Computational Modeling of Perovskite Solar Cells

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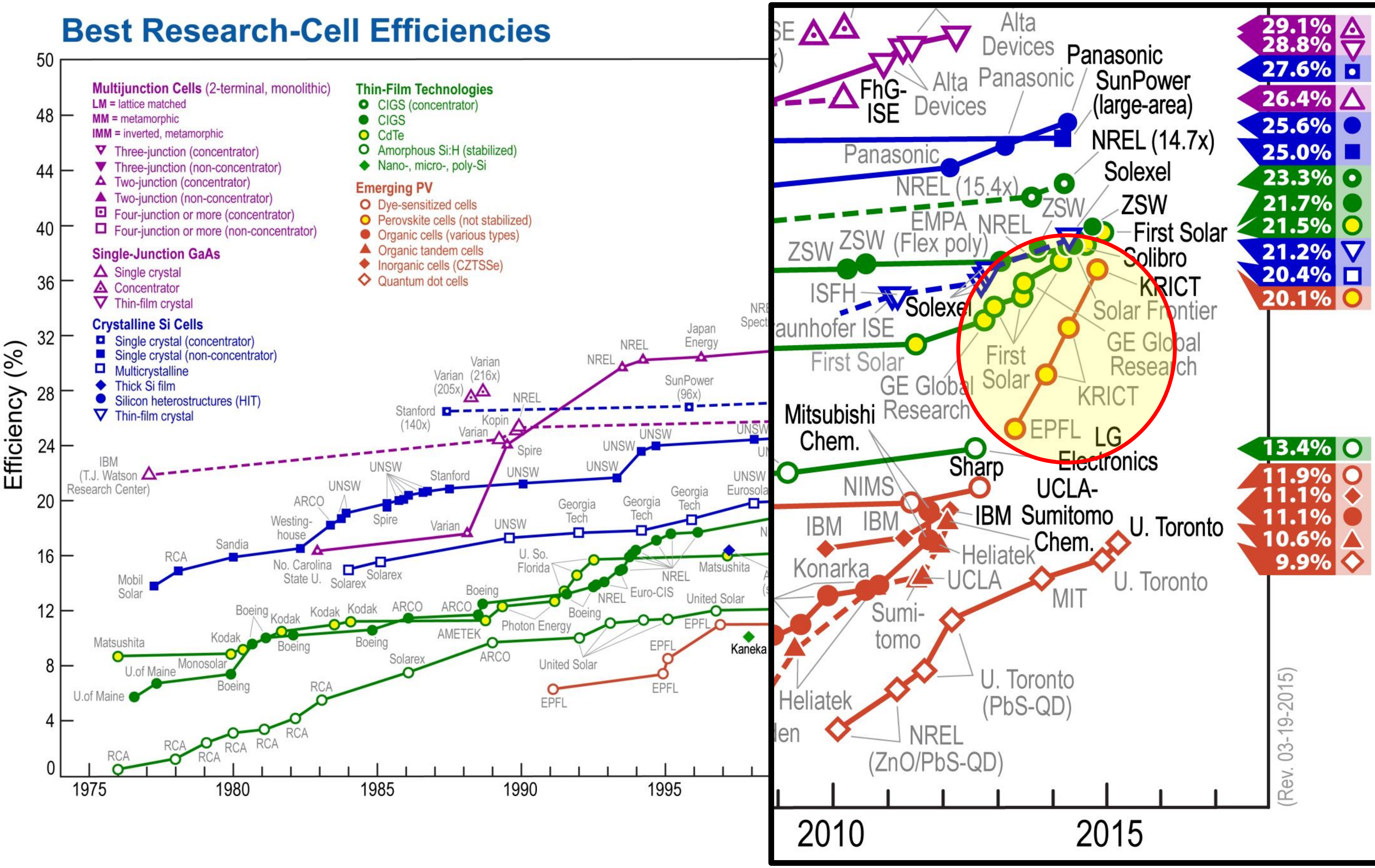
CNR- ISTM Perugia, Italy

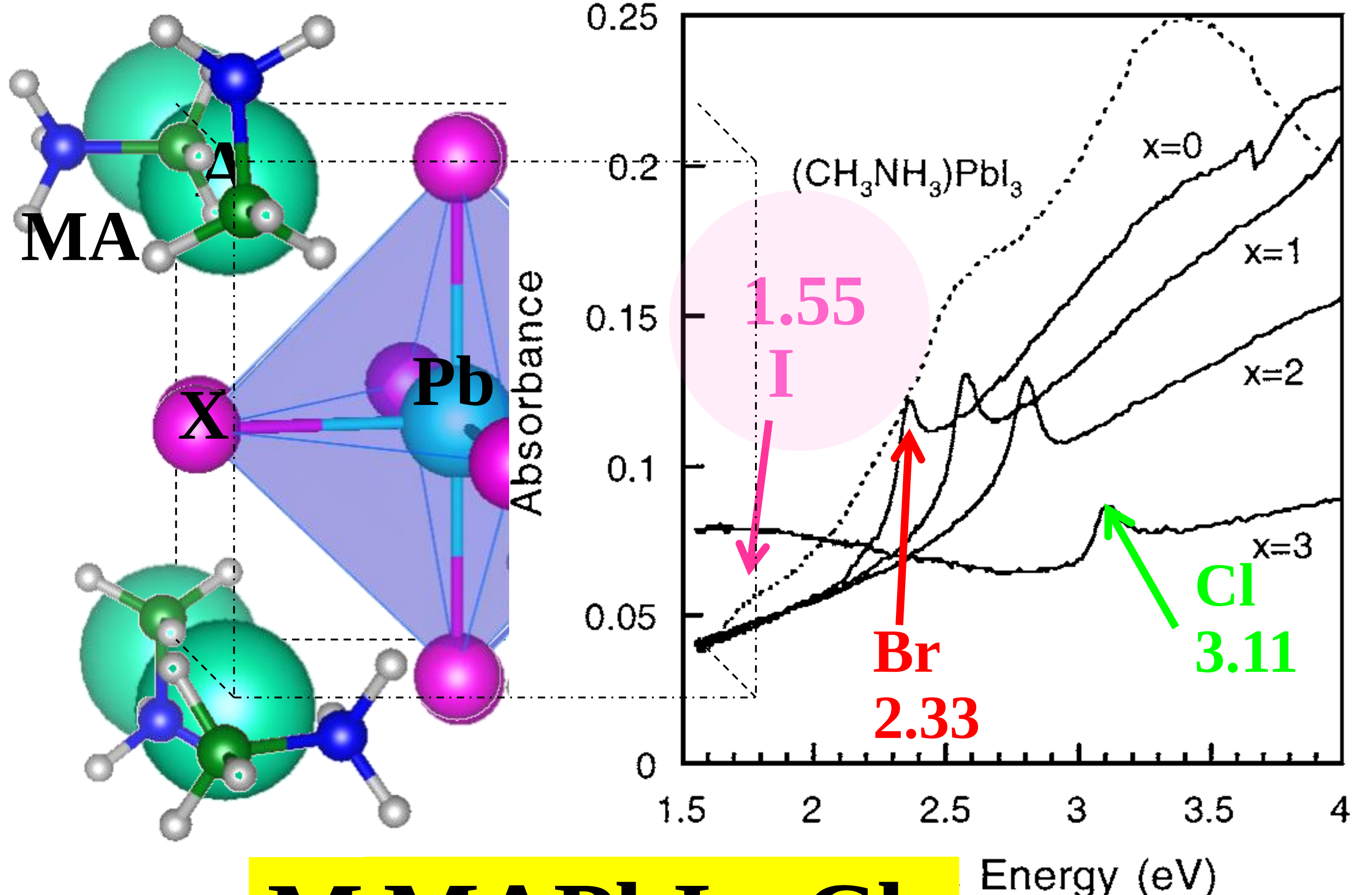
Outline

- **Introduction**
- **Computational Approach**
- **Interfaces in PSC**
- **Mobile Ions in PSC**

