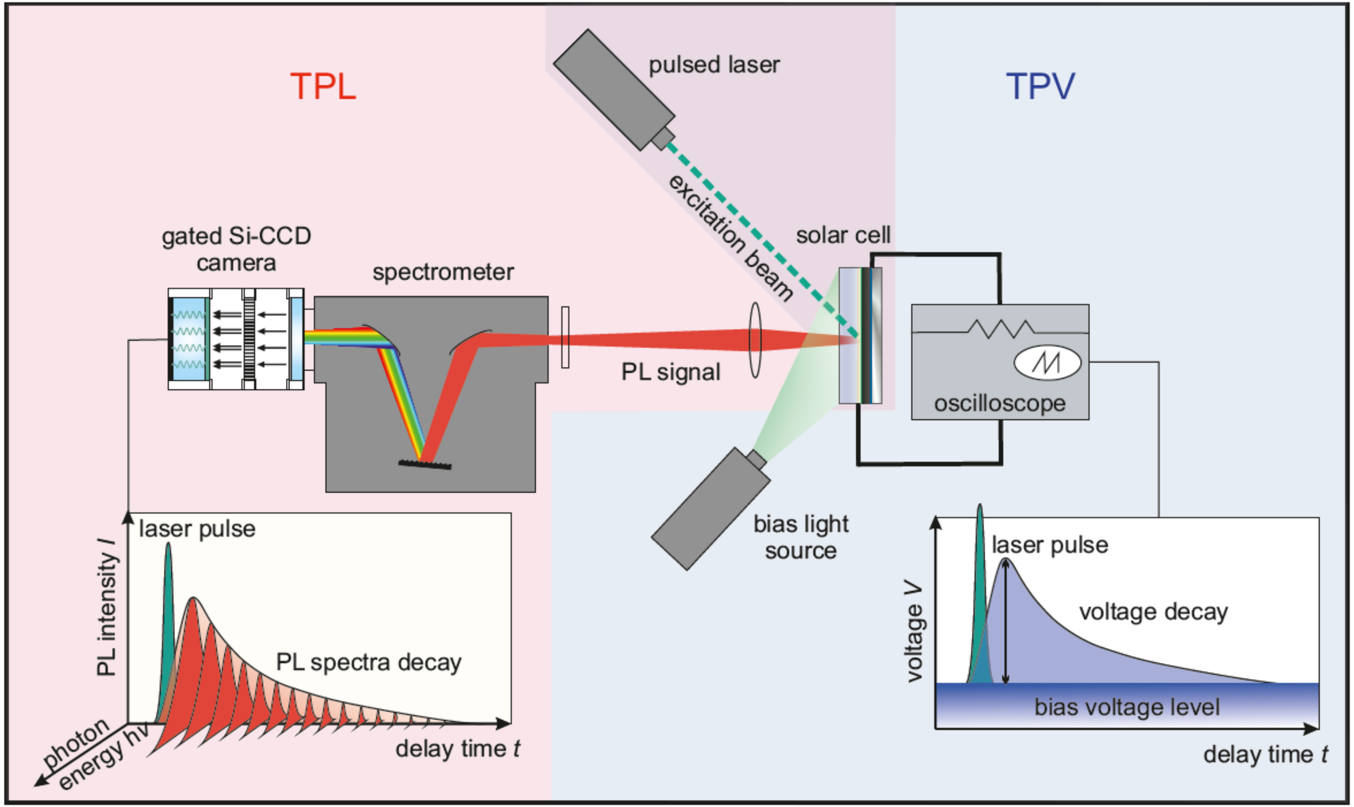


Transient Photoluminescence (TPL)

