ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANO SCIENCE AND TECHNOLOGY

Solution processable photovoltaics: Science and technology

The Jacob Blaustein Center for Scientific Cooperation
The Jacob Blaustein Institutes for Desert Research
Ben-Gurion University of the Negev

IKI
Ilse Katz Institute for Nanoscale Science and Technology

ENEA
Italian National Agency for New Technologies, Energy and Sustainable Economic Development

Via the Italian Ministry of Foreign Affairs and International Cooperation (MAECI)

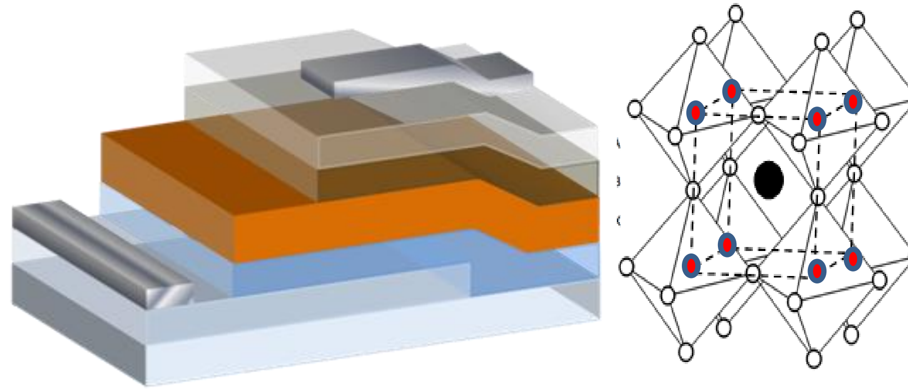
Ministry of National infrastructure, Energy and Water Resources
www.energy.gov.il

20th Sede Boqer Symposium
on Solar Electricity Production
jointly with the
IKI Annual Nano-Day
and the
BGU-ENEA WORKSHOP
September 26-28, 2016

Guglielmo Lanzani

CNST@POLIMI Istituto Italiano di Tecnologia, Milan Italy

ribes TECH



Perovskite

iit @POLIMI

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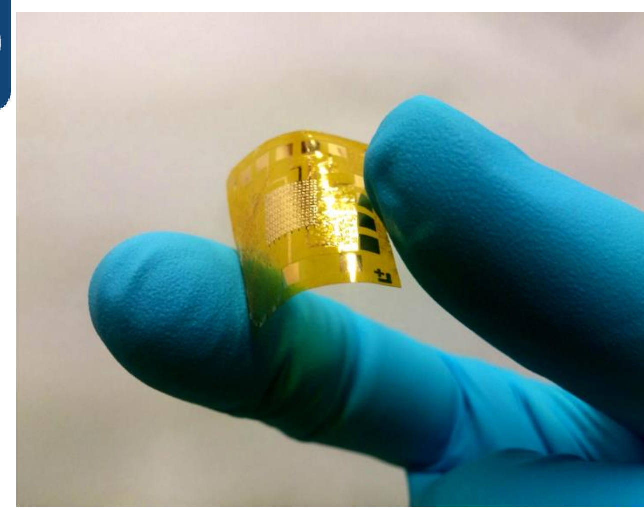

Photo-catalytic Water Splitting

Organic thermoelectricity

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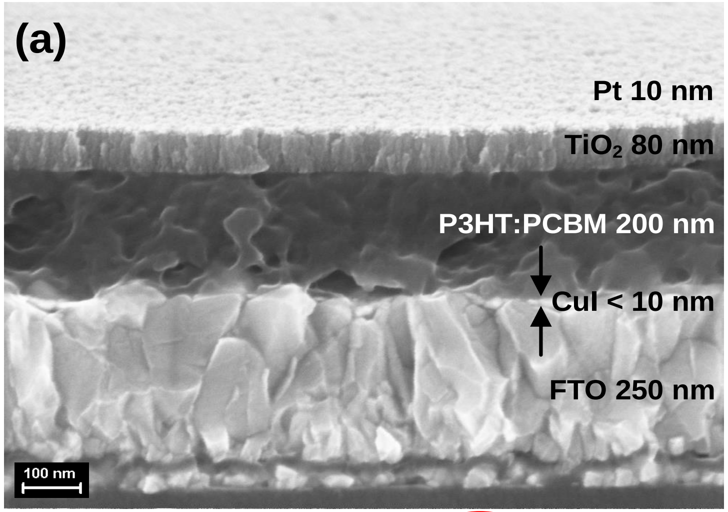
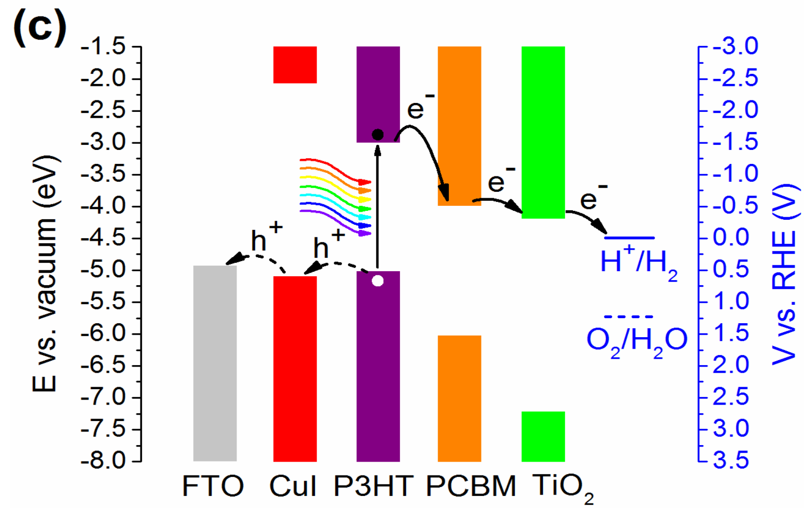
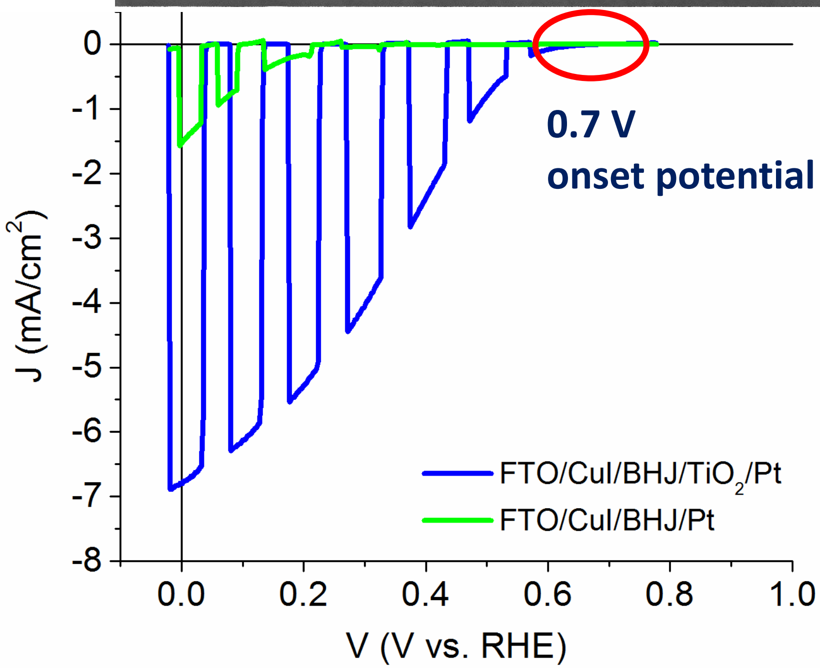
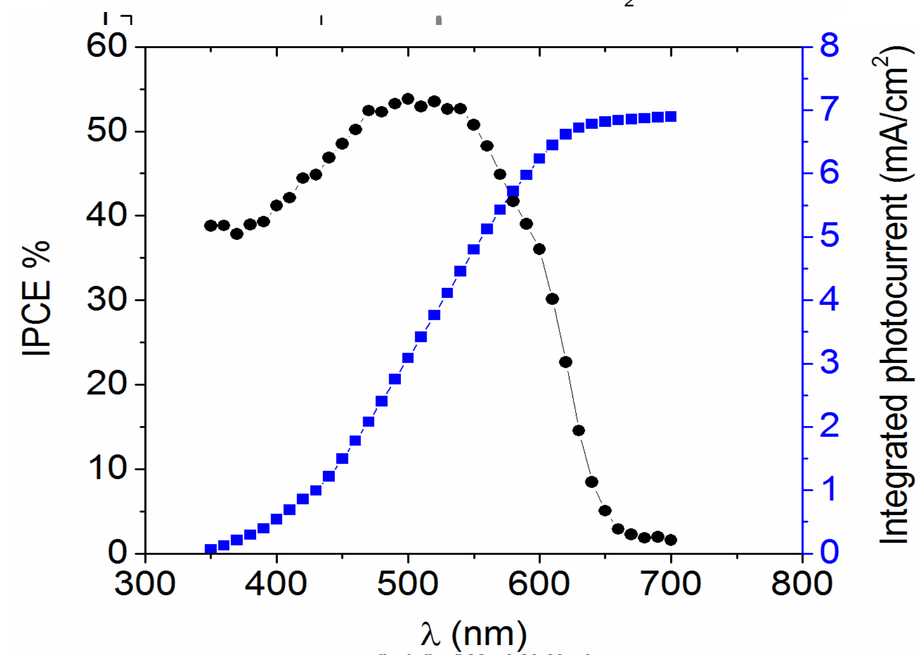
Hybrid Organic Photoelecrochemical Water Splitting

Fumagalli et al. JMCA (2016), Comas et al. EES (2016)









ribes TECHNOLOGIES

Ribes Technologies will produce plastic photovoltaic (PV) foils

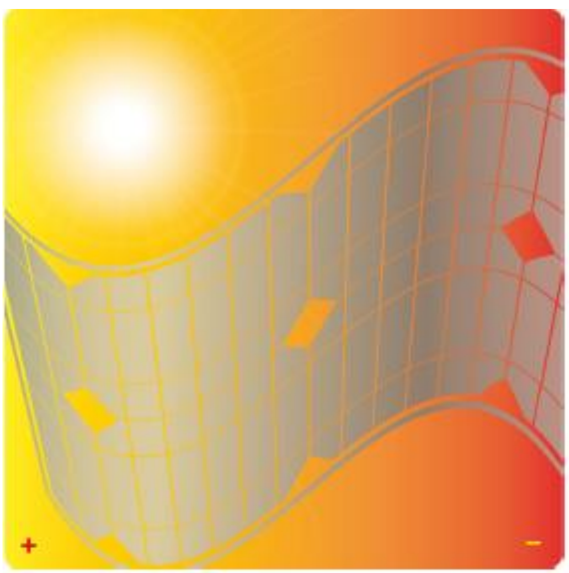
Wireless power supply for the internet of things