Perovskite Solar Cells Efficiency



Perovskite solar cells:
Organohalide lead perovskites



M $MAPbI_{3-x}Cl_x$

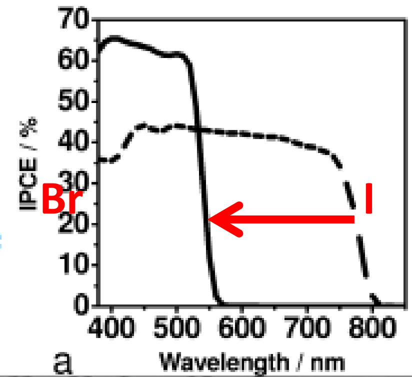
J. Am. Chem. Soc. **2009,** *131*, 6050

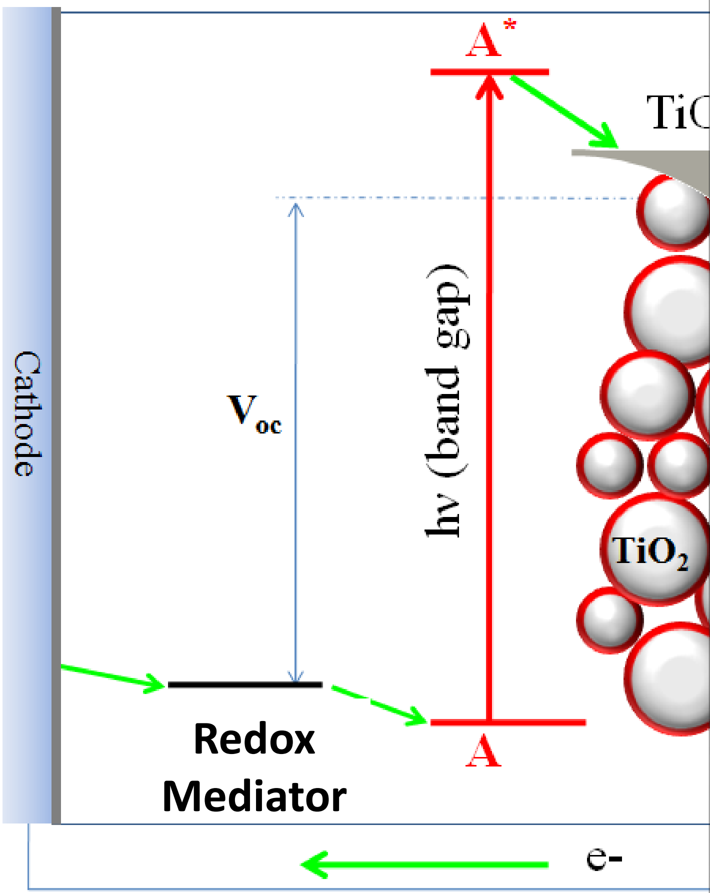
J|A|C|S
COMMUNICATIONS

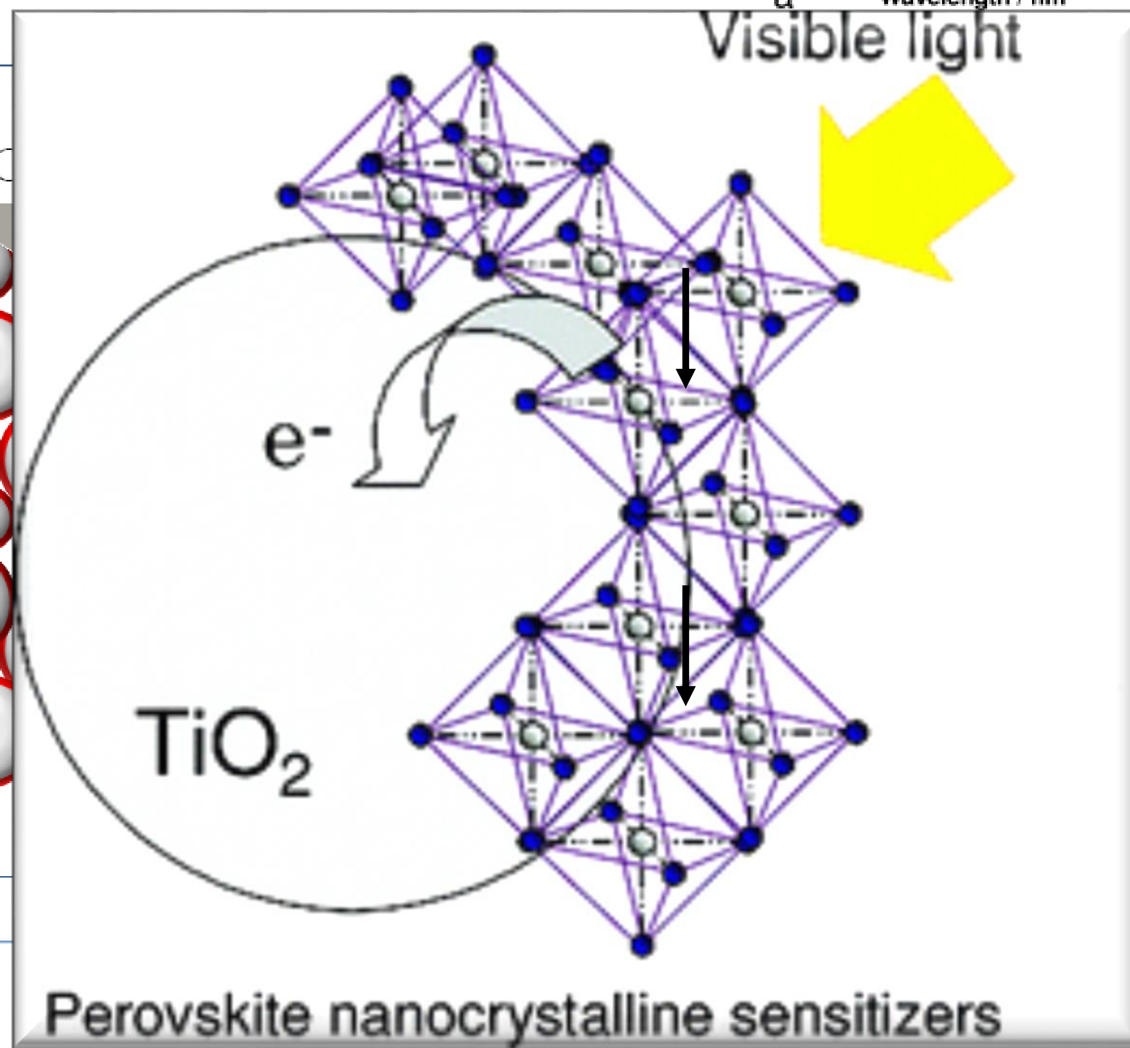
Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*[,†,‡,∥]

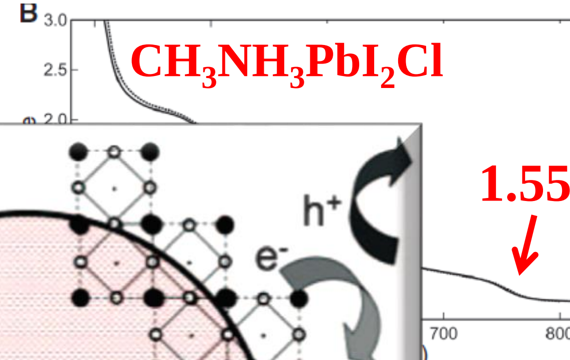


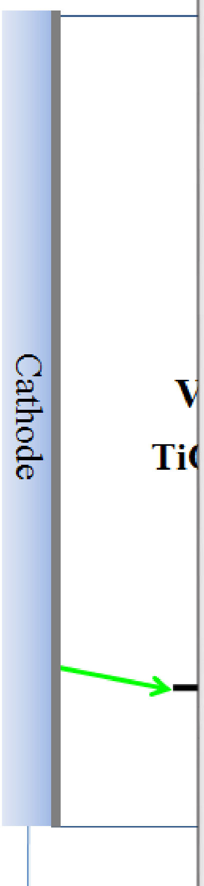


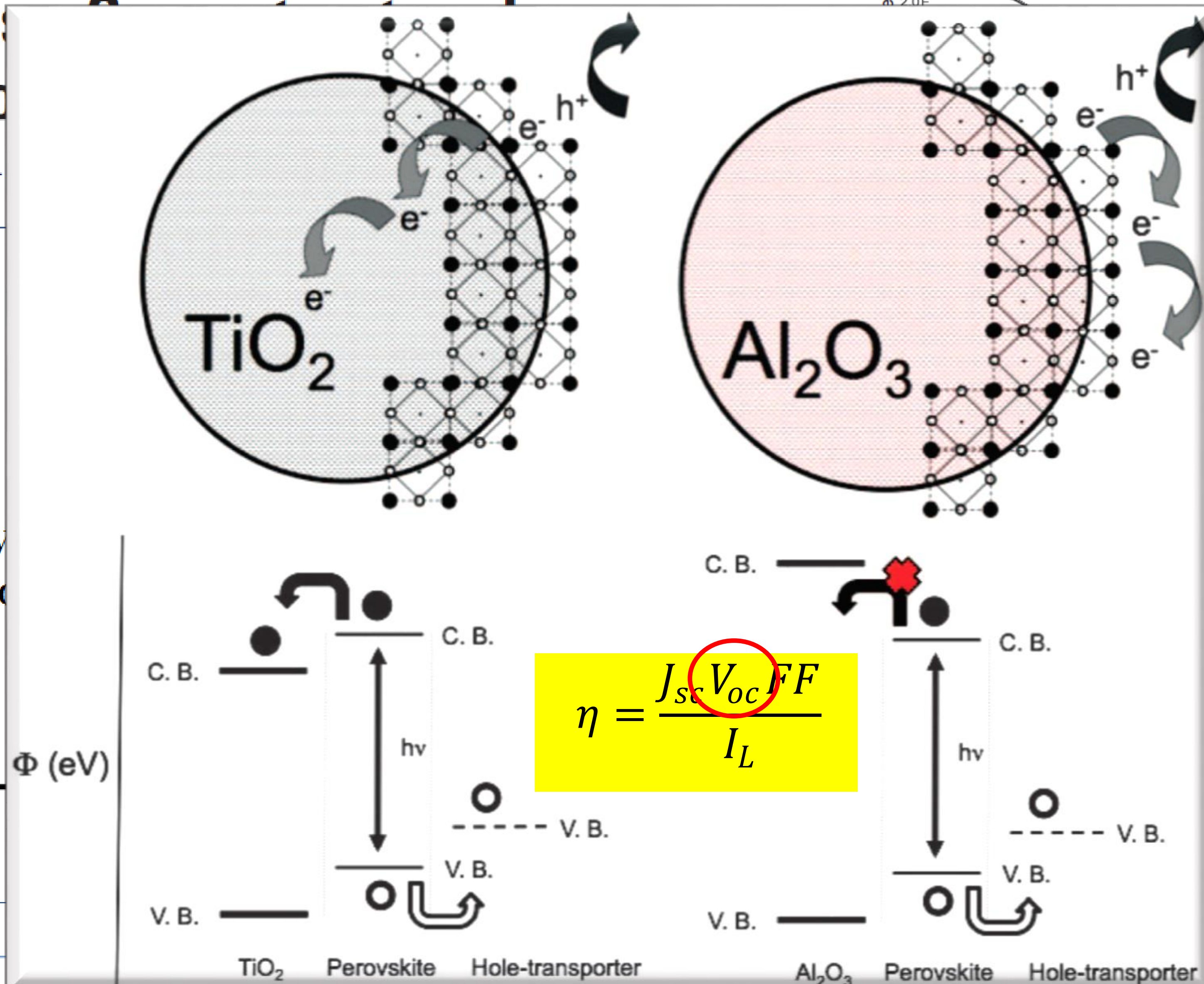


Efficient Hybrid Solar Cells Based on Me… Organ…

Michael M. Lee,[1]





