ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANO SCIENCE AND TECHNOLOGY

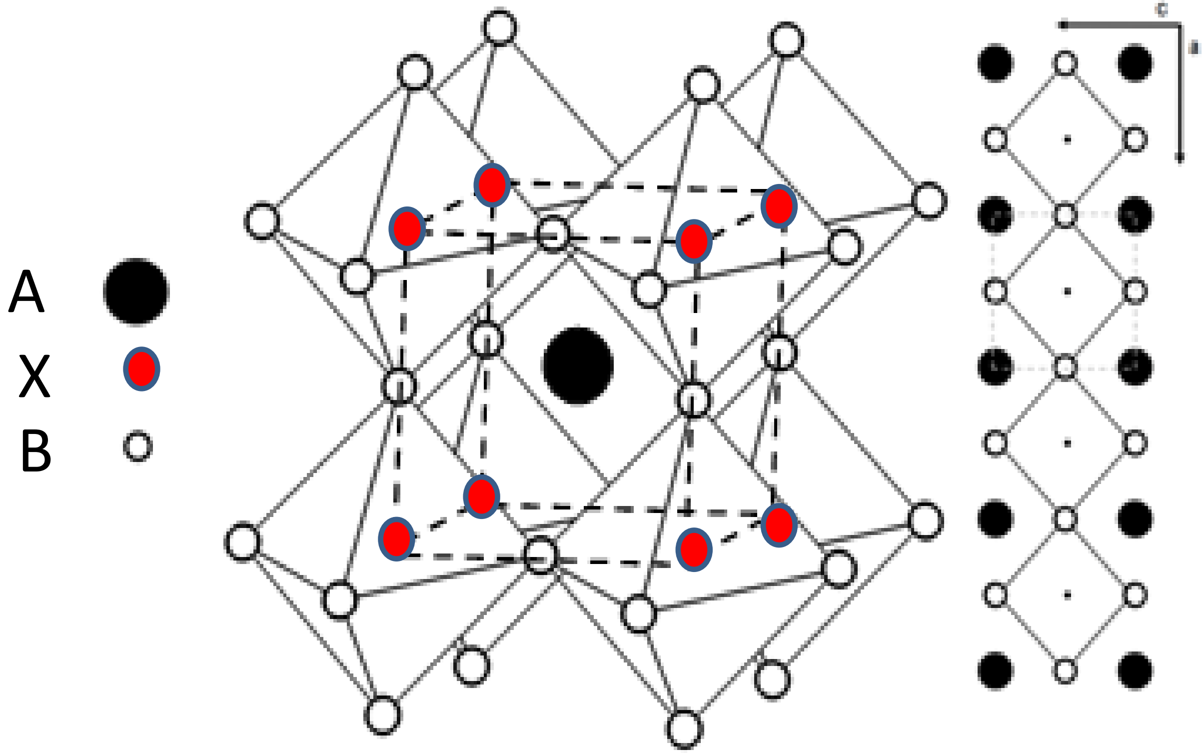
Hybrid Perovskite Solar Cells

Annamaria Petrozza

"ORGANIC ELECTRONICS : principles, devices and applications"

Milan, Novembre 27th, 2015

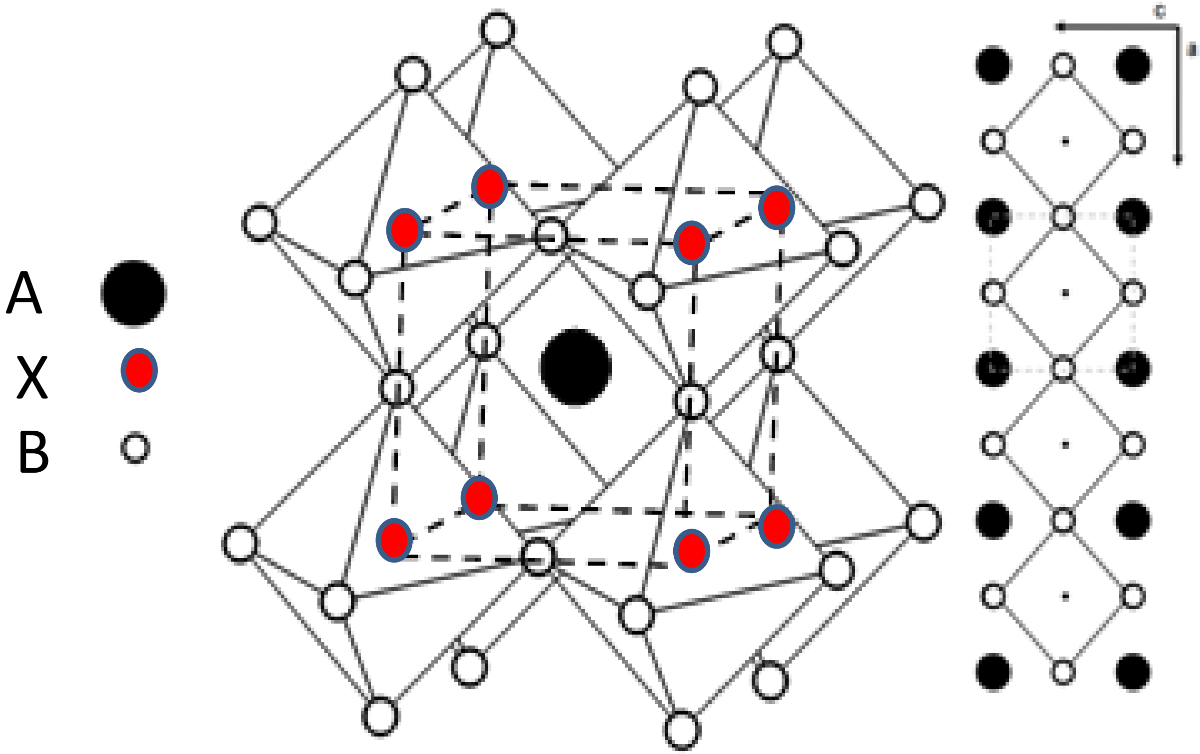
Perovskite Crystal with ABX_3 stoichiometry



I-V-O3, II-IV-O3 and III-III-O3 e.g KTaO3, SrTiO3 and GdFeO3

I-II-X3, e.g. CsSnI3, CH3NH3PbI3,

It is not only a matter of stoichiometry....



The Goldschmidt tolerance factor:

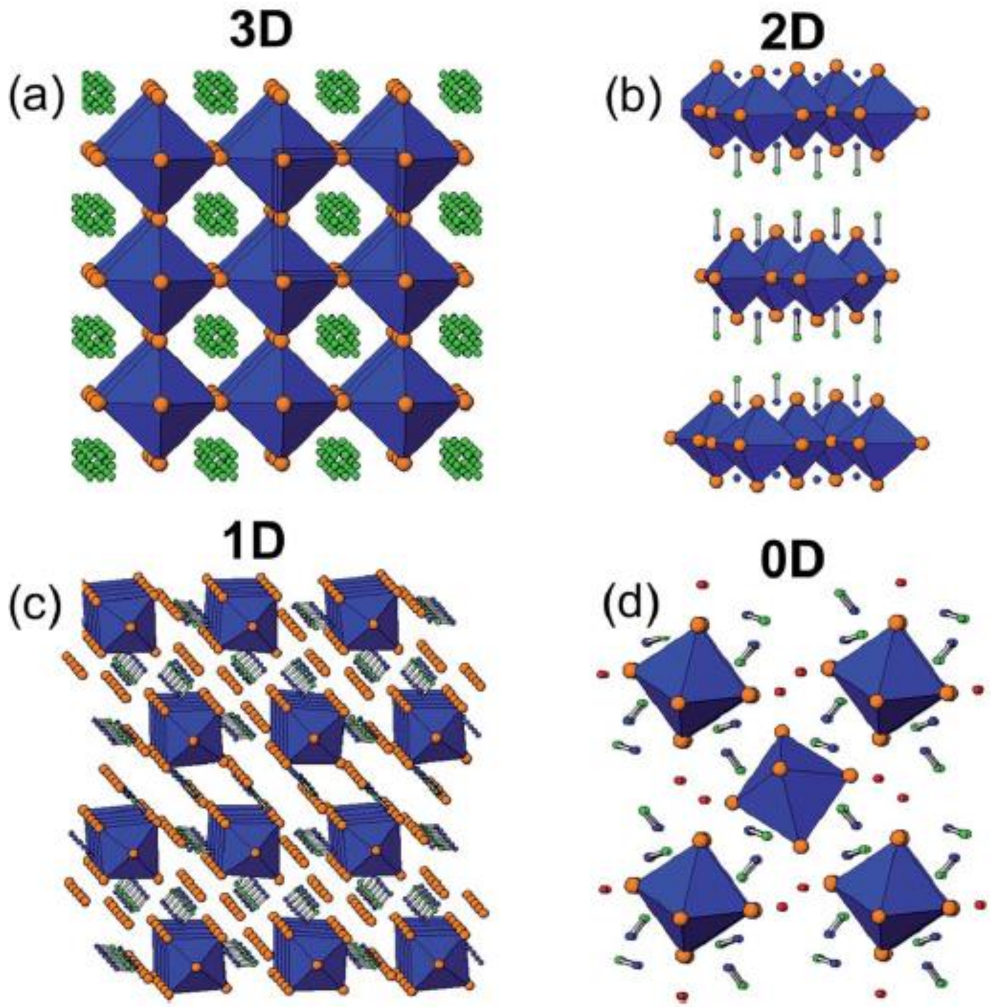
$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

t< 0.7 the perovskite falls apart
t >1 towards 2D structures…

Playing with Dimensionality

$CH_3NH_3PbI_3$

$(CH_3NH_3)_2PbI_4$

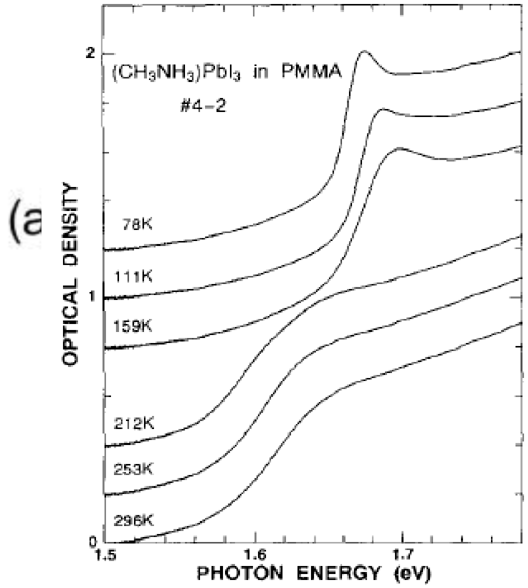


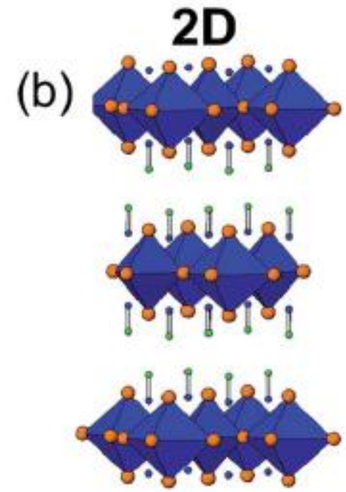
$(C_{10}H_{21}NH_3)_2PbI_4$

$(CH_3NH_3)_4PbI_6{*}H_2O$

Dielectric Confinement

$CH_3NH_3PbI_3$





$(CH_3NH_3)_2PbI_4$

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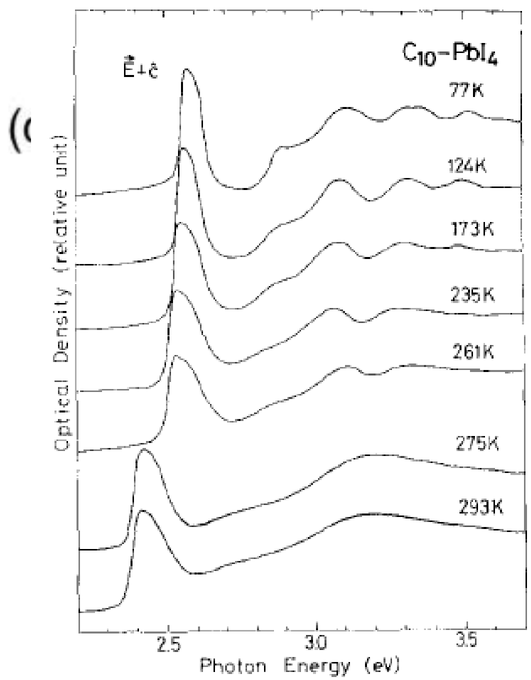

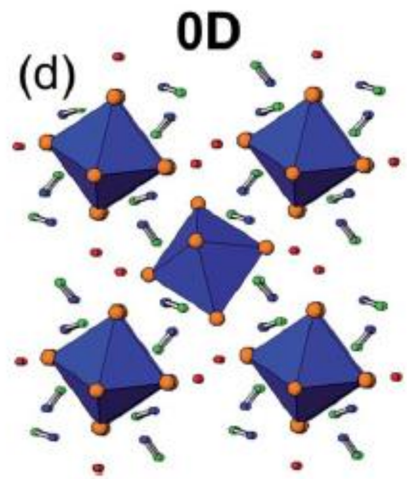

$(CH_3NH_3)_4PbI_6*H_2O$

Ishihara, J. Lum, 1994.

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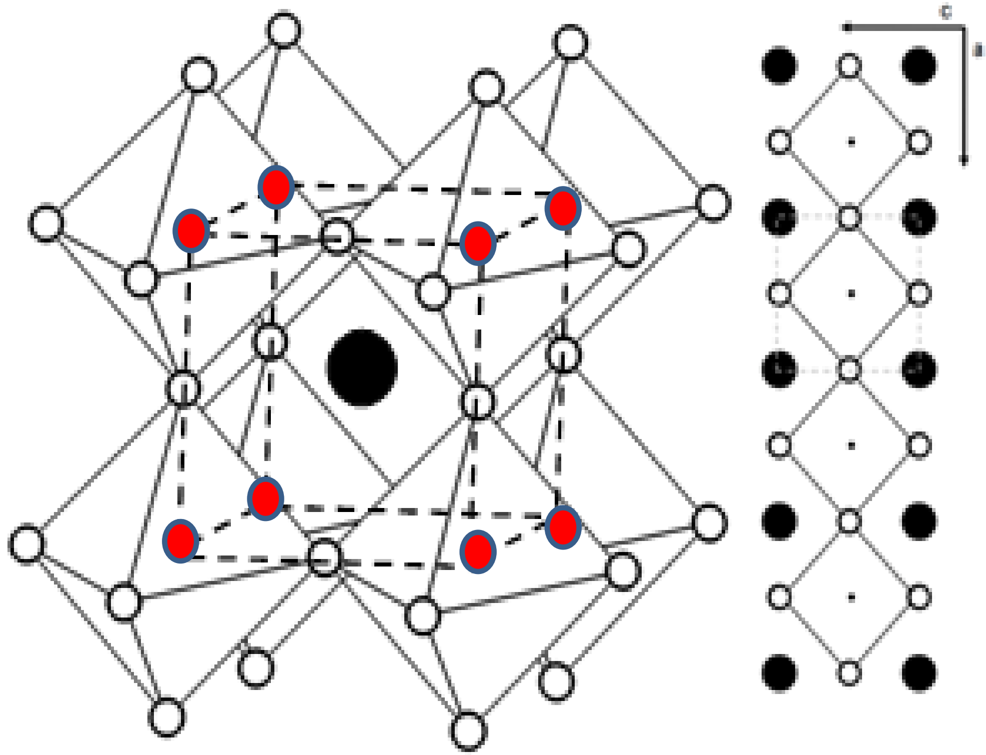
Organo-Metal Halide Crystalline Perovskite

ABX_3

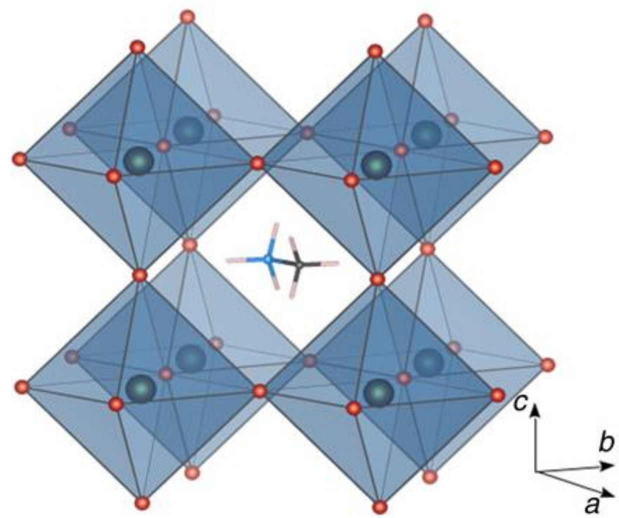
B = $(CH_3NH_3^+)_x$

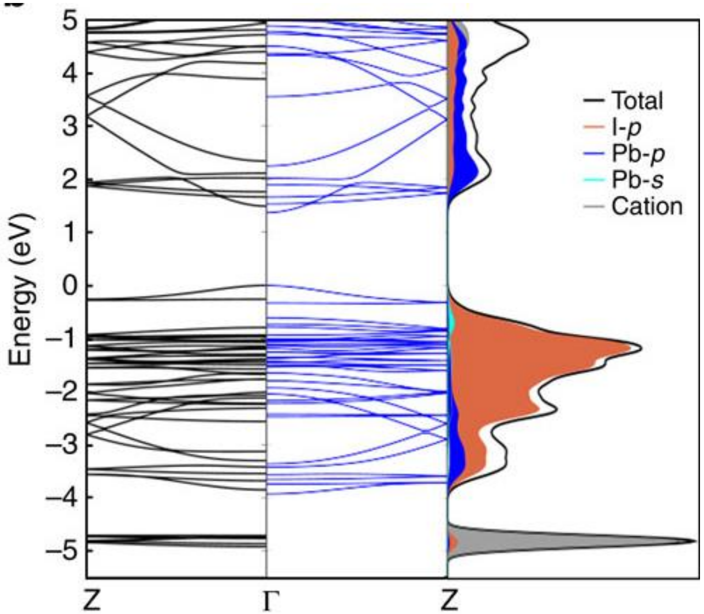
X= I^-, Cl^-, Br^-

A= Pb^{2+}

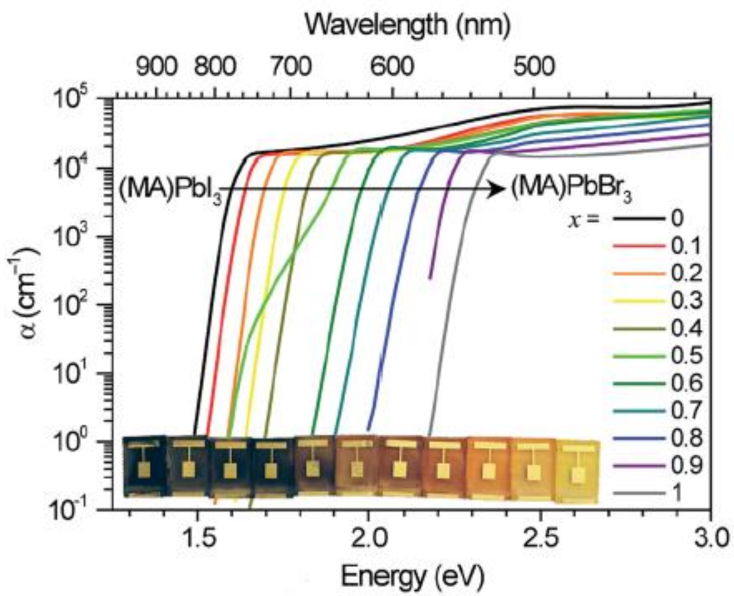


Organo-Metal Halide Crystalline Perovskite



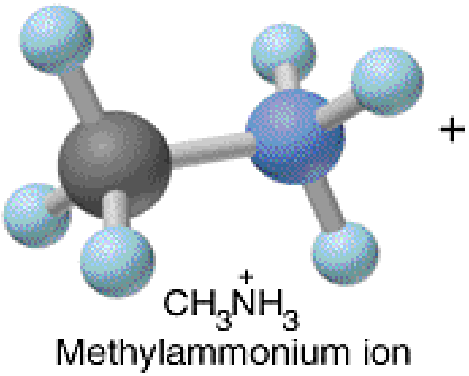


Filip et al, Nat Comm, 2014



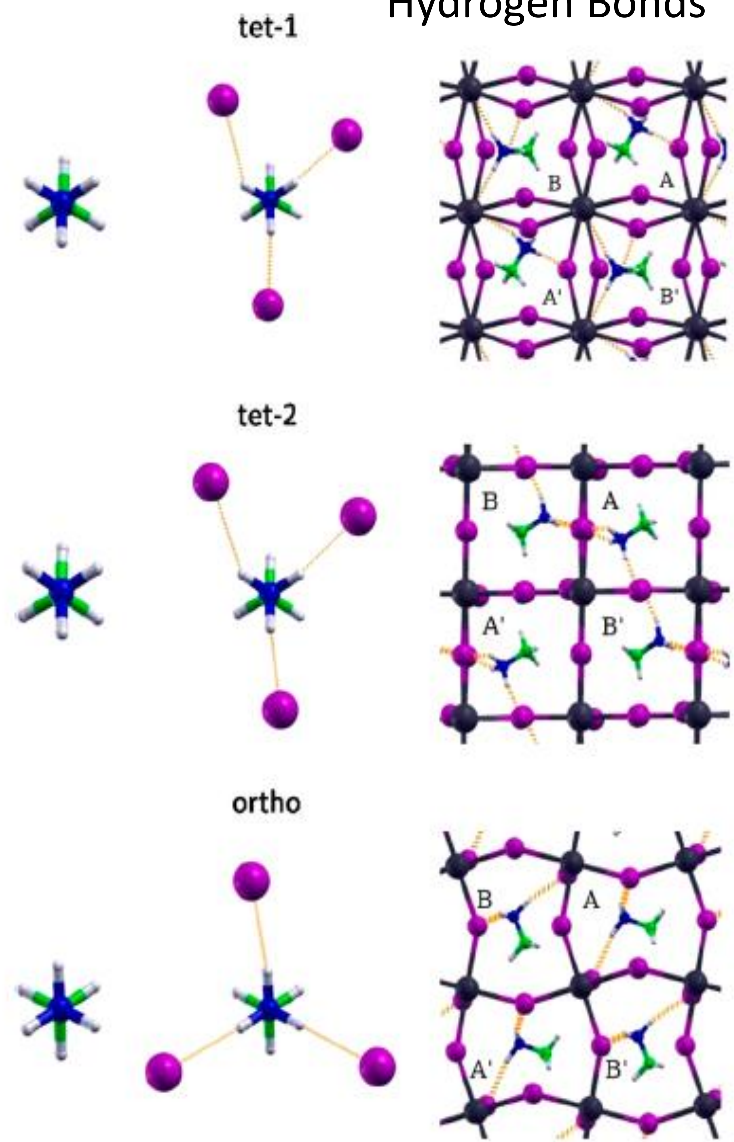
Eric Hoke et al, Chem Sci, 2015

Organo-Metal Halide Crystalline Perovskite

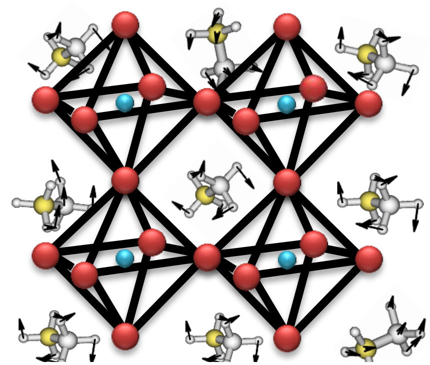


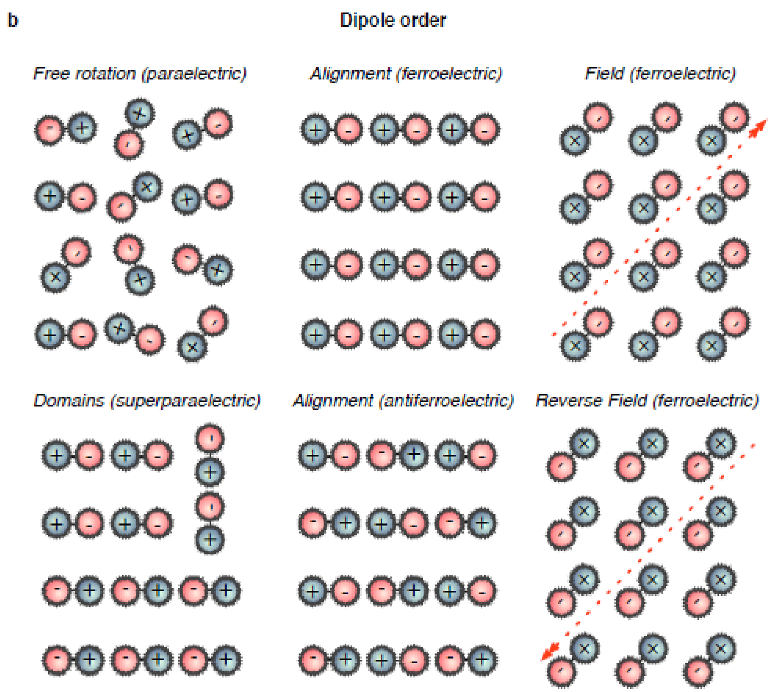
$CH3NH3^+$:Orientational disorder and Polarizability