WORLD ECONOMIC FORUM

COMMITTED TO IMPROVING THE STATE OF THE WORLD

Global Agenda

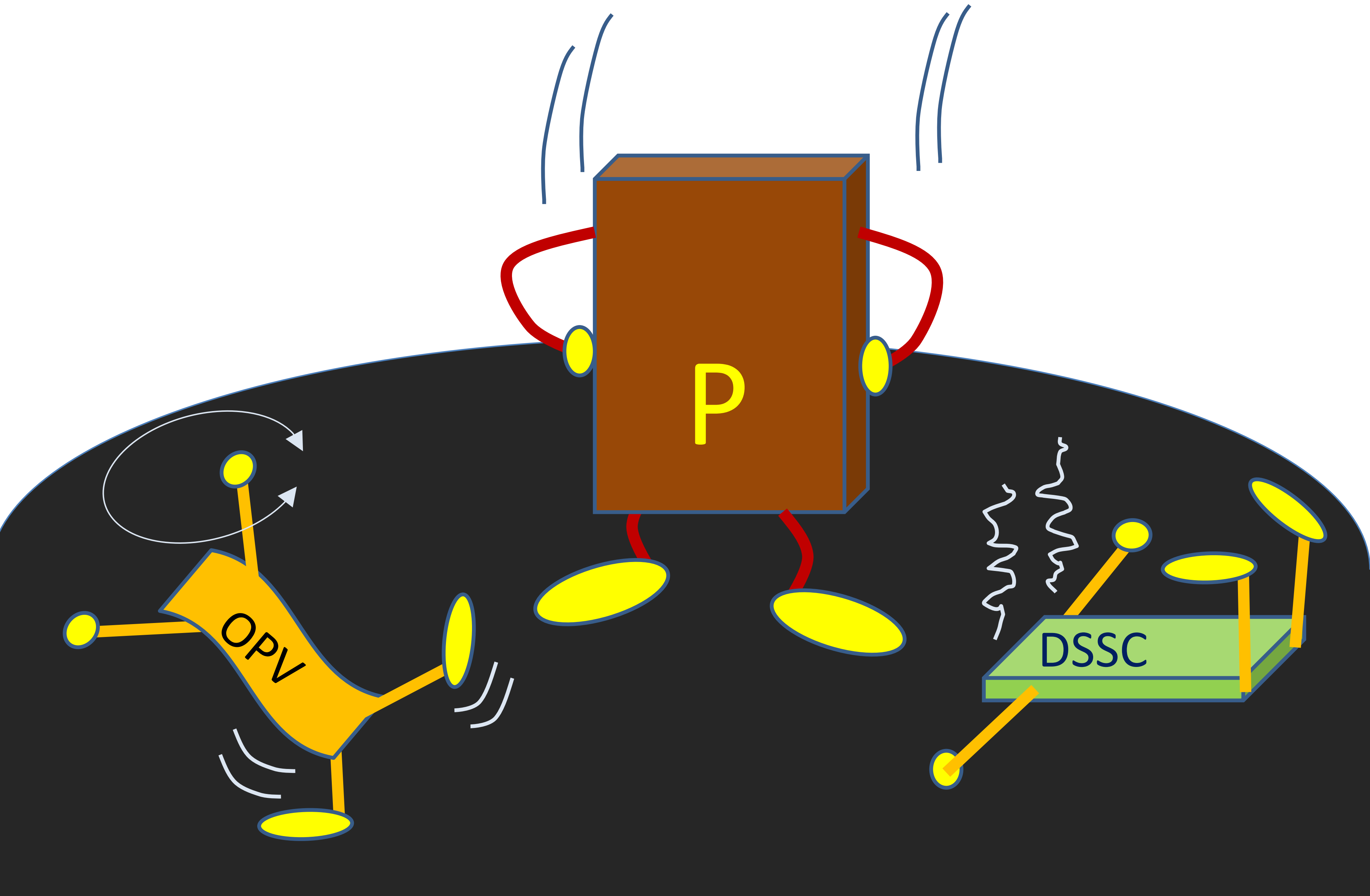
Top 10 Emerging Technologies of 2016



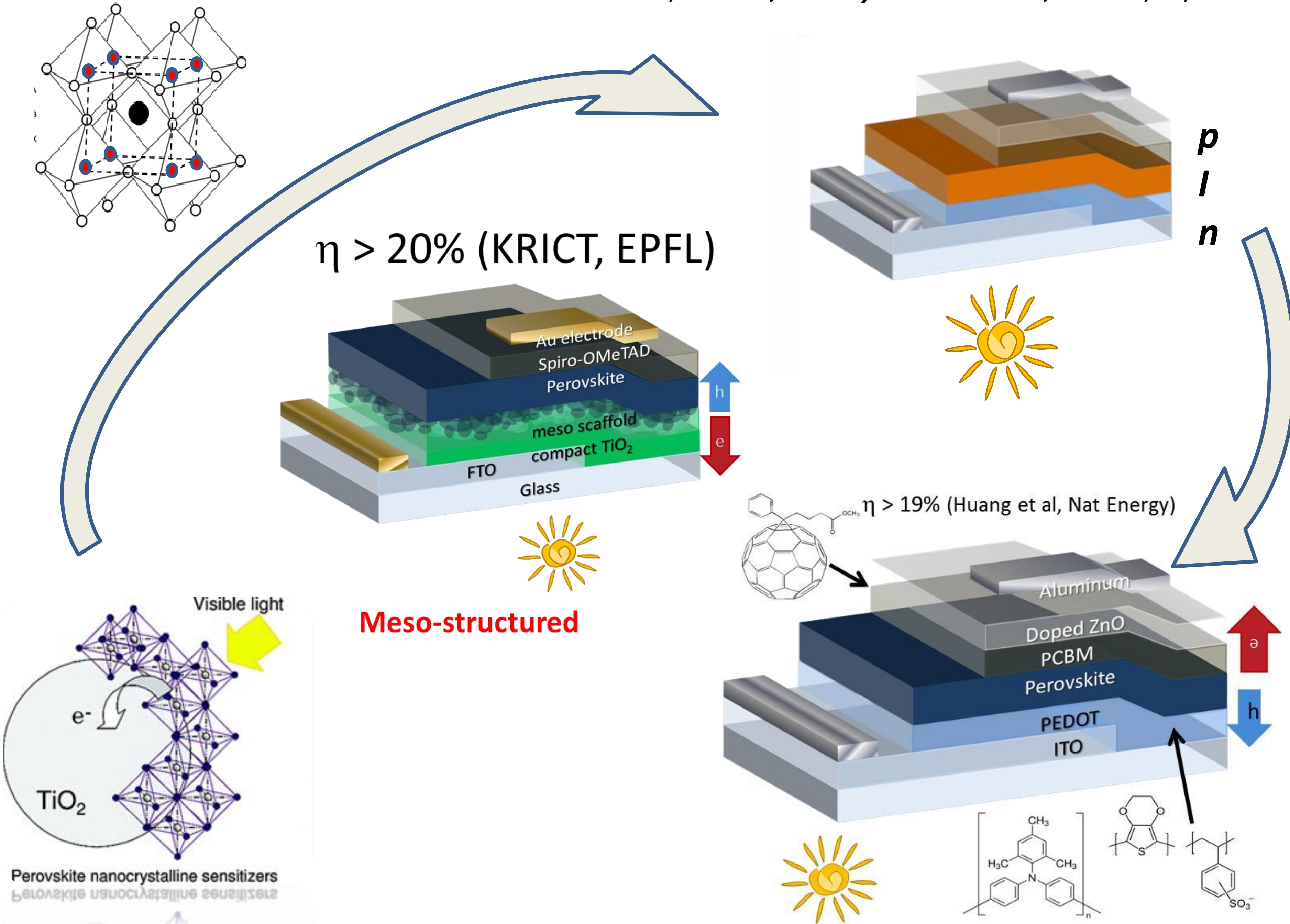
Perovskite Solar Cells

Making progress towards ubiquitous solar power generation

The Perovskite Revolution



H. Snaith, et al., *J. Phys.Chem. L.*, 2014, **5**, 1511



Planar Solar Cells For Tandem Structure

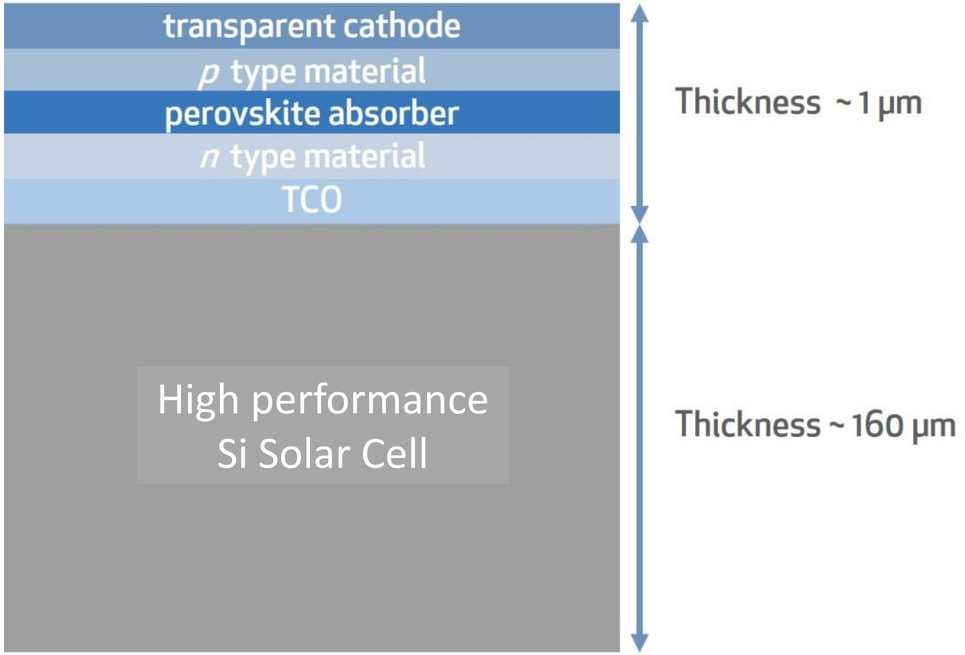
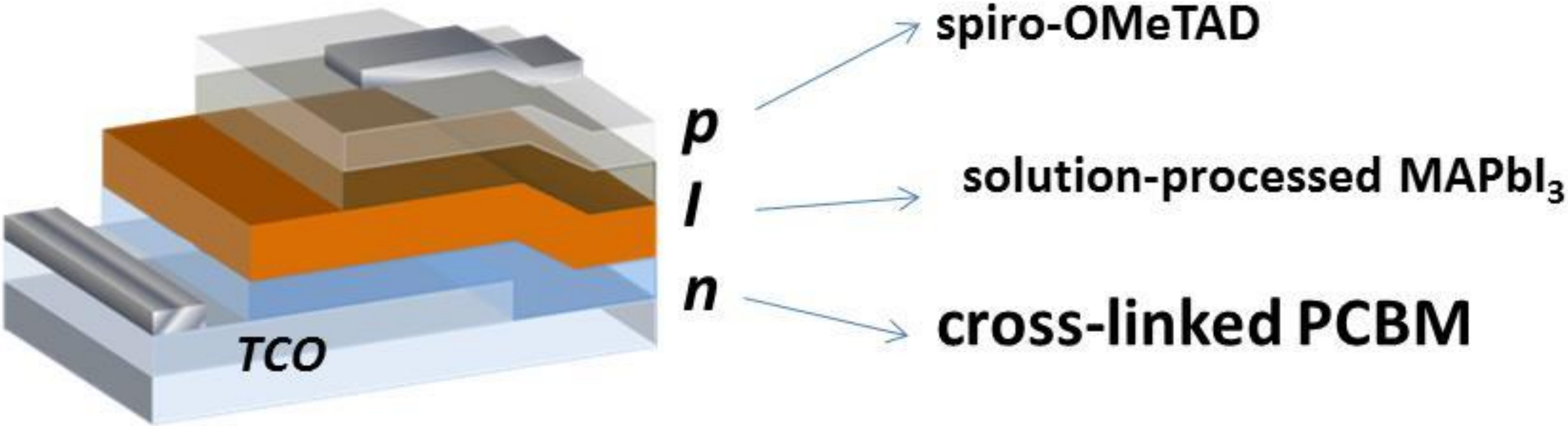


Figure credit: OxfordPV Ltd website

- ✓ Low temperature processing
- ✓ High Efficiency in Steady State Conditions
- ✓ Multi-layers processing

All-Solution Low T Planar Solar Cells

Chen Tao (陶 晨)