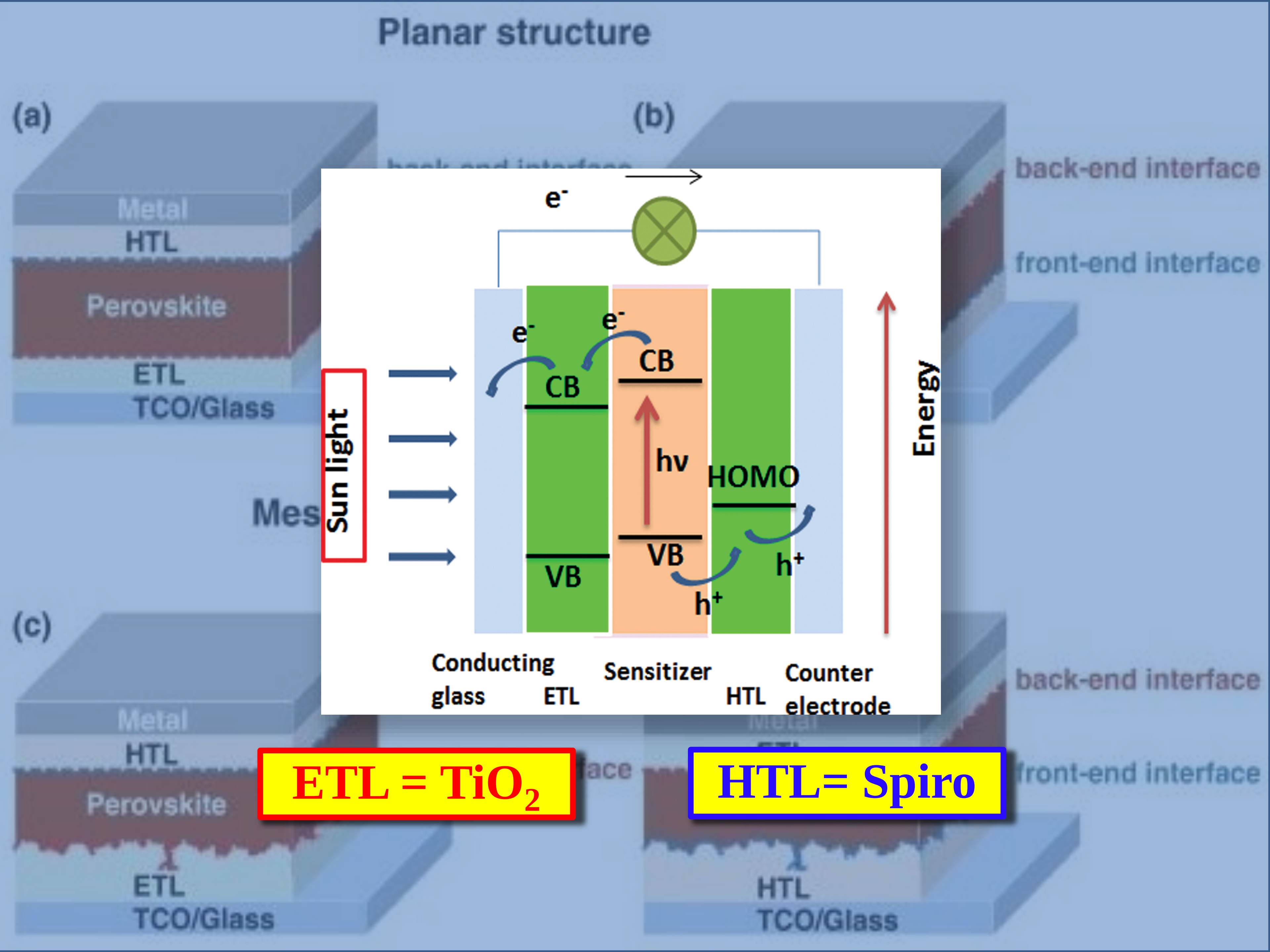


$$\eta = \frac{J_{sc} V_{oc} FF}{I_L}$$

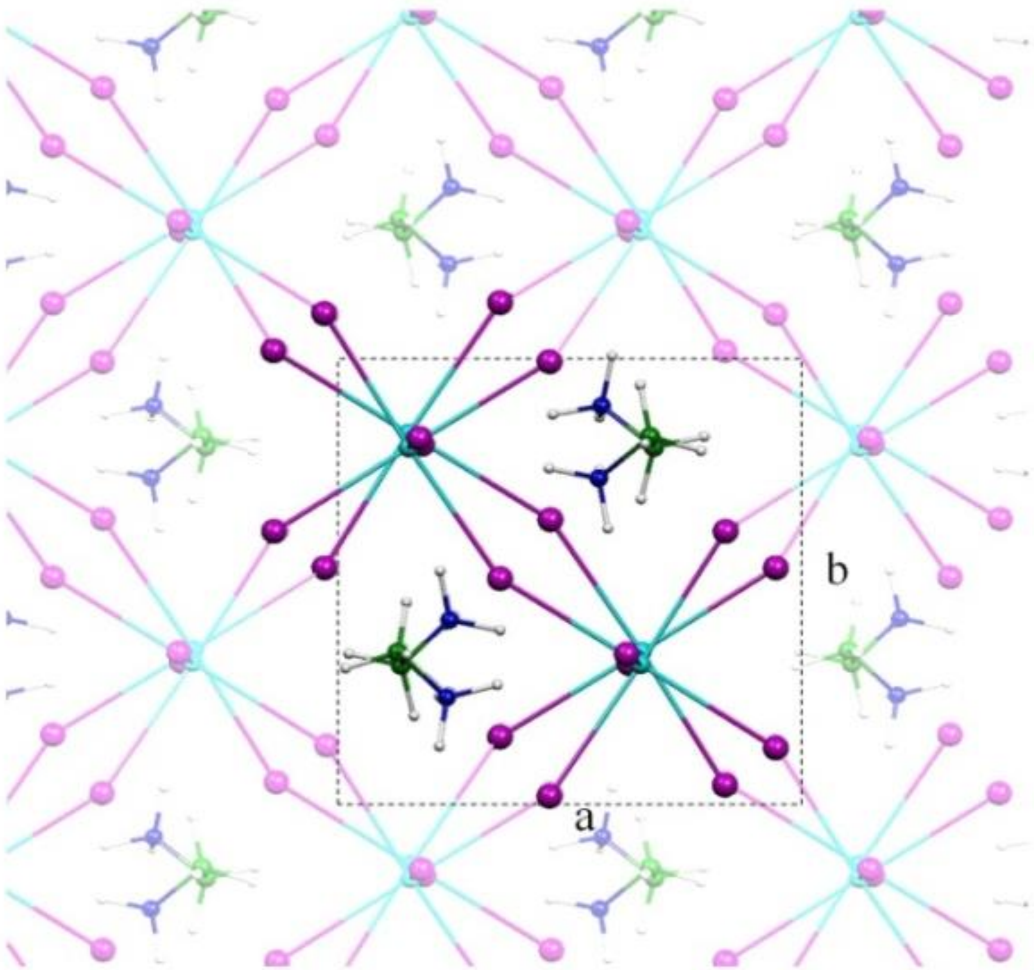
TiO$_2$ and

vskite

H.S. Kim et al *Sci. Rep.* **2012,** *2;* M. Lee et al. *Science* **2012**, 338, 643;
L. Etgar et al. *J. Am. Chem. Soc.* **2012,** *134*, 17396; H. Zhou et al. *Science*, **2014**, 354, 543.


Planar structure
(a)
Metal
HTL
Perovskite
ETL
TCO/Glass
(b)
back-end interface
front-end interface
(c)
back-end interface
front-end interface
Metal
HTL
Perovskite
ETL
TCO/Glass
HTL
TCO/Glass
e-
Sun light
e-
e-
CB
CB
hv
HOMO
VB
VB
h+
h+
Energy
Conducting glass
ETL
Sensitizer
HTL
Counter electrode
ETL = TiO2
HTL= Spiro

Tetragonal $MAPbI_3$: I4cm



Model:

I4cm unit cell
48 atoms

Geometry:

SR-DFT (PBE)
VdW corrections
Lattice parameters 1%

Electronic structure:

Direct band-gap at Γ

Band-gap 1.65 eV
Exp. 1.6-1.7 eV

Fortuitous agreement!!!
Spin-orbit coupling?

E. Mosconi et al. *J. Phys. Chem. C* **2013**, 114, 13092.

J. Even et al. *J. Phys. Chem. Lett.* **2013**, 114, 2999.
G. Giorgi et al. *J. Phys. Chem. Lett.* **2013**, 114, 4213.

Band-gap 0.6 eV

Perovskites Electronic Structure

SCIENTIFIC REPORTS

OPEN

Relativistic GW calculations on $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$ Perovskites for Solar Cell Applications

SUBJECT AREAS:
SOLAR CELLS
MATERIALS SCIENCE

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Correspondence and requests for materials should be addressed to F.D.A. (filippo@thch.unipg.it)

Paolo Umari[1,2], Edoardo Mosconi[3] & Filippo De Angelis[3]

[1]Dipartimento di Fisica e Astronomia, Università di Padova, via Marzolo 8, I-35131 Padova, Italy, [2]CNR-IOM DEMOCRITOS, Theory@Elettra Group, c/o Sincrotrone Trieste, Area Science Park, Basovizza, I-34012 Trieste, Italy, [3]Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, I-06123, Perugia, Italy.