Hydrogen Bonds

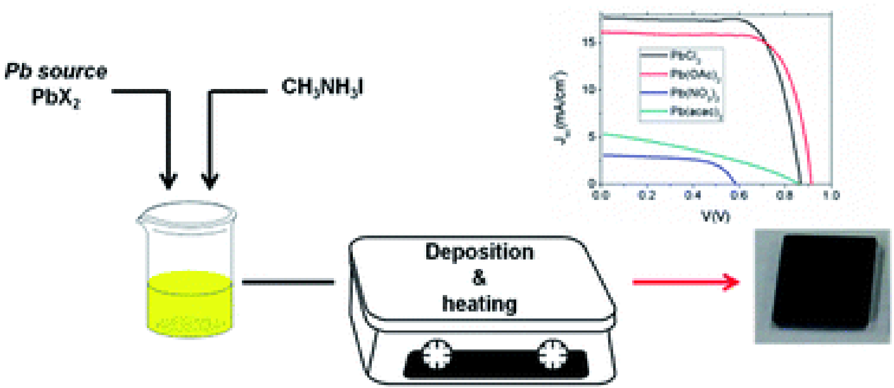


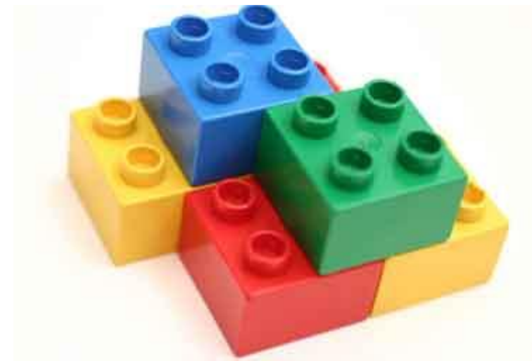
Dipole "nearly" free to move

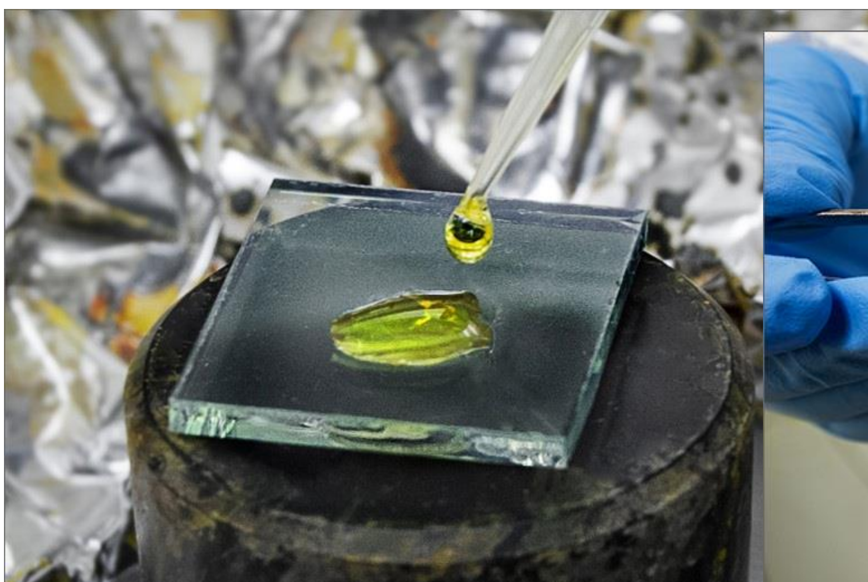


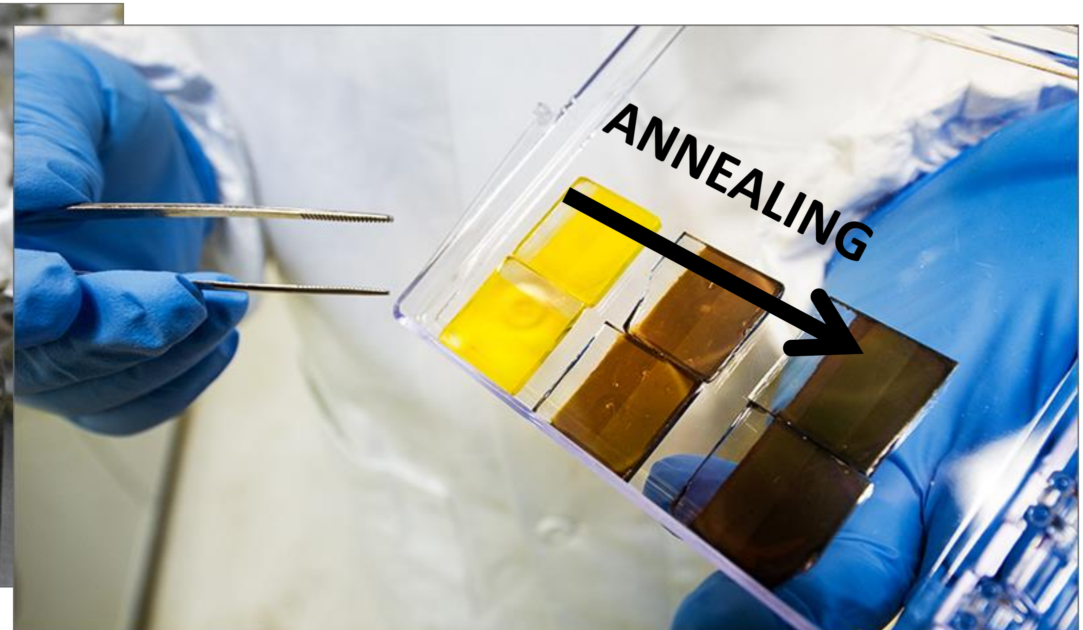


Modular Structure

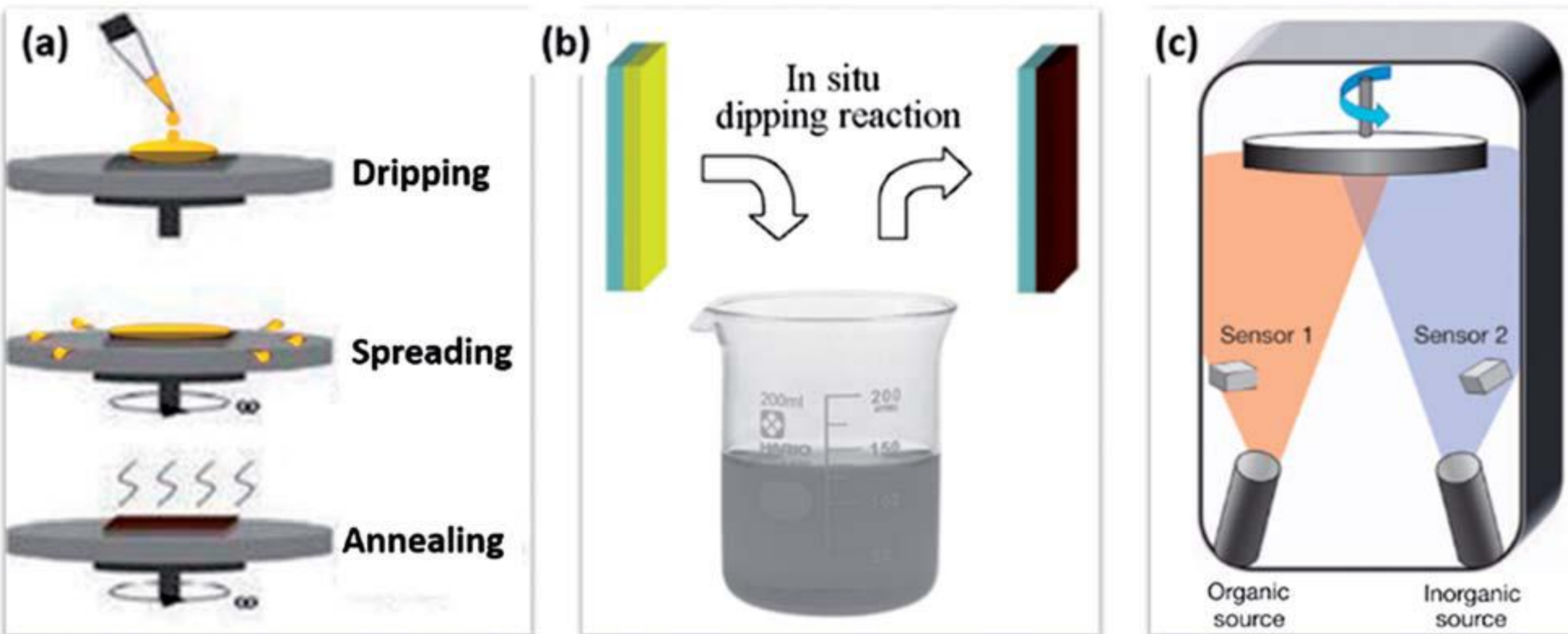






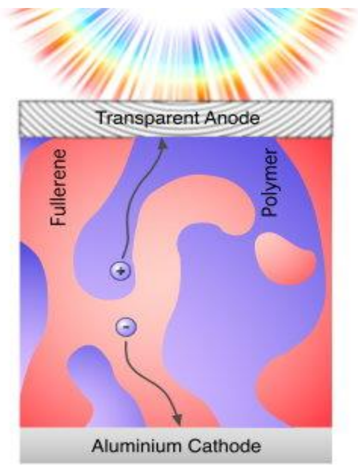


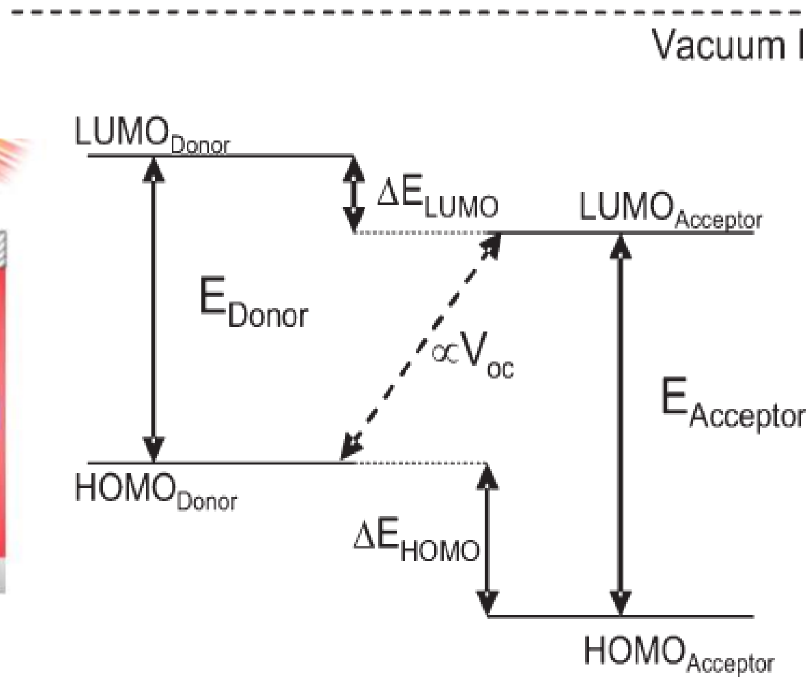
Prone to a variety of processing methods



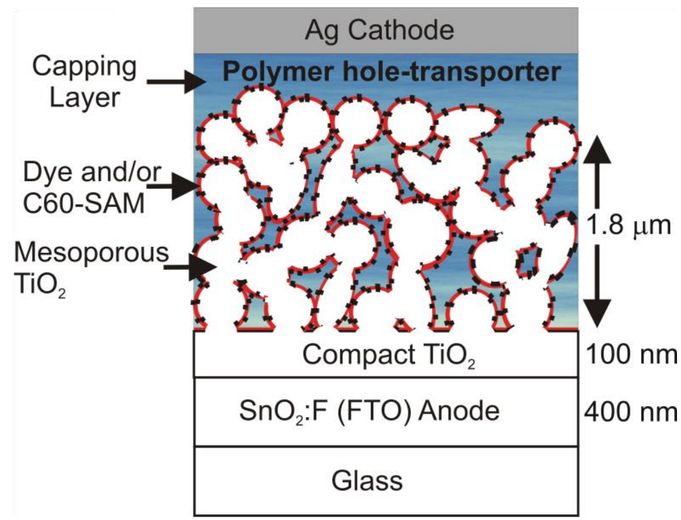
Excitonic Solar Cells

OPV



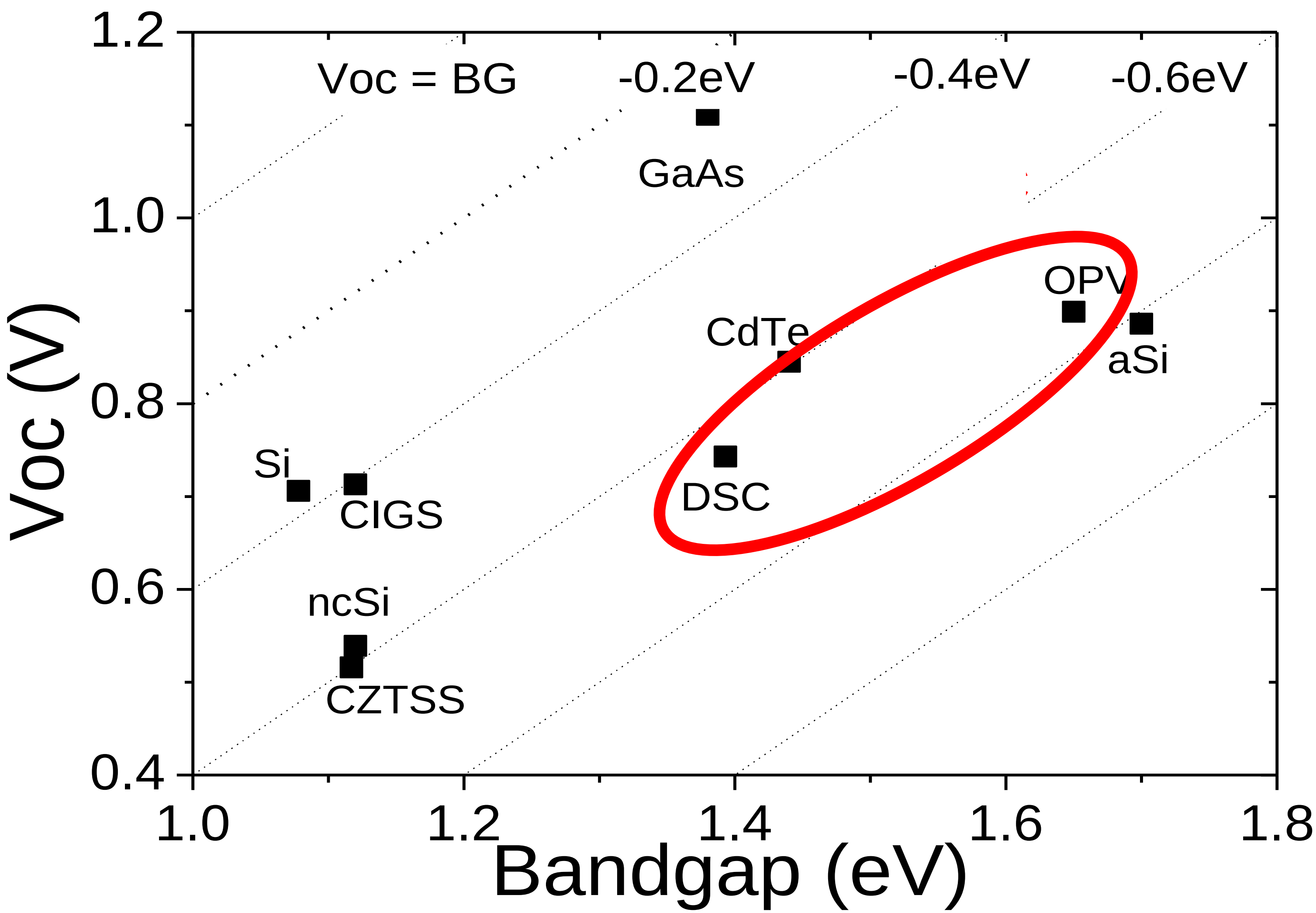


DSSC



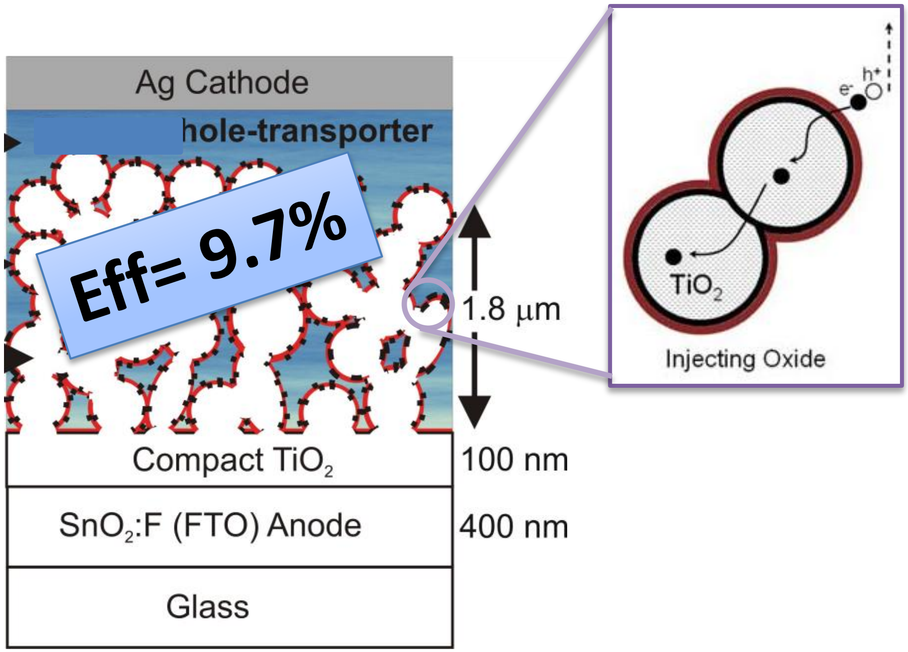
Type II Hetero-Junction

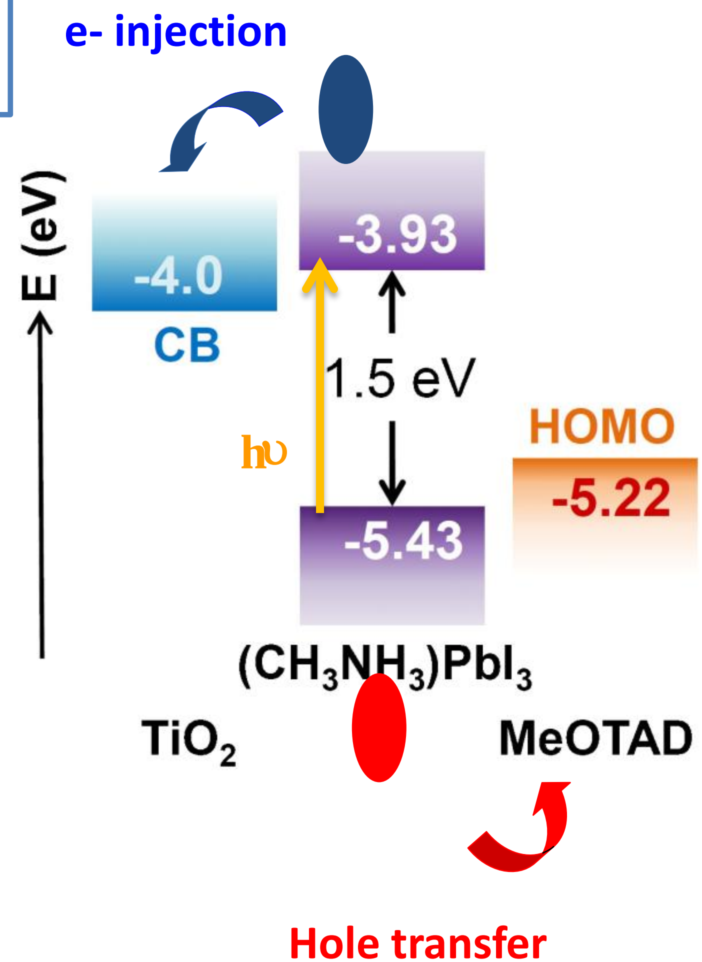
Intrinsic Loss in Excitonic Solar Cells



Hybrid Crystals in DSSC Devices

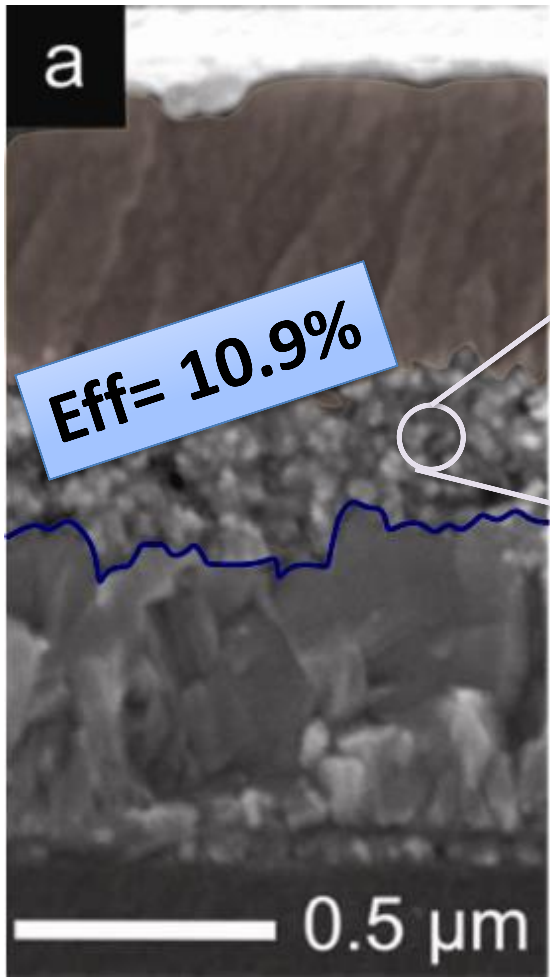
$CH_3NH_3PbI_3$ perovskite as light antenna in the **DSSC concept**