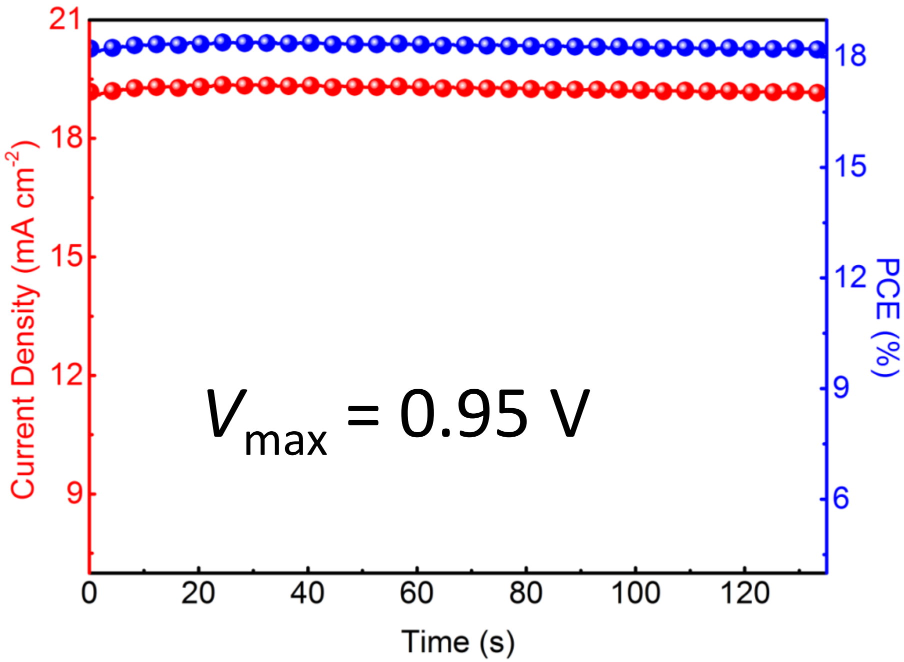
Direct Architecture

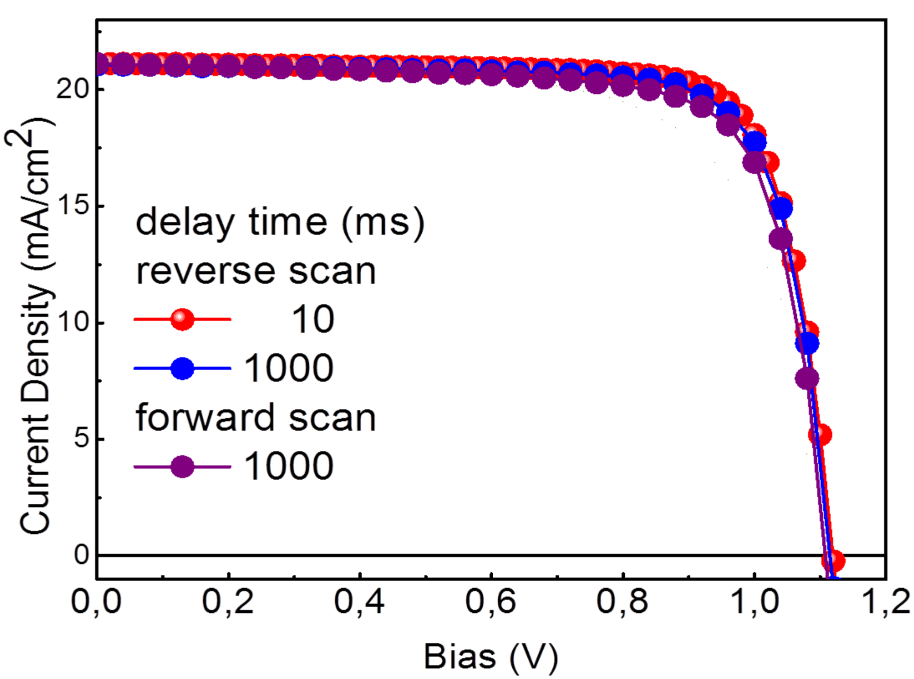
C. Tao et al, *submitted.*

All-Solution Processed Planar Solar Cells

Device performance

TiO_2/x-PCBM

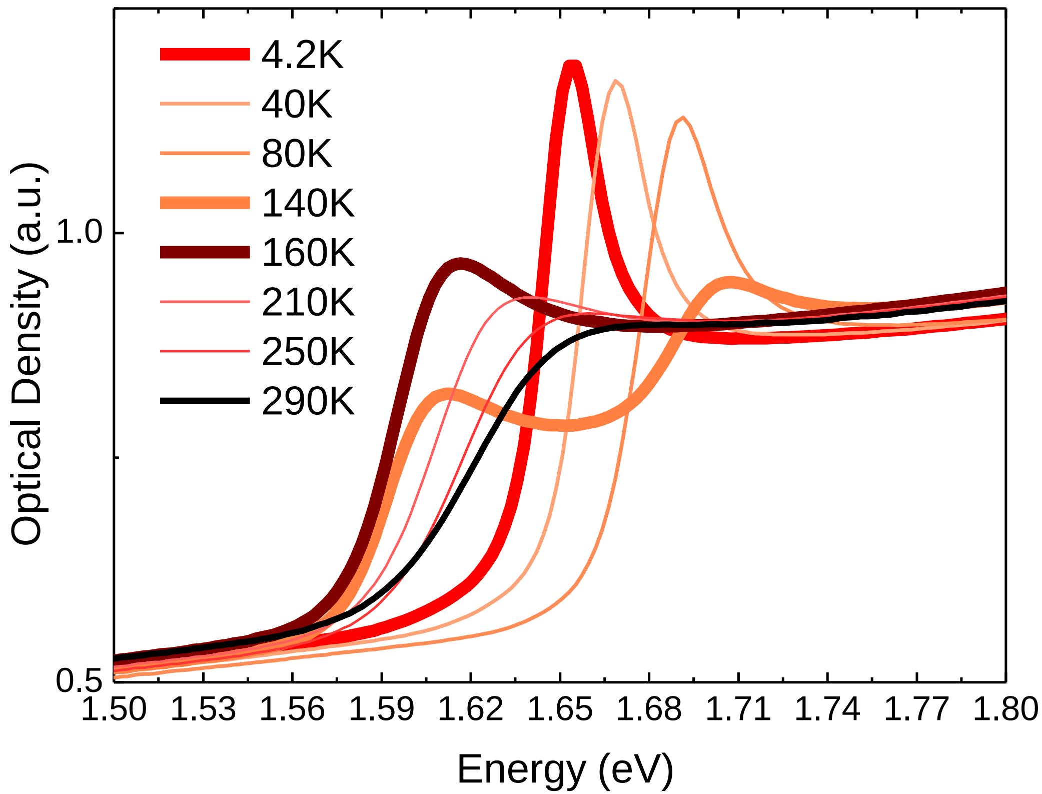




V_{OC} (V)	J_{SC} ($mA\ cm^{-2}$)	FF (%)	PCE (%)
1.12	21.1	79	18.7

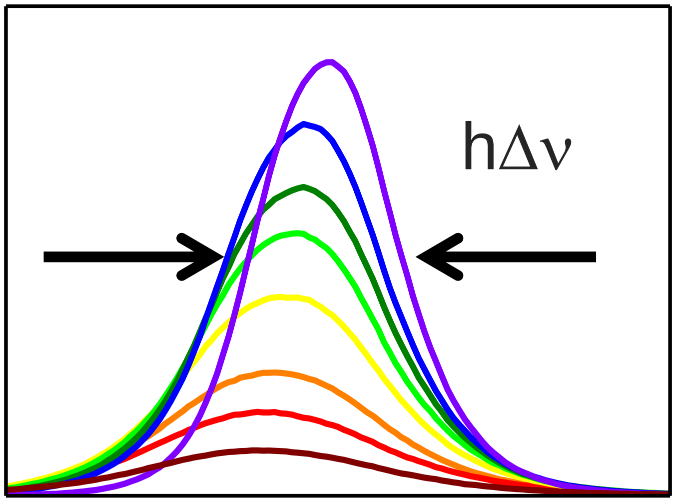
C. Tao et al, *submitted.*

Which Photoexcitation in working devices?



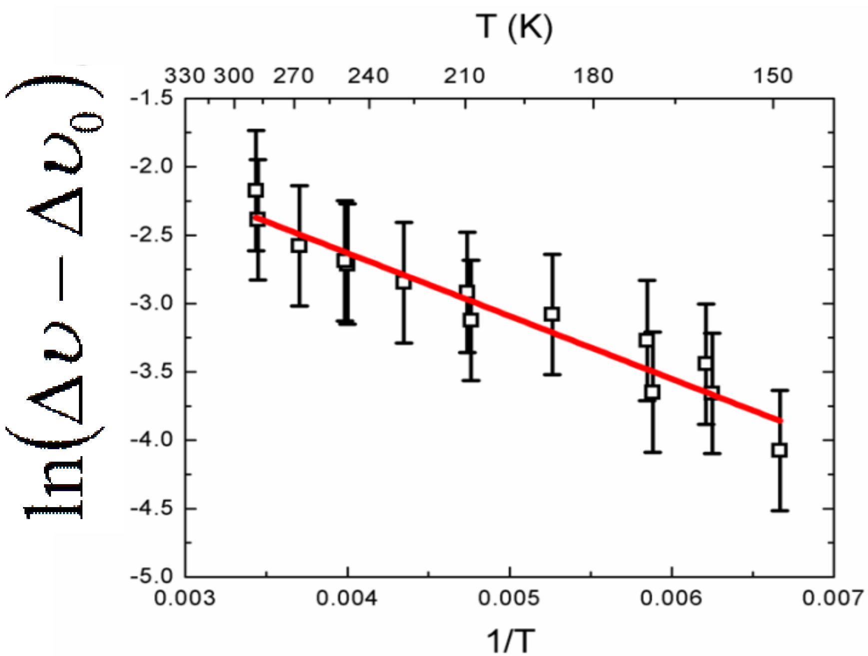
$CH_3NH_3PbI_{3-x}Cl_x$ on glass substrate

Exciton Binding Energy in $CH_3NH_3PbI_{3-x}Cl_x$



Exciton Binding Energy

$$\Delta\upsilon = \Delta\upsilon_0 + \upsilon_T \exp(-\frac{E_b}{k_B T})$$



E_b = (50±20)meV

Nat Comm. DOI: 10.1038/ncomms4586

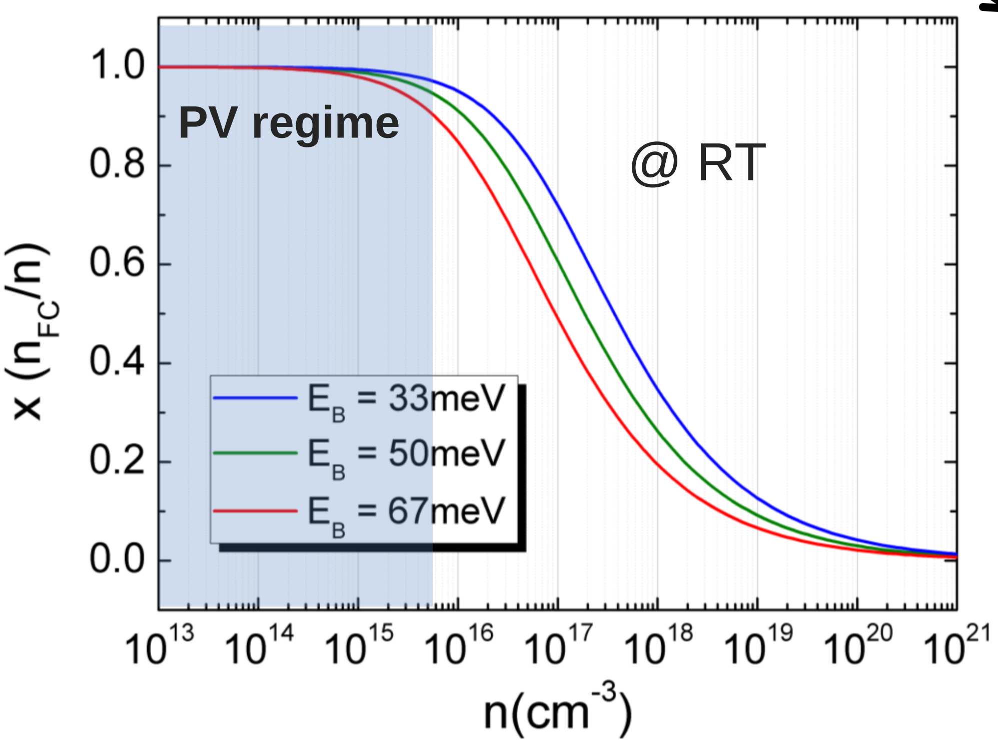
Exciton Vs Free Charges at the Thermodynamic Equilibrium

Total excitation density

Excitons

$$n = n_{FC} + n_{exc}$$

Free charges



$$\frac{n_{FC}}{n_{exc}} = \left(\frac{2\pi\mu k_B T}{h^2}\right)^{3/2} e^{-\frac{E_b}{k_B T}}$$

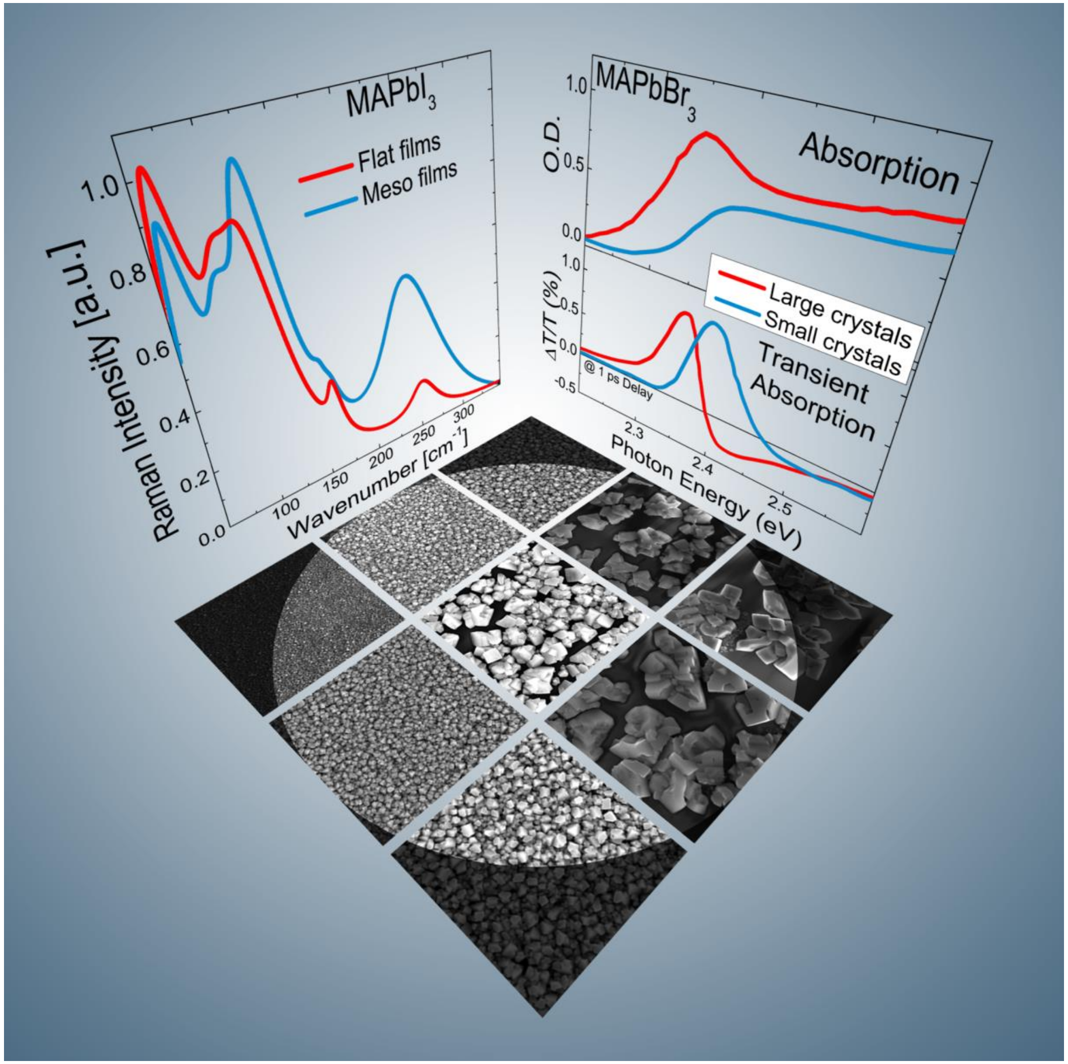
$$x = \frac{n_{FC}}{n}$$

Cingolani, R. *et al*. *JOS*,**13,** 1268 (1996).
Saha, M. N. **99**, 135–153 (1921).

Nat Comm. DOI: 10.1038/ncomms4586

Photo-physics and Micro-structure

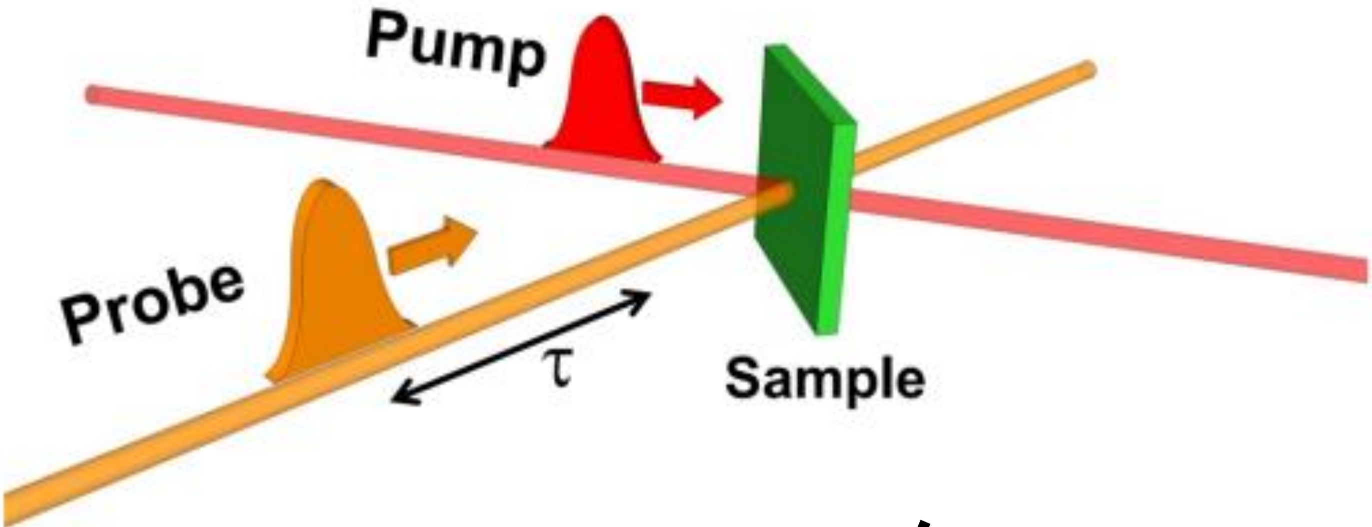
Courtesy: Stefanie Neutzner

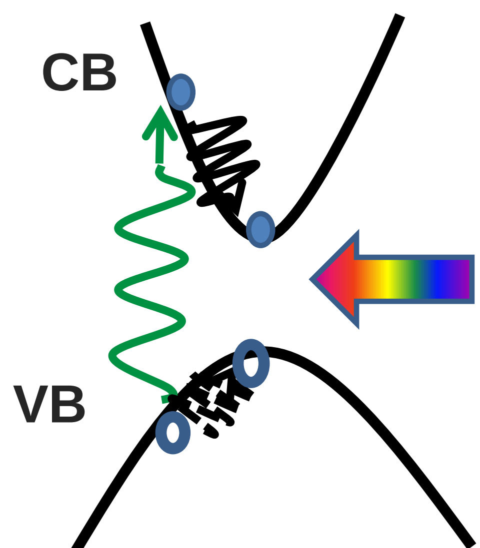


- •Excitonic effects and Microstructure
- •Related to order/disorder in the material
- •Modulation of the dielectric constant?