measures the luminescence decay

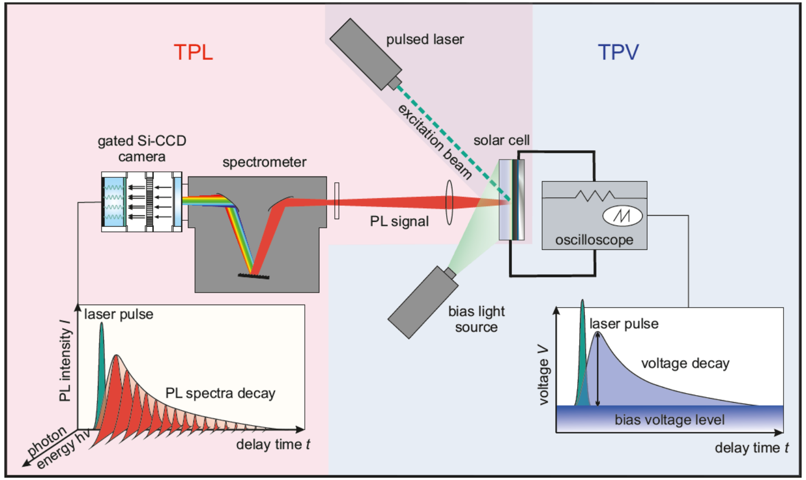
Transient Photovoltage (TPV)

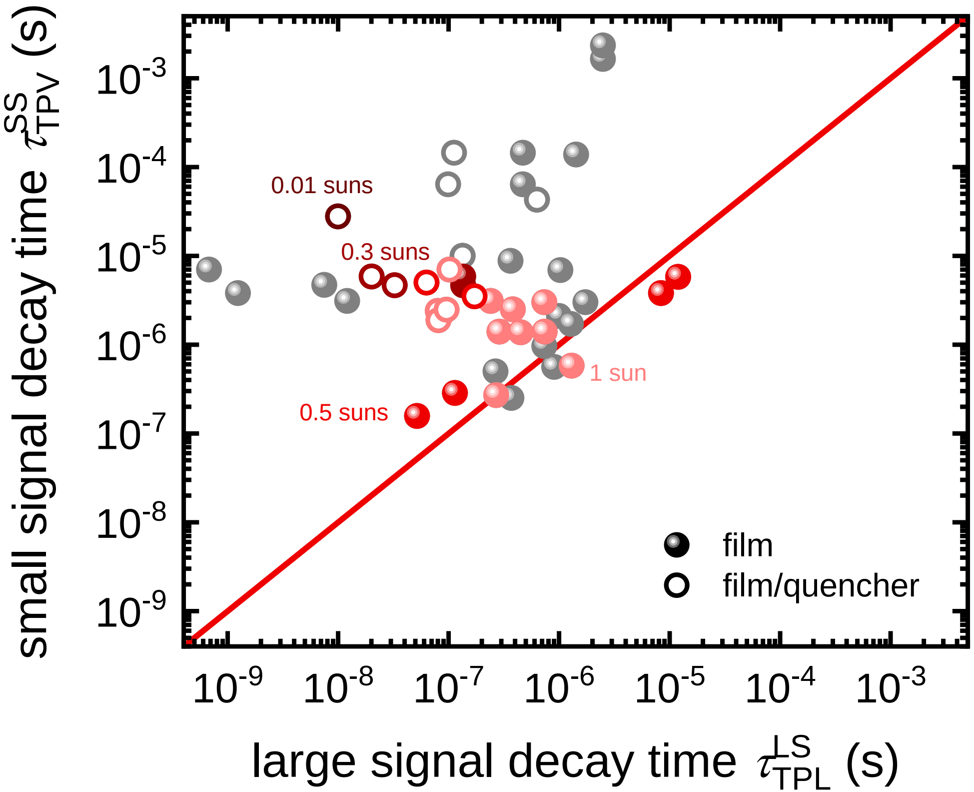
measures the decay of an external voltage



Metaanalysis: TPV vs. TPL

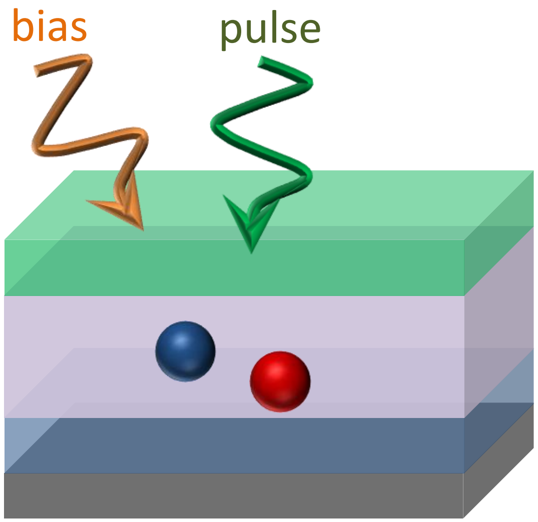
Fairly poor correlation between the two decay times. Why?