H. S. Kim et al. Sci Rep. 2: 591 **(2012)**

Hybrid Crystals in Hybrid Solar Cells

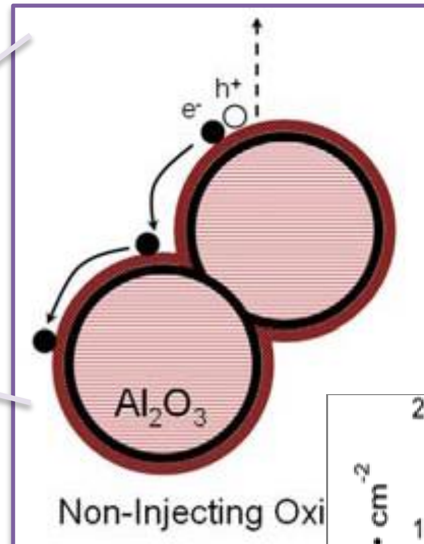


Silver

HTL

FTO

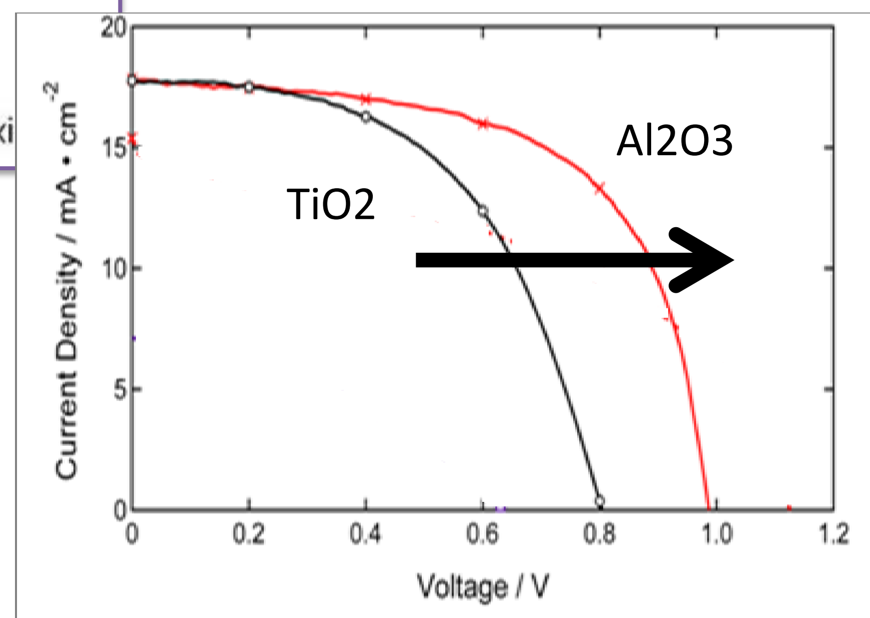
Glass



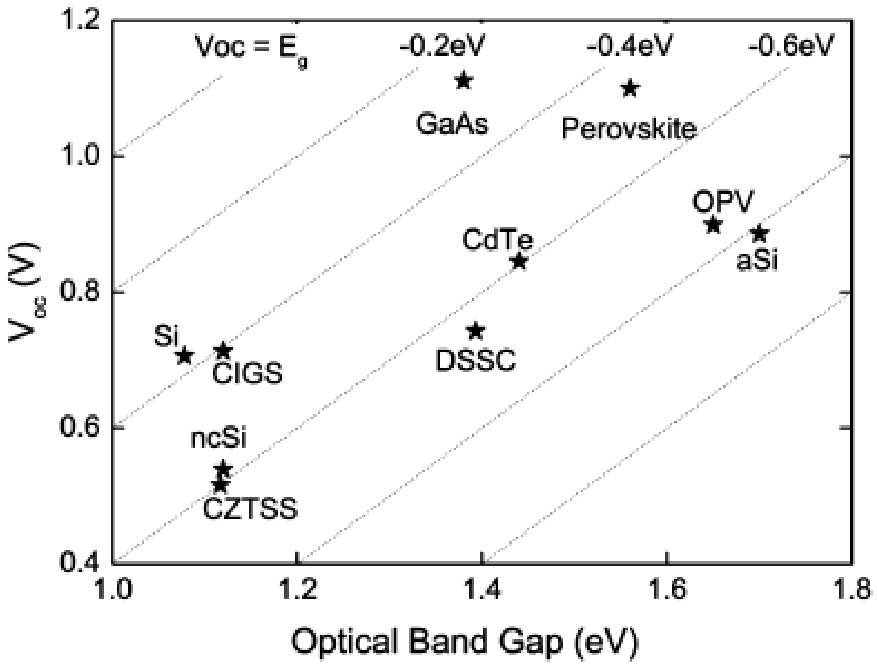
M.Lee et al. *Science 338, 643* **(2012)**

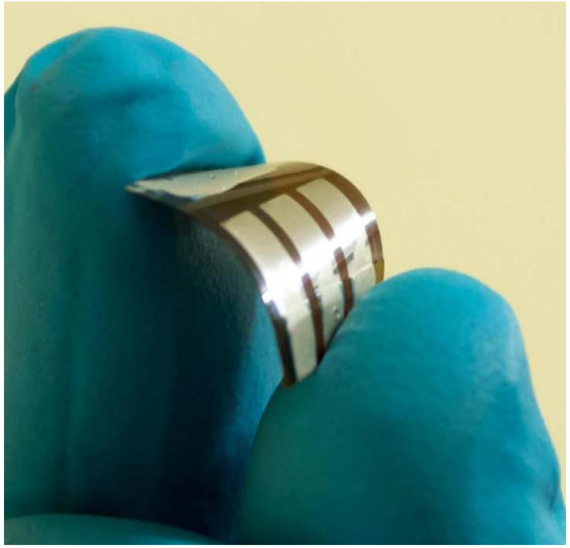
Perovskite role:

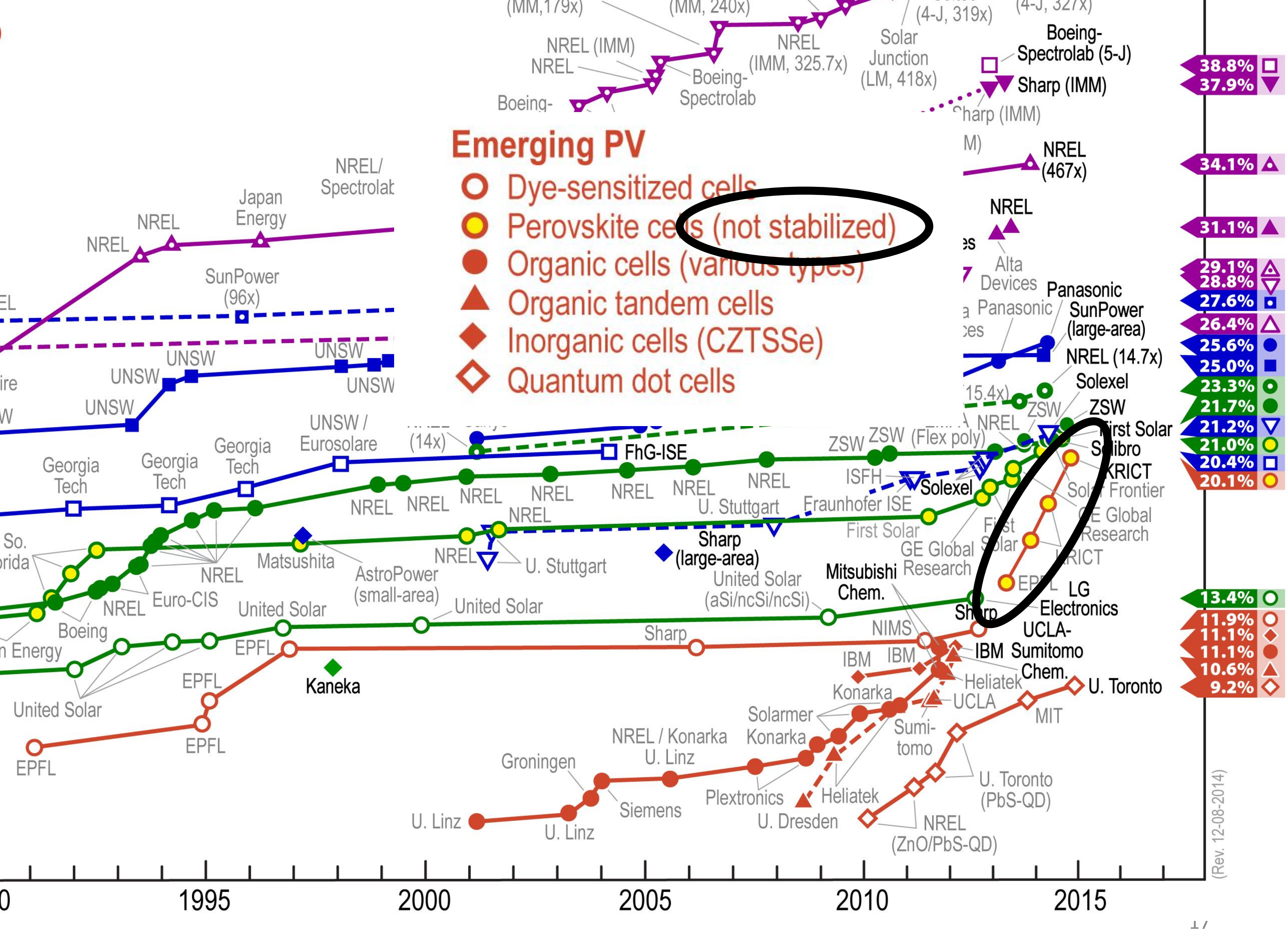
- Absorber
- Electron-transporter



Which is their strength?

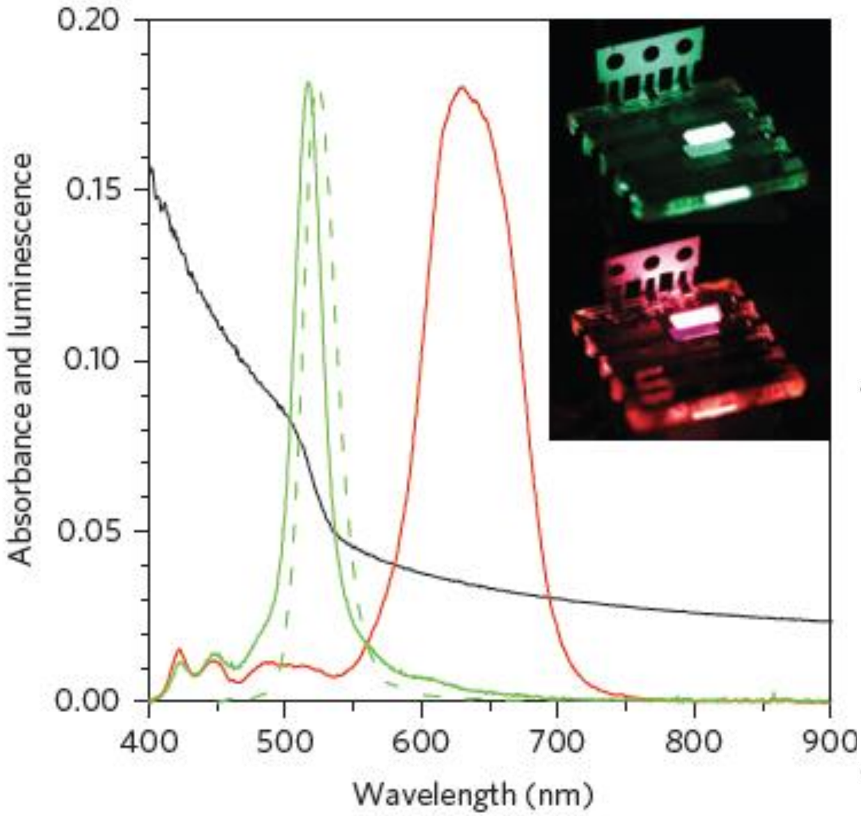






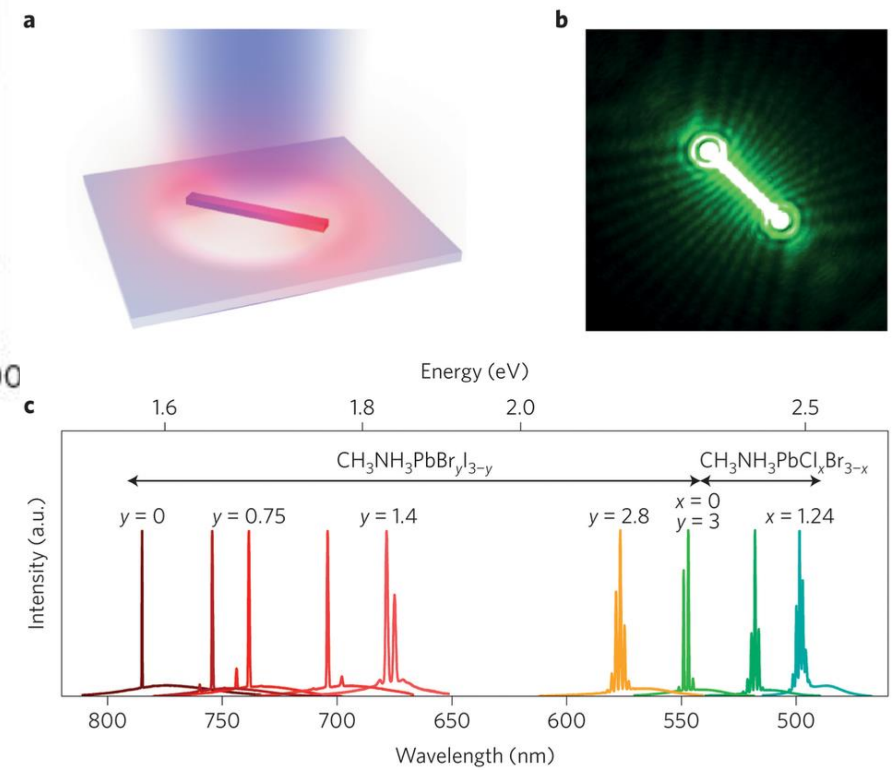
Emerging PV
Dye-sensitized cells
Perovskite cells (not stabilized)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells
38.8%
37.9%
34.1%
31.1%
29.1%
28.8%
27.6%
26.4%
25.6%
25.0%
23.3%
21.7%
21.2%
21.0%
20.4%
20.1%
13.4%
11.9%
11.1%
11.1%
10.6%
9.2%
1995
2000
2005
2010
2015
(Rev. 12-08-2014)

Optoelectronic Devices

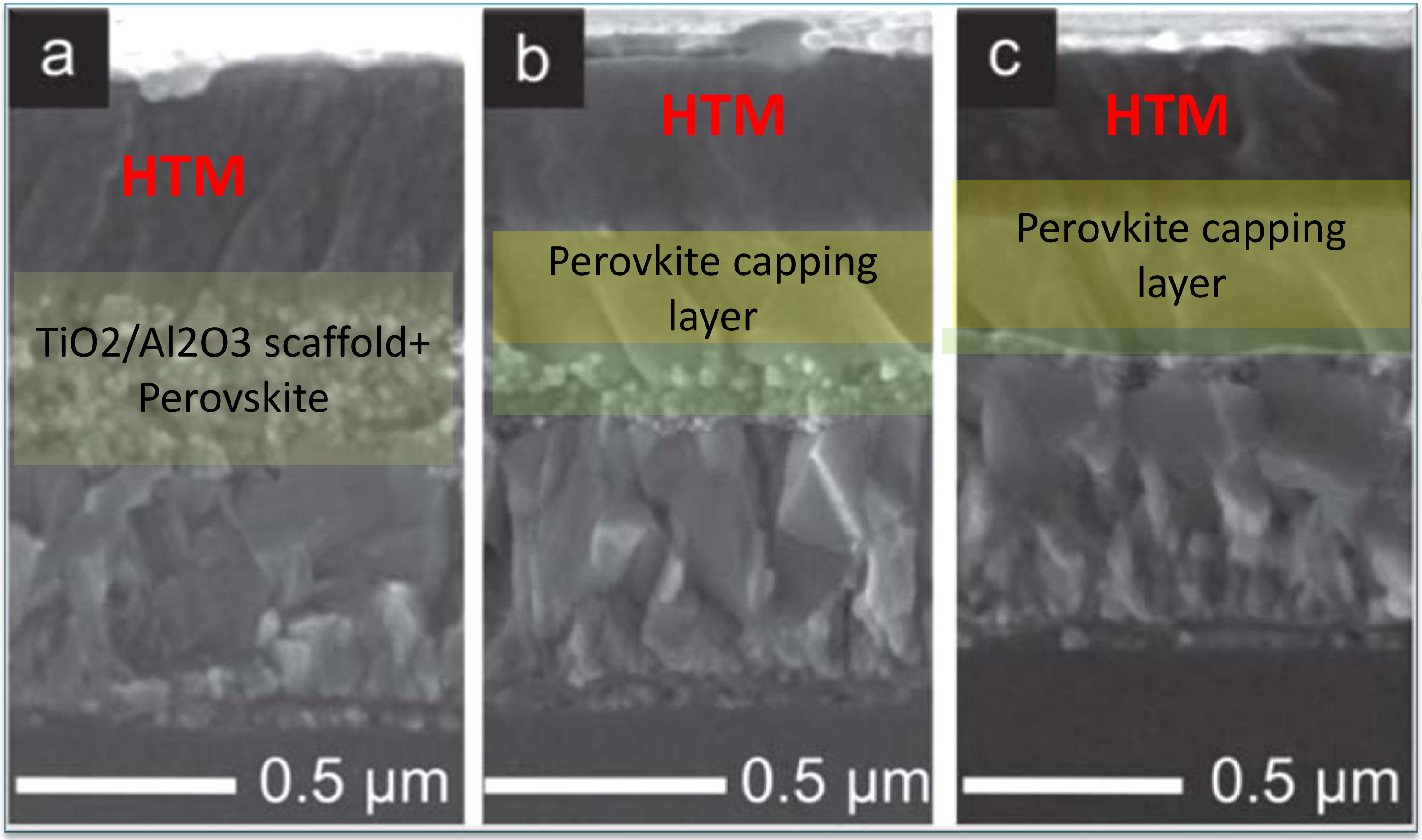


Tan et al, Nat Nanotech, 2014

Zhu et al, Nat Mat, 2015



Designing the Device Architecture



Nano-structured vs Thin Film

J. Ball, EES, 2013

Designing the Device Architecture

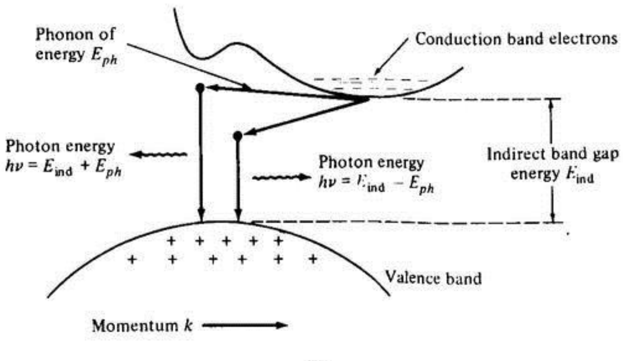
- Light Absorption
- Charge Generation
- Photo-carriers Transport

Designing the Device Architecture

- **Light Absorption**
- Charge Generation
- Photo-carriers Transport

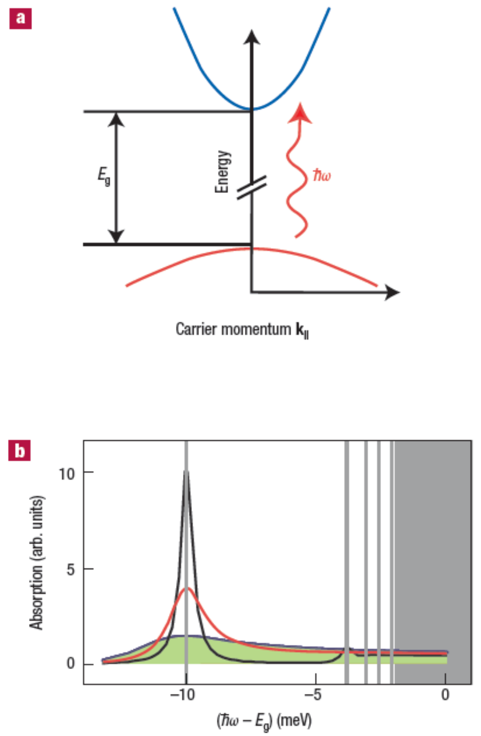
Light Absorption

Silicon



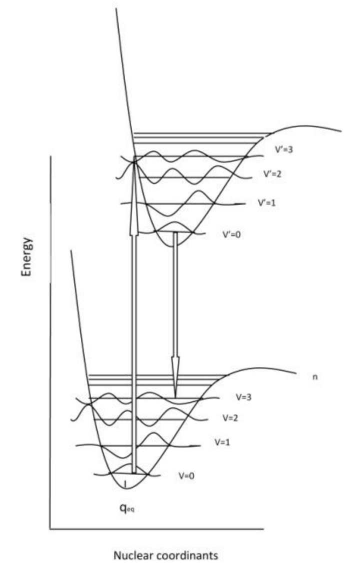
- ➢ In direct band-gap Phonon assisted
- ➢um range sun light penetration depth
- ➢ thick solar cells
- ➢ no light emission

GaAs



- ➢ direct band-gap
- ➢ excitonic effects at absorption edge
- ➢ good light penetration depth

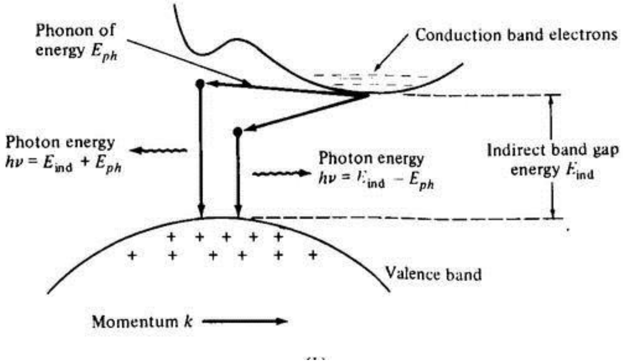
Dyes/conjugated polymers



- ➢ localized states
- ➢ excitonic effects
- ➢ large absorption cross-section/ efficient carrier recombination