Grancini, Kandada et al, Nature Photonics 9 (10), 695-701 (2015)
Kandada and Petrozza, Acc. Chem. Res (2016)

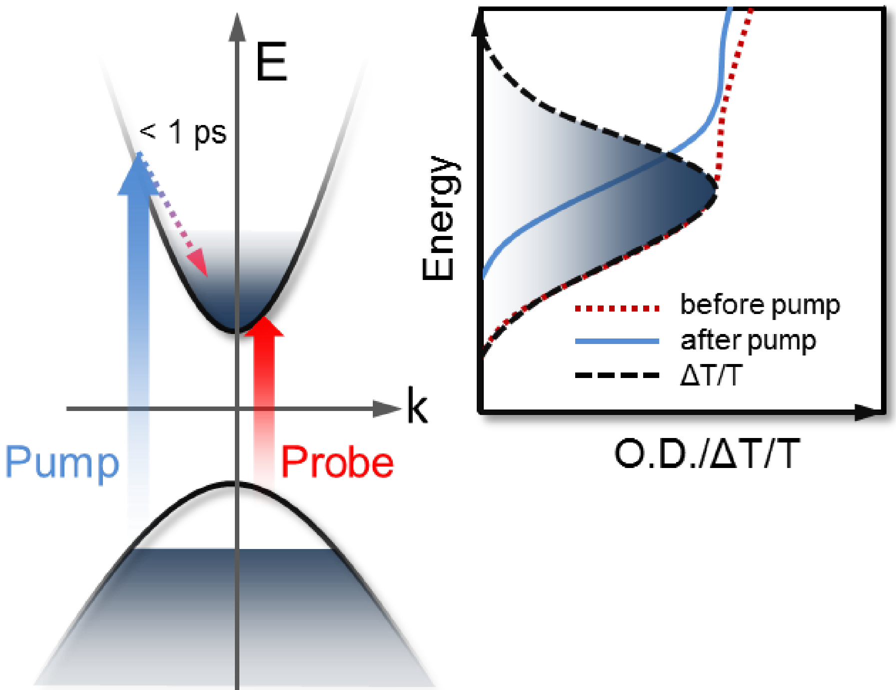
Role of Microstructure in the Electron-Hole Interaction of Hybrid Lead-Halide Perovskites

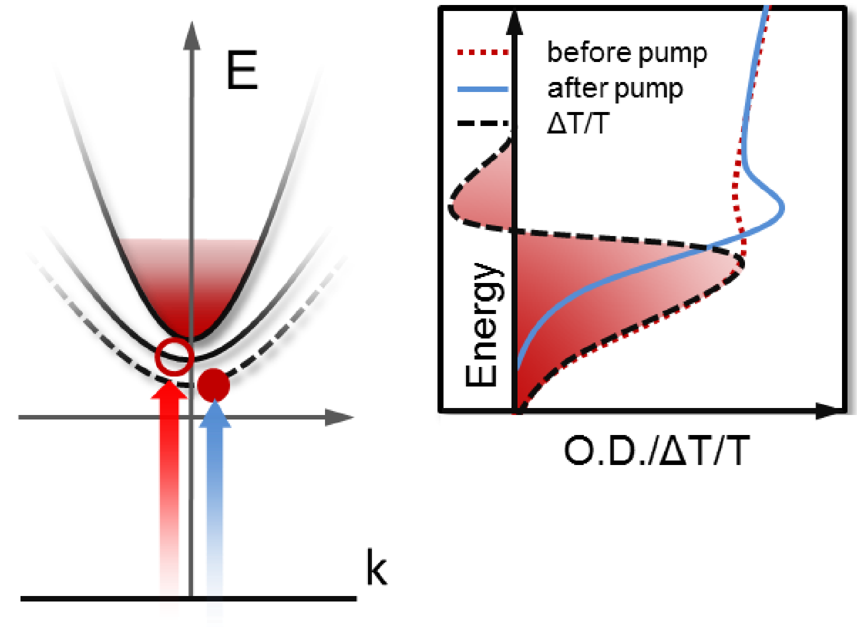




Nature Photonics 9, 695–701(2015)

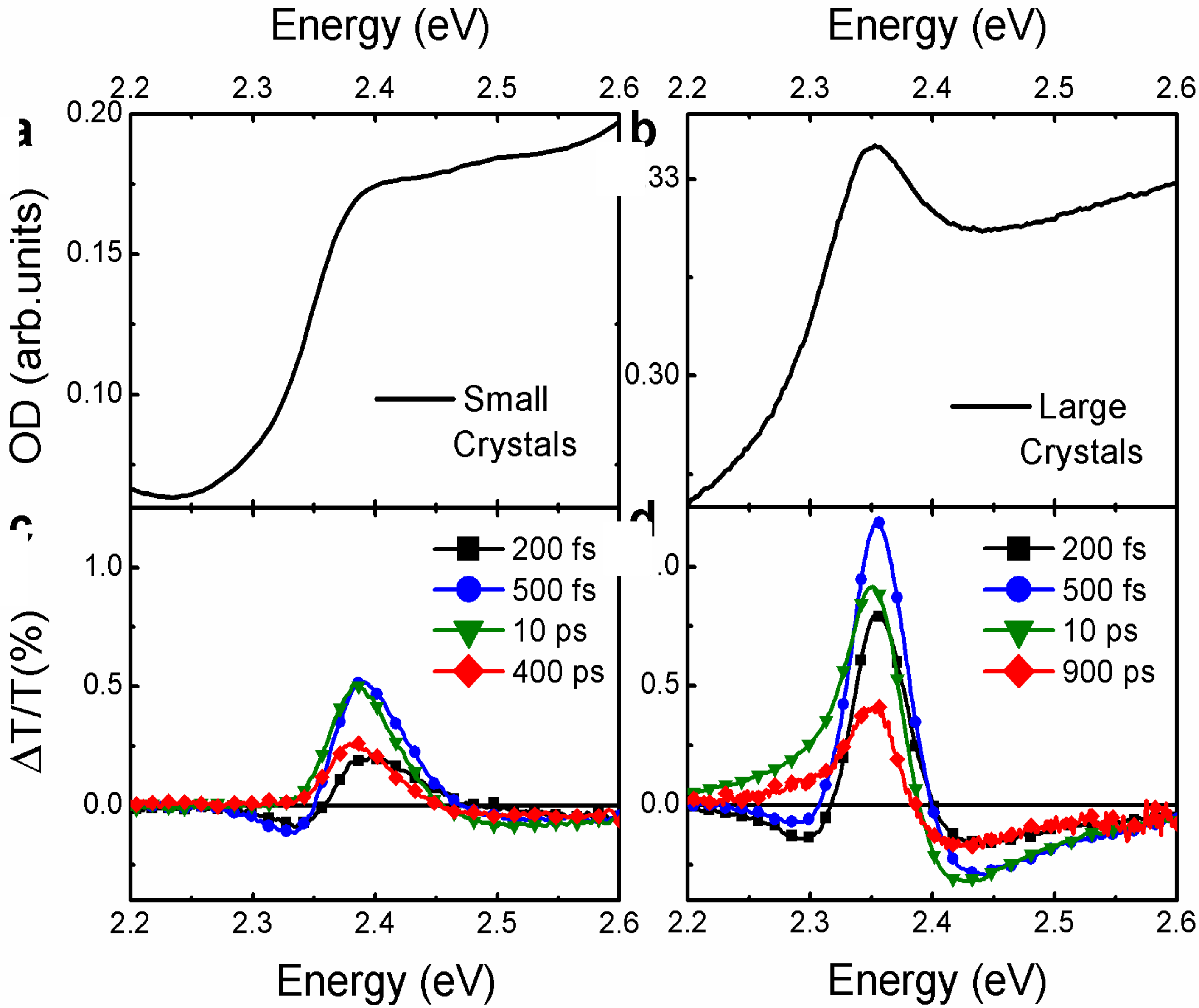
Intepretation of the transient spectra





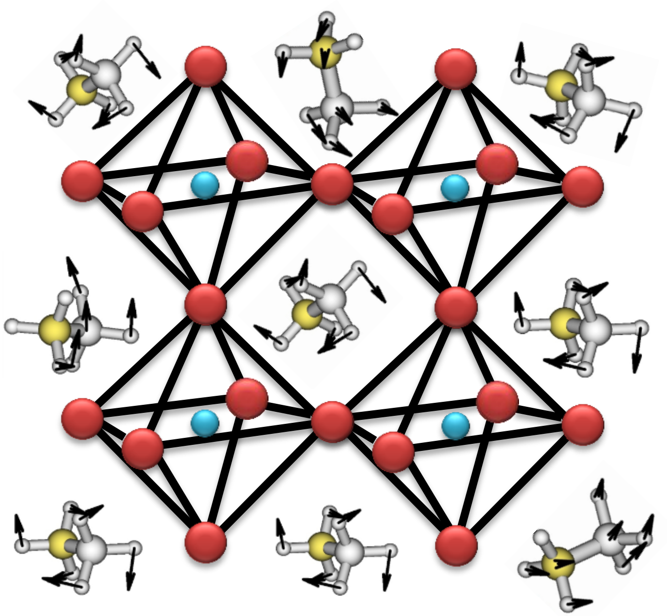
FREE CARRIERS vs EXCITON

Stable Exciton (RT) $MAPbBr_3$



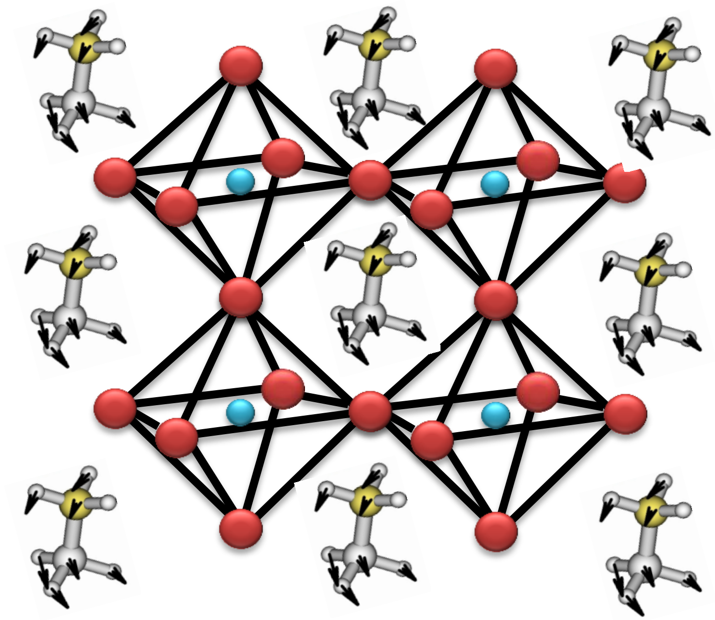
Nature Photonics 9, 695–701(2015)

Screening in Perovskites



Free Dipoles

Langevin model: $\varepsilon_r \approx 8$



Dipoles twinning

Ferroeletric order

Nature Photonics 9, 695–701(2015)

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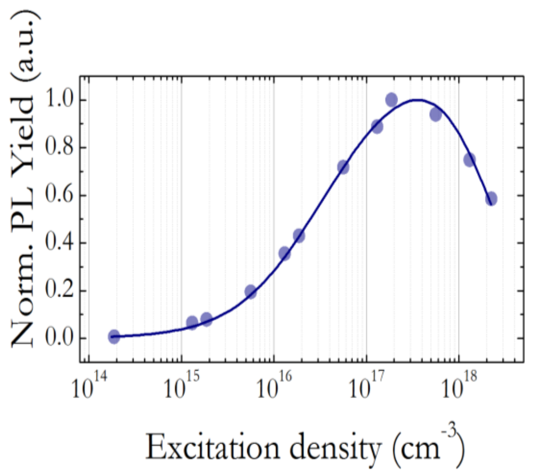
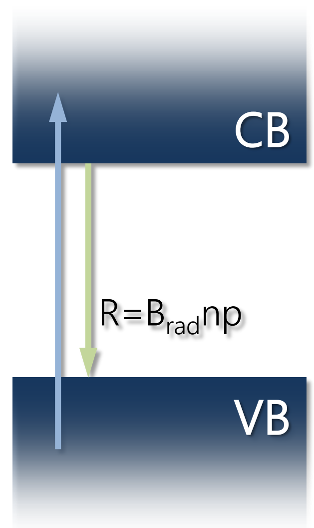
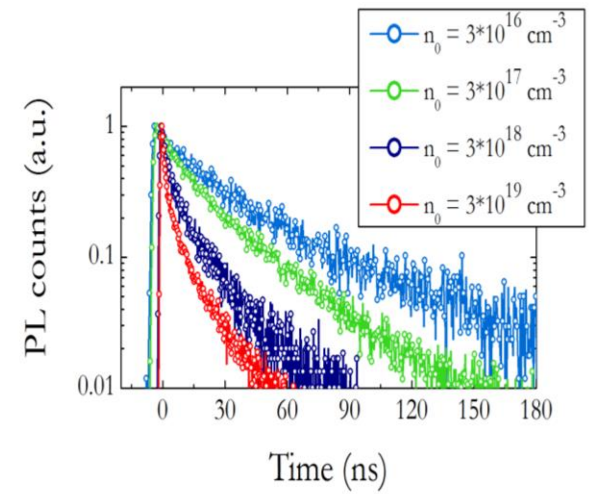
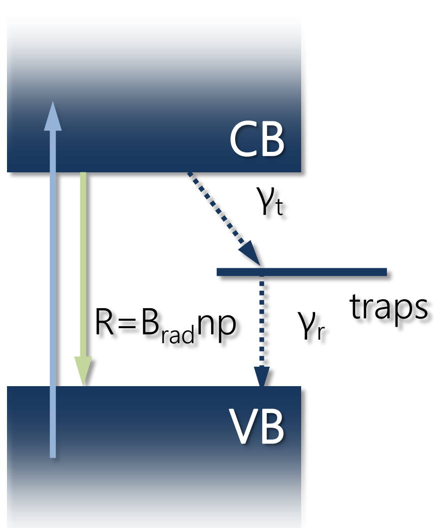
PL in Perovskites