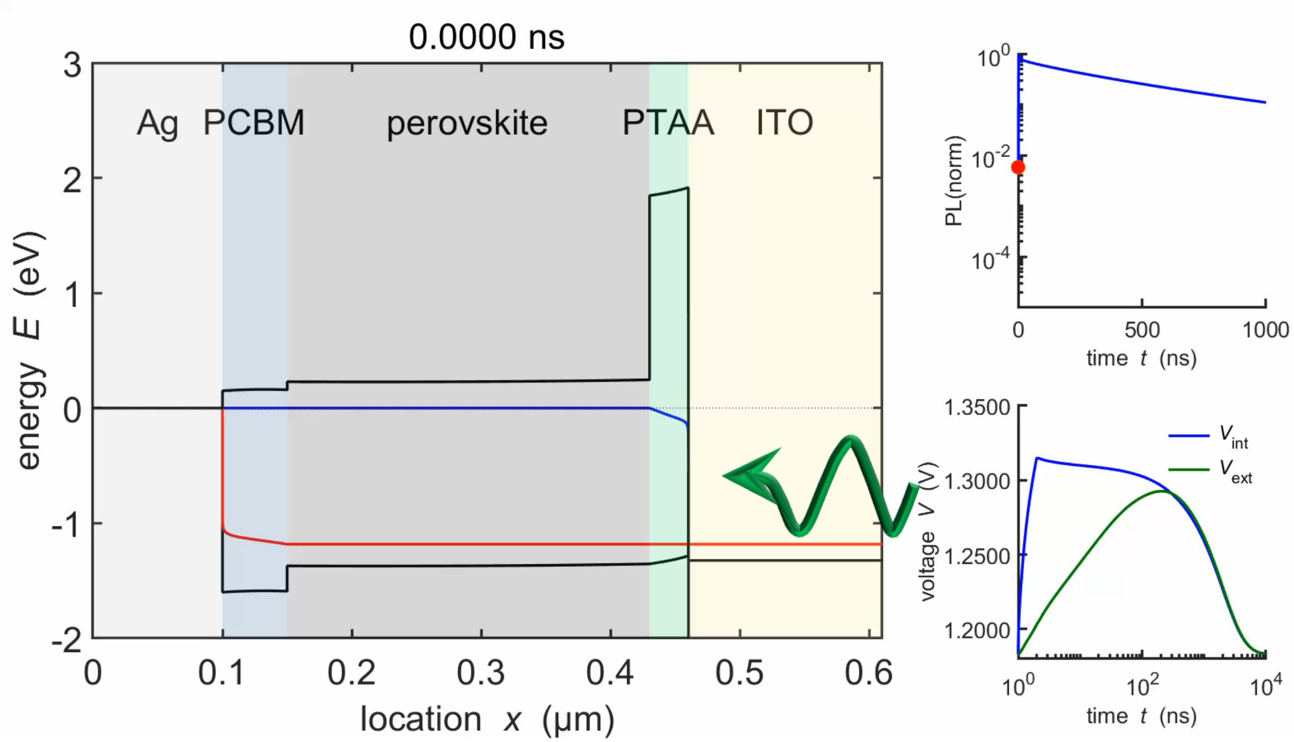




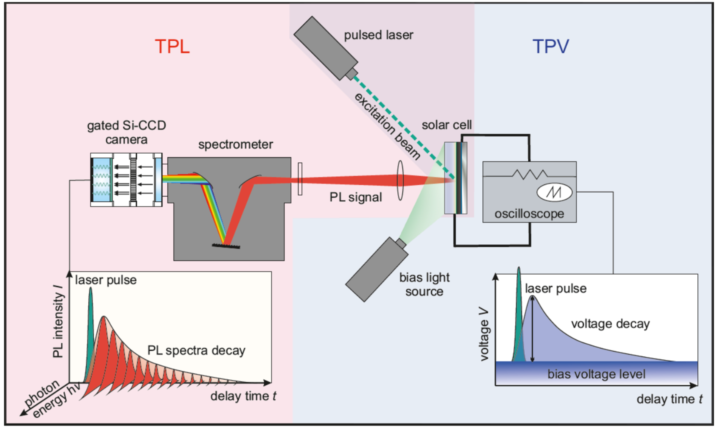