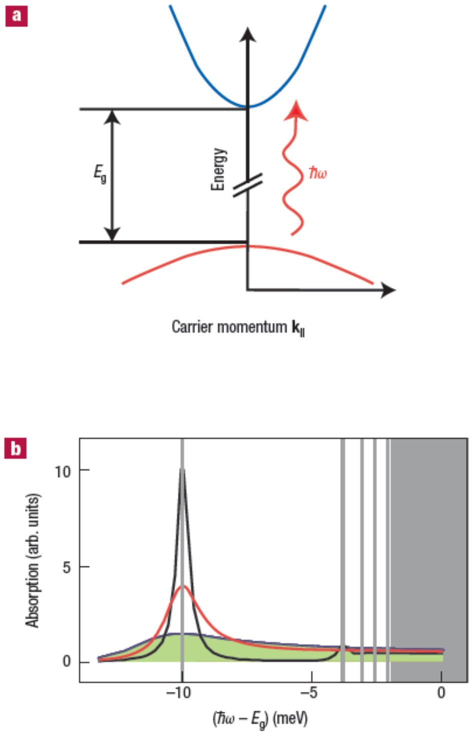
Light Absorption

Silicon



- ➢ In direct band-gapPhonon assisted
- ➢um range visible light penetration dept
- ➢ thick solar cells
- ➢ no light emission

GaAs



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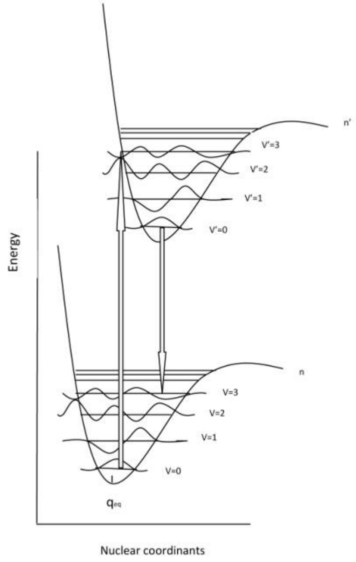

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Light Absorption

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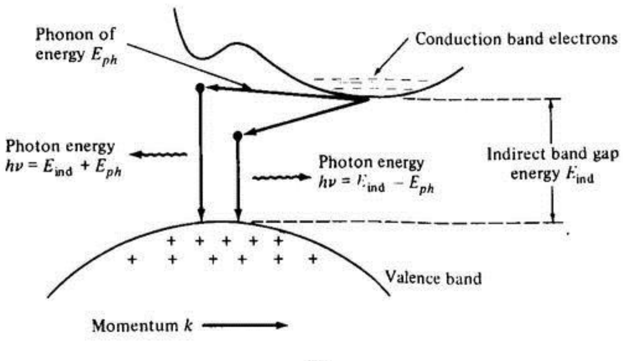

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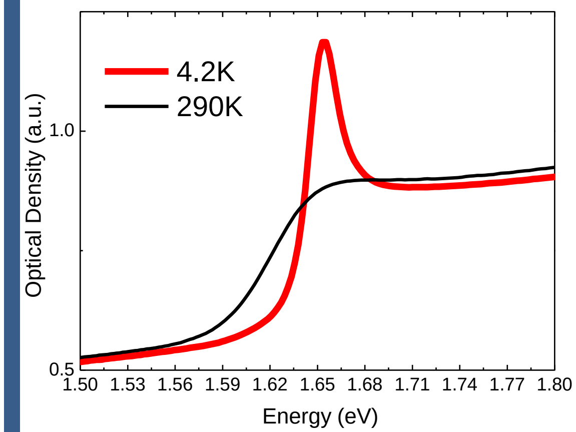
Hybrid Perovskites



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- ➢ excitonic effects at absorption edge
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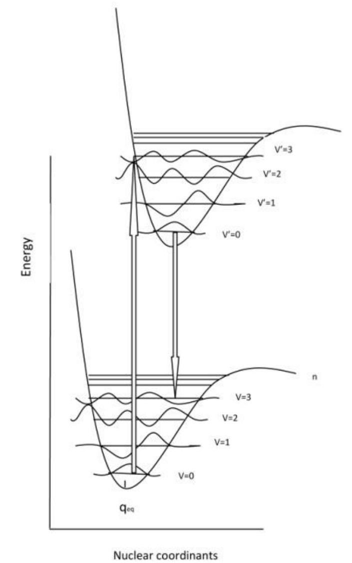
Dyes/conjugated polymers



- ➢ localized states
- ➢ excitonic effects
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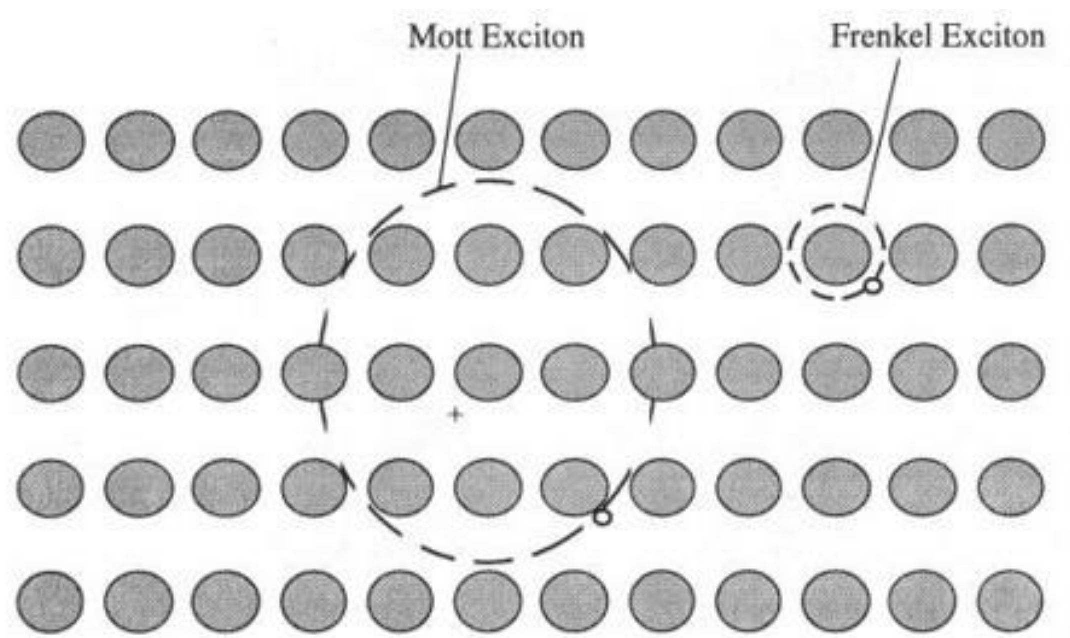
Exciton

" ..is a quasi-particle that represents a collective excited state of an ensable of atoms or molecules. It is represented by a wavepacket for which we can define mass and speed which transports Energy"

How many kind of excitons??

Wannier-Mott **Frenkel**



Binding energy

Delocalization

Oscillator strength

Triplet

Singlet

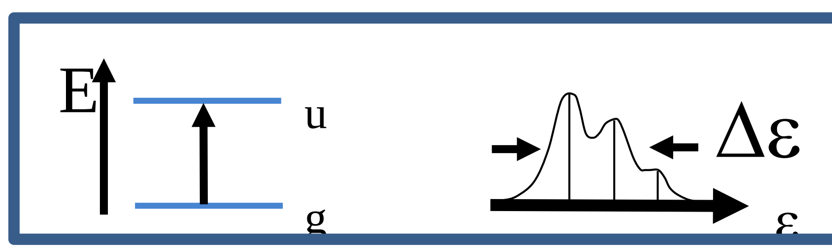
Lifetime

Frenkel Exciton

- Solids made by weakly interacting units (e.g organic crystals, inter-molecular coupling weaker than the intra-molecular ones).

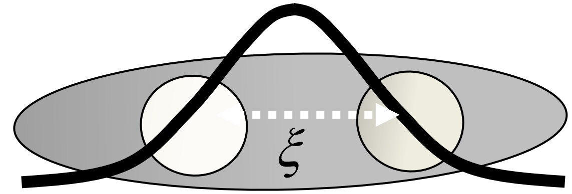
- General case of a Molecular Excitation **(DSSC)**

- The wavefunction squared amplitude is the probability of finding the excited state in the lattice.

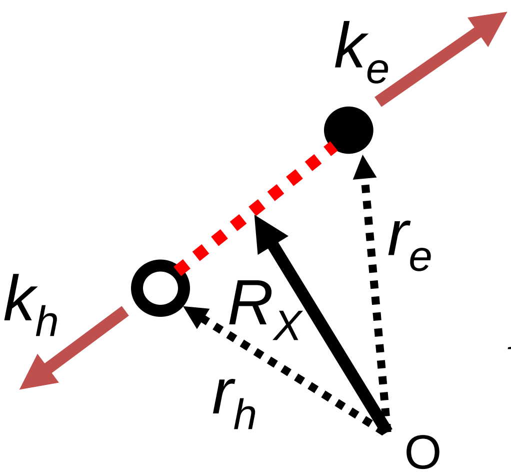


G. Lanzani, "The Photophysics behind Photovoltaics and Photonics" Wiley-VCH

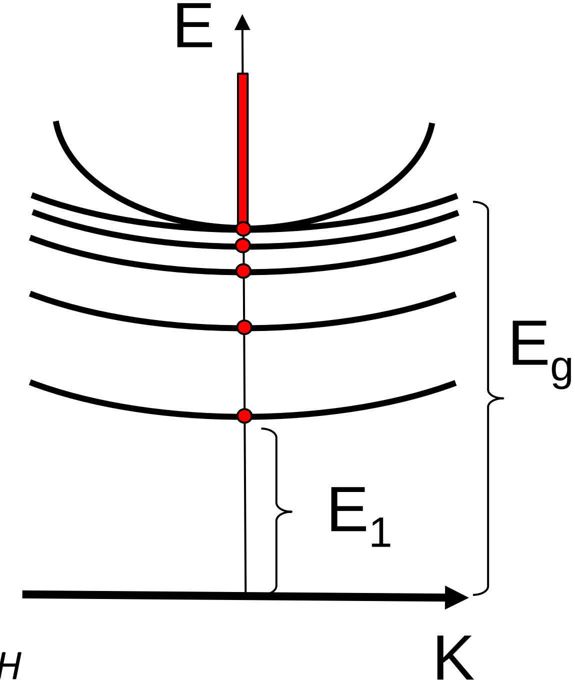
Wannier-Mott



- Solids with tightly bounded atoms
- Low Screening → Coulomb attraction does not allow the generation of FREE e-h pairs
- Hydrogenoid system.
- Center of Mass/Exciton radius (LARGER than the lattice constant)



$$E_{K_X,n} = E_g - \frac{E_b}{n^2} + \frac{\hbar^2 K_X^2}{\left(m_e^* + m_h^*\right)}$$



G. Lanzani, "The Photophysics behind Photovoltaics and Photonics" Wiley-VCH

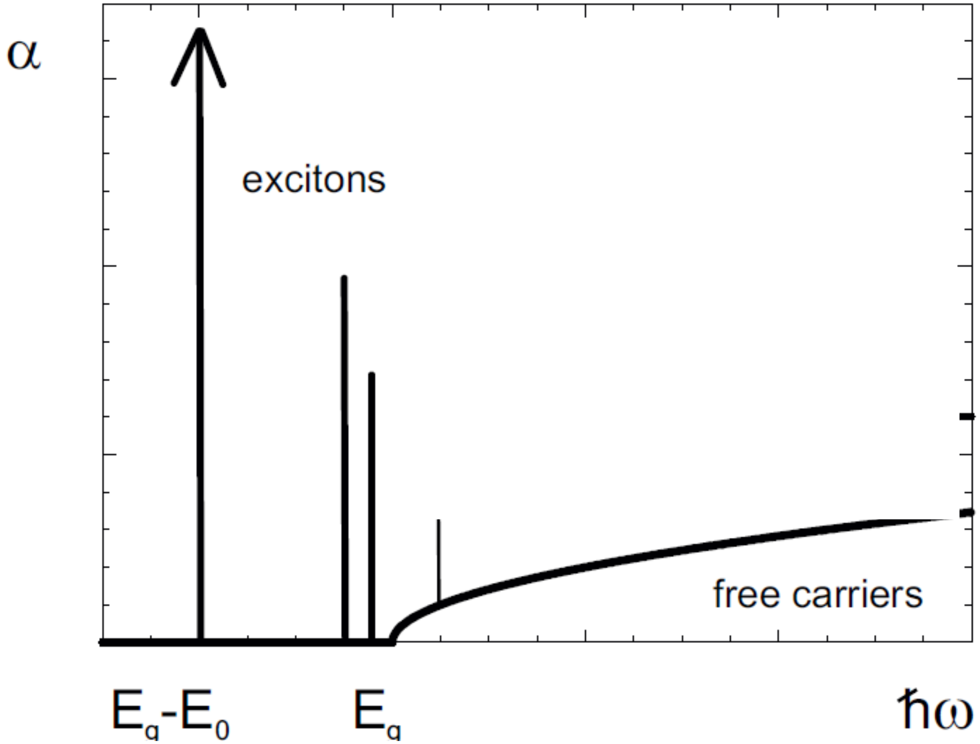
Why do we need to know the details?

- **Energy spent in the exciton dissociation**

Why do we need to know the details?

- **Energy spent in the exciton dissociation**

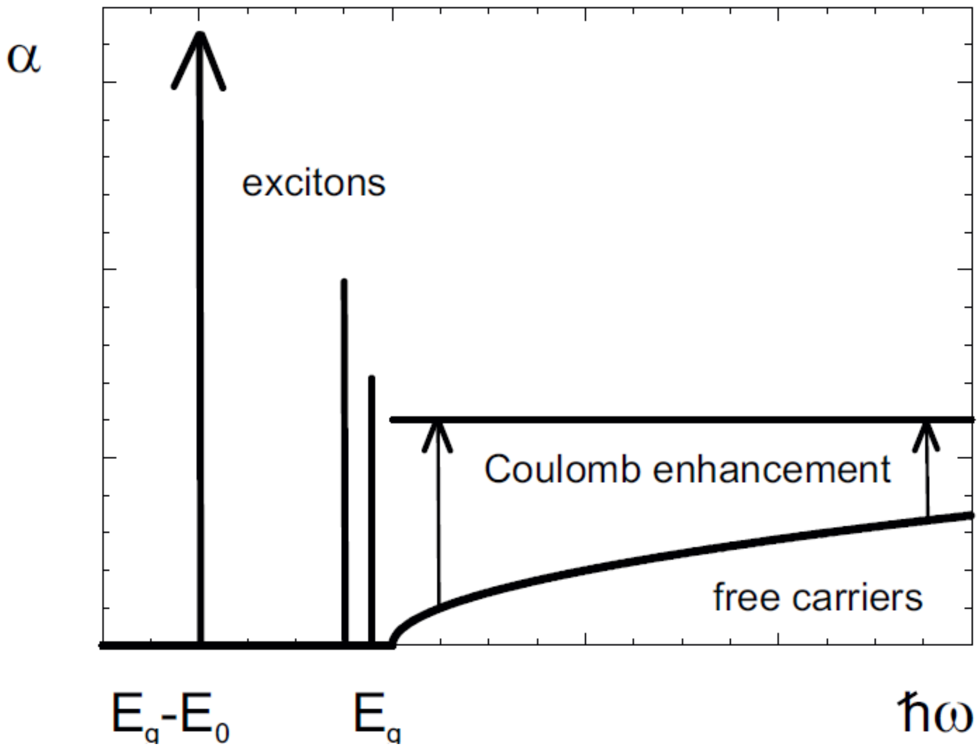
- **Absoprtion cross section enhancement**



$$\alpha_X \propto \frac{1}{\pi (a_B)^3}$$

Why do we need to know the details?

- **Energy spent in the exciton dissociation**
- **Absoprtion cross section enhancement**



$$\alpha_{cont} = \alpha_{free} C(\omega)$$

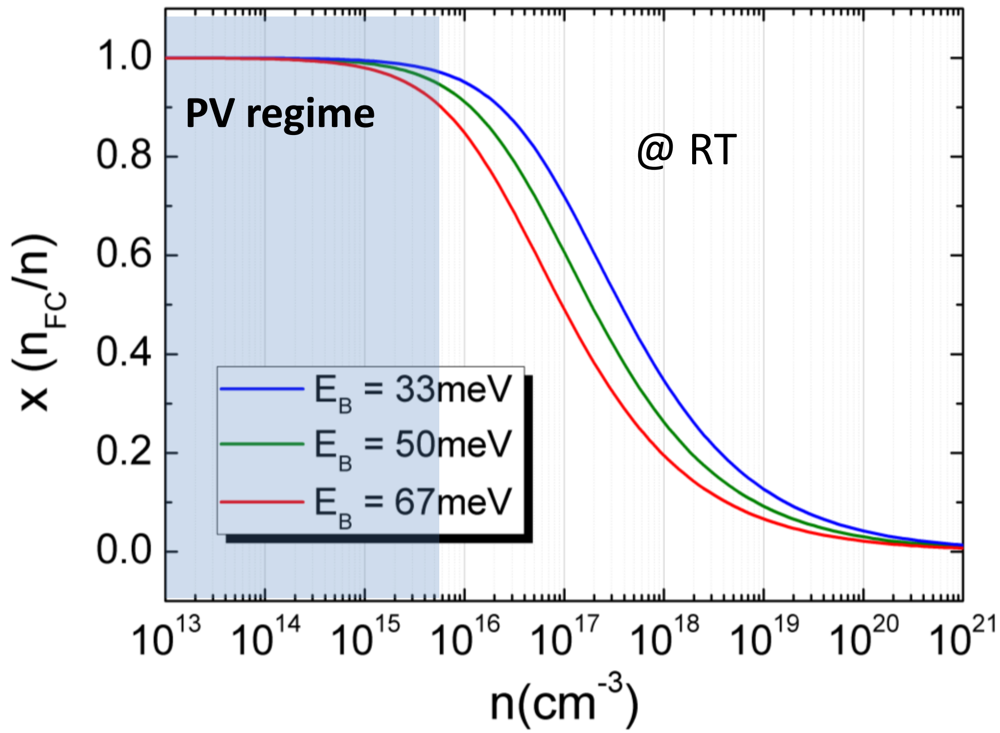
$$C(\omega) = \frac{\frac{\pi}{\sqrt{\Delta}} e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})}$$

$$\Delta = (\hbar\omega - E_g)/E_0$$

Elliott's Theory (1963)

Exciton Vs Free Charges

at the Thermodynamic Equilibrium



Total excitation density

Excitons

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

Free charges

Law of mass action

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

Saha-Langmiur equation

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

D'Innocenzo et al, Nat Comm. 5, 3586, 2014

Exciton Binding Energy

$$a_B = \frac{\hbar^2 \varepsilon}{\mu e^2}$$

Exciton Reduced mass

$$\mu = \frac{m_e m_h}{m_e + m_h}$$

$$E_B = \frac{\mu e^4}{2\hbar^2 \varepsilon^2} = \frac{\hbar^2}{2\mu a_B^2}$$

Dielectric constant

Bohr Radius

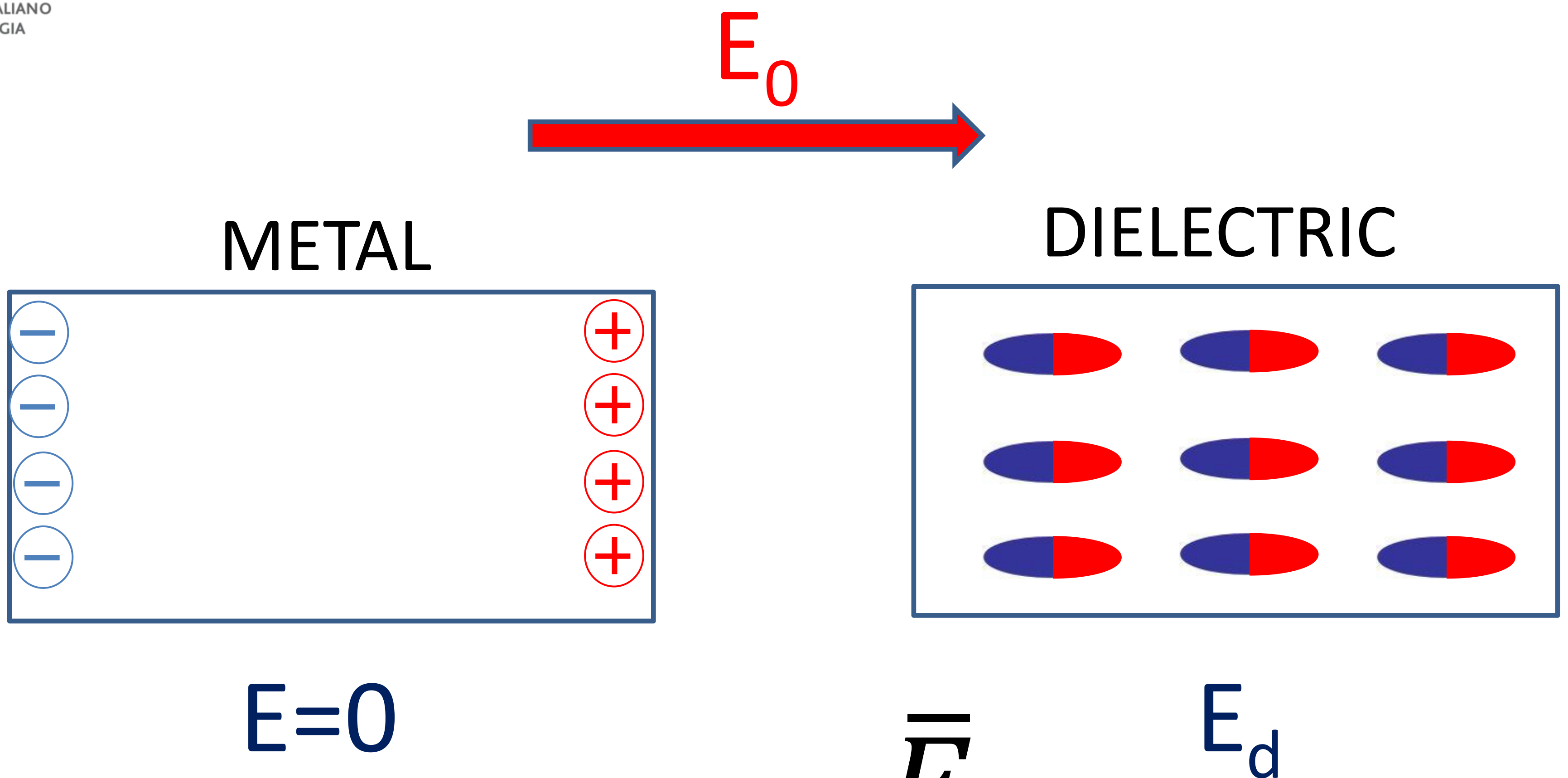
The golden rule:

"the Bohr orbital frequency (E_b/h) must be compared with the optical phonon frequency"

Dielectric constant **(ε):**

A measure of a substance's ability to insulate charges from each other.