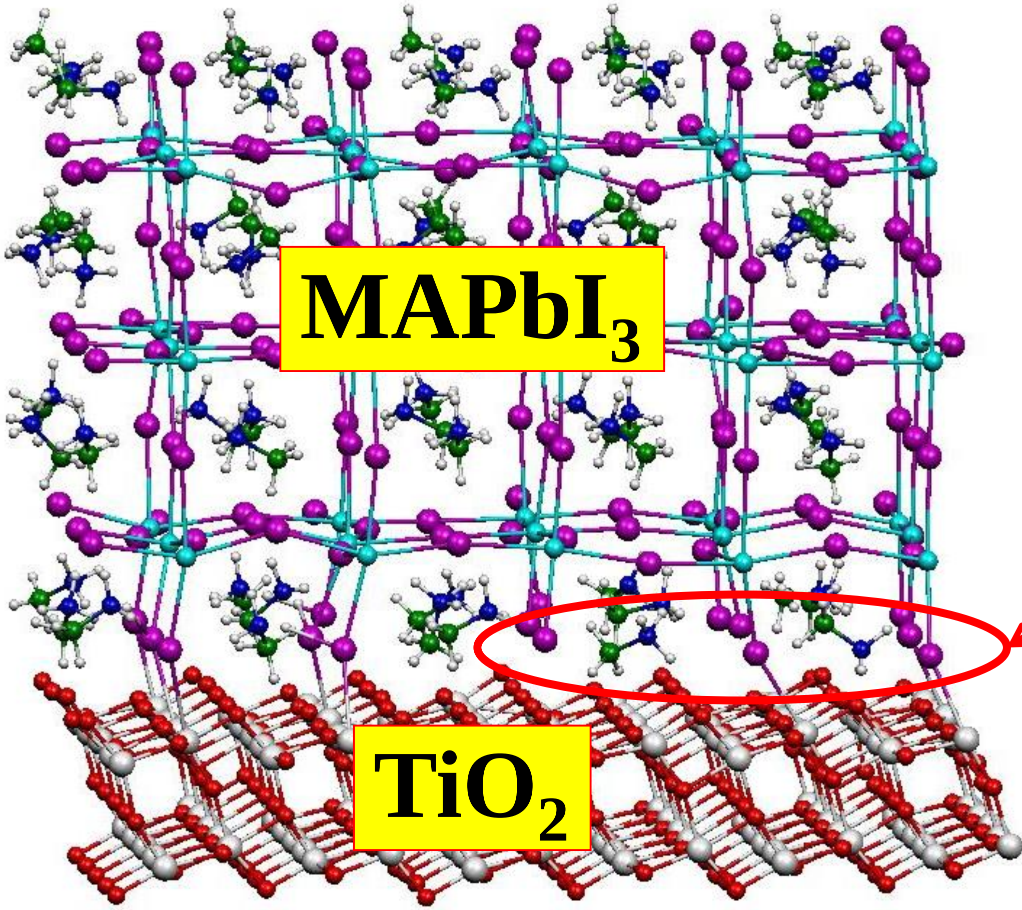
Hybrid AMX_3 perovskites (A = Cs, CH_3NH_3; M = Sn, Pb; X = halide) have revolutionized the scenario of emerging photovoltaic technologies, with very recent results demonstrating 15% efficient solar cells. The $CH_3NH_3PbI_3$/$MAPb(I_{1-x}Cl_x)_3$ perovskites have dominated the field, while the similar $CH_3NH_3SnI_3$ has not been exploited for photovoltaic applications. Replacement of Pb by Sn would facilitate the large uptake of perovskite-based photovoltaics. Despite the extremely fast progress, the materials electronic properties which are key to the photovoltaic performance are relatively little understood. Density Functional Theory electronic structure methods have so far delivered an unbalanced description of Pb- and Sn-based perovskites. Here we develop an effective GW method incorporating spin-orbit coupling which allows us to accurately model the electronic, optical and transport properties of $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$, opening the way to new materials design. The different $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ electronic properties are discussed in light of their exploitation for solar cells, and found to be dominantly due to relativistic effects. These effects stabilize the $CH_3NH_3PbI_3$ material towards oxidation, by inducing a deeper valence band edge. Relativistic effects, however, also increase the material band-gap compared to $CH_3NH_3SnI_3$, due to the valence band energy downshift (~0.7 eV) being only partly compensated by the conduction band downshift (~0.2 eV).

P. Umari, E. Mosconi, F. De Angelis *Sci. Rep.* **2014**, *4*, 4467.

Perovskite/TiO_2 interface: Structural features

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Vittoria Roiati,[†,‡,#] Edoardo Mosconi,[§] Andrea Listorti,*[,†,∥] Silvia Colella,[∥] Giuseppe Gigli,[†,∥,⊥]
and Filippo De Angelis*[,§]



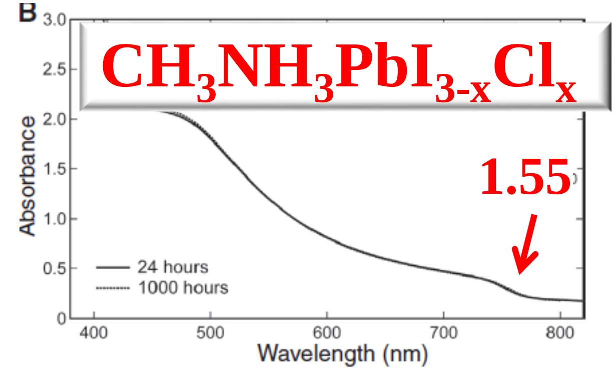
$MAPbI_3/TiO_2$ interaction via I-Ti bonds

V. Roiati, E. Mosconi, et al. *Nano Lett.* **2014,** *14*, 2168.

TiO_2/perovskites interfaces: Role of Cl doping

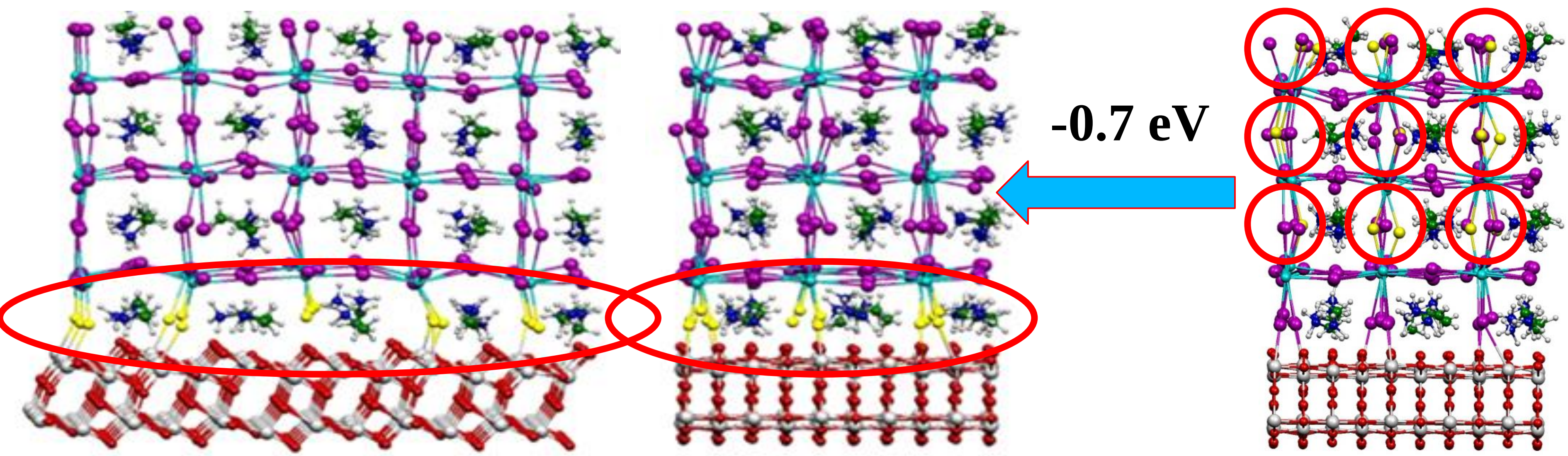
Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1]*



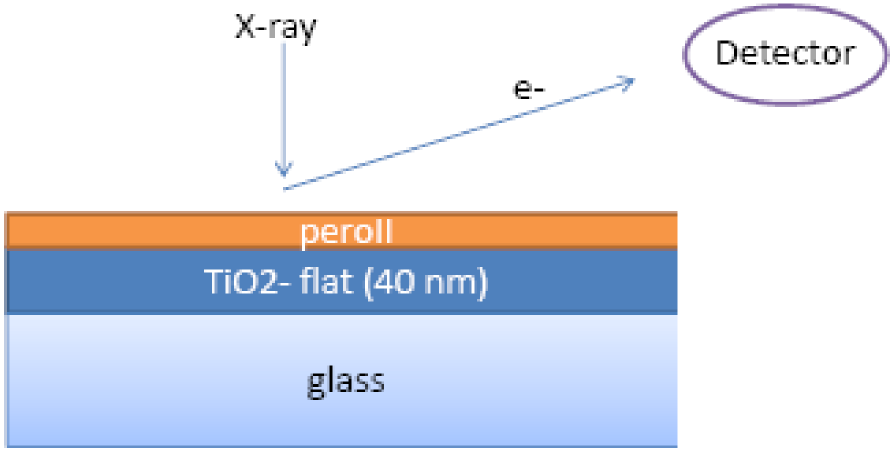
XRD -> 0.7% volume contraction → **~1% Cl**

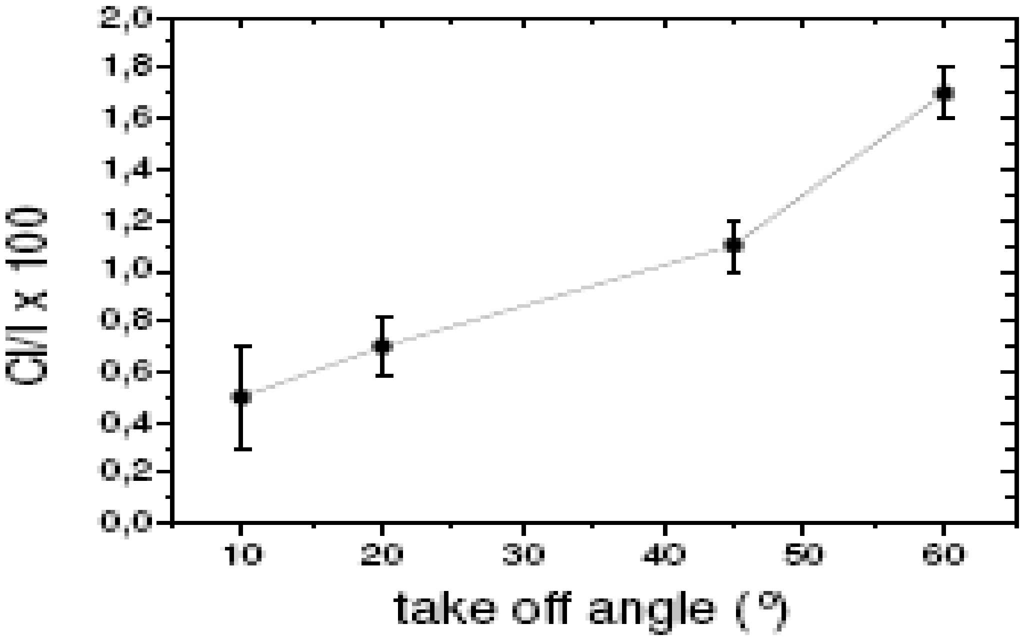
S. Colella, E. Mosconi, et al. *Chem. Mater.* **2013**, *25*, 4613.

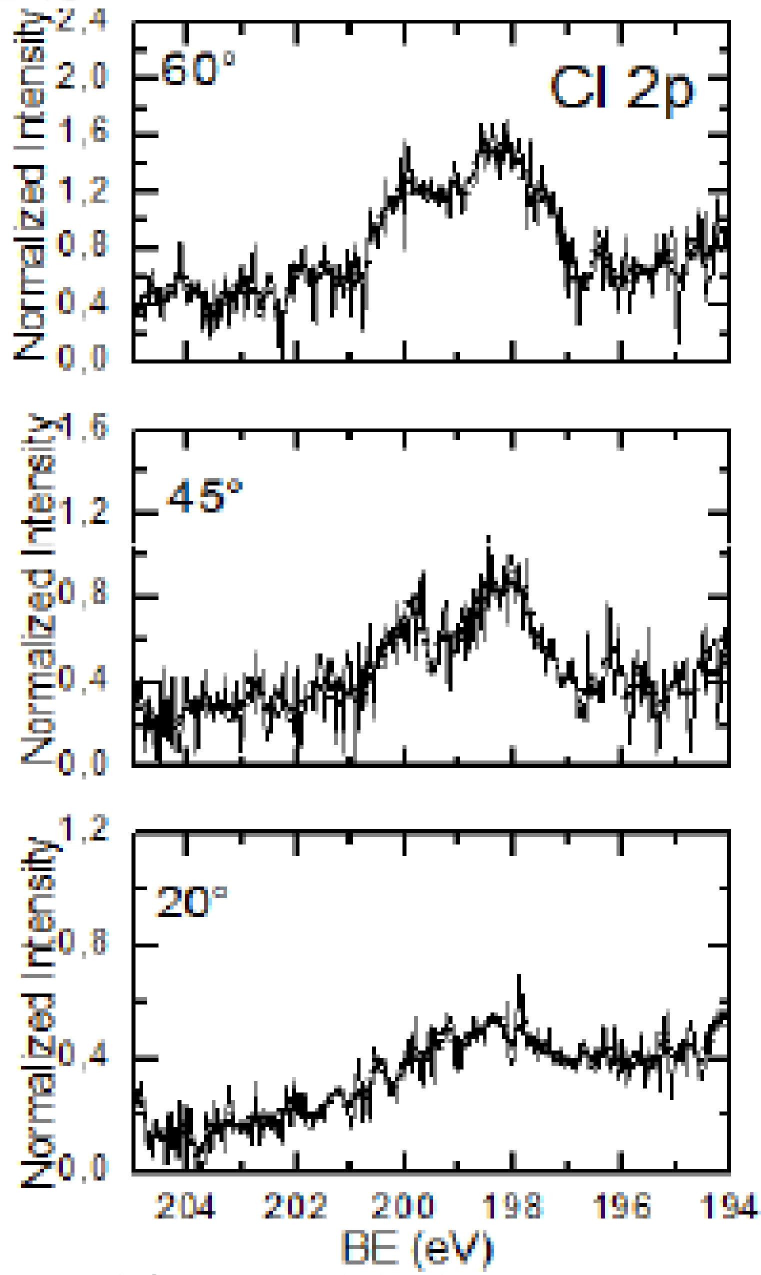


E. Mosconi, et al. *J. Phys. Chem. Lett.* **2014,** *5*, 2619.

Variable angle XPS

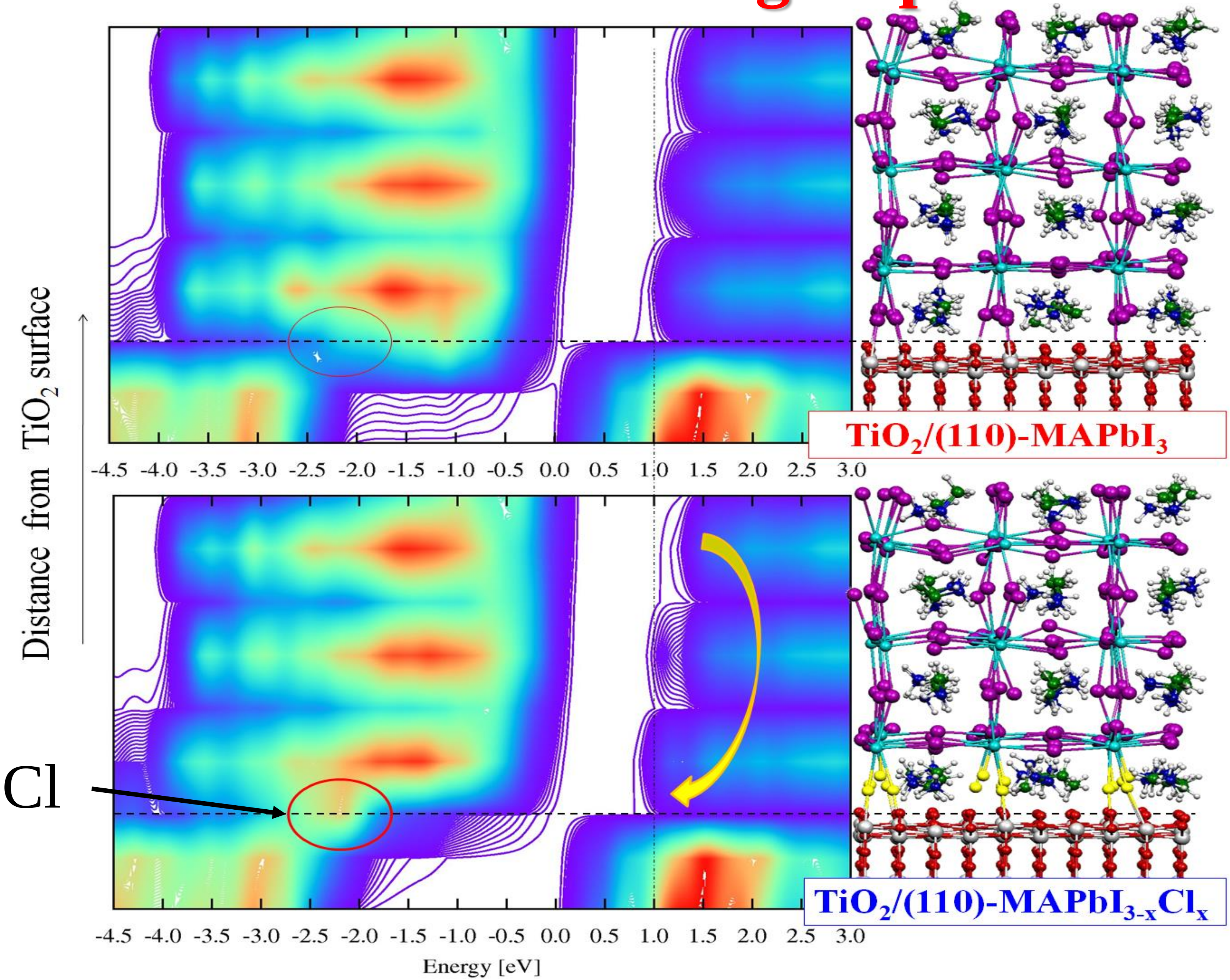






E. Mosconi, et al. *J. Phys. Chem. Lett.* **2014,** *5*, 2619.

Chloride effect: Charge separation



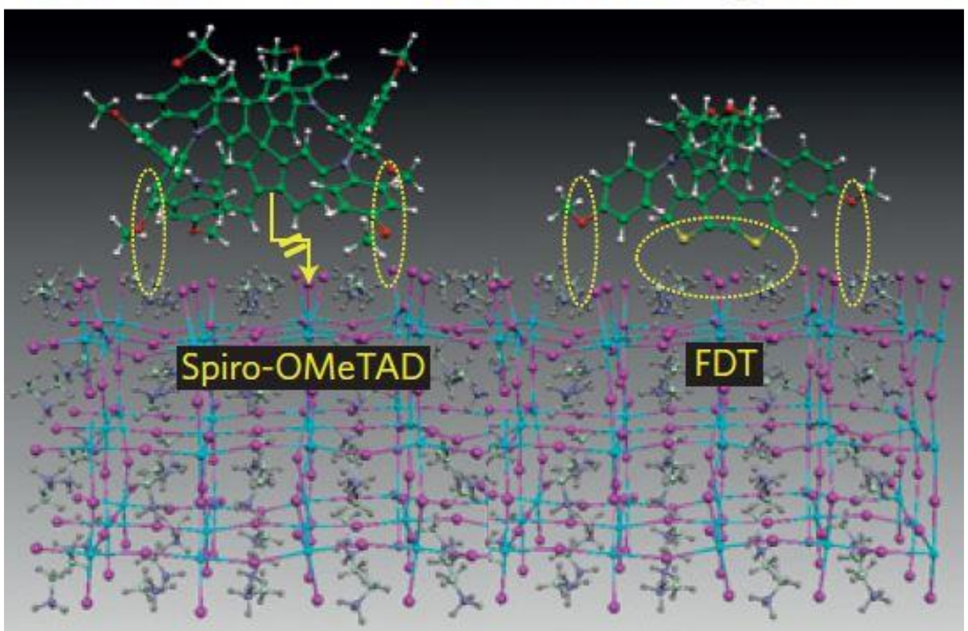
nature energy

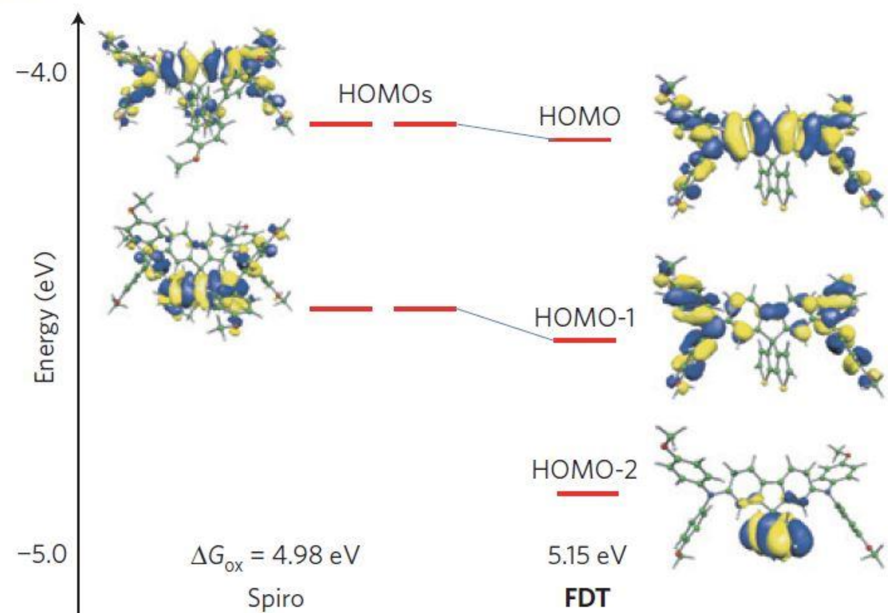
ARTICLES

PUBLISHED: 18 JANUARY 2016 | ARTICLE NUMBER: 15017 | DOI: 10.1038/NENERGY.2015.17

A molecularly engineered hole-transporting material for efficient perovskite solar cells

Michael Saliba[1], Simonetta Orlandi[2], Taisuke Matsui[3], Sadig Aghazada[1], Marco Cavazzini[2], Juan-Pablo Correa-Baena[4], Peng Gao[1], Rosario Scopelliti[1], Edoardo Mosconi[5], Klaus-Hermann Dahmen[6], Filippo De Angelis[5], Antonio Abate[7], Anders Hagfeldt[4], Gianluca Pozzi[2], Michael Graetzel[7] and Mohammad Khaja Nazeeruddin[1]*





Ion (Defects) Migration in $MAPbI_3$: Activation energies

<u>Unwanted phenomena:</u>
Slow photo conductivity response
Hysteresis

→ <u>Ions migration</u>

	E_a (eV)			
Defect	**Azpiroz - CNR**	Haruyama	Eames	Meloni
I Vacancy	**0.08**	**0.33**	**0.58**	**0.13**
MA Vacancy	**0.46**	**0.55**	**0.84**	**0.60**
Pb Vacancy	**1.06**	**-**	**2.31**	**1.39**
I Interstitial	**0.08**	**-**	**-**	**-**

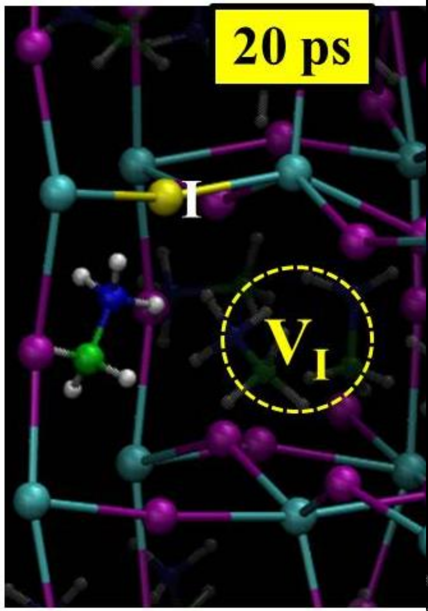
Azpiroz, J. M.; Mosconi, E.; Bisquert, J.; De Angelis, F. *Energy Environ. Sci. 2015, 8, 2118.*

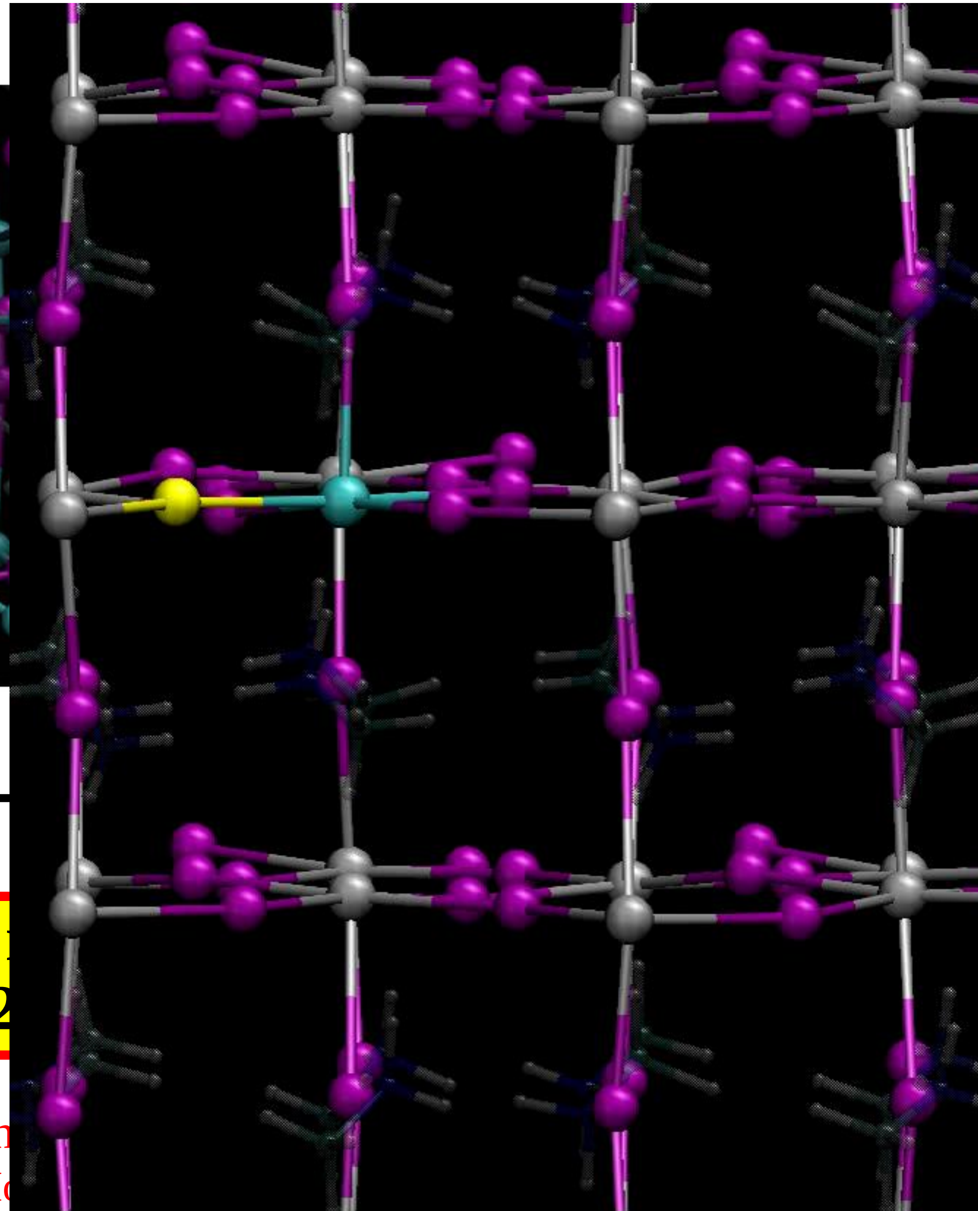
Haruyama, J.; Sodeyama, K.; Han, L.; Tateyama, Y. *J. Am. Chem. Soc. 2015, 137, 10048.*

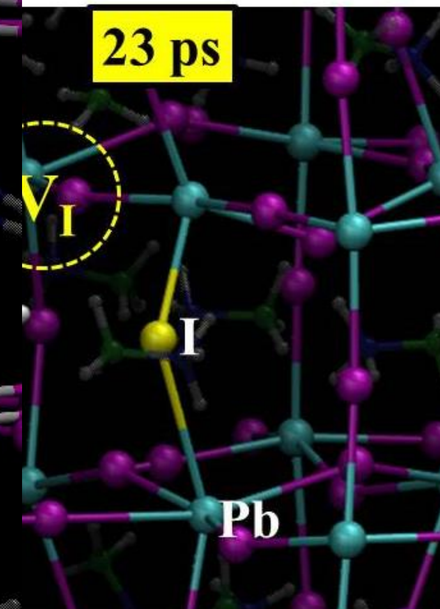
Eames, C.; Frost, J. M.; Barnes, P. R. F.; O'Regan, B. C.; Walsh, A.; Islam, M. S. *Nat Commun 2015, 6,* 7497

Meloni, S. ; Moehl, T.; Tress,…Rothlisberger, U.; Graetzel, M. *Nat Commun* 2016, *7*, 10334.

I^- Vacancy Migration: Car-Parrinello MD





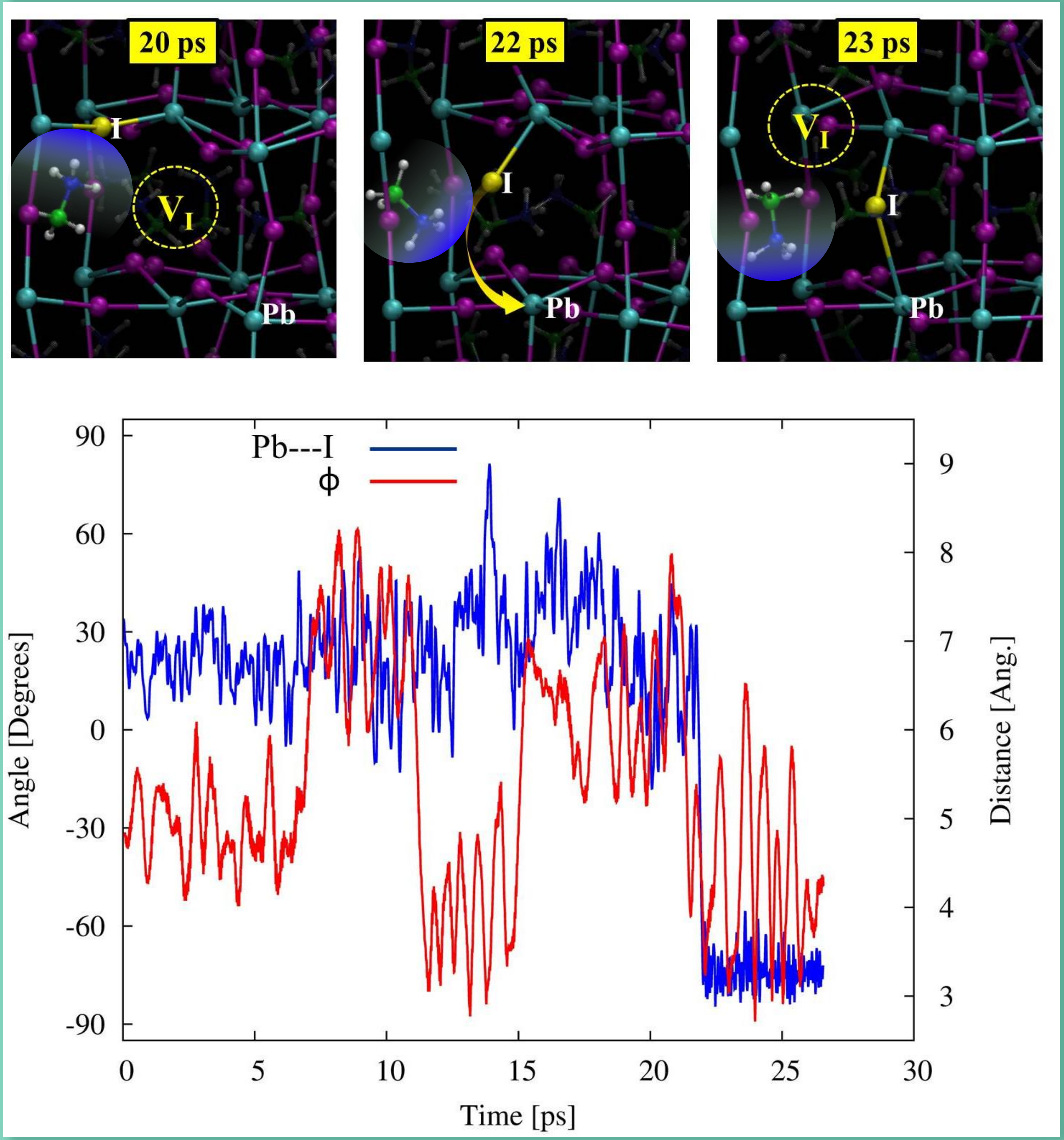


1 … in 2…

…eV

Azpiroz, J. M.; Moscon… *…ci. 2015, 8, 2118-2127.*
Mo… …8.

I^- Vacancy Migration: Car-Parrinello MD



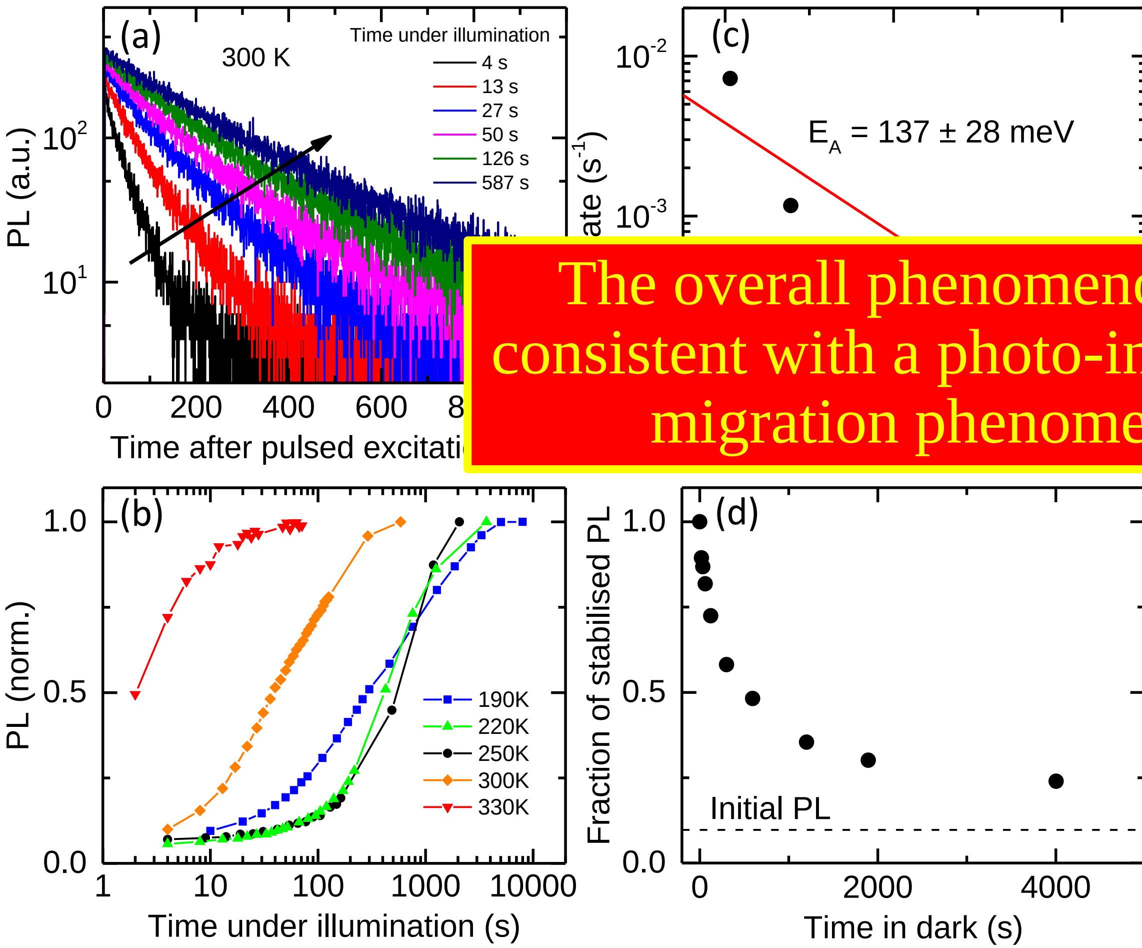
MA dynamics and ion/defect migration are essentially coupled:

MA assists defect migration by reorienting its charge distribution along with the ionic motion, providing a local charge screening mechanism which may further speed up the ionic migration

Energy & Environmental Science

Light-induced annihilation of Frenkel defects in organo-lead halide perovskites†

Edoardo Mosconi,[ab] Daniele Meggiolaro,[b] Henry J. Snaith,[c] Samuel D. Stranks*[de] and Filippo De Angelis*[ab]



The overall phenomenology is consistent with a photo-induced ion migration phenomenon

Over a period of time under illumination, the PL lifetime and total intensity both increase and eventually stabilize, **consistent with a substantial reduction of** **ive decay pathways**

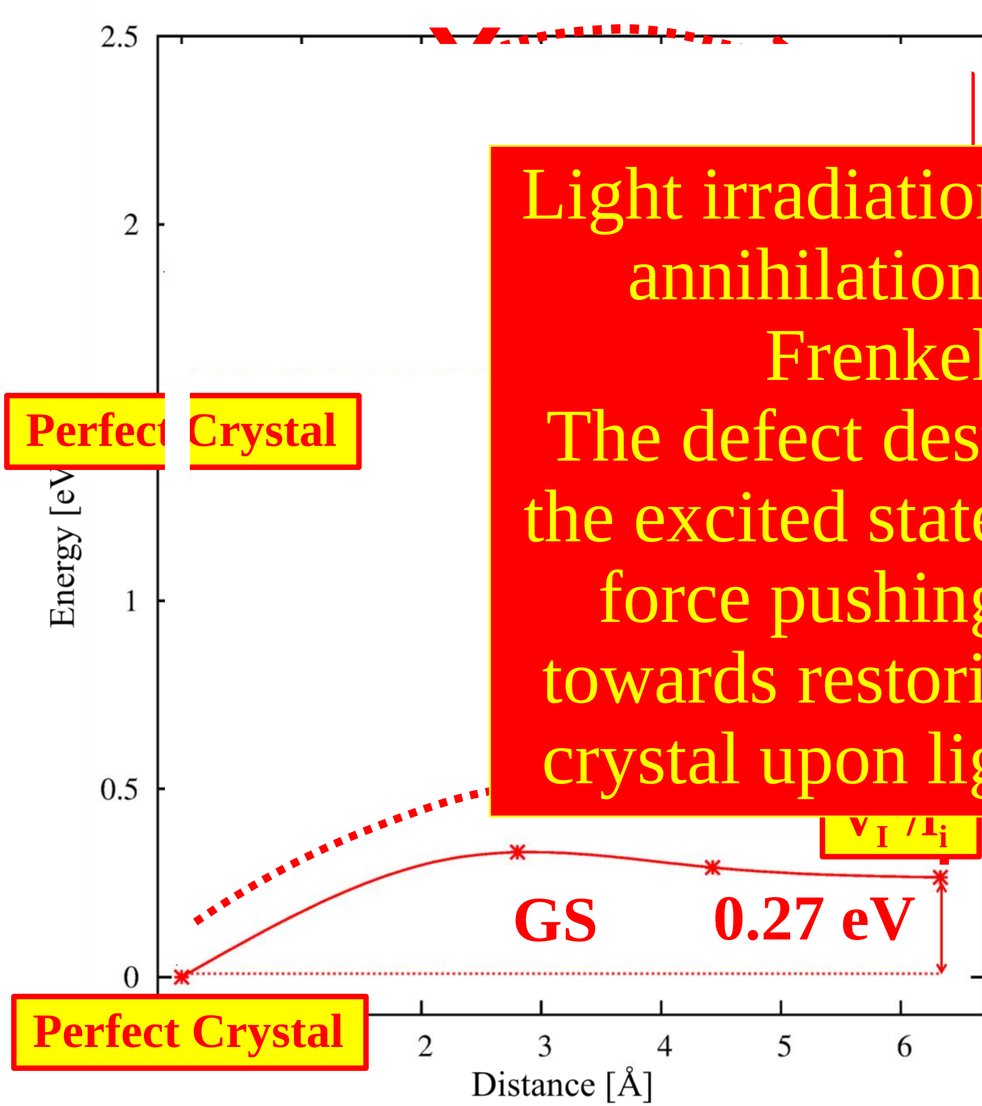
ng of trap density: from ~10^{17} to ~10^{16} cm^{-3}

The observed temperature-dependent PLQE rise was fitted by an Arrhenius exponential behavior, delivering an **activation energy of 0.14 ± 0.03 eV in line with the calculated barriers of V_I and I_i**

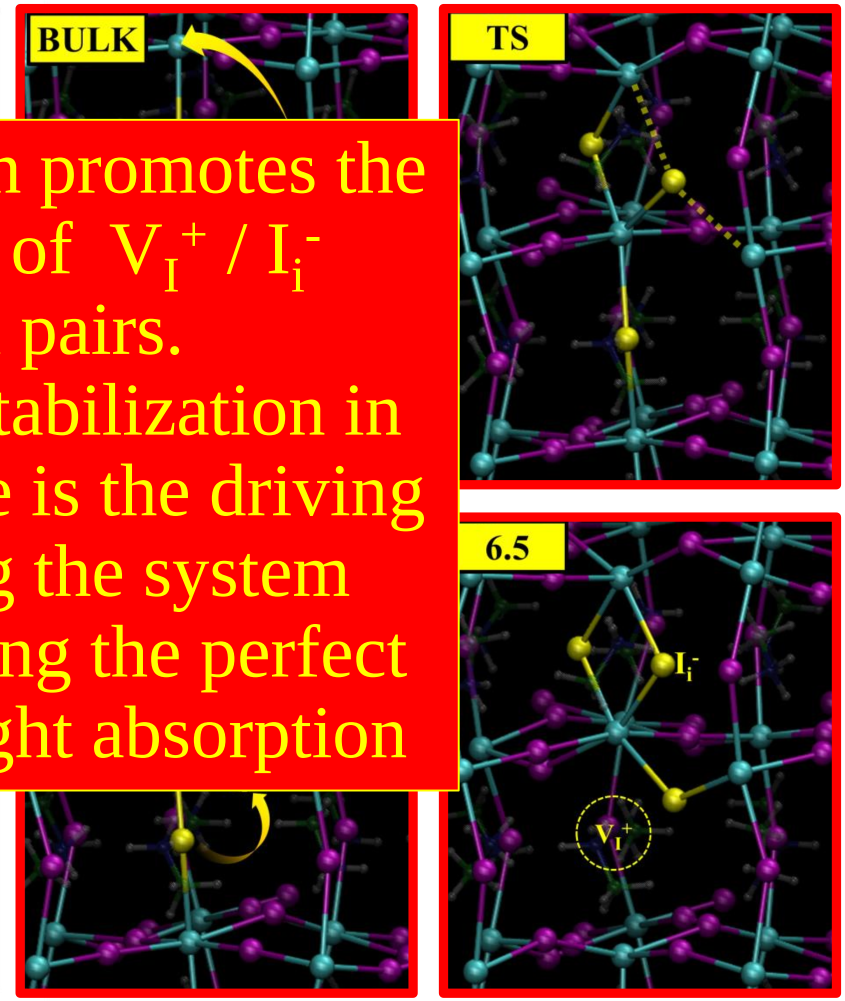
Mosconi, E.; Meggiolaro, D.; Snaith, H. J.; Stranks, S. D.; De Angelis, F. *Energy Environ. Sci.* **2016**, DOI: 10.1039/C6EE01504B

D. W. deQuilettes et al. *Nat Comms*, 2016, DOI: 10.1038/ncomms11683

Light-induced Annihilation of Frenkel Defects in Organo-Lead Halide Perovskites



Light irradiation promotes the annihilation of V_I^+ / I_i^- Frenkel pairs.
The defect destabilization in the excited state is the driving force pushing the system towards restoring the perfect crystal upon light absorption



Mosconi, E.; Meggiolaro, D.; Snaith, H. J.; Stranks, S. D.; De Angelis, F. *Energy Environ. Sci.* **2016**, DOI: 10.1039/C6EE01504B

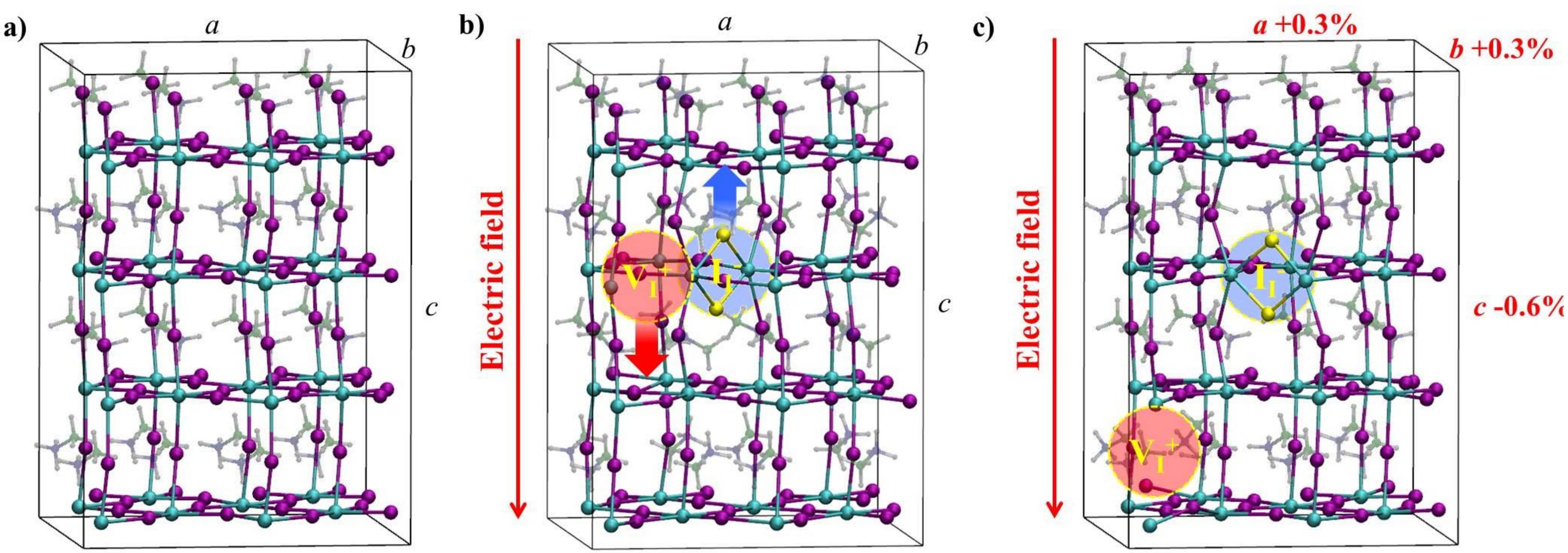
MENU

nature materials

Article Published: 24 September 2018

Large electrostrictive response in lead halide perovskites

Bo Chen, Tao Li, Qingfeng Dong, Edoardo Mosconi, Jingfeng Song, Zhaolai Chen, Yehao Deng, Ye Liu, Stephen Ducharme, Alexei Gruverman, Filippo De Angelis & Jinsong Huang



Conclusions and Remarks

- Electronic and Optical properties of $MAPbI_3$

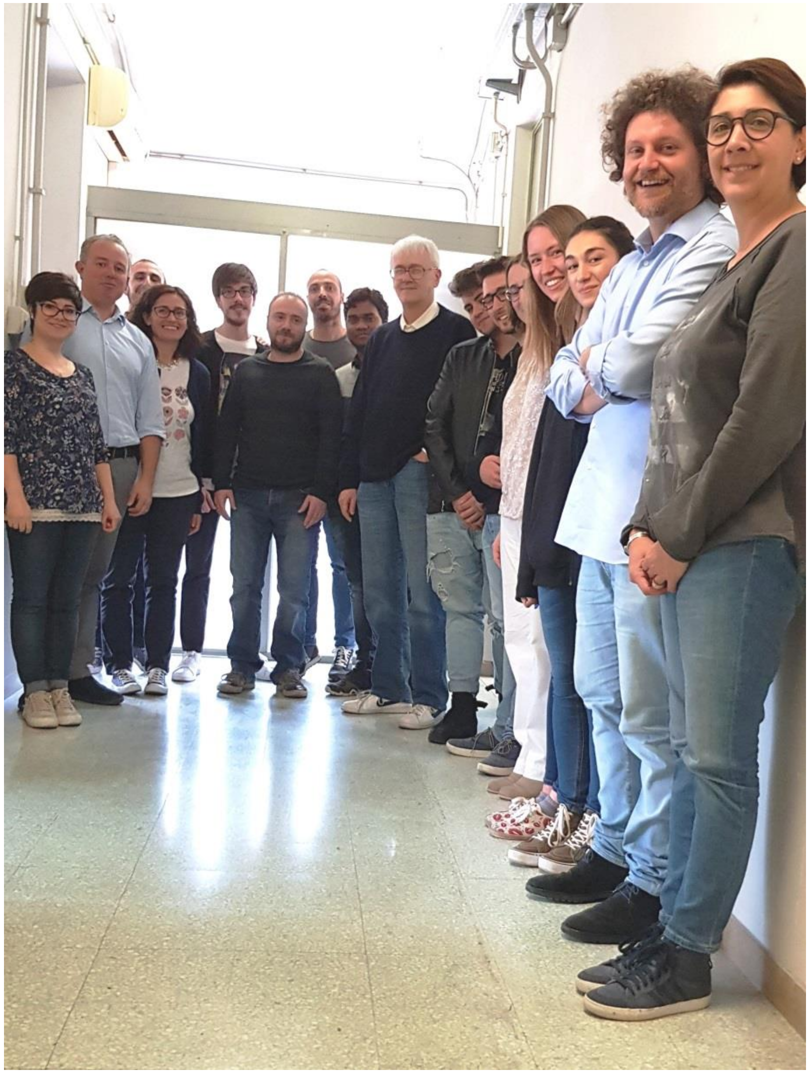
  GW-SOC, HSE06-SOC, PBE0-SOC

- Role of Cl doping

- Role of MA^+ in determining the migration meachanism

- Light-induced Annihilation of Frenkel Defects

Computational Laboratory for Hybrid/Organic Photovoltaics



Collaborations

- CNR-IMM (Alberti, Pellegrino)
- CNR-IMEM (Mosca)
- CNR-NANO (Colella, Listorti, Gigli)
- CNR-ISMN (Ruani)
- IIT (Petrozza)
- LPI-EPFL (Nazeeruddin, Graetzel)
- UOXF (Snaith)

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FP7-NMP-2013-**MESO**
H2020-LCE-2017-RES-RIA-**ESPResSo**
LCE-07-2016-2017-**PERTPV**