Transients with bias light

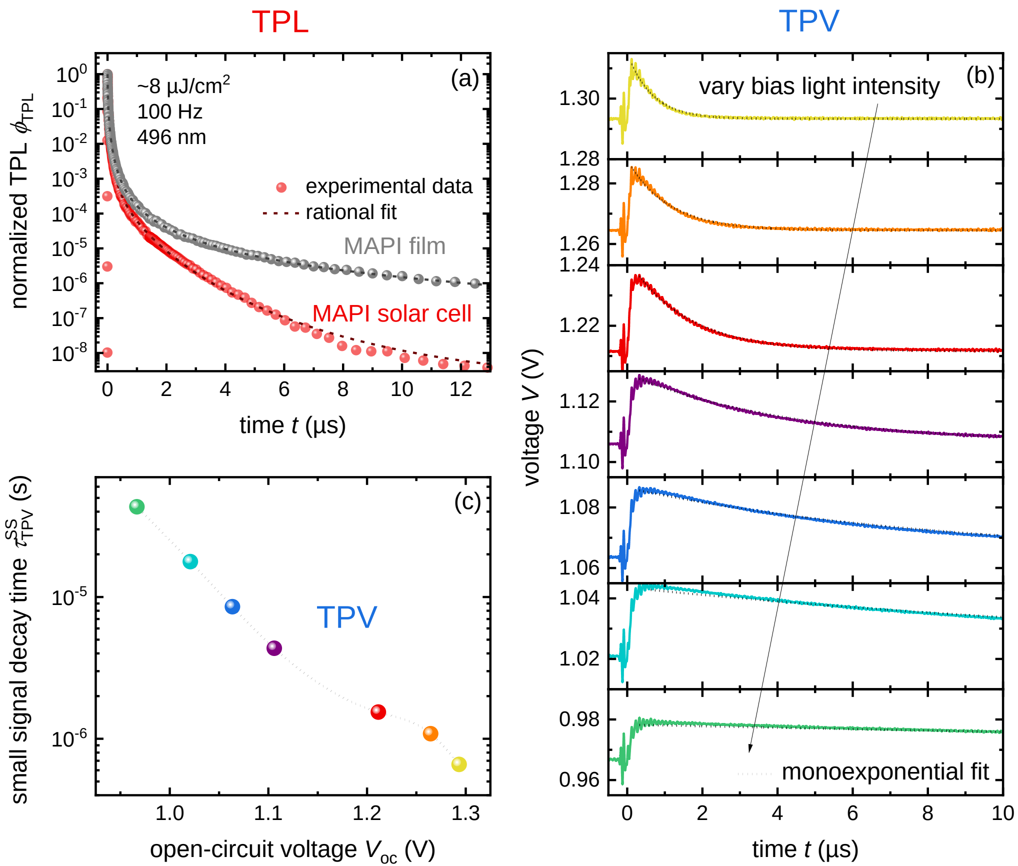
Video TPV vs. TPL