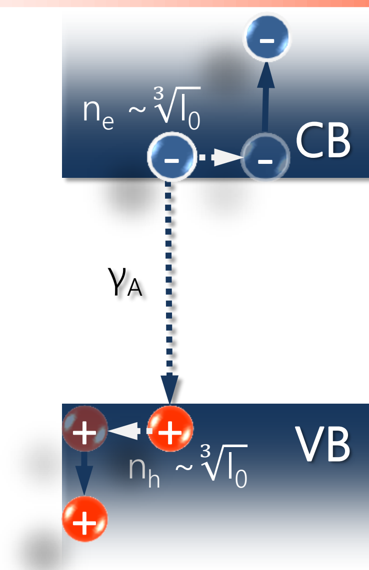






PV regime

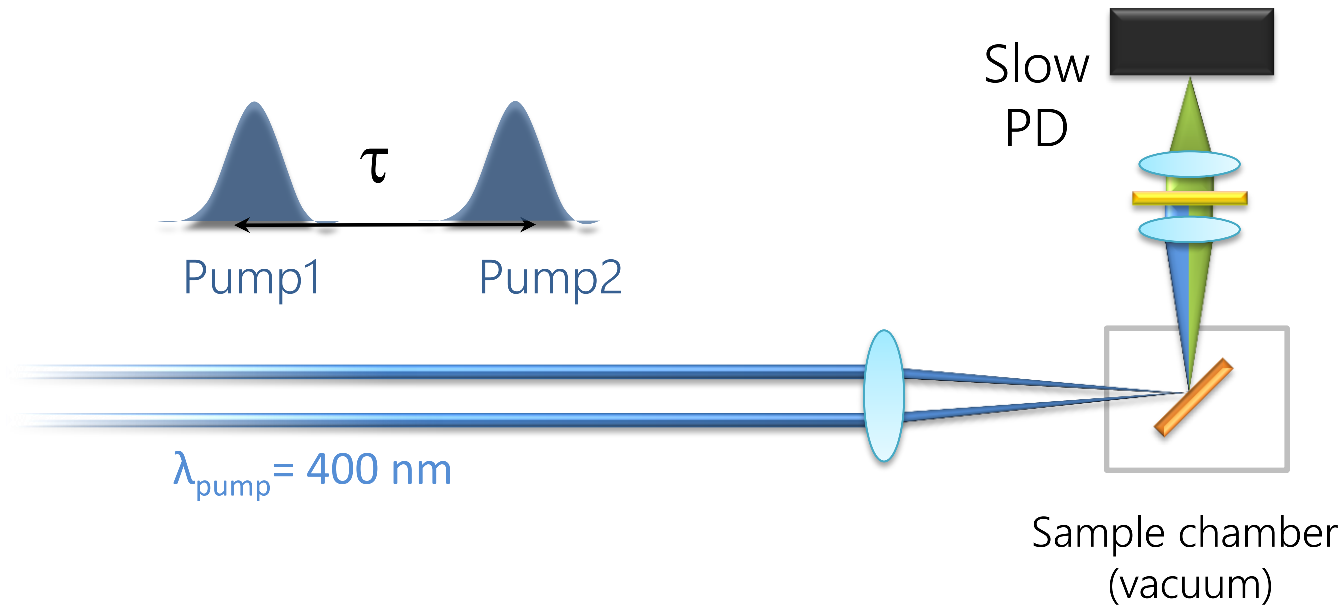




Lasing

Kandada et al. http://pubs.acs.org/doi/abs/10.1021/jacs.6b06463

ECPL : Experimental Principle



Total intensity at photo detector:

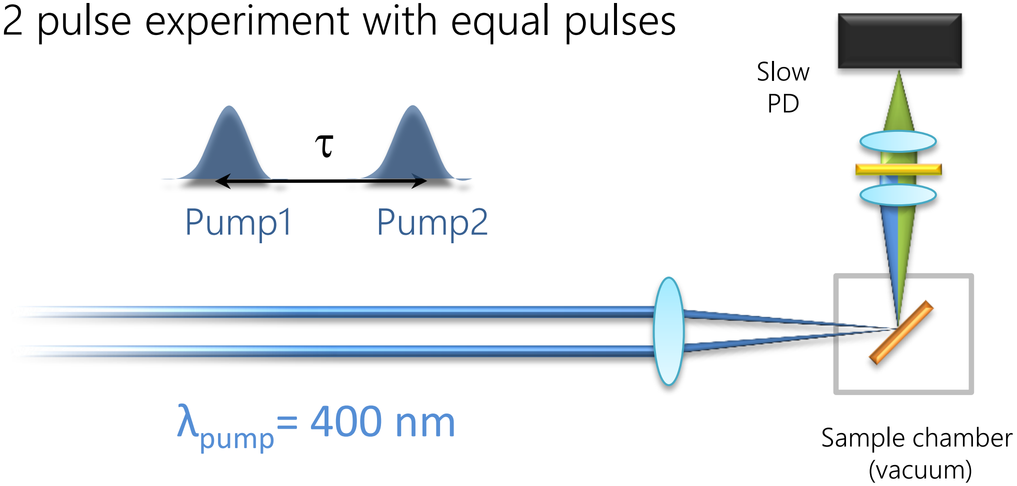
$$I(I_0,\tau) = \int_0^{\infty} PL_1(I_0,t)dt + \int_{\tau}^{\infty} PL_2(I_0,t-\tau)dt + \int_{\tau}^{\infty} PL_{cross}(2I_0,t,t-\tau)dt$$

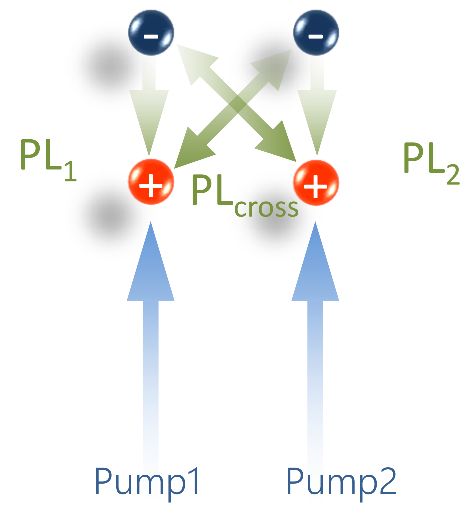
Von der Linde et al, J. Lumin, 24, 675 (1981).
Rosen, Appl. Phys. Lett, 39, 935 (1981).
Borgwardt et al, J. Appl. Phys. 117, 215702(2015)

Kandada *et al*. JACS in press

ECPL : Experimental Principle

2 pulse experiment with equal pulses





Total intensity at photo detector:

$$ECPL\,(\tau = 0, I) = \frac{PL(2I) - 2PL\,(I)}{PL(2I)}$$

Von der Linde et al, J. Lumin, 24, 675 (1981).
Rosen, Appl. Phys. Lett, 39, 935 (1981).
Borgwardt et al, J. Appl. Phys. 117, 215702(2015)

Kandada *et al*. JACS in press

Understanding ECPL Signals

	Rate equation	Steady-state PL TIME INTEGRATED	$\frac{ECPL\ (\tau = 0, I)}{PL(2I) - 2PL\ (I)}{PL(2I)}$
Radiative recombination	$\frac{dn}{dt} = G - Bn^2$	$\propto I$	0
Trap-limited recombination	$\frac{dn}{dt} = G - \gamma_t N_t n - Bnp$	$\propto I^{3/2}$	> 0 ≈ 30%
Auger recombination	$\frac{dn}{dt} = G - Bn^2 - \gamma_{auger} n^3$	$\propto I^{2/3}$	< 0

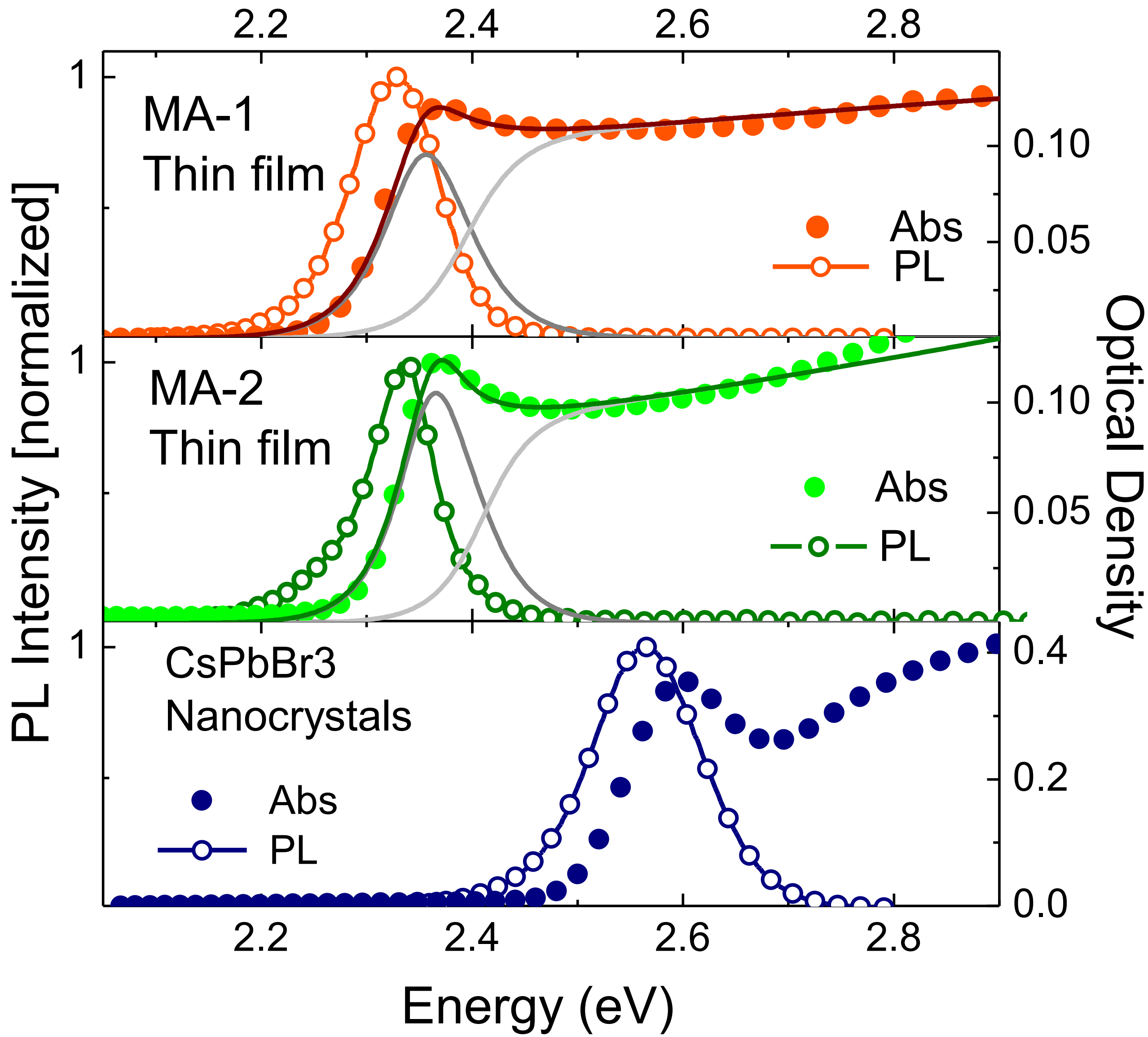
Kandada et al. http://pubs.acs.org/doi/abs/10.1021/jacs.6b06463

Investigated Systems

- **MA-1** MAPbBr$_3$: with equal molar precursors
  PLQY of < 1%

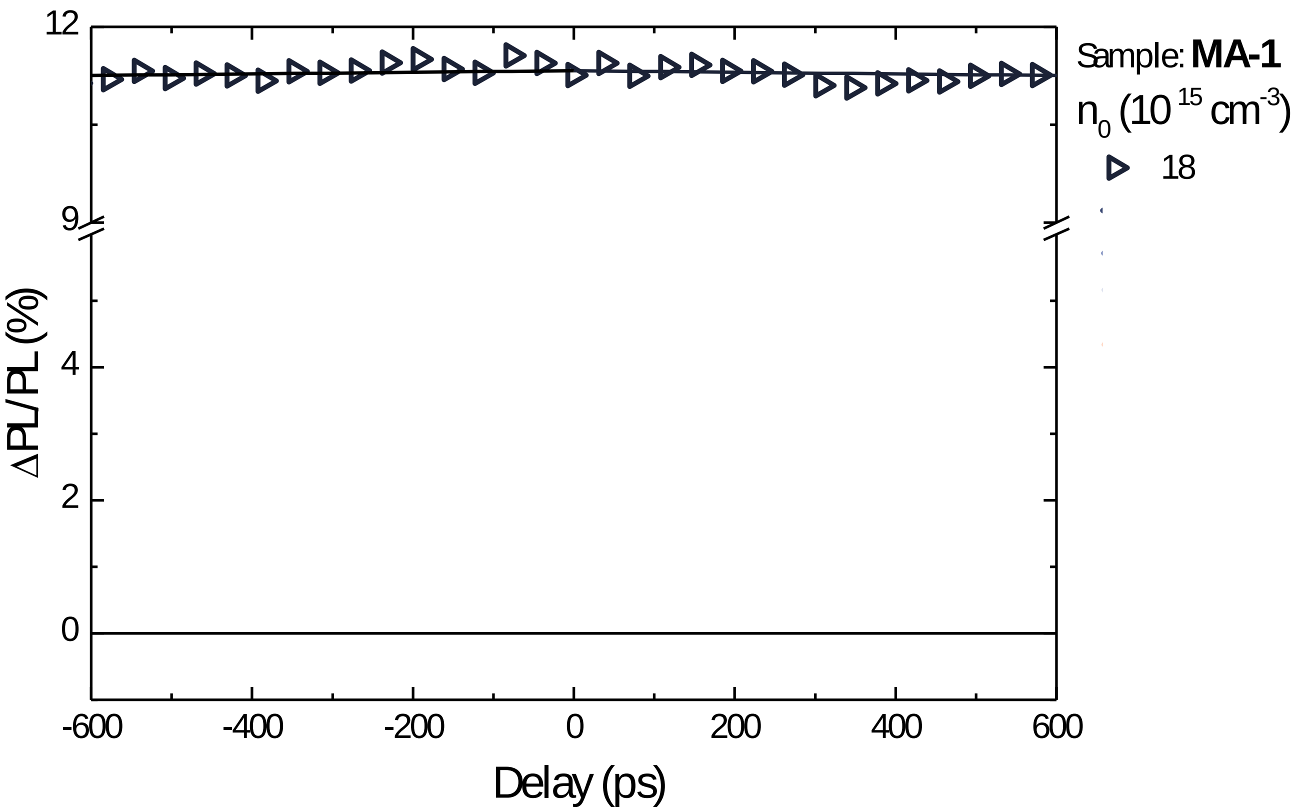
- **MA-2** MAPbBr$_3$: with excess MABr (1:1.05)
  PLQY > **4%**