Screening in solids: basic concept

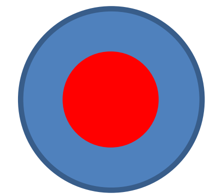


$$\overline{E_d} = \frac{\bar{E}_0}{\varepsilon}$$

Screening mechanisms

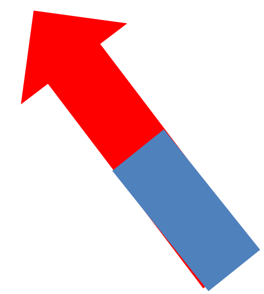
Electronic Polarizability
(Electron Cloud Distortion)

$10^{15}\ s^{-1}$



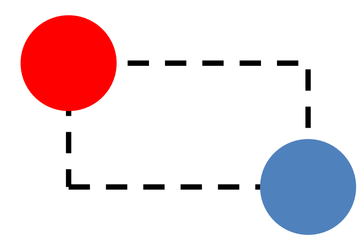
Dipole Re Orientation
(Langevin Mechanism)

$10^{8} - 10^{10}\ s^{-1}$

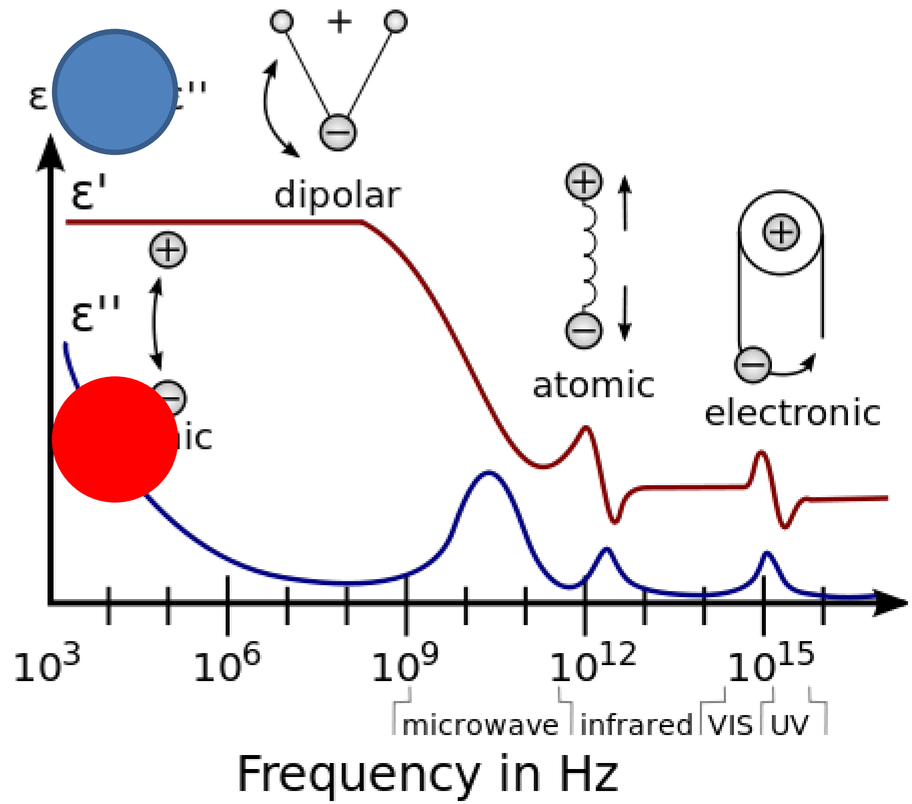


Ions Displacement
(Optical Phonons)

$10^{10} - 10^{0}\ s^{-1}$



Screening mechanisms

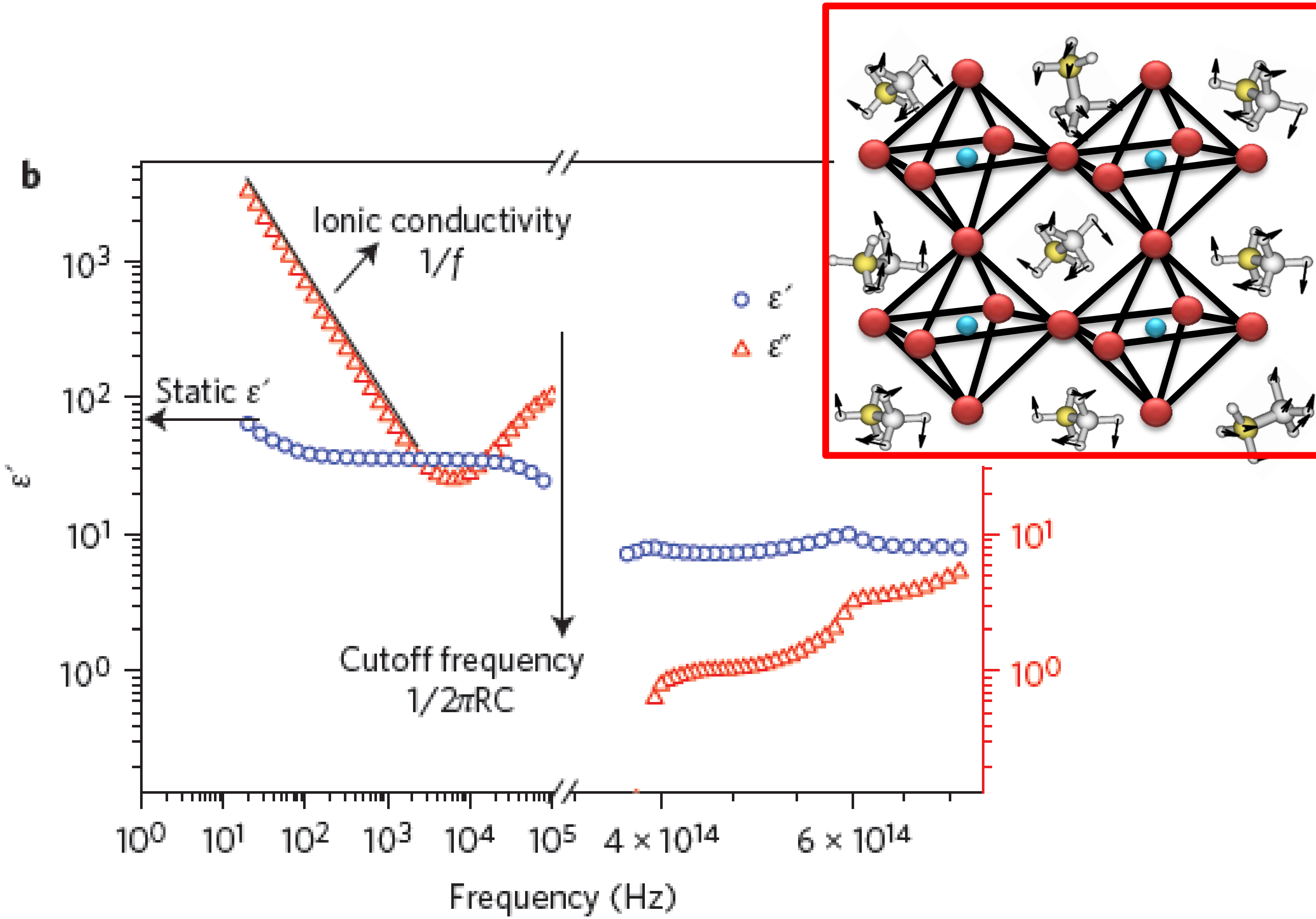


$$\prod_i \left(\frac{\omega_{Li}}{\omega_{Ti}}\right)^2 = \frac{\varepsilon_0}{\varepsilon_\infty}$$

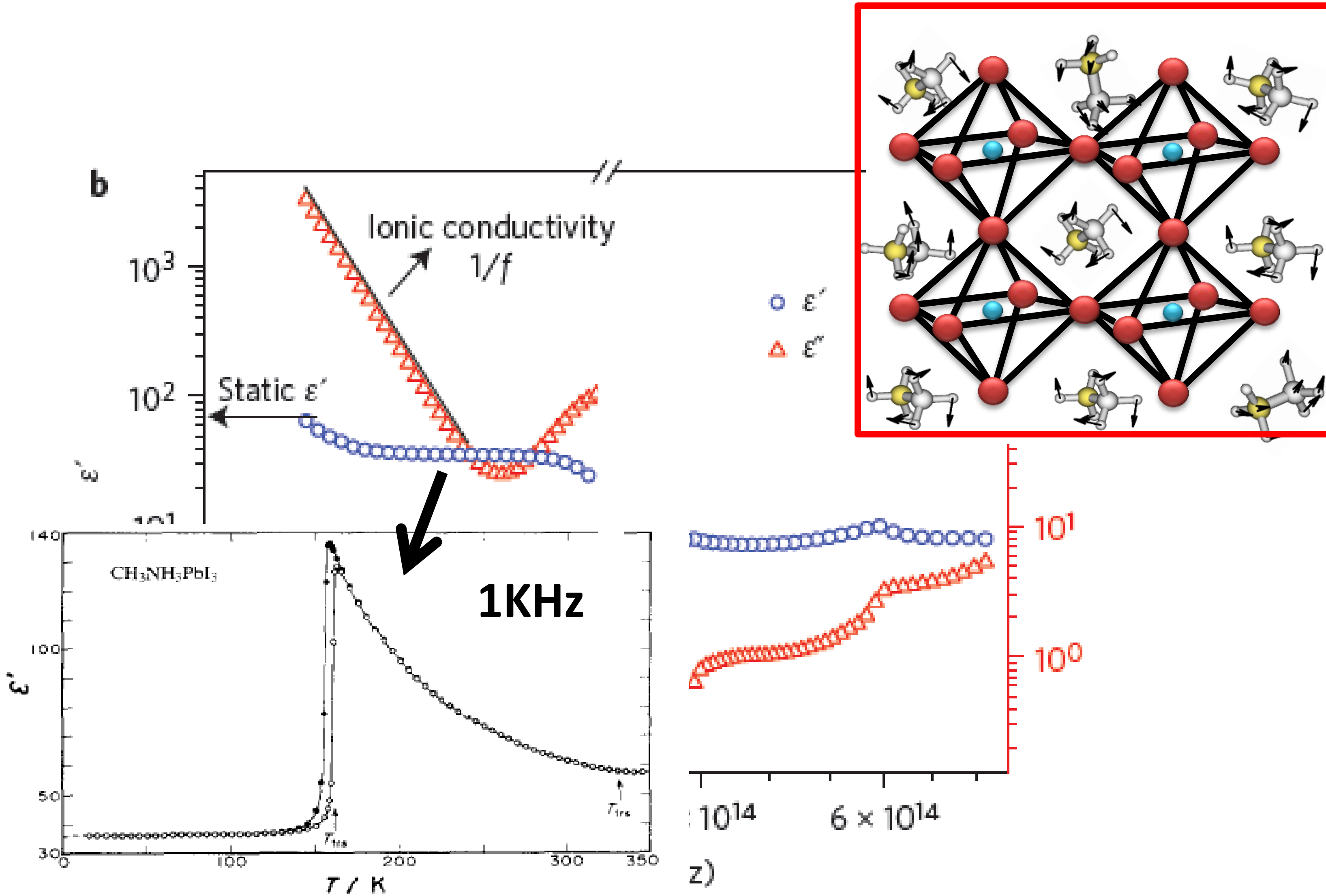
Dielectric constant of GaAs. Why it is so easy

- $\dfrac{\varepsilon_0}{\varepsilon_\infty} = 2$
- $\varepsilon_0\,(T) = 12.4 + 0.00012*T$
- $\omega_{LO} = 36\text{meV}$ $\omega_{TO} = 38\text{meV}$

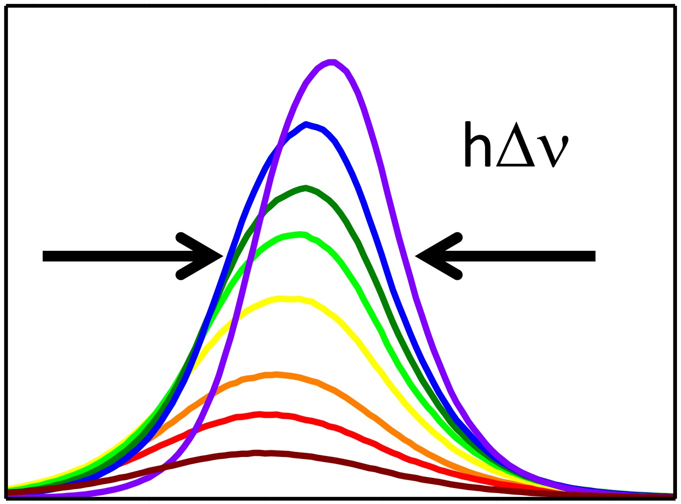
Dielectric constants of CH3NH3PbI3, real and imaginary parts

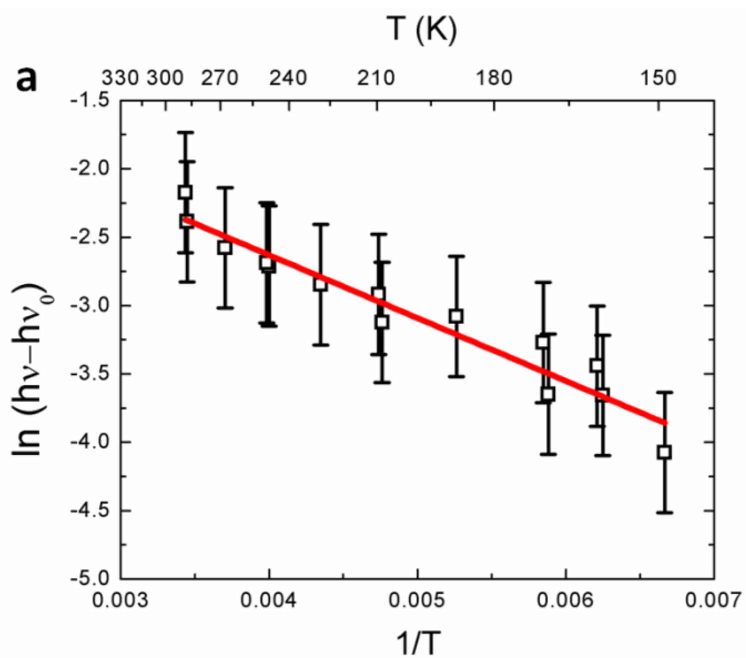


Dielectric constants of CH3NH3PbI3, real and imaginary parts



(I) Direct Measurement of Exciton Binding Energy in $CH_3NH_3PbI_3$





Exciton Binding Energy

$$\Delta\upsilon = k_1 + \upsilon \exp\left(-\frac{E_b}{k_B T}\right)$$

E_b (upper limit)= 50meV

Limitations:

→It is assumed that exciton-phonon interaction induces only exciton dissociation

→ though in a limited range – it assumes the exciton binding energy constant in T

D'Innocenzo et al, Nat Comm. 5, 3586, 2014

(I) Direct Measurement of Exciton Binding Energy in $CH_3NH_3PbI_3$

$$\Delta\nu = \frac{1}{\pi \mathrm{T}_2}$$

$$\frac{1}{\mathrm{T}_2} = \frac{1}{2T_1} + \gamma$$

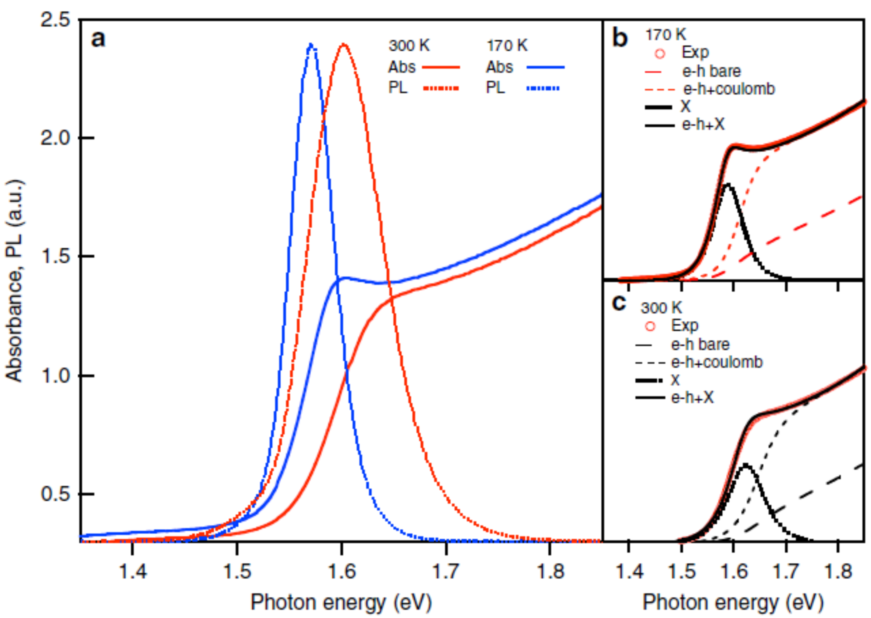
$$\frac{1}{\mathrm{T}_1} = k_0 + k_T$$

$$k_T = \nu_T e^{-E_B/k_B T}$$

(II) Direct Measurement of Exciton Binding Energy in $CH_3NH_3PbI_3$

Numerical modelling of band-edge absorption by using Elliot's theory of Wannier excitons

$$\alpha(\hbar\omega) \propto \mu_{cv}{}^2 \frac{\hbar\omega}{E_b}\left[\sum_j \frac{4\pi E_b}{j^3}\cdot Sech\left(\frac{\hbar\omega - E_g + E_b/j^2}{\Gamma}\right) + \int_{E_g}^{\infty} Sech\left(\frac{\hbar\omega-\varepsilon}{\Gamma}\right)\cdot\frac{2\pi}{1-e^{-2\pi\sqrt{E_b/\varepsilon - E_g}}}\cdot\frac{1}{1-\frac{8\mu b}{\hbar^3}(\varepsilon - E_g)}\,d\varepsilon\right]$$

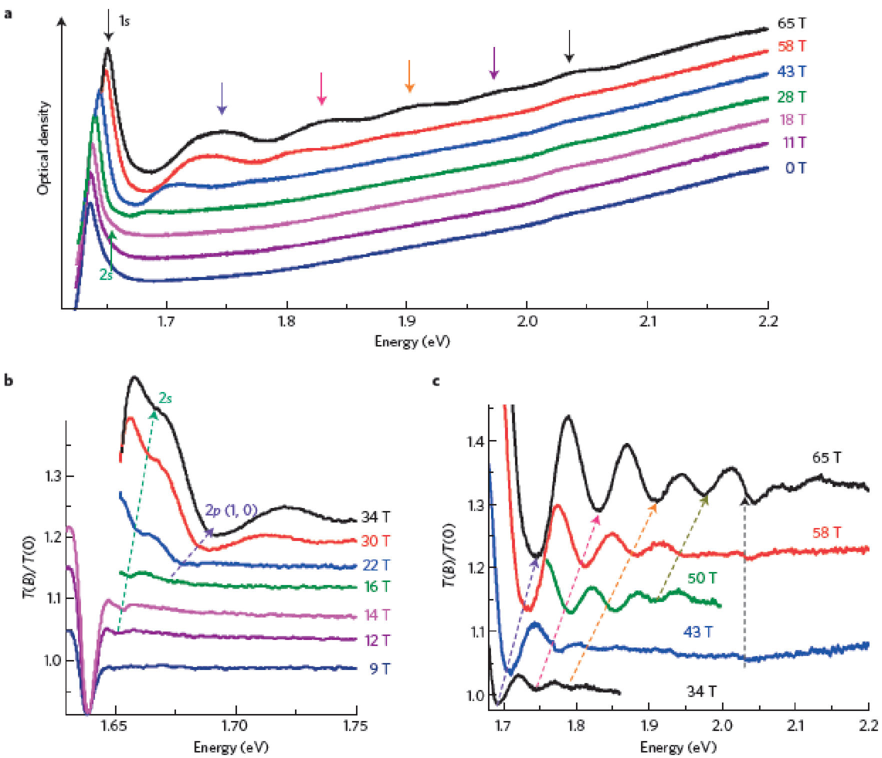


E_b = 25meV

<u>Note:</u> This simple formalism does not consider the frequency dependance of the exciton-phonon interaction

Saba et al, Nat Comm. 5, 5049, 2014

(III) Direct Measurement of Exciton Binding Energy in $CH_3NH_3PbI_3$



$$E(B) = E_g + (N + 1/2)\hbar\left(\frac{eB}{m^*}\right)$$

$$E_n = E_g - \frac{R}{n}$$

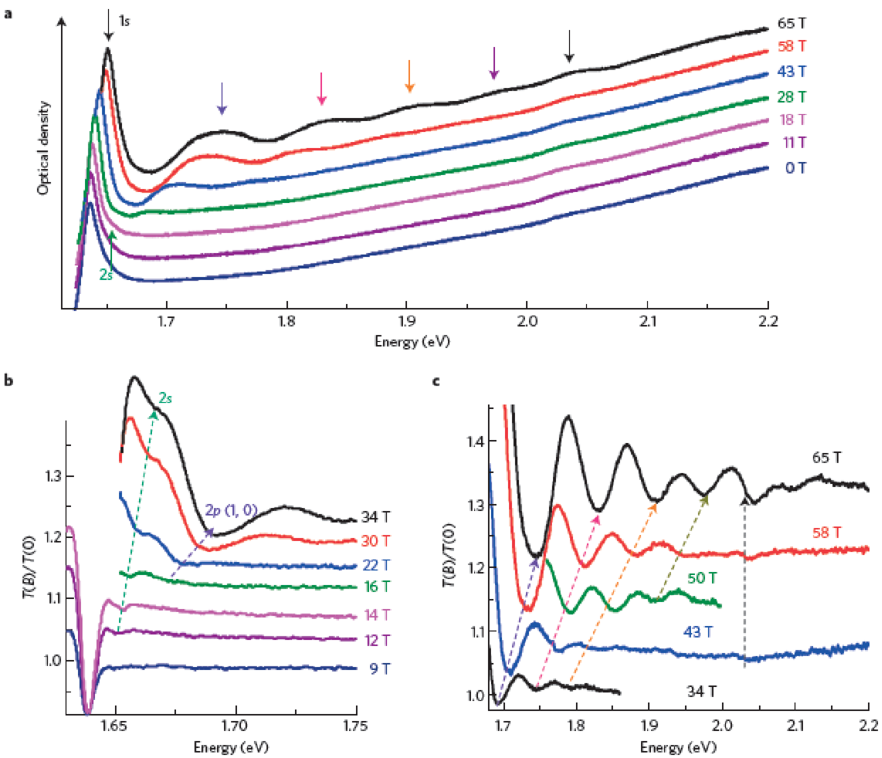
At 4K

$m^* = 0.1m$; E_b = 16meV

$\varepsilon \sim 9$

Miyata et al, Nature Physics 11, 582–587 (2015)