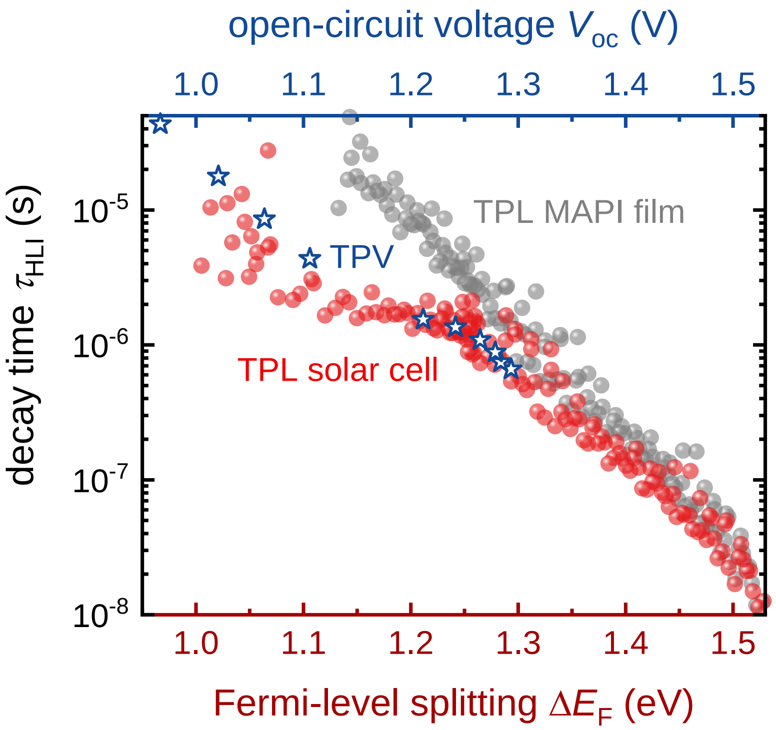


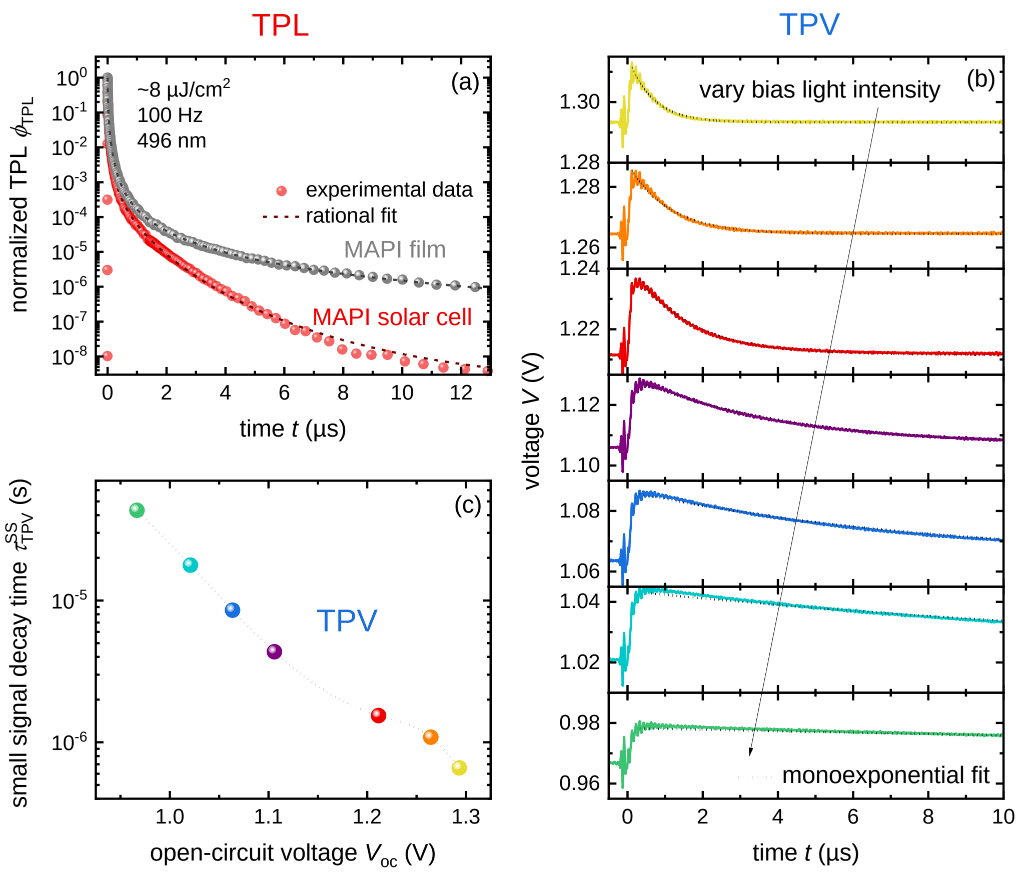
What is typically measured?