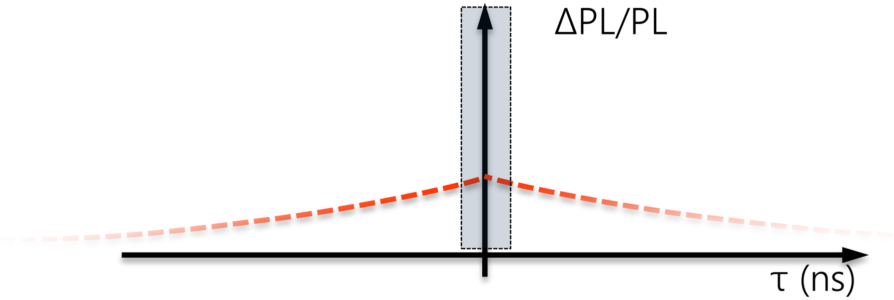
- **CsPbBr$_3$ NX** nanocrystals (7.5 nm)



Kandada et al. http://pubs.acs.org/doi/abs/10.1021/jacs.6b06463

ECPL: MA-1



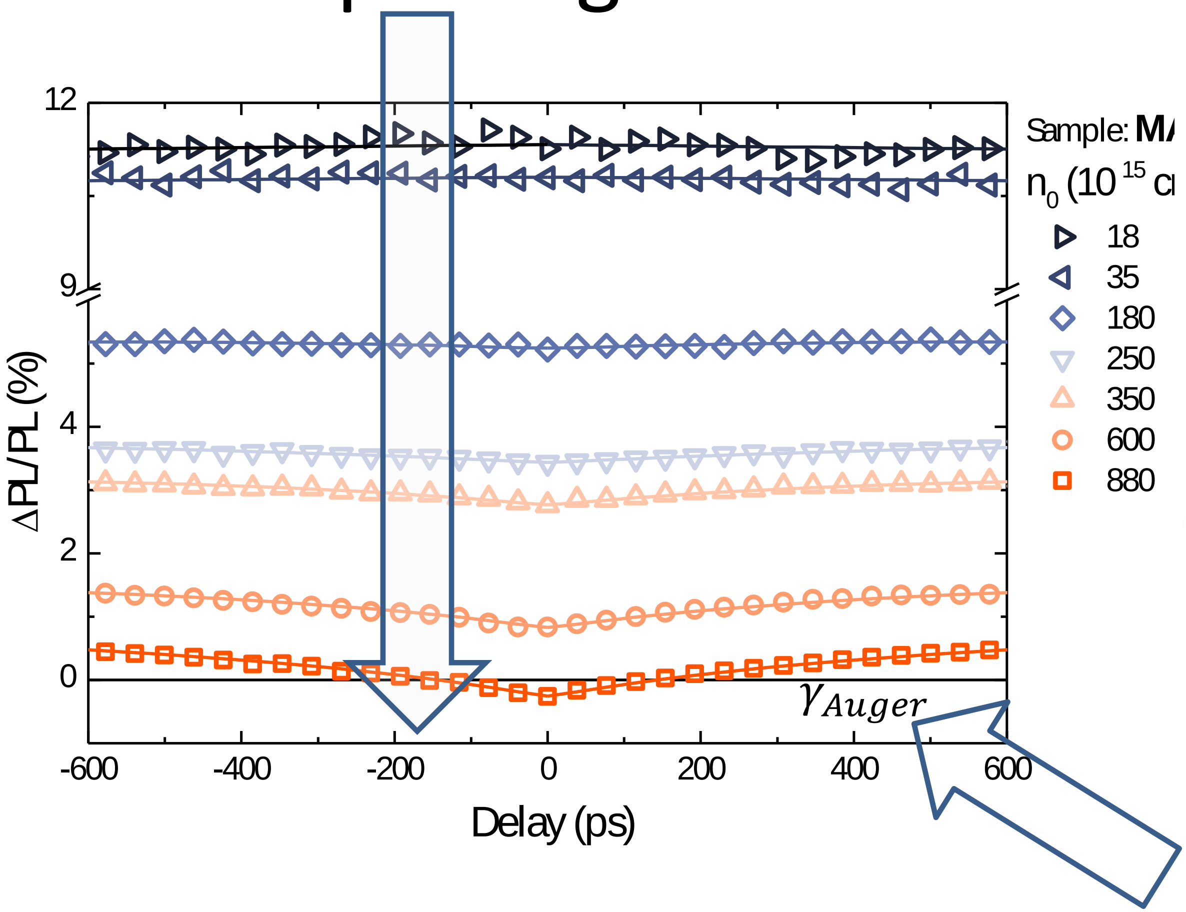


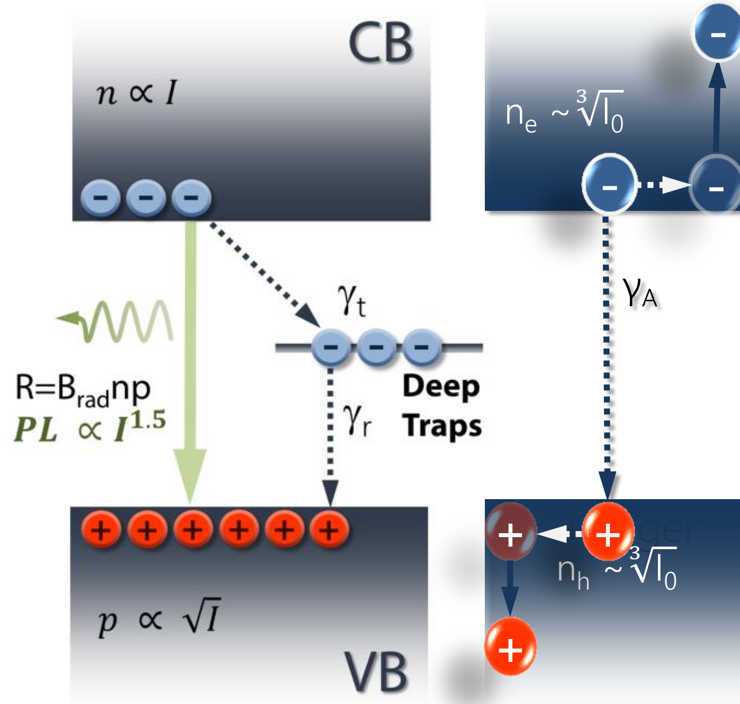
Kandada *et al*. JACS in press

Trap limited (SRH) electron-hole recombination

ECPL: MA-1

Trap filling





Auger

$N_T = 1 \times 10^{17} cm^{-3}$; $B_{rad} = 2 \times 10^{-9} cm^3 s^{-1}$;

$\gamma_{Auger} = 1 \times 10^{-27} cm^6 s^{-1}$; $\gamma_t = 0.84 \times 10^{-9} cm^3 s^{-1}$ $\gamma_r = 0.19 \times 10^{-9} cm^3 s^{-1}$

Rate Equation Model

$$\frac{dn}{dt} = G - R - \gamma_t(N_t - n_t)n + \gamma_d n_t - \gamma_{auger} n^2 p$$

$$\frac{dp}{dt} = G - R - \gamma_r n_t p - \gamma_{auger} n^2 p$$

$$\frac{dn_t}{dt} = \gamma_t(N_t - n_t)n - \gamma_r n_t p - \gamma_d n_t$$

$N_t = 1 \times 10^{17} cm^{-3}$; $B_{rad} = 2 \times 10^{-9} cm^3 s^{-1}$;
$\gamma_{Auger} = 1 \times 10^{-27} cm^6 s^{-1}$; $\gamma_t = 0.84 \times 10^{-9} cm^3 s^{-1}$
$\gamma_r = 0.19 \times 10^{-9}\, cm^3 s^{-1}$

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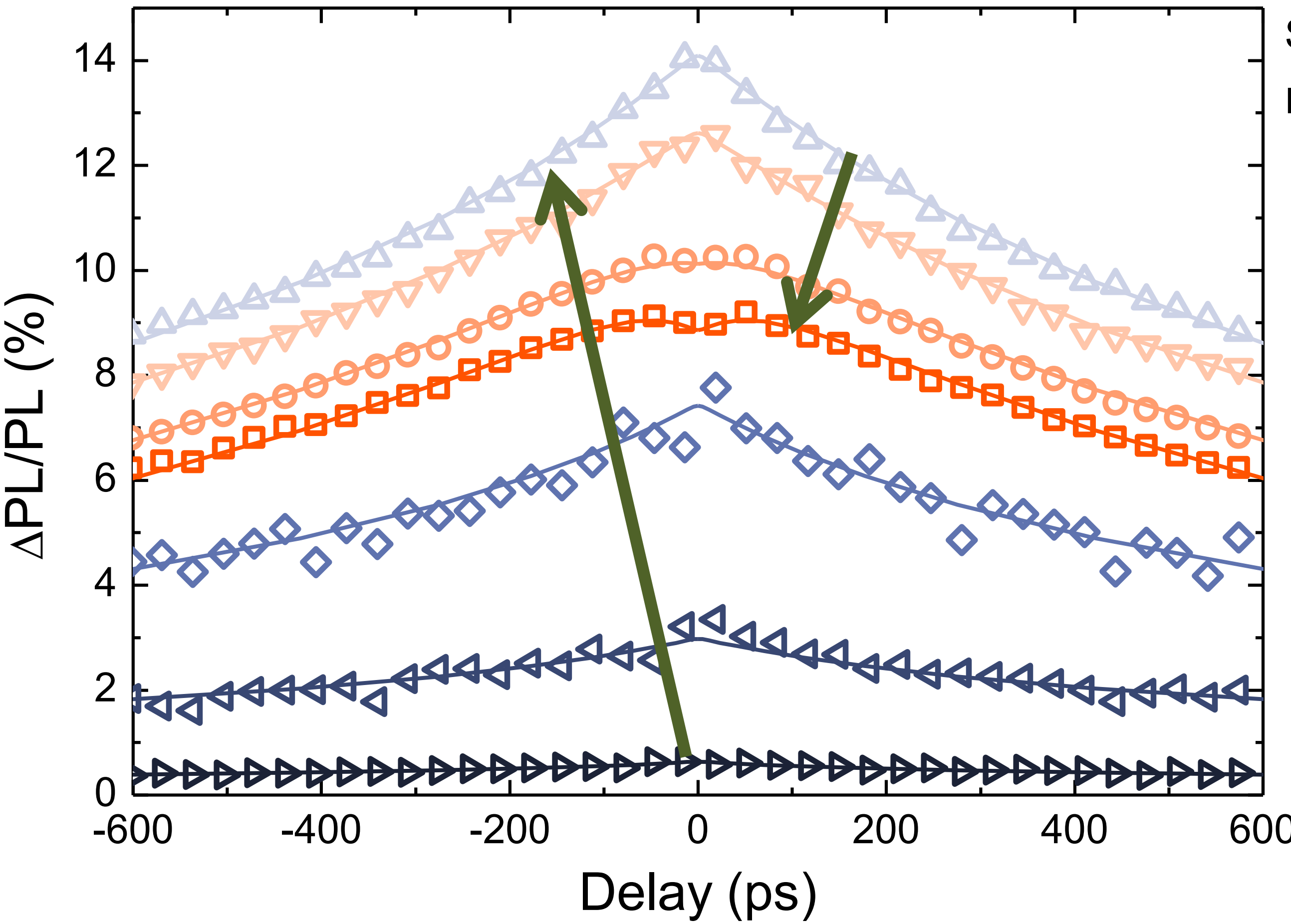
ECPL: MA-2 Vs MA-1



ECPL reminder:

Traps:

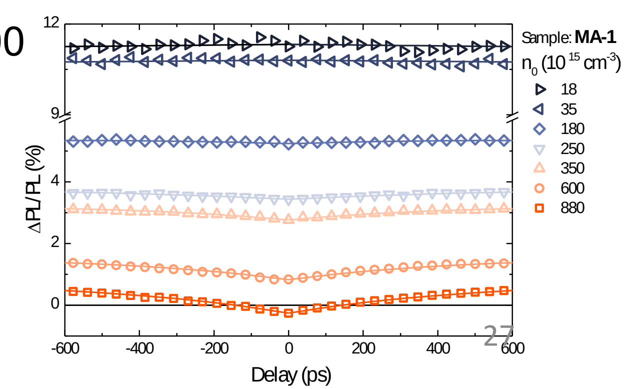
$PL_{bi} \propto \sqrt[2]{I^3}$ *ECPL>0*

Pure radiative:

$PL_{bi,mono} \propto I_0$, *ECPL=0*

Auger:

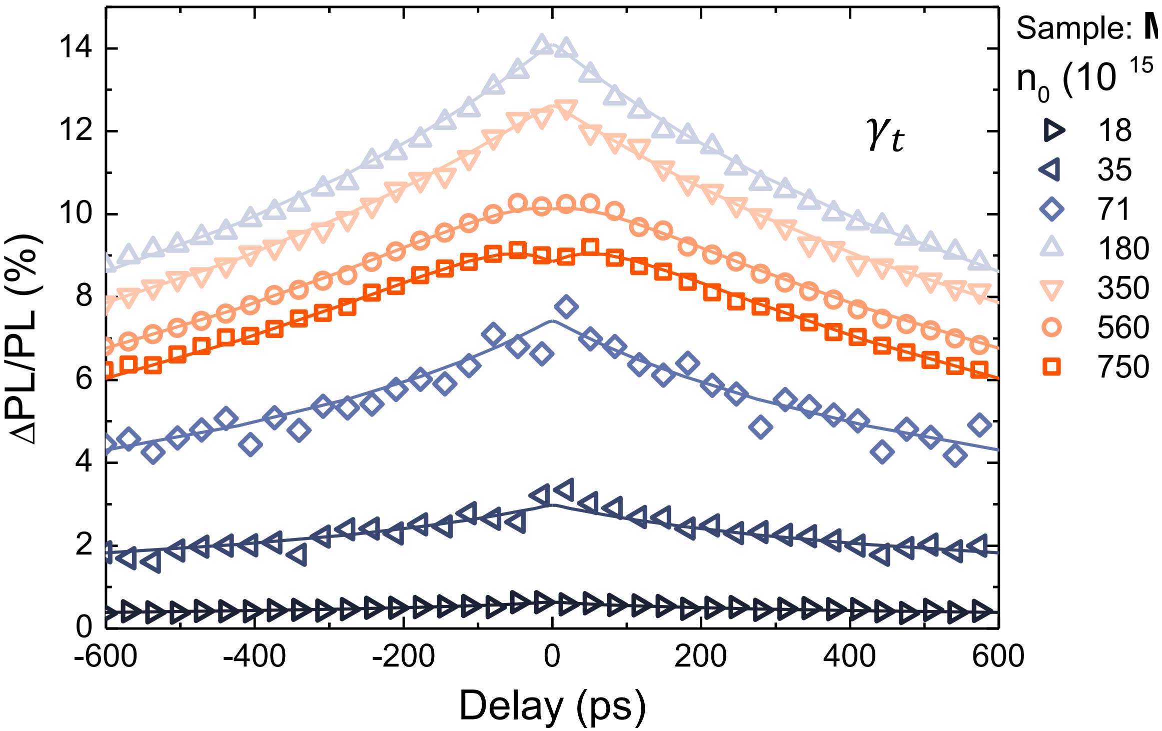
$PL_{bi} \propto \sqrt[3]{I^2}$, *ECPL<0*

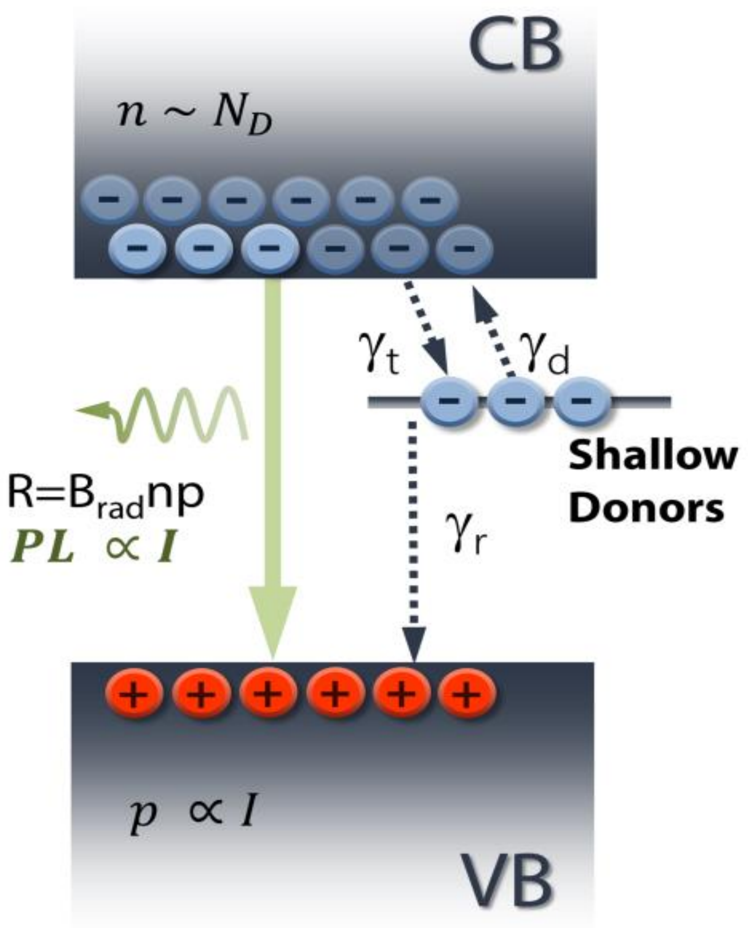


Kandada *et al*. JACS in press

ECPL: MA-2

Shallow defects doping





ECPL reminder:

Traps:

$PL_{bi} \propto \sqrt[2]{I^3}$ ECPL>0

Pure radiative:

$PL_{bi,mono} \propto I_0$, ECPL=0

Auger:

$PL_{bi} \propto \sqrt[3]{I^2}$, ECPL<0

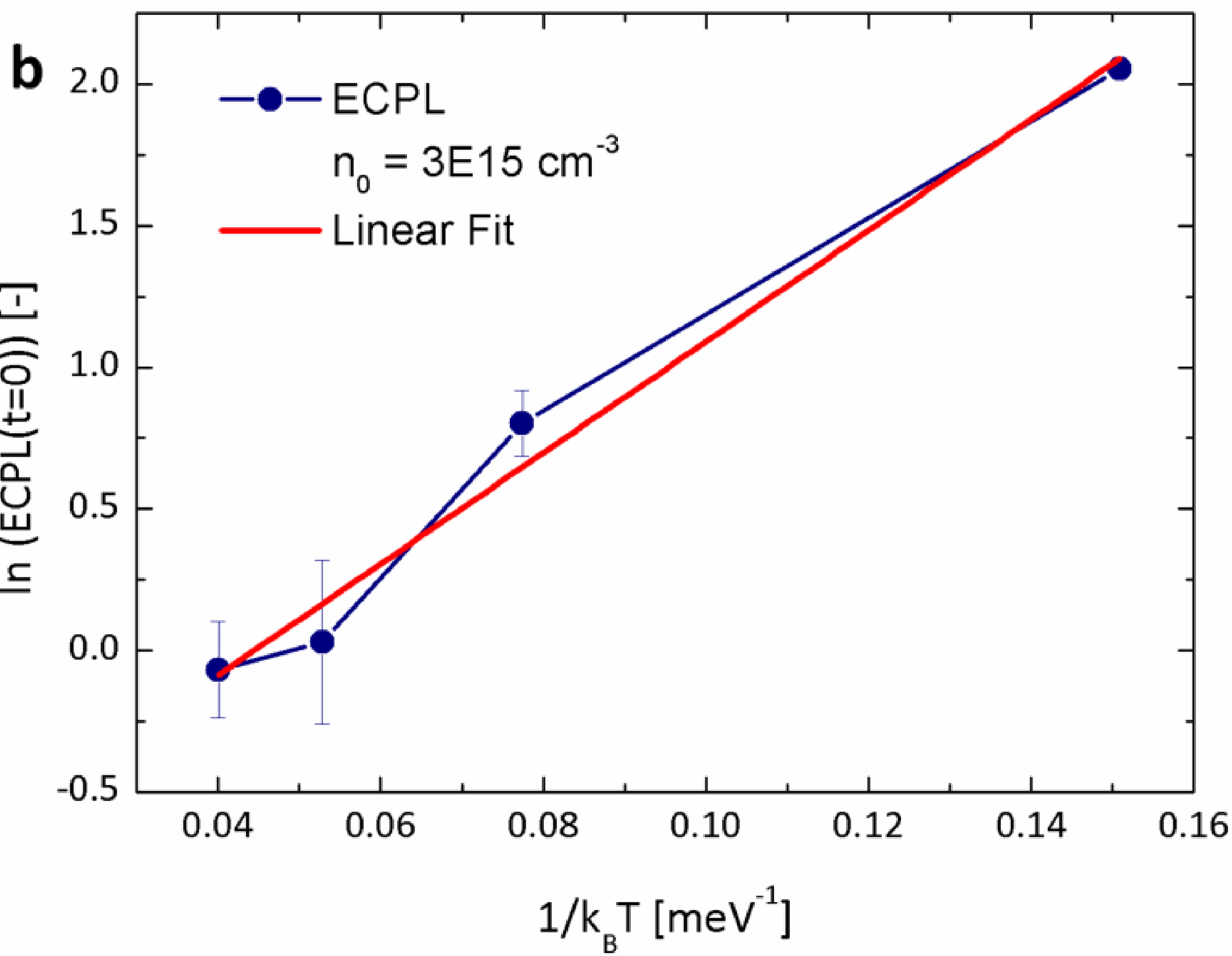
$$N_T = 2 \times 10^{18} cm^{-3}$$

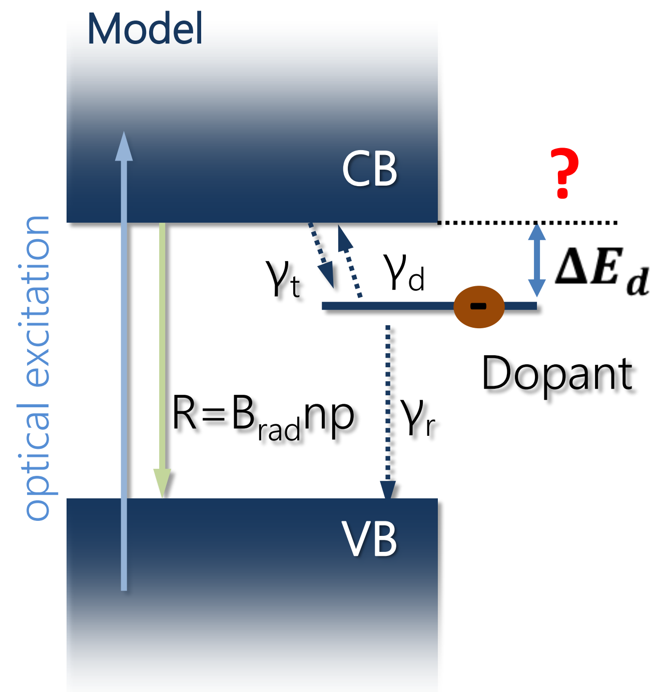
$$\gamma_t = 3 \times 10^{-8}\ cm^3 s^{-1}$$

ECPL: MA-2

Energetics of the Dopant?

Temperature dependence of ECPL



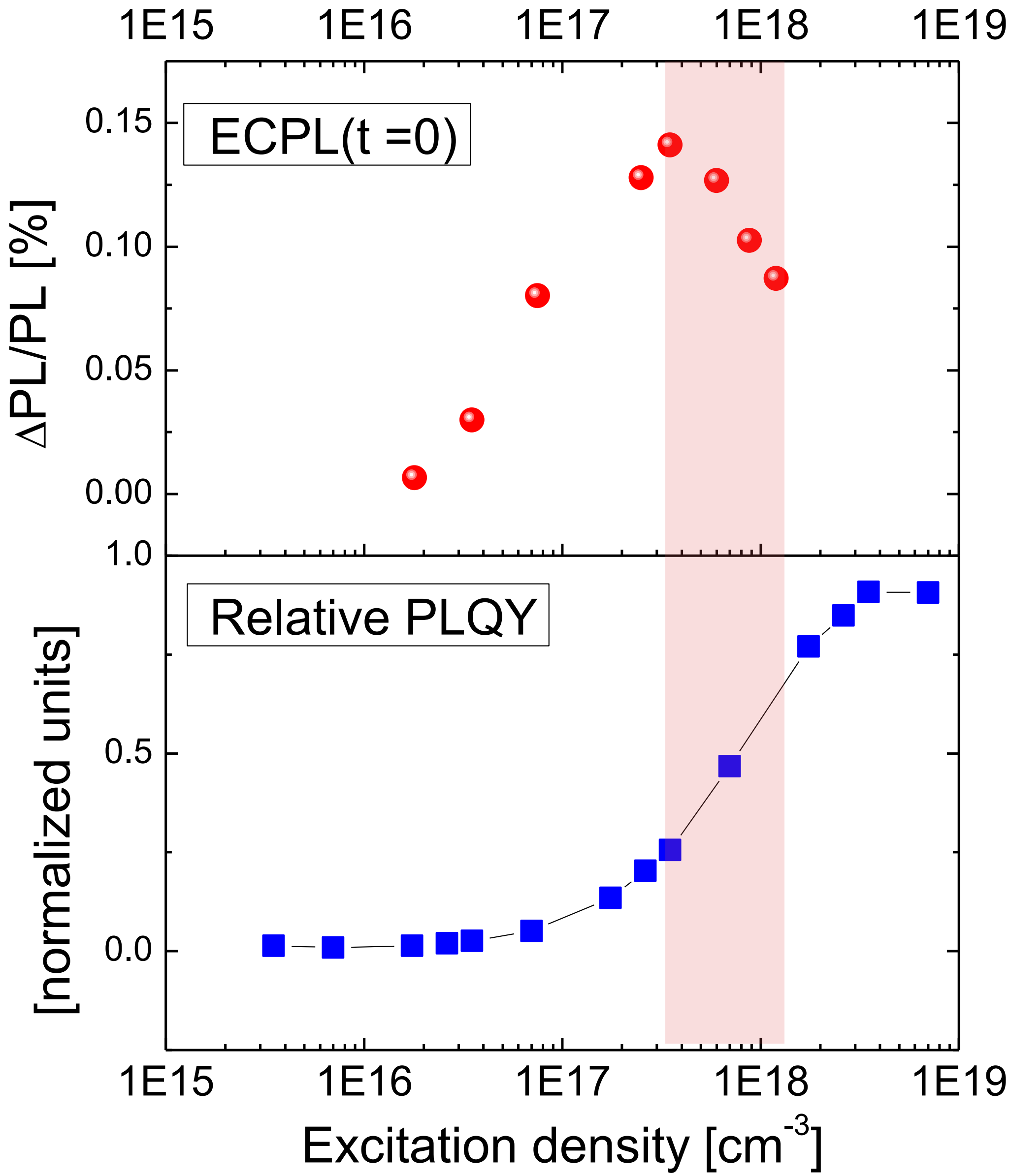


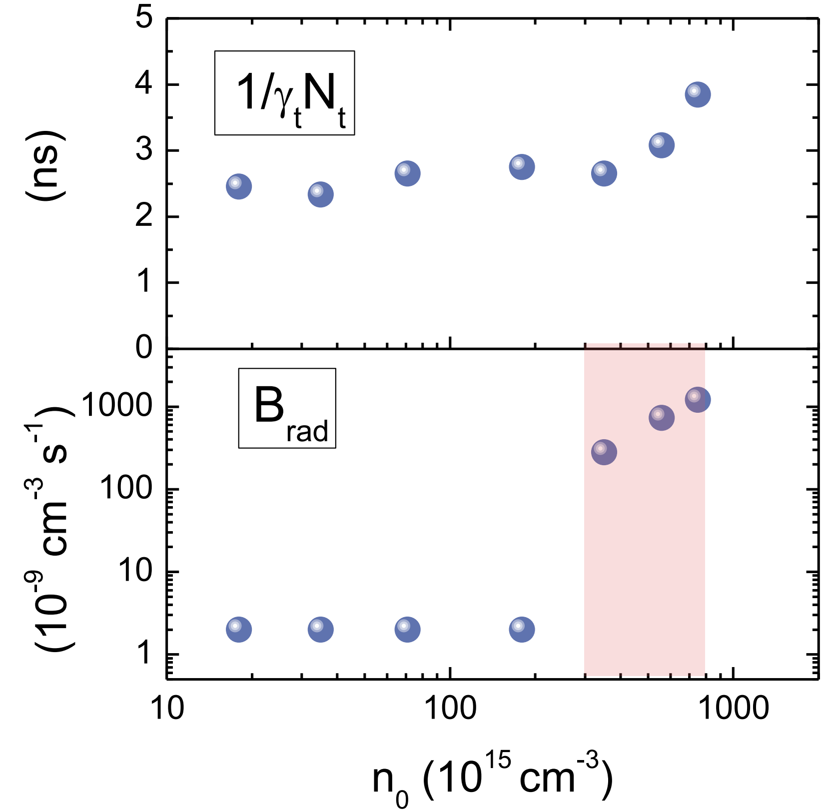
$$N_D \propto \exp(-\frac{\Delta E_D}{kT})$$

$$N_D(77K) \sim 0.1\, N_D(290K)$$

$$\rightarrow \boldsymbol{\Delta E_d \sim 20\ meV}$$

ECPL: MA-2

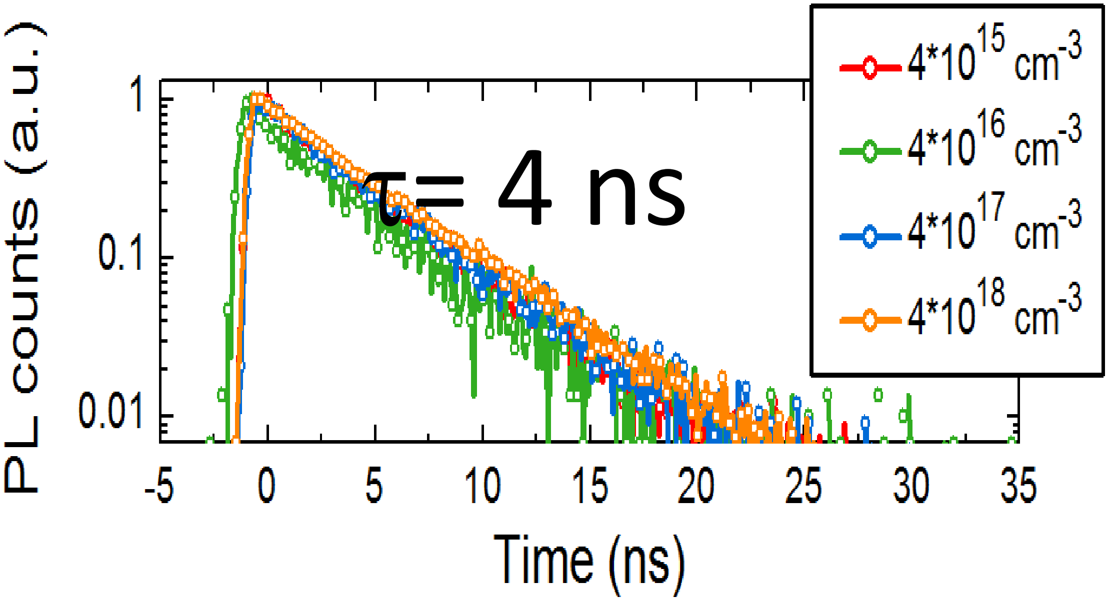




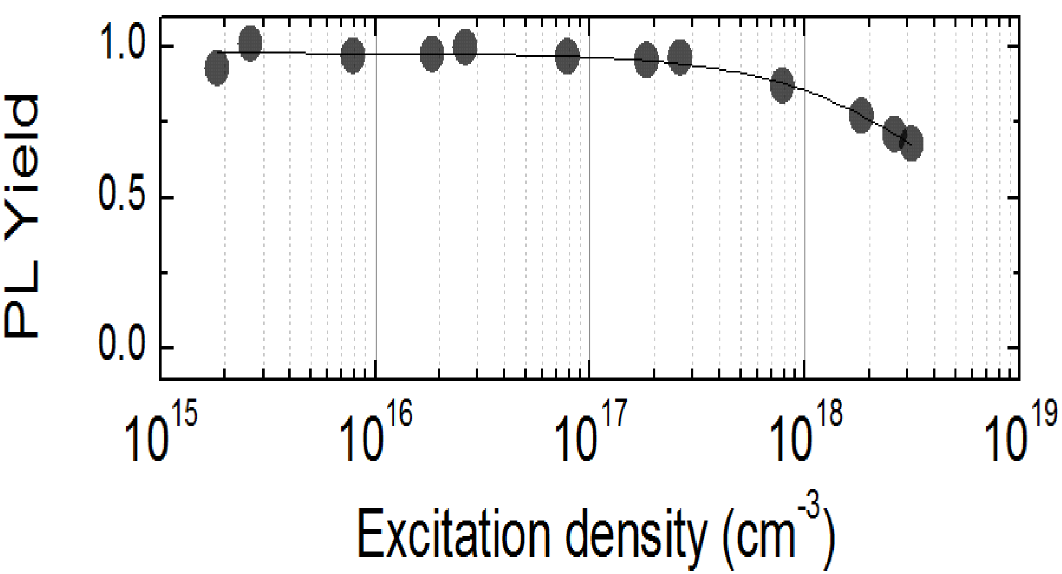
Correlated Regime

Kandada *et al*. JACS in press

PL from $CsPbBr_3$ NCs 6.7 ± 1 nm



$$\frac{dn}{dt} = -\frac{n}{\tau} - k_{nr}n$$



- No trap limited recombination
- **Exciton emission**

Kandada *et al*. JACS in press

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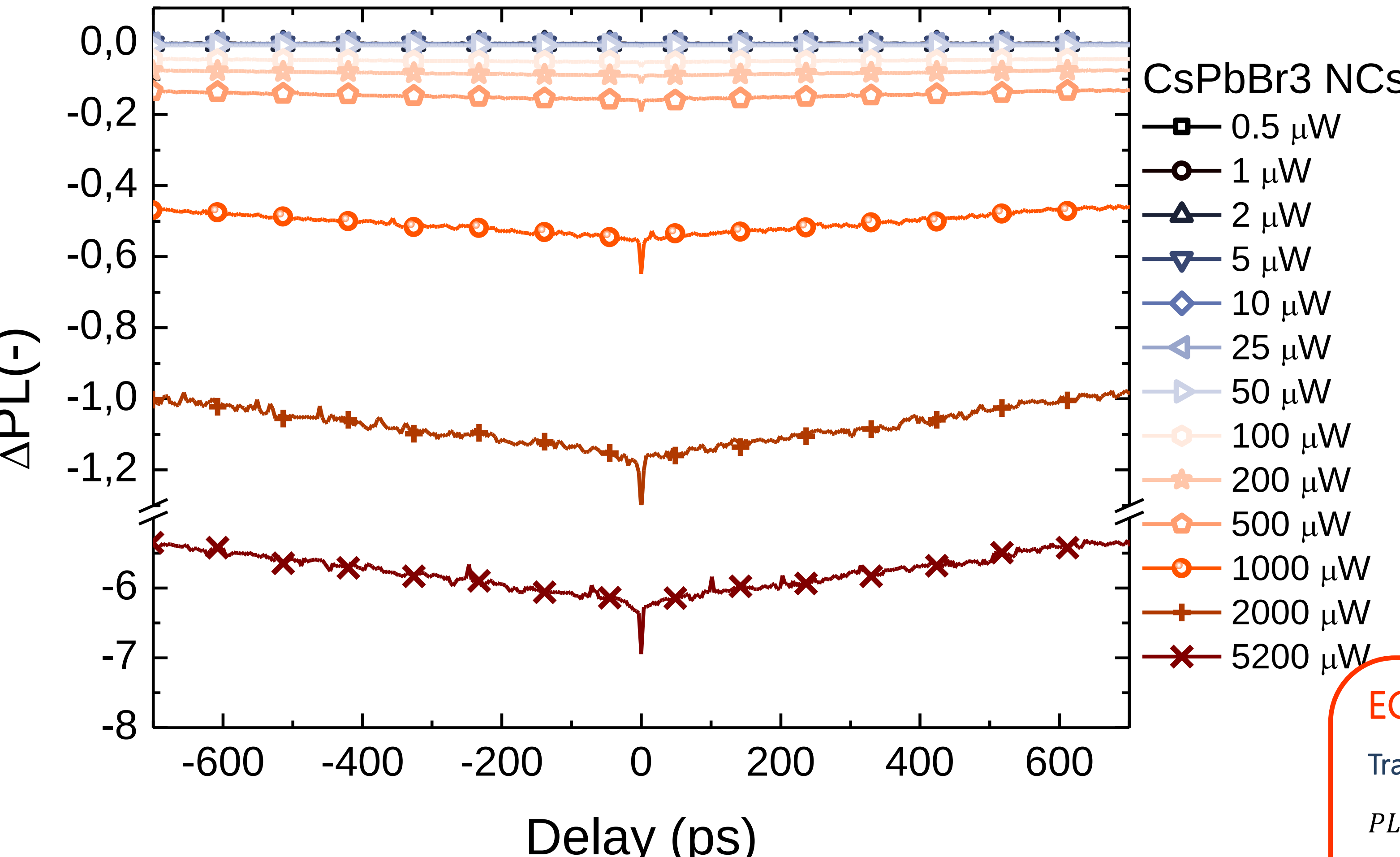
ECPL: CsPbBr3 NCs



Sub-ps Auger Recombination

Sub ns Exciton Lifetime

ECPL reminder:

Traps:

$PL_{bi} \propto \sqrt[2]{I^3}$ *ECPL>0*

Pure radiative:

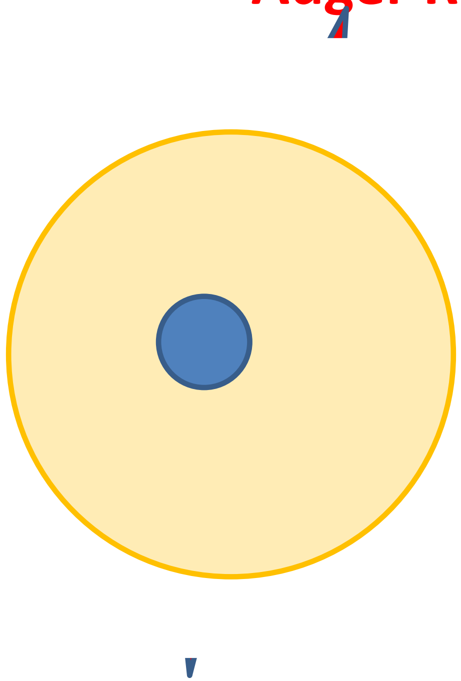
$PL_{bi,mono} \propto I_0,$ *ECPL=0*

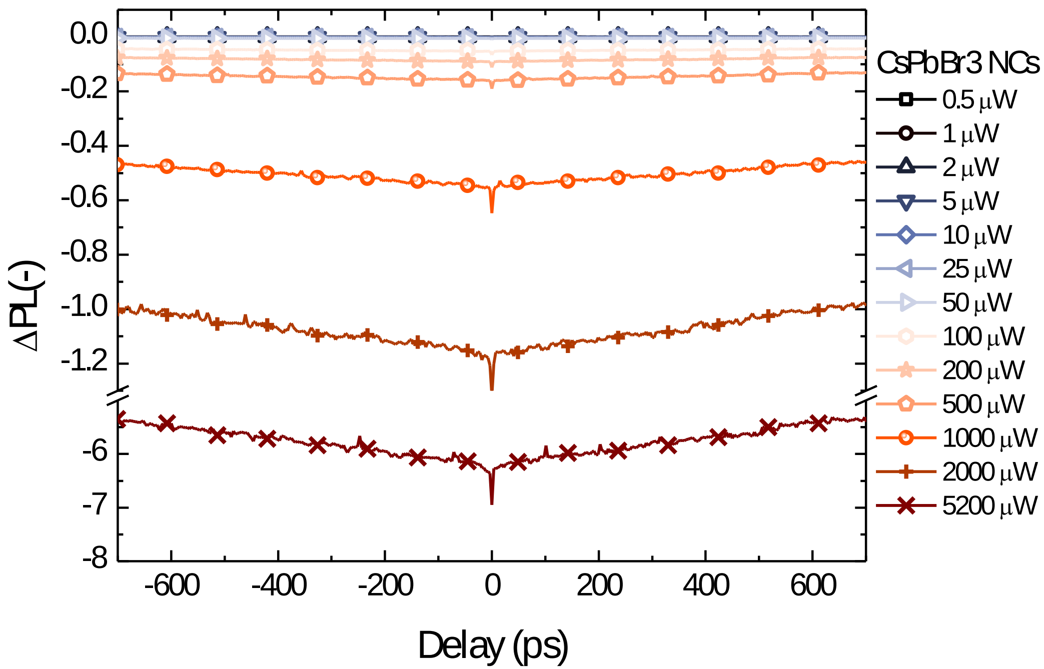
Auger:

$PL_{bi} \propto \sqrt[3]{I^2},$ *ECPL<0*

ECPL: CsPbBr3 NCs

Auger Recombination in sub-ps timescales





Assuming Poissonian distribution

$$PLQY = \frac{1 - e^{-\langle N \rangle}}{\langle N \rangle} \qquad ECPL = (1 - e^{-2\langle N \rangle}) - 2(1 - e^{-\langle N \rangle})$$

Kandada et al. http://pubs.acs.org/doi/abs/10.1021/jacs.6b06463

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