(III) Direct Measurement of Exciton Binding Energy in $CH_3NH_3PbI_3$



$$E(B) = E_g + (N + 1/2)\hbar\left(\frac{eB}{m^*}\right)$$

$$E_n = E_g - \frac{R}{n}$$

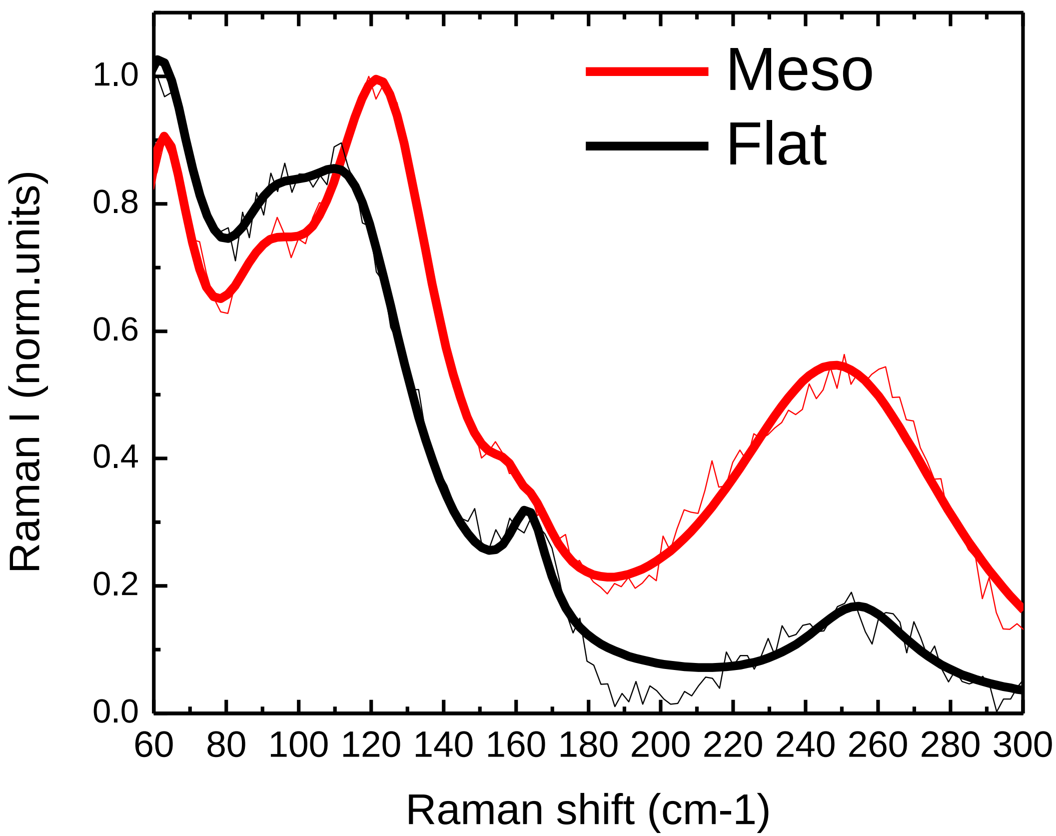
At 161K

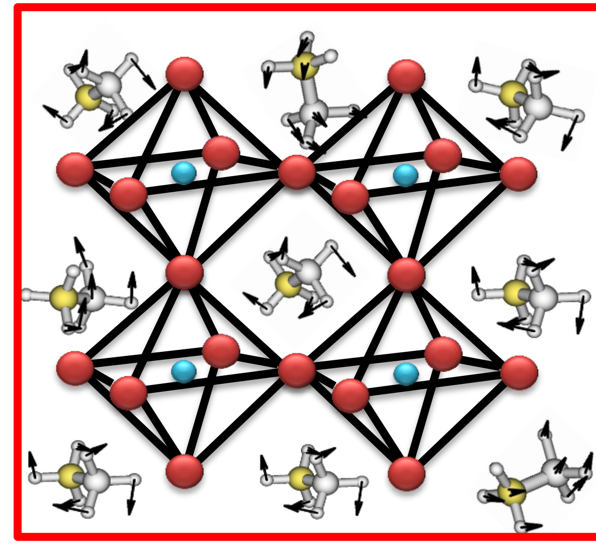
$E_b \sim 10$ meV

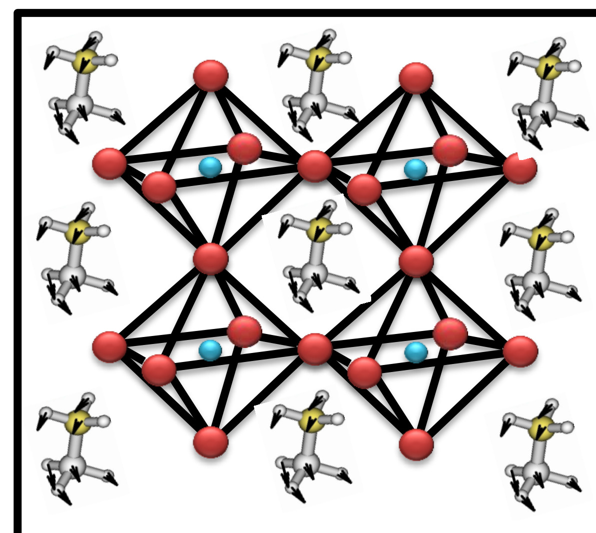
$\varepsilon > 9$

Miyata et al, Nature Physics 11, 582–587 (2015)

Organic-Inorganic Interplay: Raman Spectroscopy as a probe







Grancini G et al, JPC Letters, 5, 3836, 2014

- Light Absorption
- **Charge Generation**
- Photo-carriers Transport

Exciton Vs Free Charges

at the Thermodynamic Equilibrium

Total excitation density

Excitons

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

Free charges

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

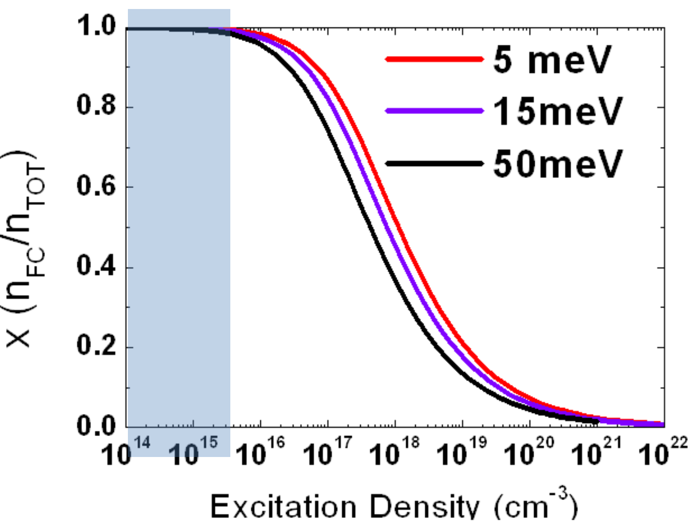
$$x = \frac{n_{FC}}{n}$$

Saha-Langmuir equation

Are there excitons around? $MAPbI_3$

- **Room Temperature**, in the typical PV regime η_{ph} **<10^{16} cm^{-3} :**

free carriers only



→**THz conductivity spectra are Drude-like in accordance with the presence of free charge carriers.** Wehrefenning et al, Adv Mater, 26, 1584, 2014, Milot et al, Adv Funct Mater, 2015 DOI: 10.1002/adfm.201502340,

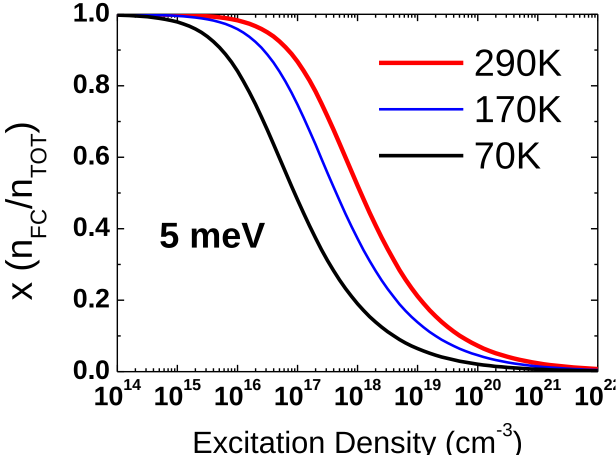
→**PL dynamics are dictated by bimolecular recombination processes.** Yamada, Y J. Am. Chem. Soc. 2014, 136, 11610. Stranks, Phys. Rev. Appl. 2014, 2 034007.

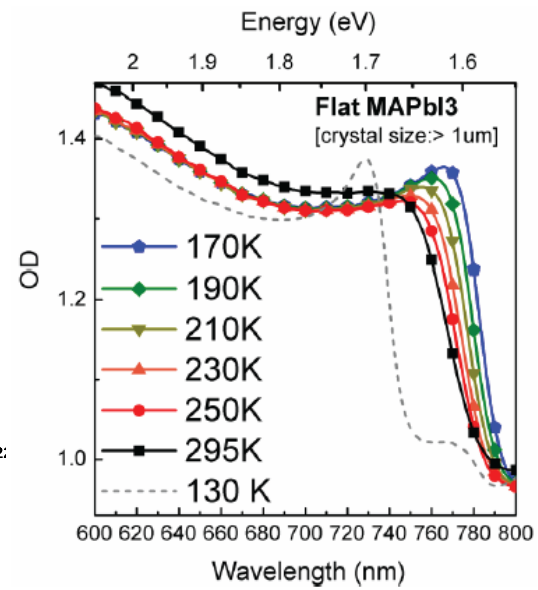
→ **fs-TA spectra show band filling effect and Varnshi –shift.** Kamat et al, Nature Photonics, 2014; Grancini&Kandada et al, Nature Photonics 2015

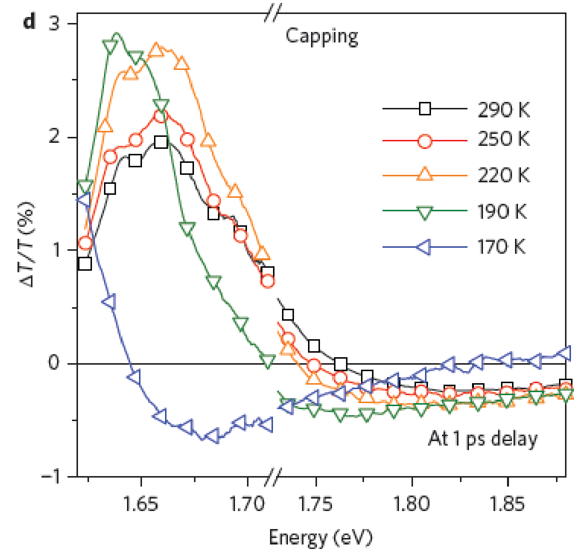
The deal for PV is:
we exploit the presence of the exciton transition for light harvesting without paying in charge dissociation

Are there excitons around? $MAPbI_3$

- **Low Temperature**, Exciton population is detectable.







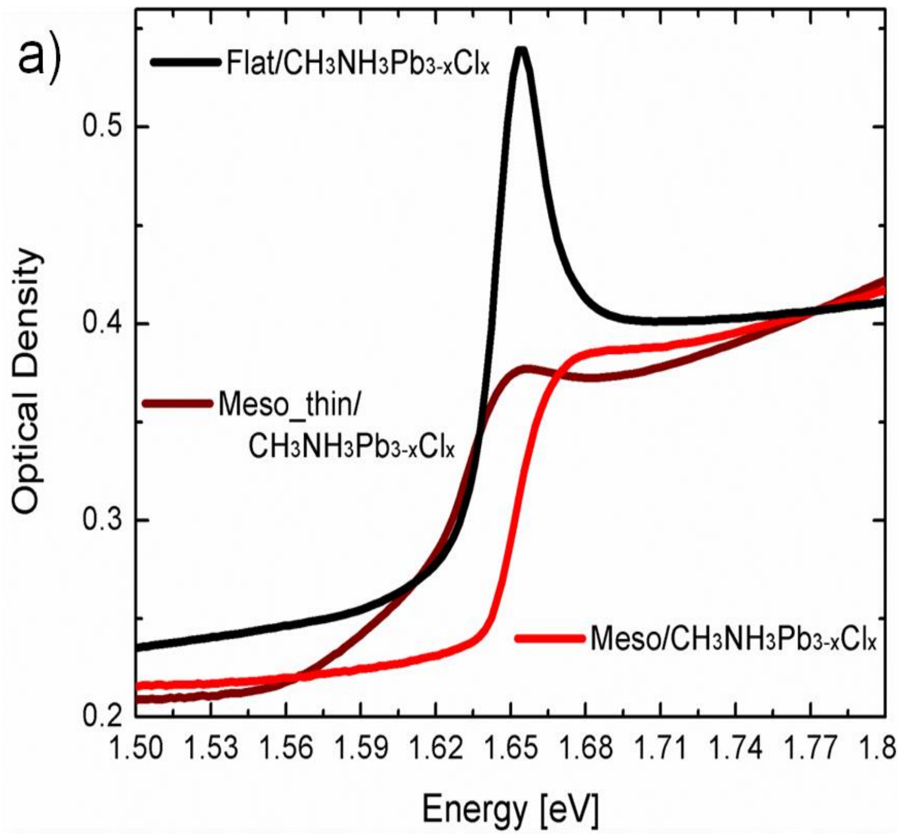
→**THz spectra probe localization effects as a consequence of exciton formation below 80K.** Milot et al, Adv Funct Mater, 2015 DOI: 10.1002/adfm.201502340,

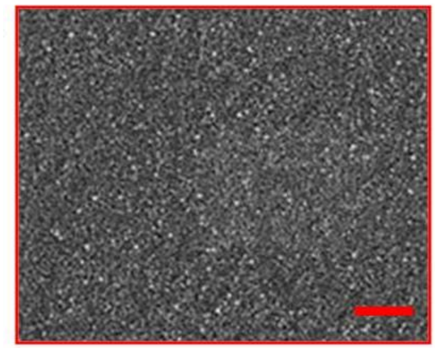
→ **fs-TA spectra show a modulation of the photo-bleach as a result of exciton-exciton interaction.** Grancini&Kandada et al, Nature Photonics 2015

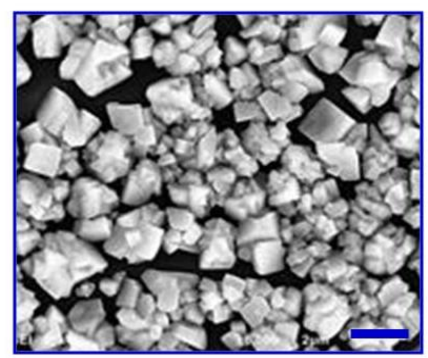
<u>WARNING: </u> The Exciton binding energy increases (the dielectric constant decreases) when cooling down! →Miyata et al, Nature Physics 11, 582–587 (2015)

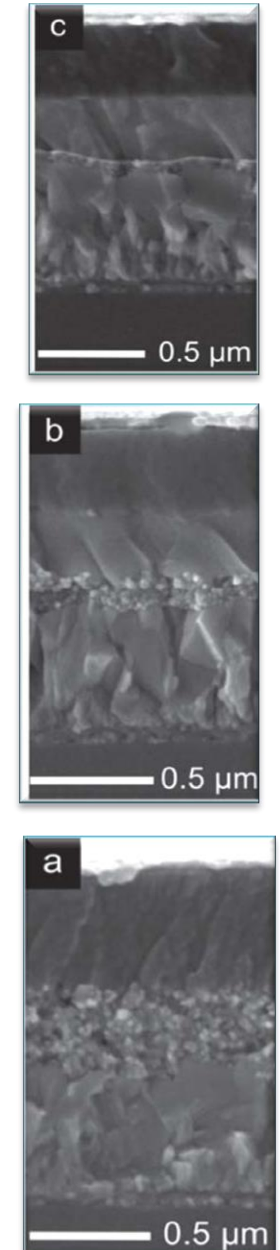
Local order/ microstructure

$MAPbI_3$









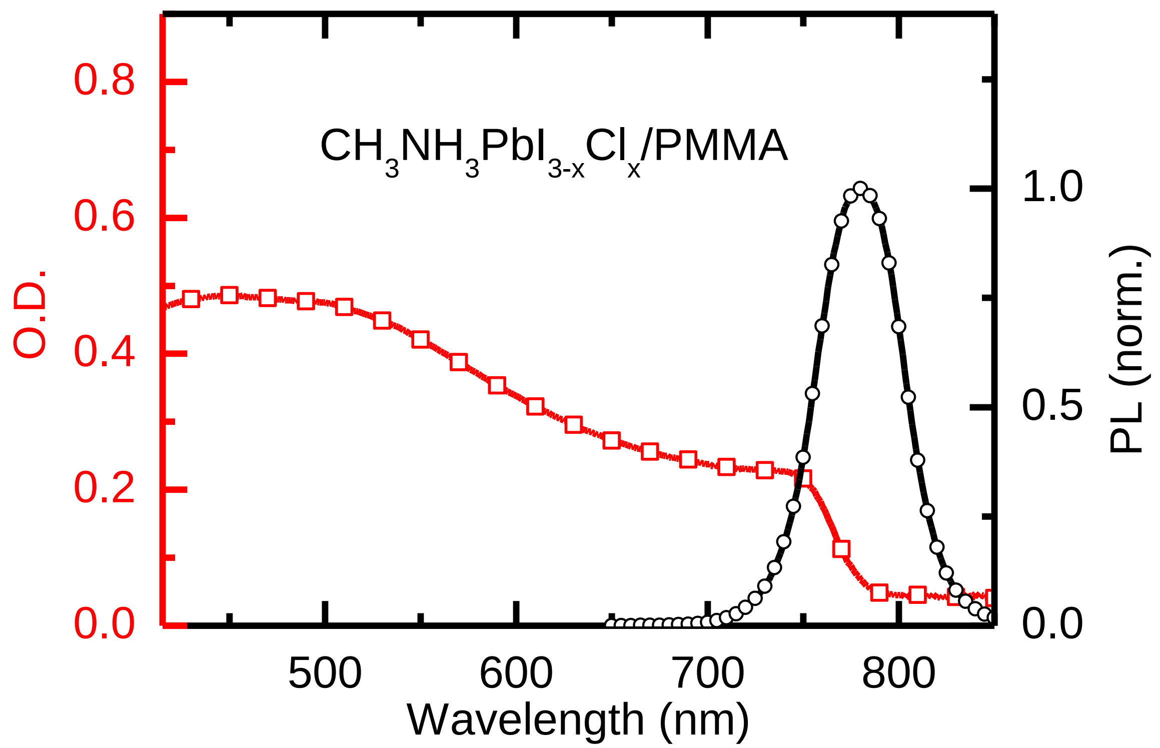
D'Innocenzo et al, Nat Comm. 5, 3586, 2014

Grancini&Kandada et al, Nature Photonics 2015

Designing the Device Architecture

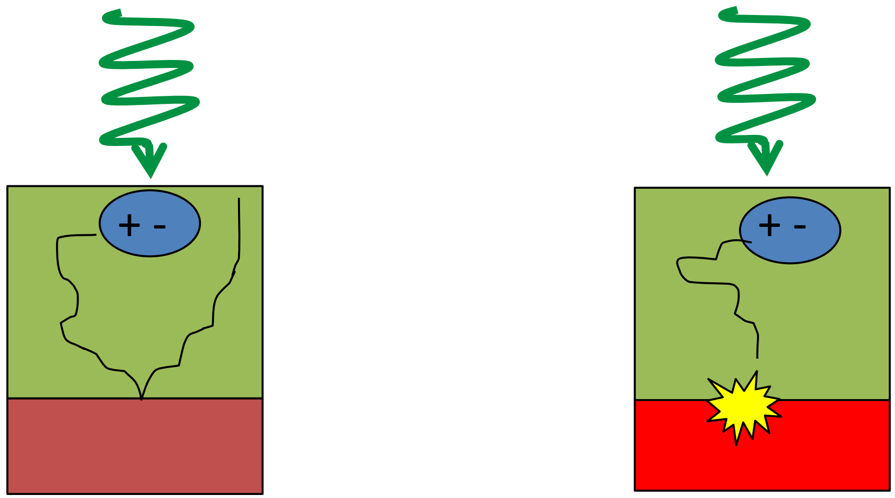
- Light Absorption
- Charge Generation
- **Photo-carriers Transport**

Photo-carriers Diffusion Length



Electron-Hole Diffusion Lengths

By Photoluminescence Quenching



Silica   Selective Quencher

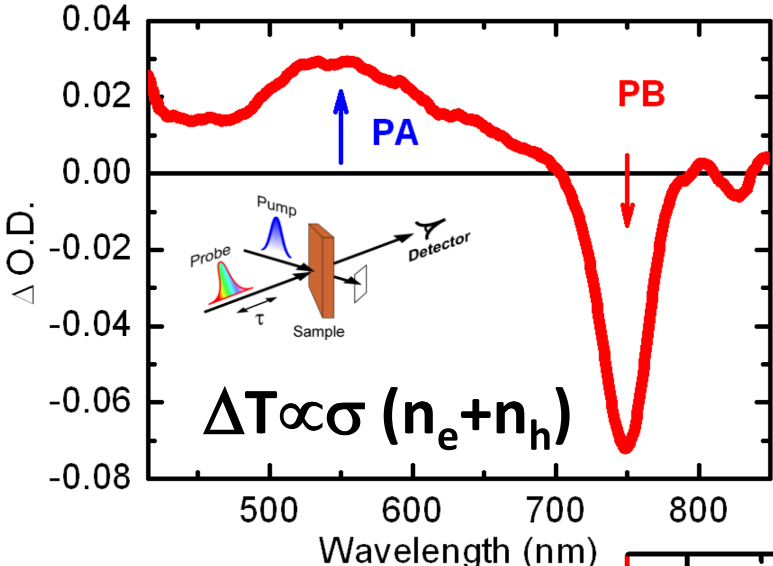
$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial z^2} - k(t)n(z,t)$$

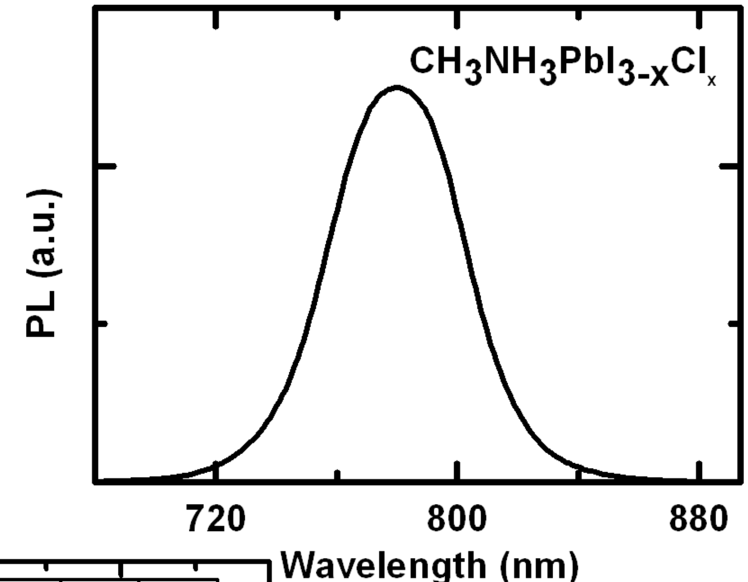
Diffusion constant

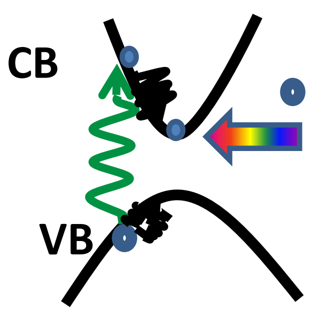
Natural decay rate (no quencher)

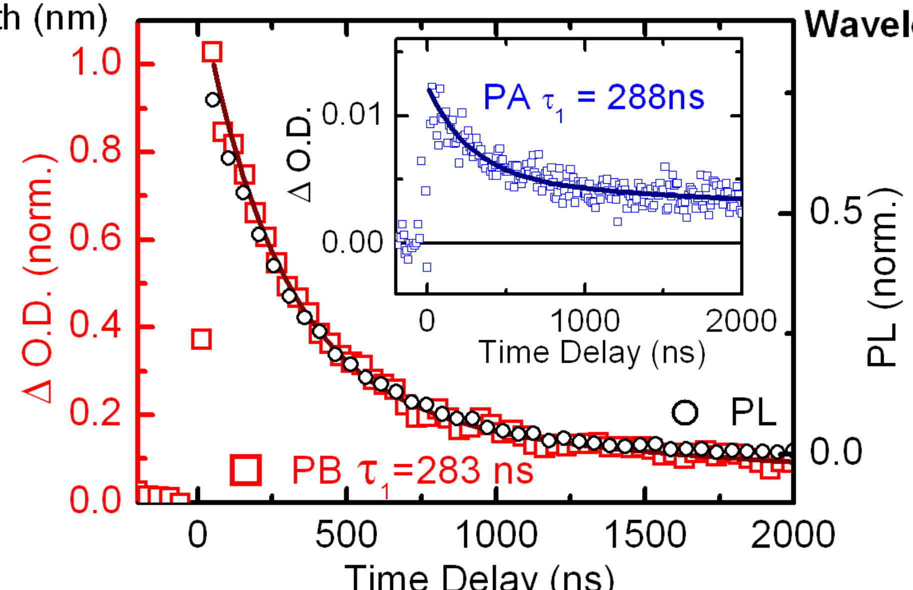
Electron-Hole Diffusion Lengths

By Photoluminescence Quenching





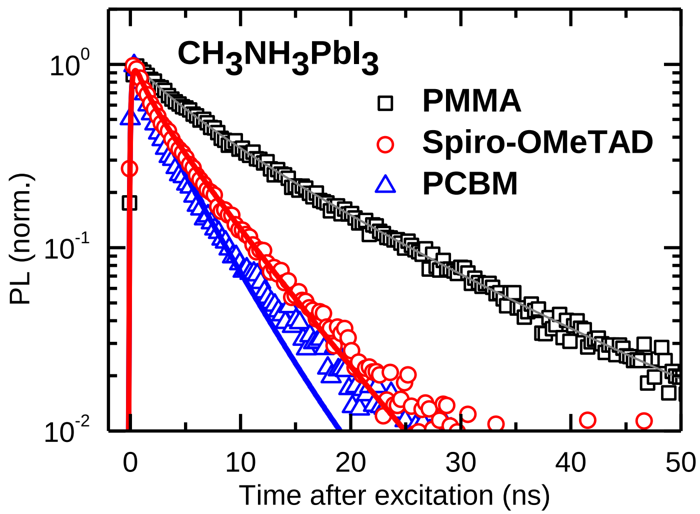


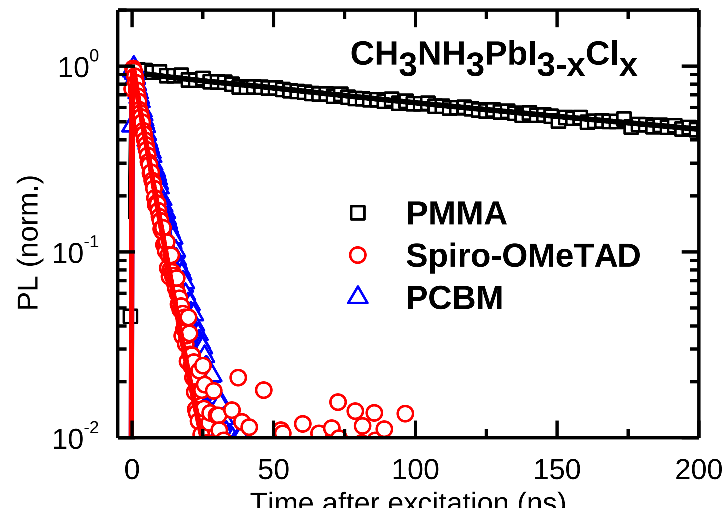


Science , 342,341, 2013

Electron-Hole Diffusion Lengths

By Photoluminescence Quenching



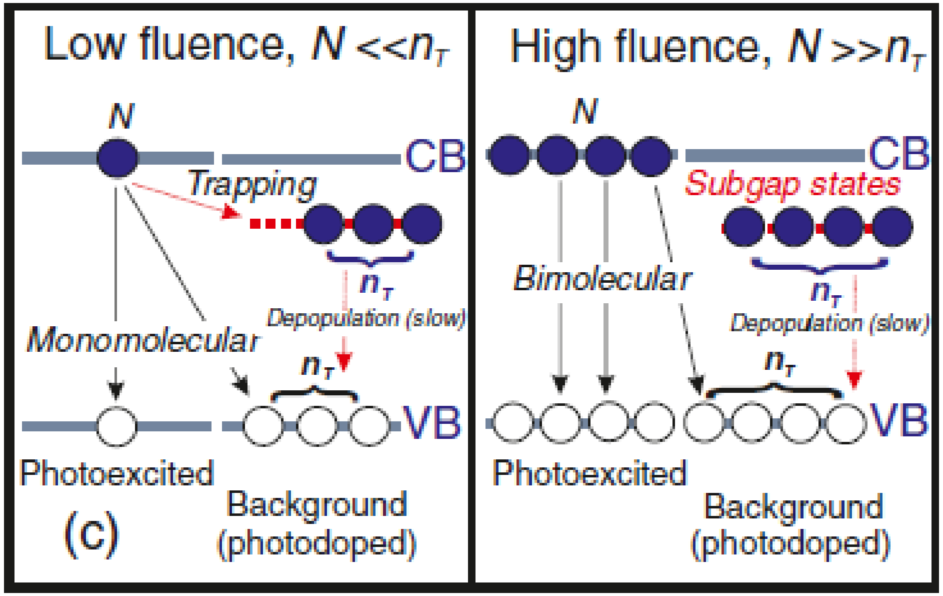


Perovskite	Species	D (cm^2s^{-1})	L_D (nm)
$CH_3NH_3PbI_{3-x}Cl_x$	Electrons	0.042 ± 0.016	1094 ± 210
	Holes	0.054 ± 0.022	1242 ± 250
$CH_3NH_3PbI_3$	Electrons	0.017 ± 0.009	117 ± 29
	Holes	0.012 ± 0.005	96 ± 22

Science , 342,341, 2013

Time-resolved Photoluminescence

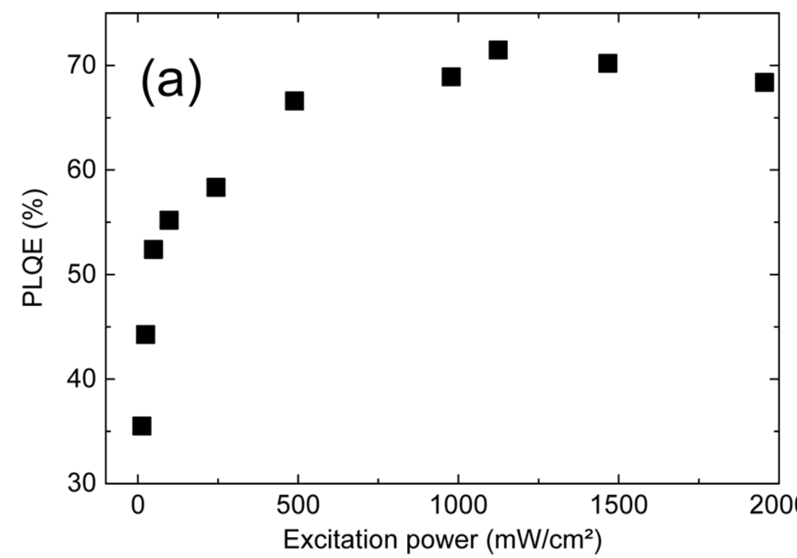
Stranks et al



$$\frac{dn}{dt} = -An - B_{rad}n^2$$

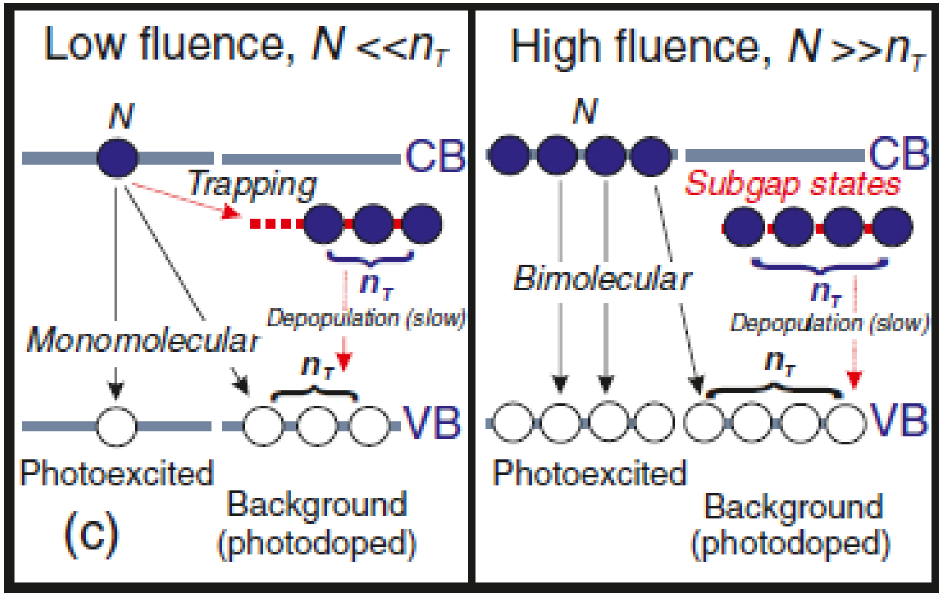
$$\left(\frac{1}{\tau_{PL}}\right) = k_{PL} = k_r + k_{nr}$$

→ Yamada, Y J. Am. Chem. Soc. 2014, 136, 11610.
→ Stranks, Phys. Rev. Appl. 2014, 2 034007.
→ Saba, M.; Nat. Commun. 2014, 5 No. 5049.
→D’Innocenzo, J. Am. Chem. Soc. 2014, 136 (51), pp 17730–1773
→ Deschler, J. Phys. Chem. Lett. 2014, 5, 1421.



Deschler, et al

Time-resolved Photoluminescence



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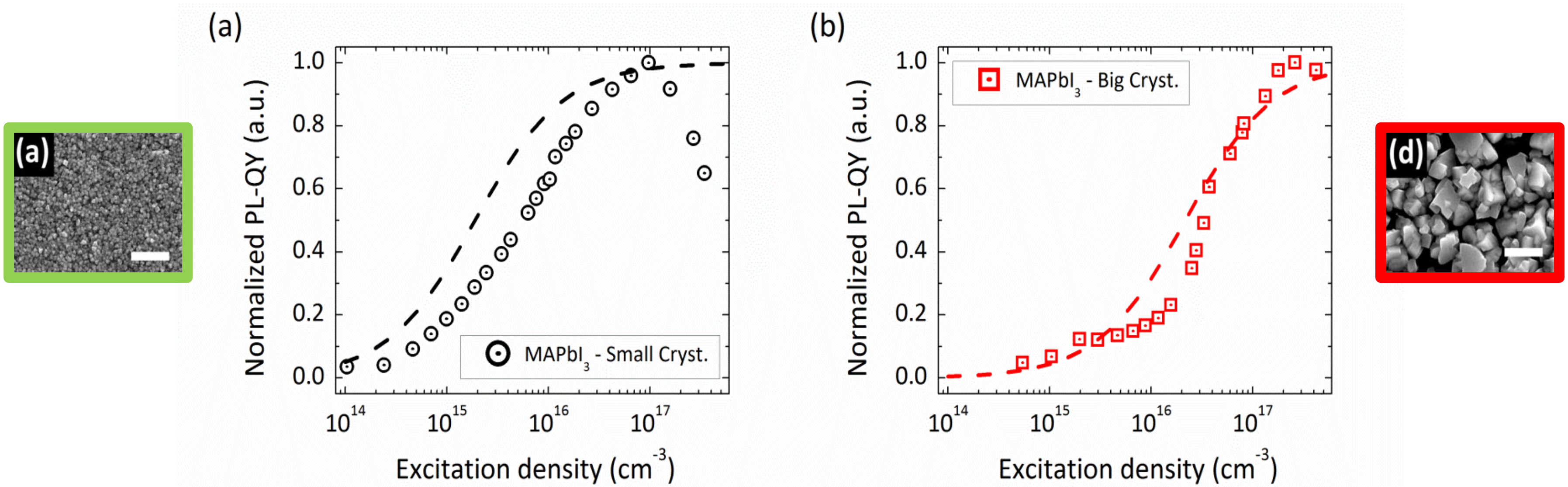
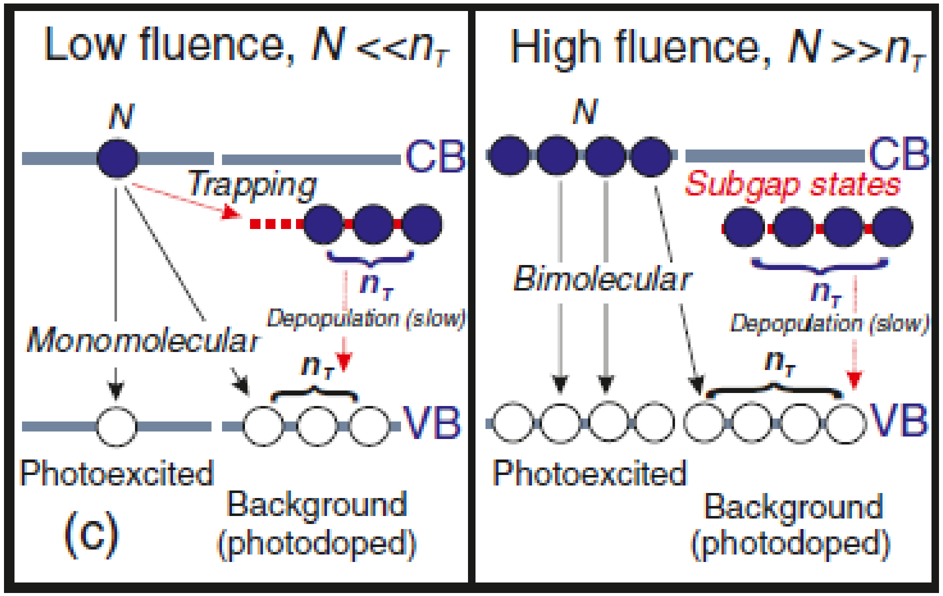


D'Innocenzo et al. *JACS*, 2014, 136 (51), pp 17730–1773

Time-resolved Photoluminescence



$$\frac{dn}{dt} = -An - B_{rad}n^2$$

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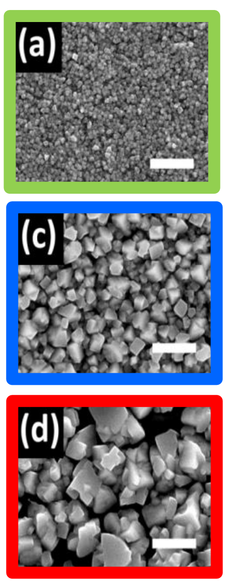
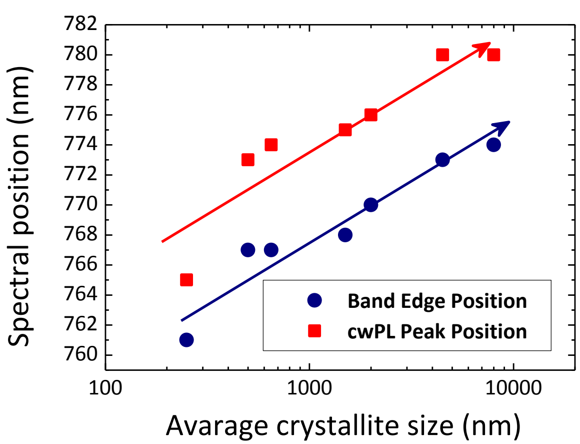




$$R_{rad}(E_G) = \int_{E_G}^{\infty} \rho_{ph}(\varepsilon)\alpha(\varepsilon)v_{ph}(\varepsilon)d\varepsilon$$

$$n_i(E_G) = \int_{E_{CBB}}^{\infty} \rho(\varepsilon)\frac{1}{1+e^{(\varepsilon-\mu)/k_BT}}d\varepsilon$$

Filippetti, et al. *J.Phys.Chem*, 2014, doi:10.1021/jp507430x

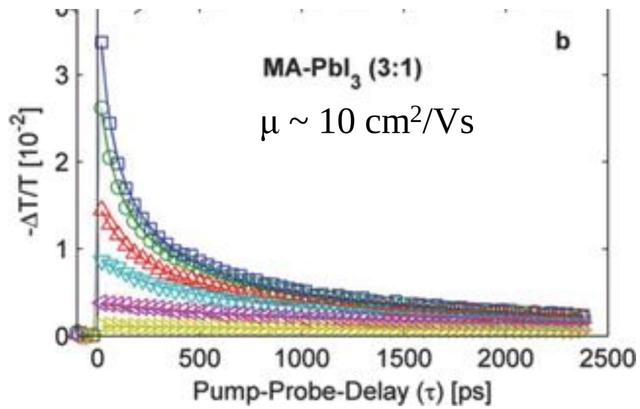
D'Innocenzo et al. *JACS*, 2014, 136 (51), pp 17730–1773

Measuring Charge-Transport in Perovskites

Terahertz/Microwave Spectroscopy

Simple sample preparation

Only informative on short length-scale

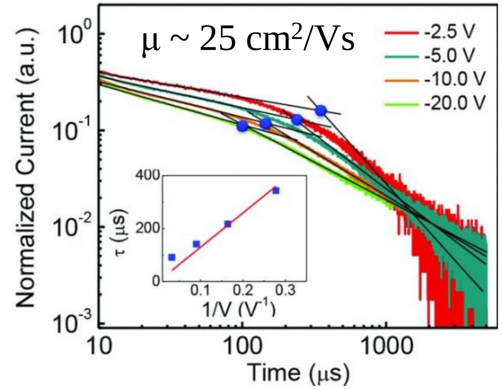


C. Wehrenfennig et al., Adv. Mat. (2013)

Time-of-flight

Relevant over longer length-scale

Time-scales difficult to measure in thin-film

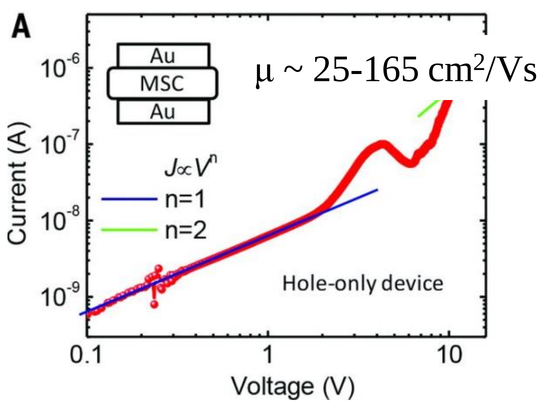


Q. Dong et al., Science (2015)

Space-charge limited current

Relevant to optoelectronic devices

Needs highly-selective non-limiting contacts

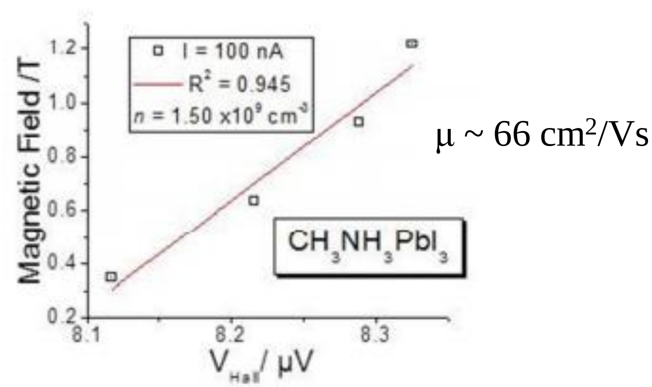


Q. Dong et al., Science (2015)

Hall-effect

Simultaneously get free-carrier density

Like THz, only band mobility obtained



C. Stoumpos et al., Inorg. Chem. (2013)

Take-home Message

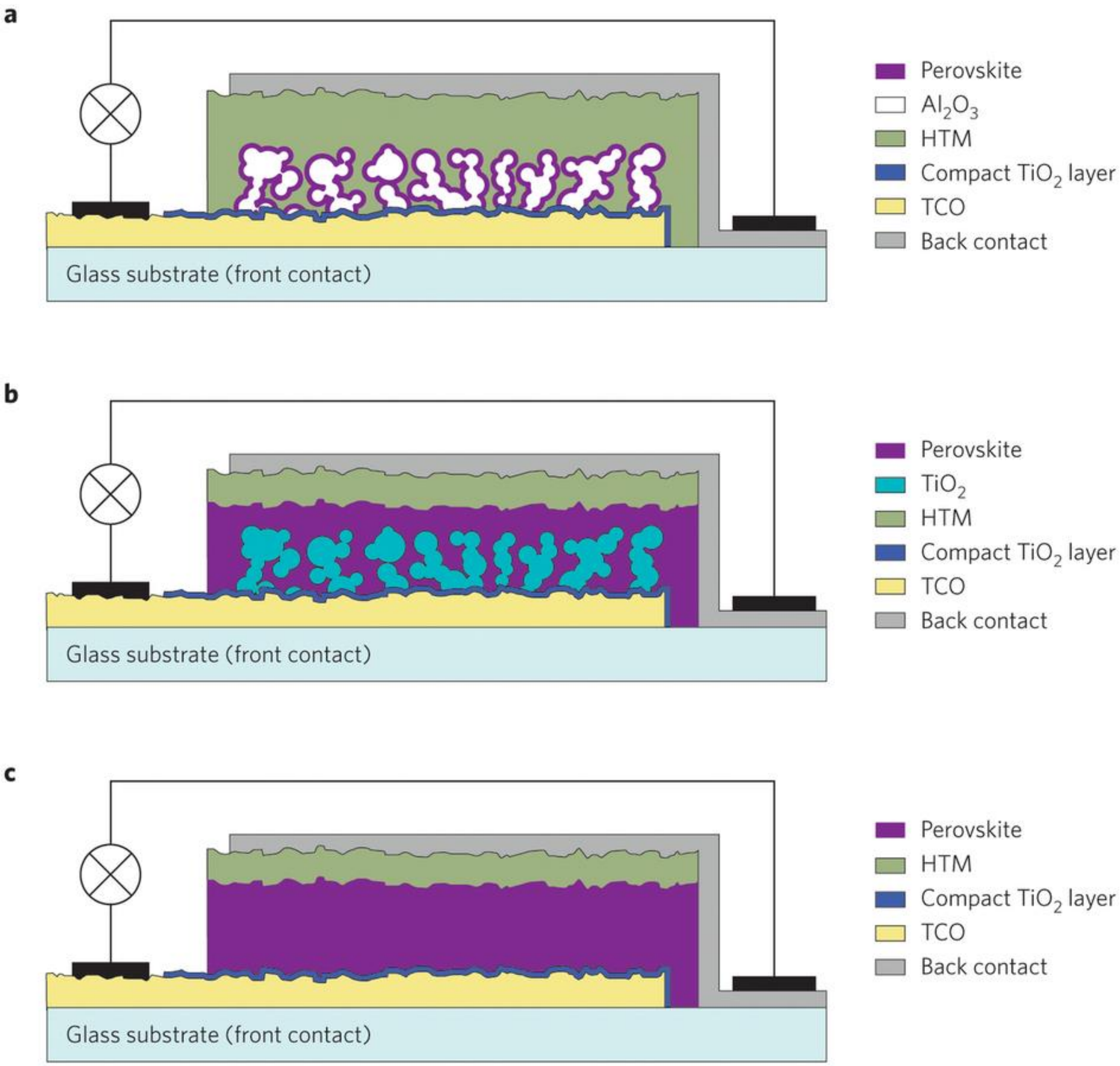
The room temperature structure of MAPbX3 is a fluctuating structure where titling and distortion of the octahedral networks and rotations and polarizability of the molecular dipole can strongly affect the optoelectronic properties of the semiconductor.

Open Questions

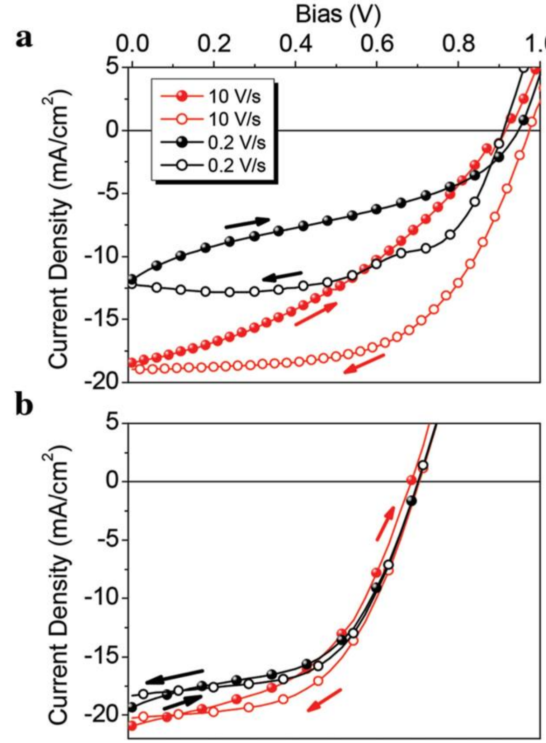
- Which is the secret of the low recombination rate
- Elucidation of the photo-carriers cooling
- Role of phonons
- Nature of carriers, localization vs delocalization
- Carriers transport mechanism

Vs Structural Properties

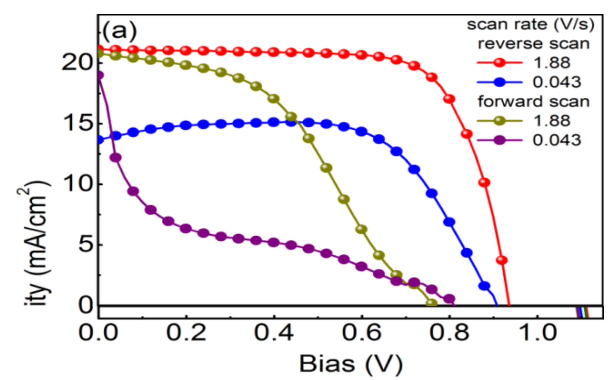
Technology



a
Perovskite
Al_2O_3
HTM
Compact TiO_2 layer
TCO
Back contact
Glass substrate (front contact)
b
Perovskite
TiO_2
HTM
Compact TiO_2 layer
TCO
Back contact
Glass substrate (front contact)
c
Perovskite
HTM
Compact TiO_2 layer
TCO
Back contact
Glass substrate (front contact)

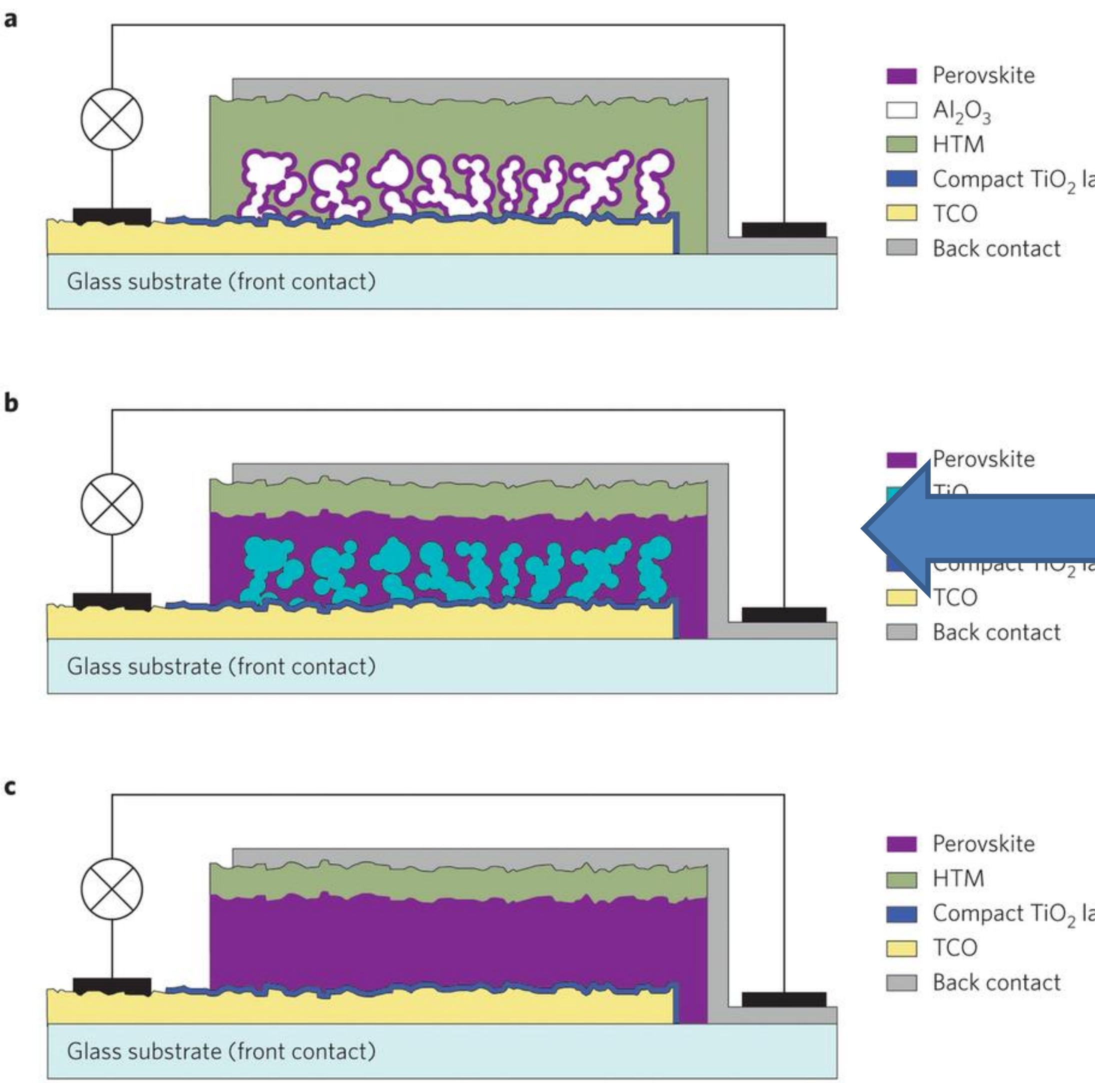


a
Bias (V)
0.0
0.2
0.4
0.6
0.8
1.0
Current Density (mA/cm^2)
5
0
-5
-10
-15
-20
10 V/s
10 V/s
0.2 V/s
0.2 V/s
b
Current Density (mA/cm^2)
5
0
-5
-10
-15
-20

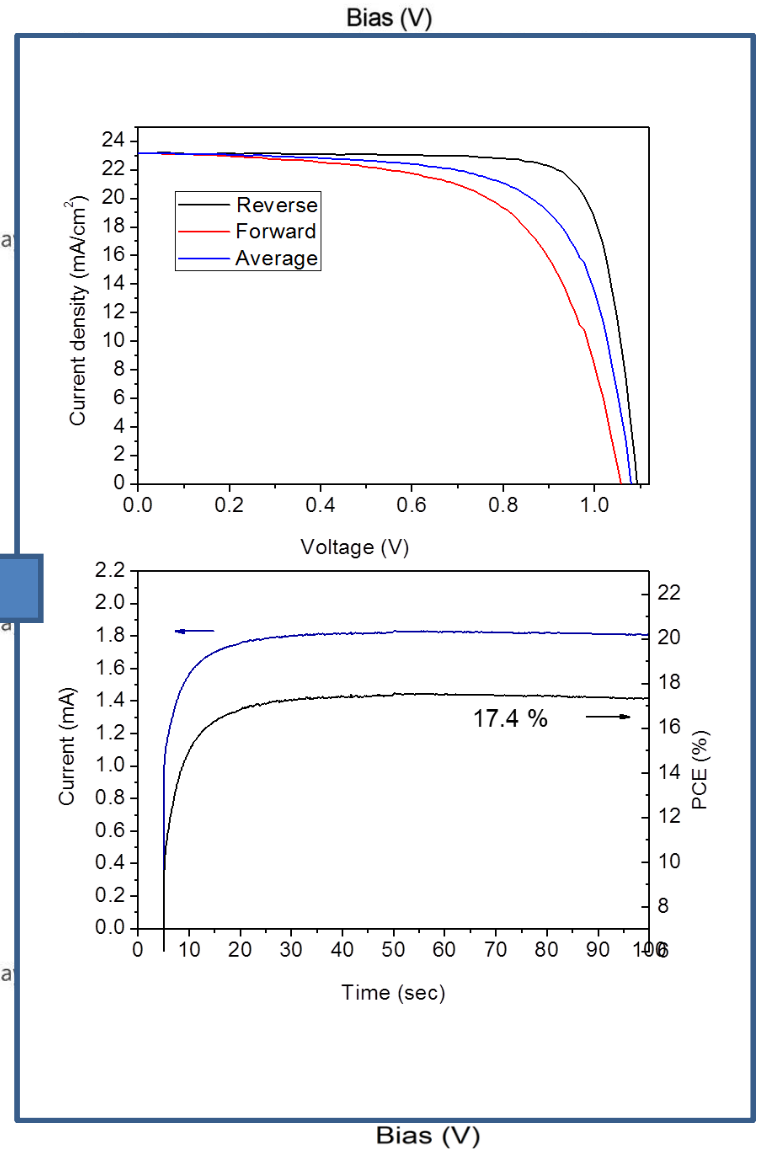


(a)
scan rate (V/s)
reverse scan
1.88
0.043
forward scan
1.88
0.043
ity (mA/cm^2)
20
15
10
5
0
0.0
0.2
0.4
0.6
0.8
1.0
Bias (V)

Technology

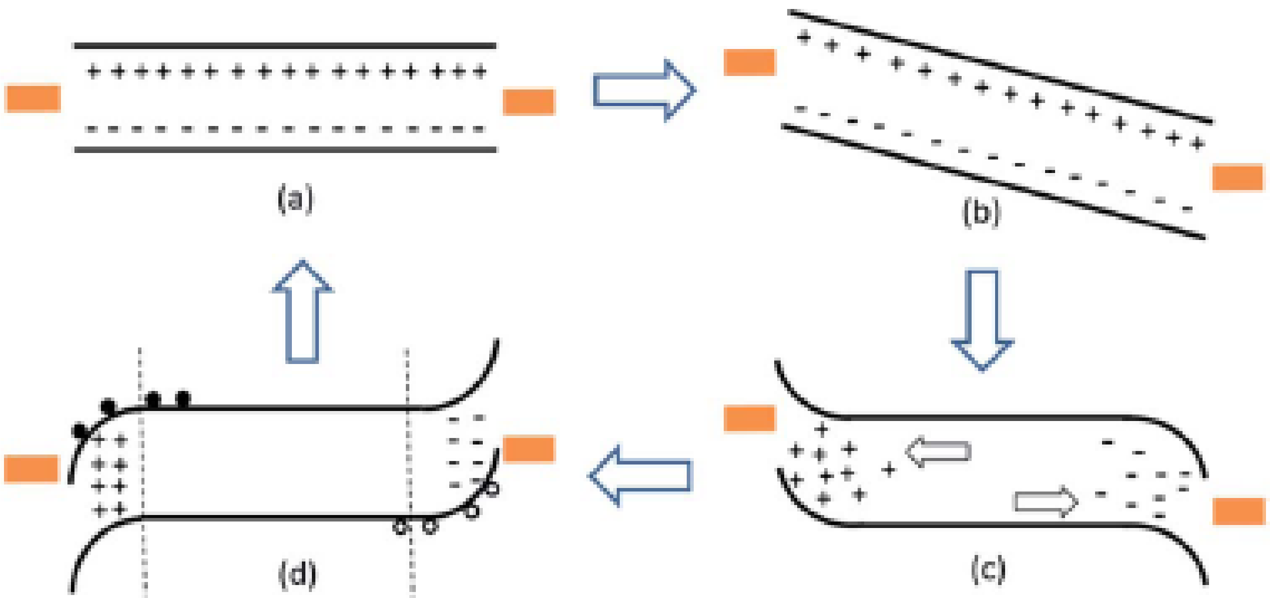


a
Perovskite
Al_2O_3
HTM
Compact TiO_2 la
TCO
Back contact
Glass substrate (front contact)
b
Perovskite
TCO
Back contact
Glass substrate (front contact)
c
Perovskite
HTM
Compact TiO_2 la
TCO
Back contact
Glass substrate (front contact)



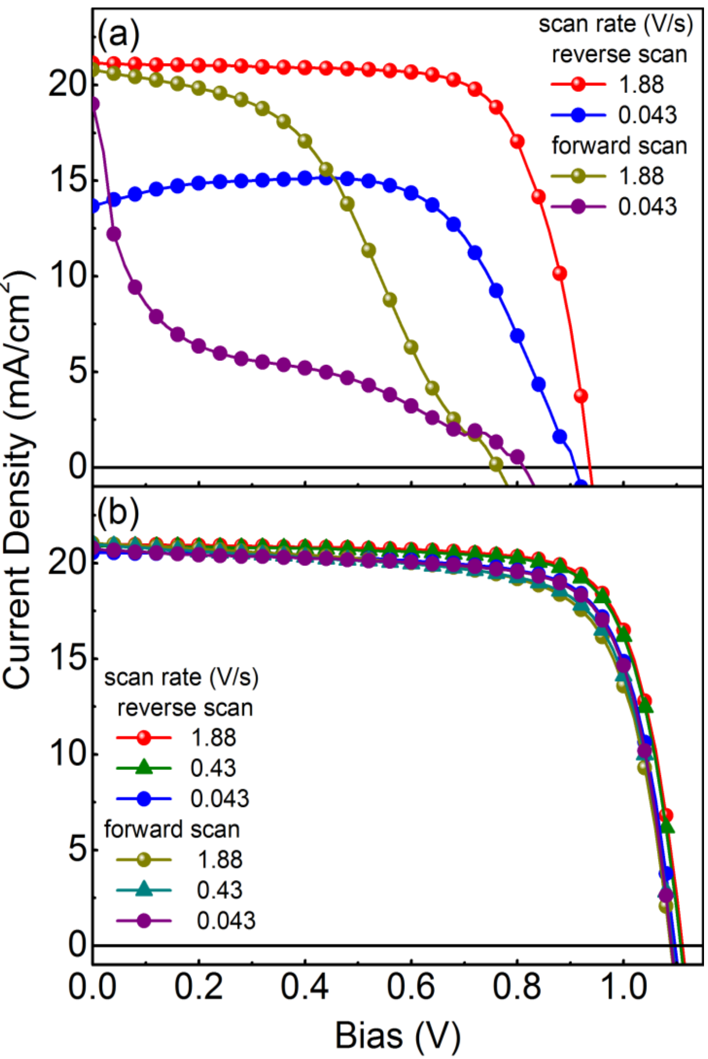
Bias (V)
Reverse
Forward
Average
Current density (mA/cm^2)
Voltage (V)
Current (mA)
PCE (%)
17.4 %
Time (sec)
Bias (V)

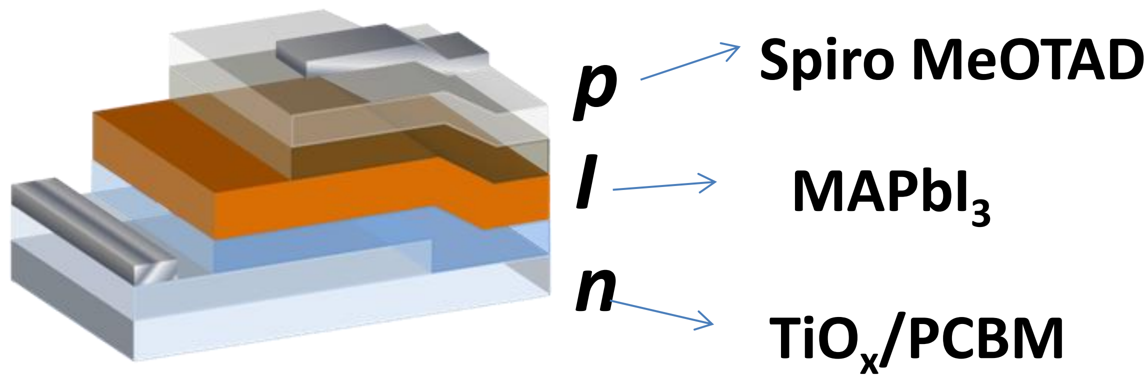
Technology

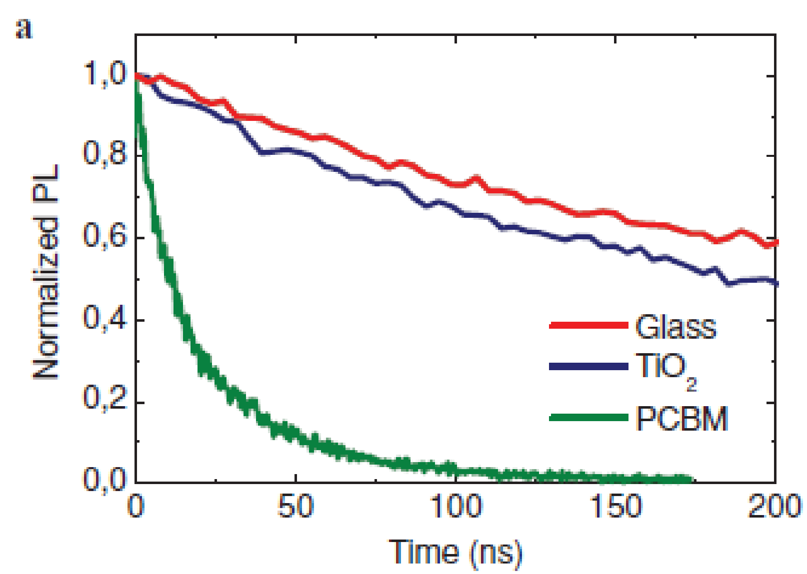


Zhang et al, Mater. Horiz., 2015, 2, 315–322

Perovskite PV at IIT

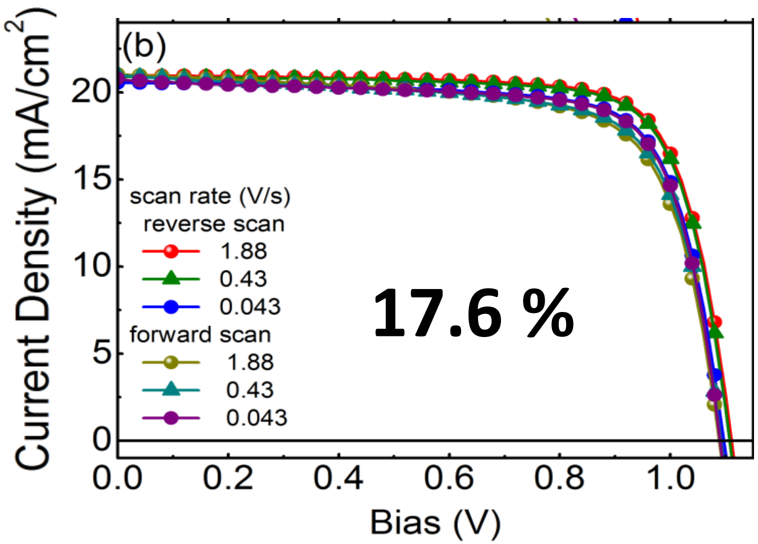


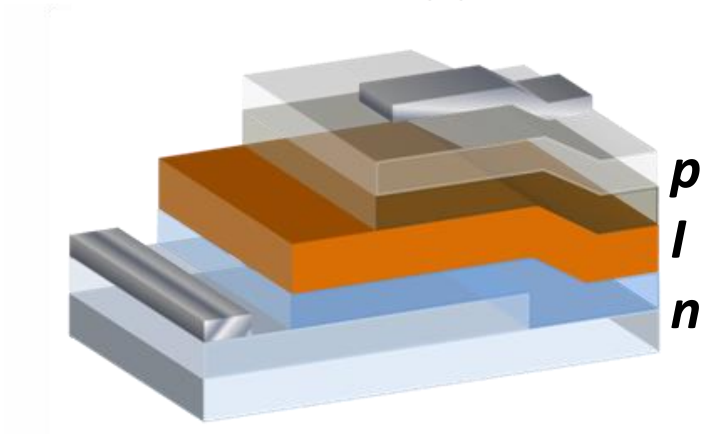




Perovskite PV at IIT

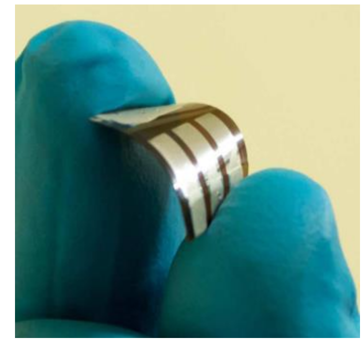
Technology Development





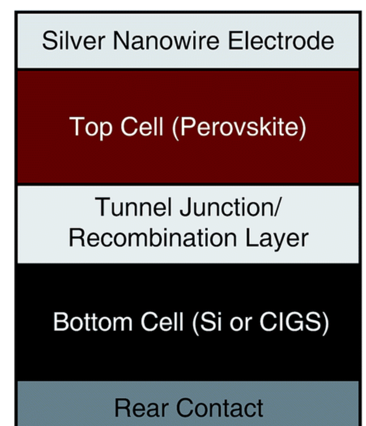
Processi a bassa temperatura
< 120 °C

Fotovoltaico leggero e flessibile, a basso costo di produzione e energetico



Aumento efficienza fotovoltaico tradizionale

Celle «TANDEM»



Further Developments

- Interface Engineering
- Stability
- Toxicity
- ..