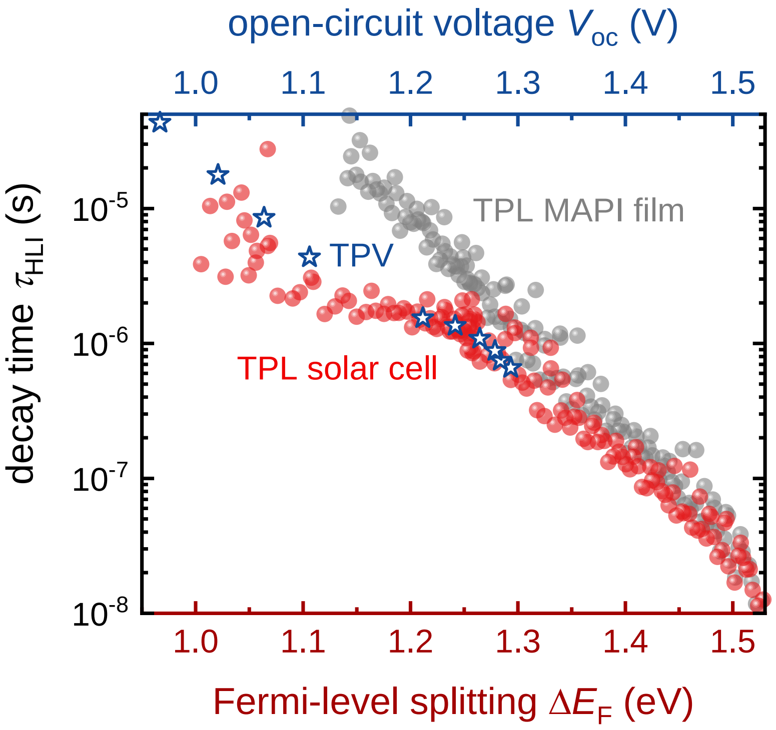


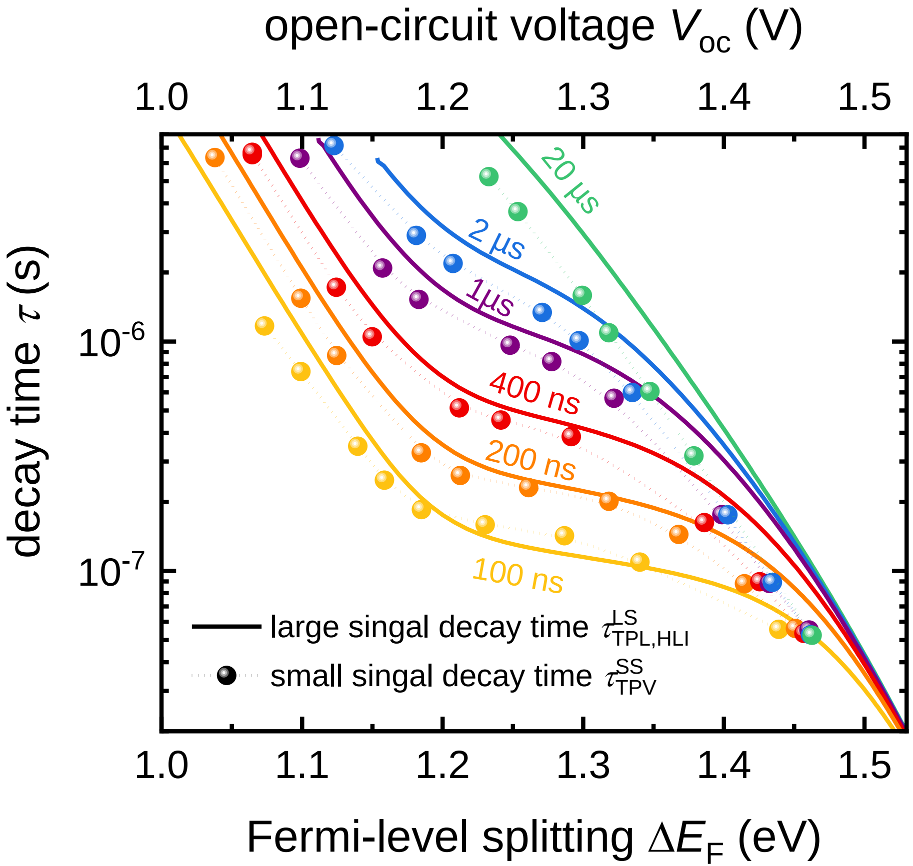
How to make sense out of it



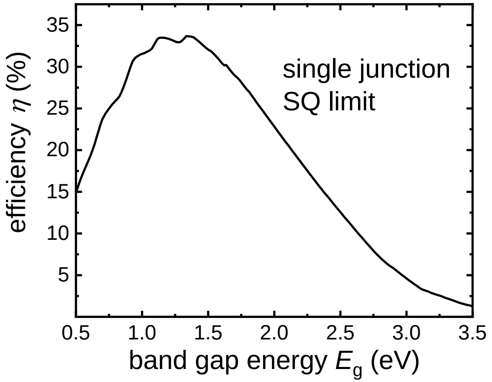


Comparison to simulations



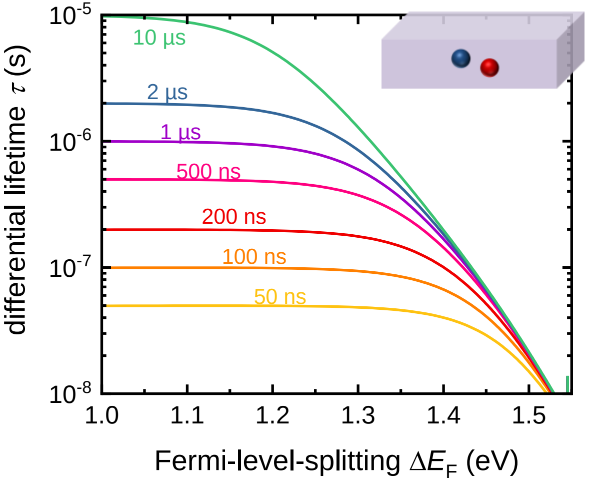


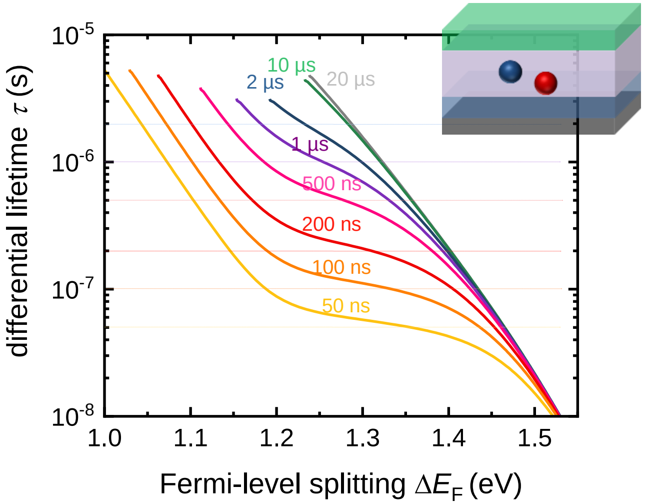
Summary



1) **From ideal solar cells (SQ model) to real solar cells. Interfaces are a substantial factor for $\eta_{real} < \eta_{SQ}$.**

2) **Interpretation of decay constants as a function of sample geometry**





Thanks to
Thomas Unold
Jose Marquez
Martin Stolterfoht
Uwe Rau
Helmholtz Association for Funding

Thank you for your attention

comment

Guide for the perplexed to the Shockley–Queisser model for solar cells

The Shockley–Queisser model is a landmark in photovoltaic device analysis by defining an ideal situation as reference for actual solar cells. However, the model and its implications are easily misunderstood. Thus, we present a guide to help understand and to avoid misinterpreting it.

Jean-Francois Guillemoles, Thomas Kirchartz, David Cahen and Uwe Rau

PROGRESS REPORT

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How to Report Record Open-Circuit Voltages in Lead-Halide Perovskite Solar Cells

Lisa Krückemeier, Uwe Rau, Martin Stolterfoht, and Thomas Kirchartz**

PROGRESS REPORT

Solar Cells

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What Makes a Good Solar Cell?

Thomas Kirchartz and Uwe Rau*

Energy & Environmental Science

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The impact of energy alignment and interfacial recombination on the internal and external open-circuit voltage of perovskite solar cells†

Martin Stolterfoht, *[a] Pietro Caprioglio, [ab] Christian M. Wolff, [a] José A. Márquez, [c] Joleik Nordmann, [a] Shanshan Zhang, [a] Daniel Rothhardt, [a] Ulrich Hörmann, [a] Yohai Amir, [a] Alex Redinger, [h] Lukas Kegelmann, [b] Fengshuo Zu, [de] Steve Albrecht, [b] Norbert Koch, [de] Thomas Kirchartz, [f] Michael Saliba, [g] Thomas Unold*[c] and Dieter Neher *[a]

PROGRESS REPORT

ADVANCED ENERGY MATERIALS

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Photoluminescence-Based Characterization of Halide Perovskites for Photovoltaics

Thomas Kirchartz, José A. Márquez, Martin Stolterfoht, and Thomas Unold**

Useful literature on the contents of the talk

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum