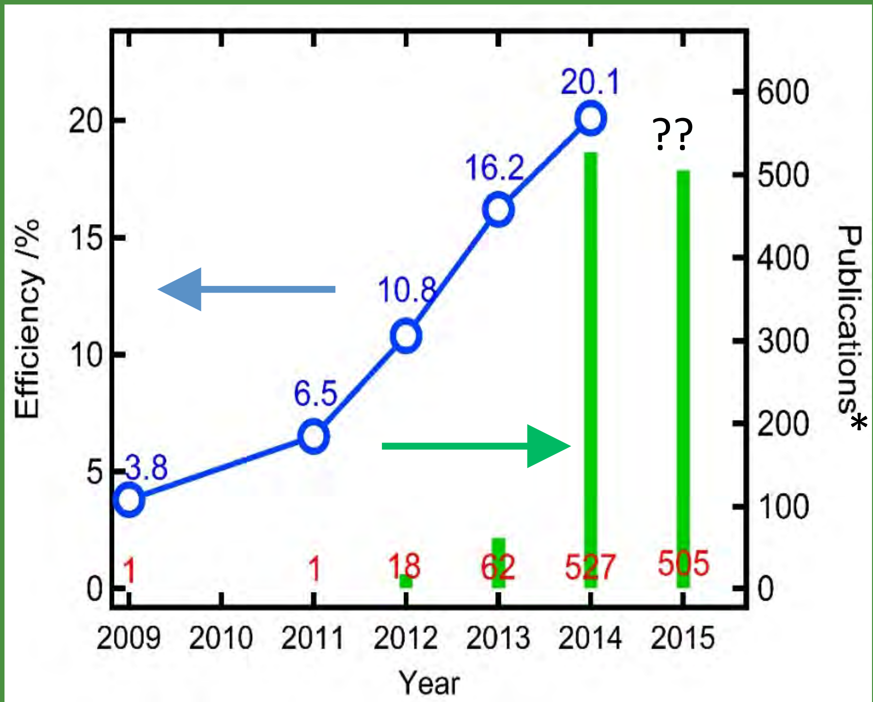
The meteoric rise of perovskite solar cells

Lecture at MSU April 12, 2016

michael.graetzel@epfl.ch

Science AAAS



Perovskite solar cell (PSC) effiiency evolution (blue9 and number of PSC - related publications

Luo, et al M. *Science* **2014**, *345*, 1593.

Solar splitting of water into hydrogen and oxygen driven by perovskite photovoltaics

EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

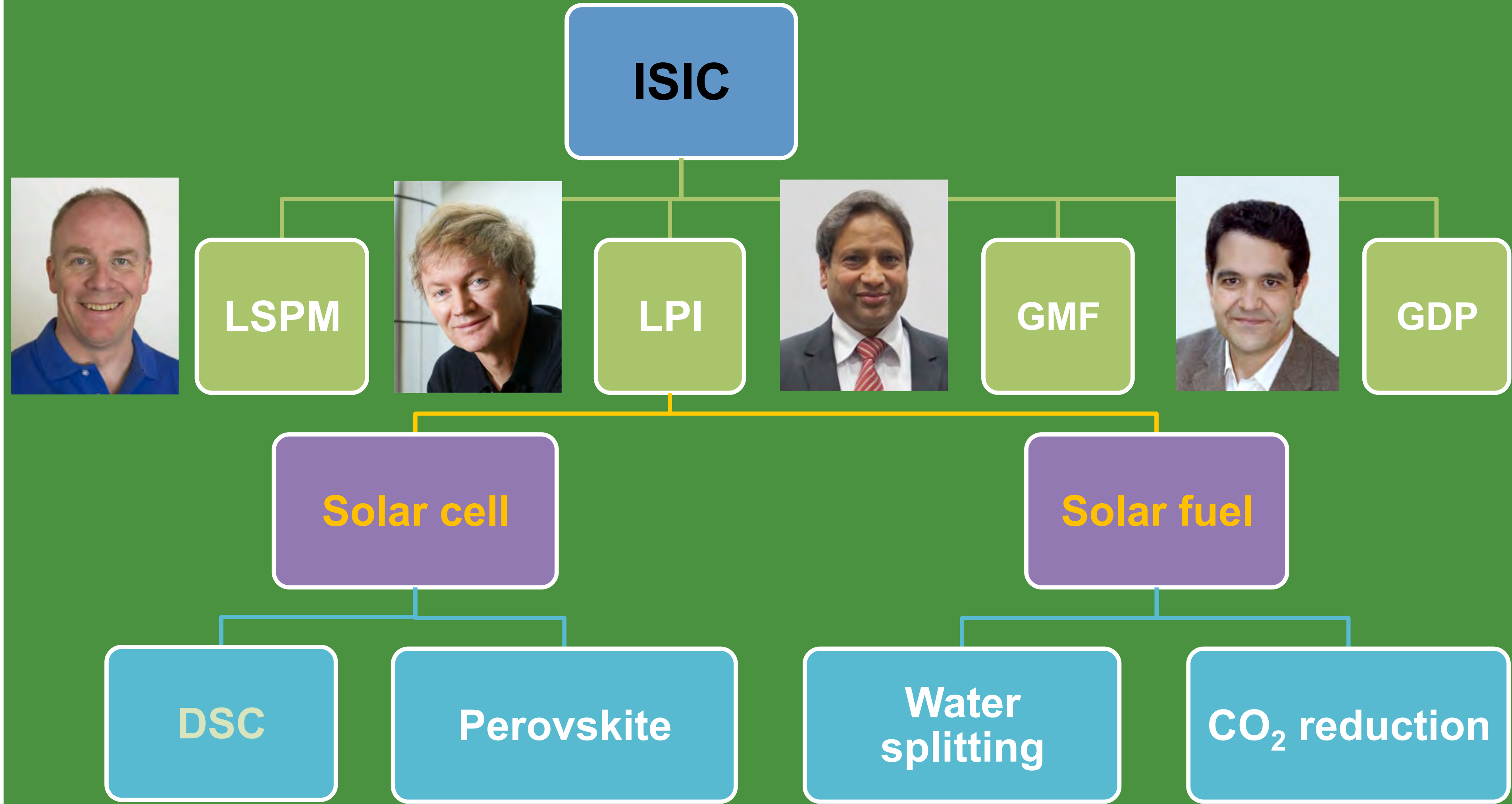
NANYANG TECHNOLOGICAL UNIVERSITY

1398

MAX-PLANCK-GESELLSCHAFT

Thank you for your attention!

Solar energy research in ISIC, EPFL



Perovskite minerals were discovered in the Russian Ural mountains

Lev Perovski (1792 - 1856)

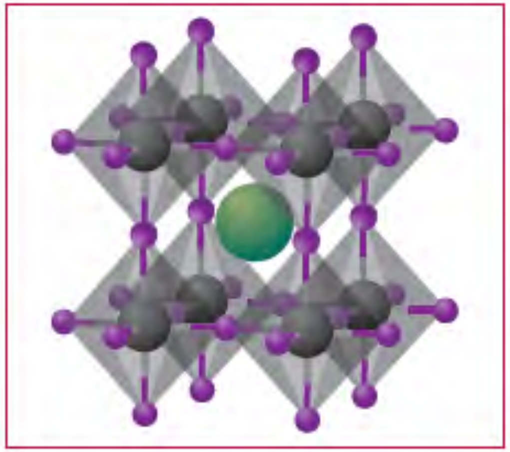
$CH_3NH_3PbI_3$

AMX_3 e.g. $CaTiO_3$ or $CH_3NH_3PbI_3$

The mineral was discovered in the Ural Mountains by the German scientist Gustav Rose in 1839, who named it perovskite to honor the famous Russian mineralogist Lev Perovski commentary

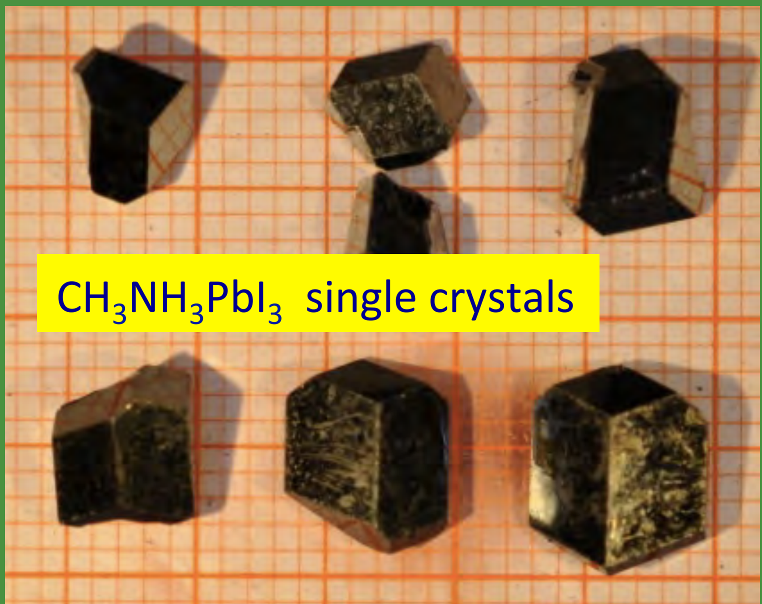
NATURE MATERIALS | VOL 13 | 2014 I 838

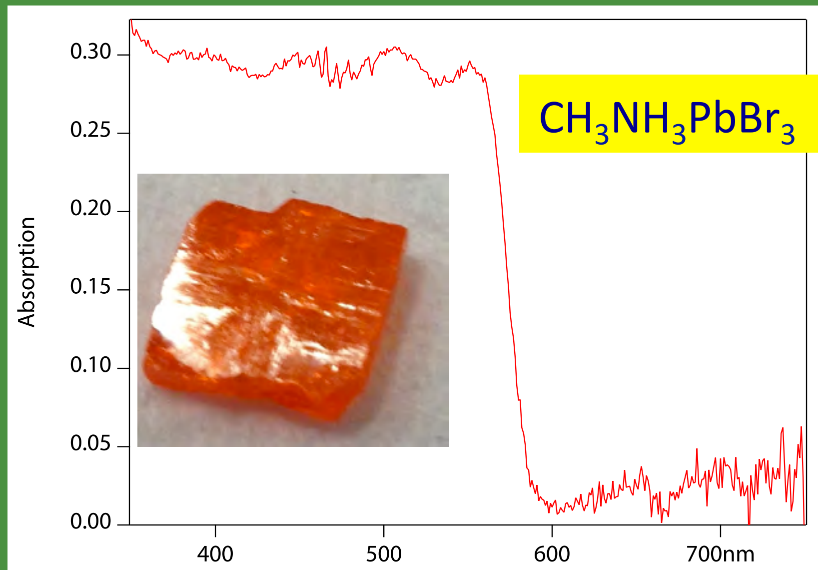
The light and shade of perovskite solar cells



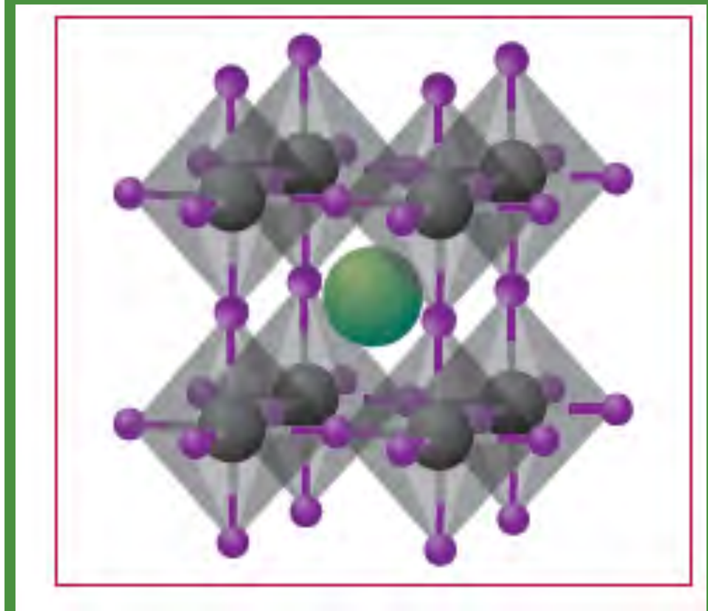
Michael Grätzel

The rise of metal halide perovskites as light harvesters has stunned the photovoltaic community. As the efficiency race continues, questions on the control of the performance of perovskite solar cells and on its characterization are being addressed.





Metal halide perovskites offer advantages as solar light harvesters



General formular: ABX_3

A (green): Cs^+ , $CH_3NH_3^+$ or $CH(NH_2)_2^+$
B (dark grey): Pb^{2+}, Sn^{2+}
X (red): Br^{-} , Cl, $^{-}$ I^{-}

$CH_3NH_3PbX_3$, ein Pb(II)-System mit kubischer Perowskitstruktur

$CH_3NH_3PbX_3$, a Pb(II)-System with Cubic Perovskite Structure

Dieter Weber

Institut für Anorganische Chemie der Universität Stuttgart

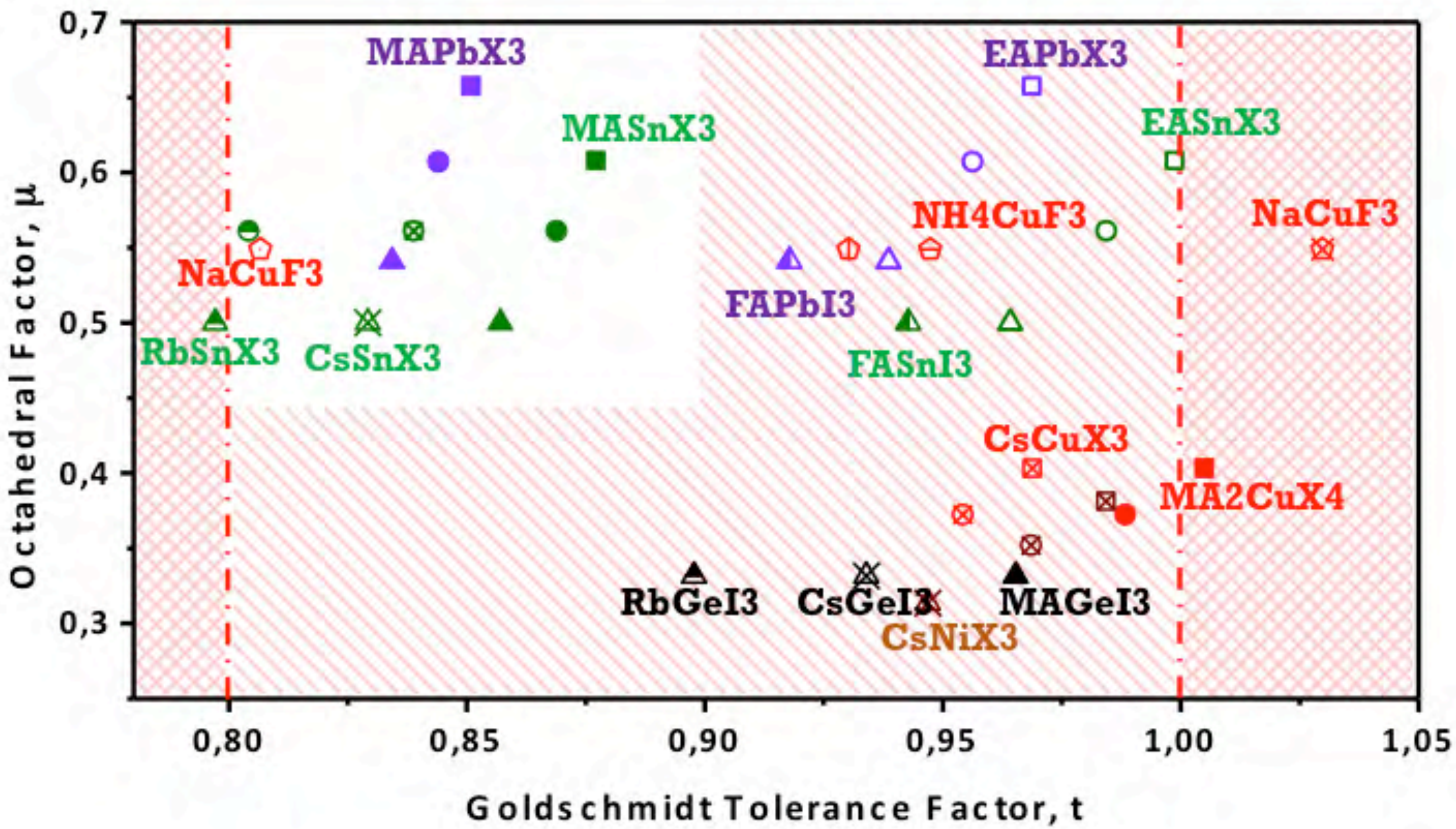
Z. Naturforsch. **33 b, ** 1443–1445 (1978); eingegangen am 21. August 1978

- Strong light absorption in the visible
- Tunable band gap
- Small exciton dissociation energy (<30 meV)
- Low defect concentration
- High open circuit voltage close to band gap energy

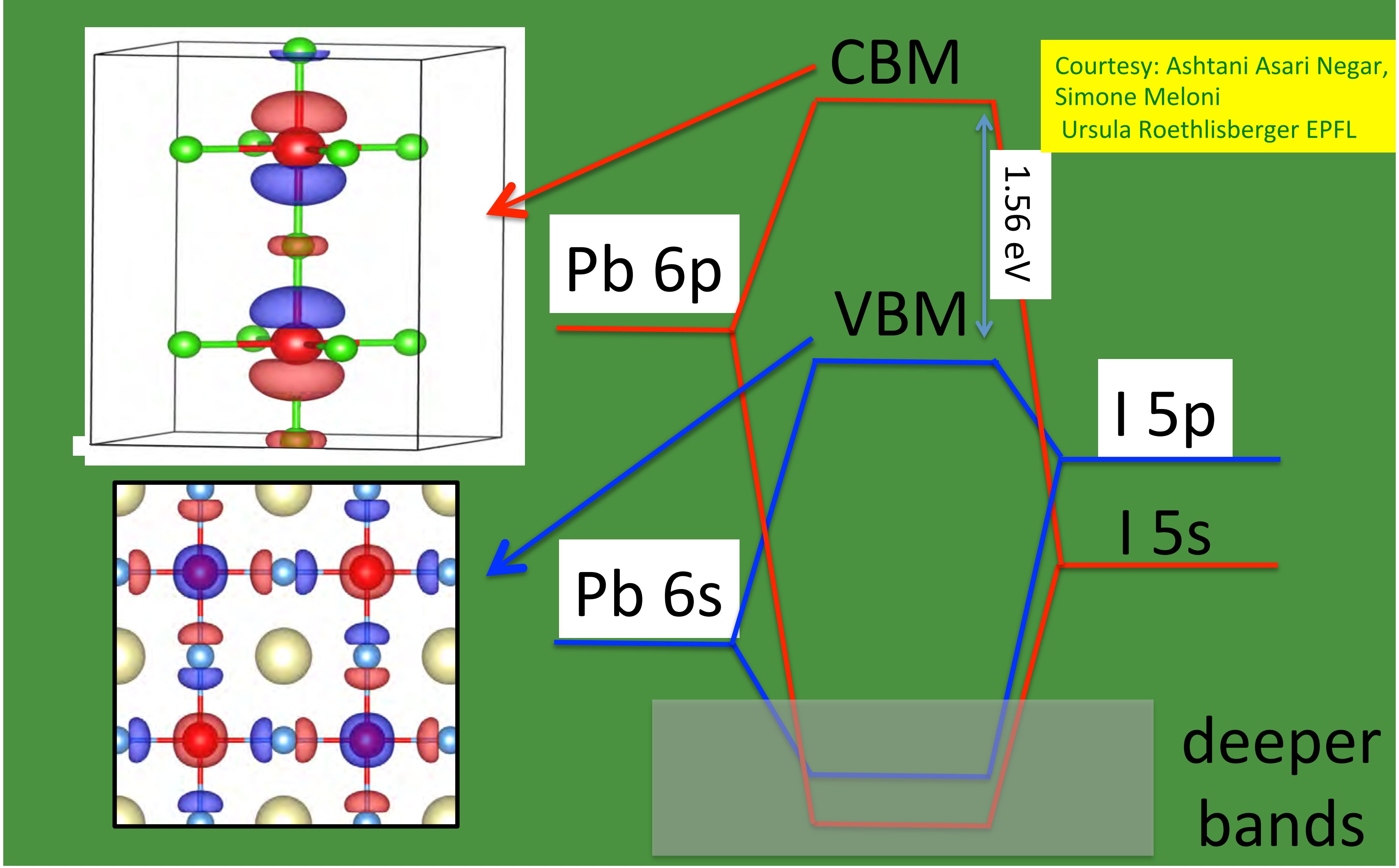
Goldschmidt tolerance factor: key criterion for feasibility of perovskite lattice formation

$$t = (R_A + R_X)/\{\sqrt{2}(R_B + R_X) = 1$$

$$\mu = R_B/R_X = 0.4$$



Band structure and orbitals for $CH_3NH_3PbI_3$

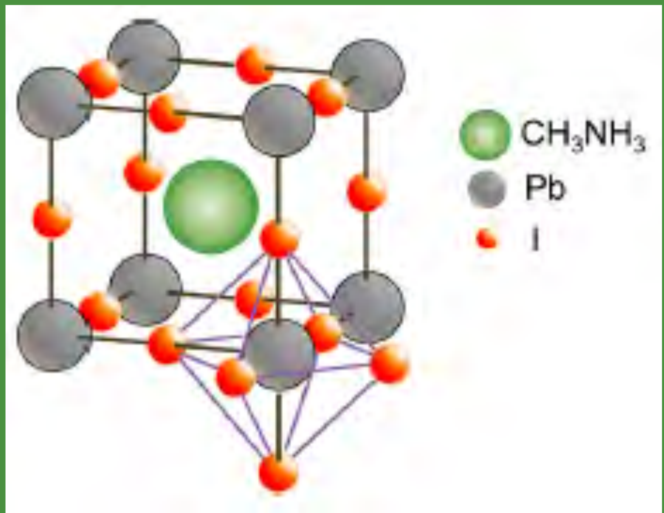


$CH_3NH_3PbI_3$ has ambipolar character (*n*-type, *p*-type conductor)

1)electronic properties of the 3D $MAPbI_3$, (frontier orbitals nature; band structure analysis; the impact of SOC; use of hybrid functionals in band gap prediction).

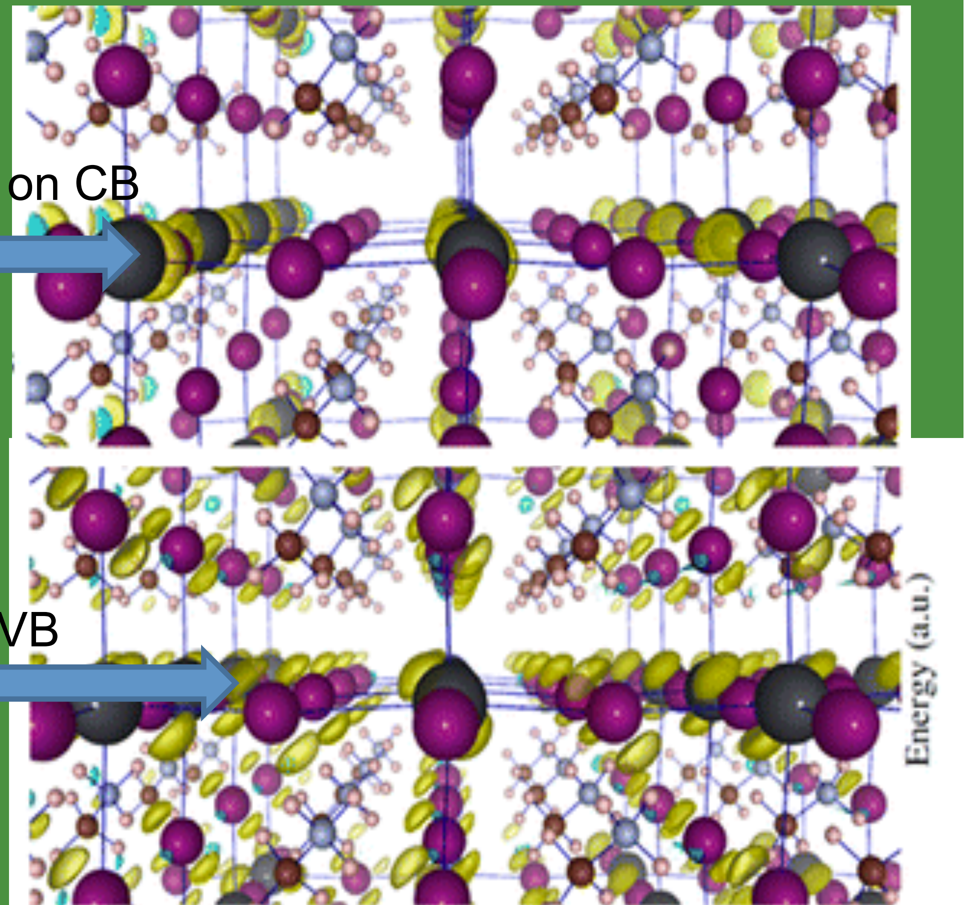
From DFT+SOC : $m_e^* = 0.228 m_0$ $m_h^* = 0.2 m_0$

G. Giorgi, J. Fujisawa, H. Segawa, K. Yamashita *J. Phys. Chem. Lett.*, 2013, 4. 4213–4216



Electron on CB

Hole on VB

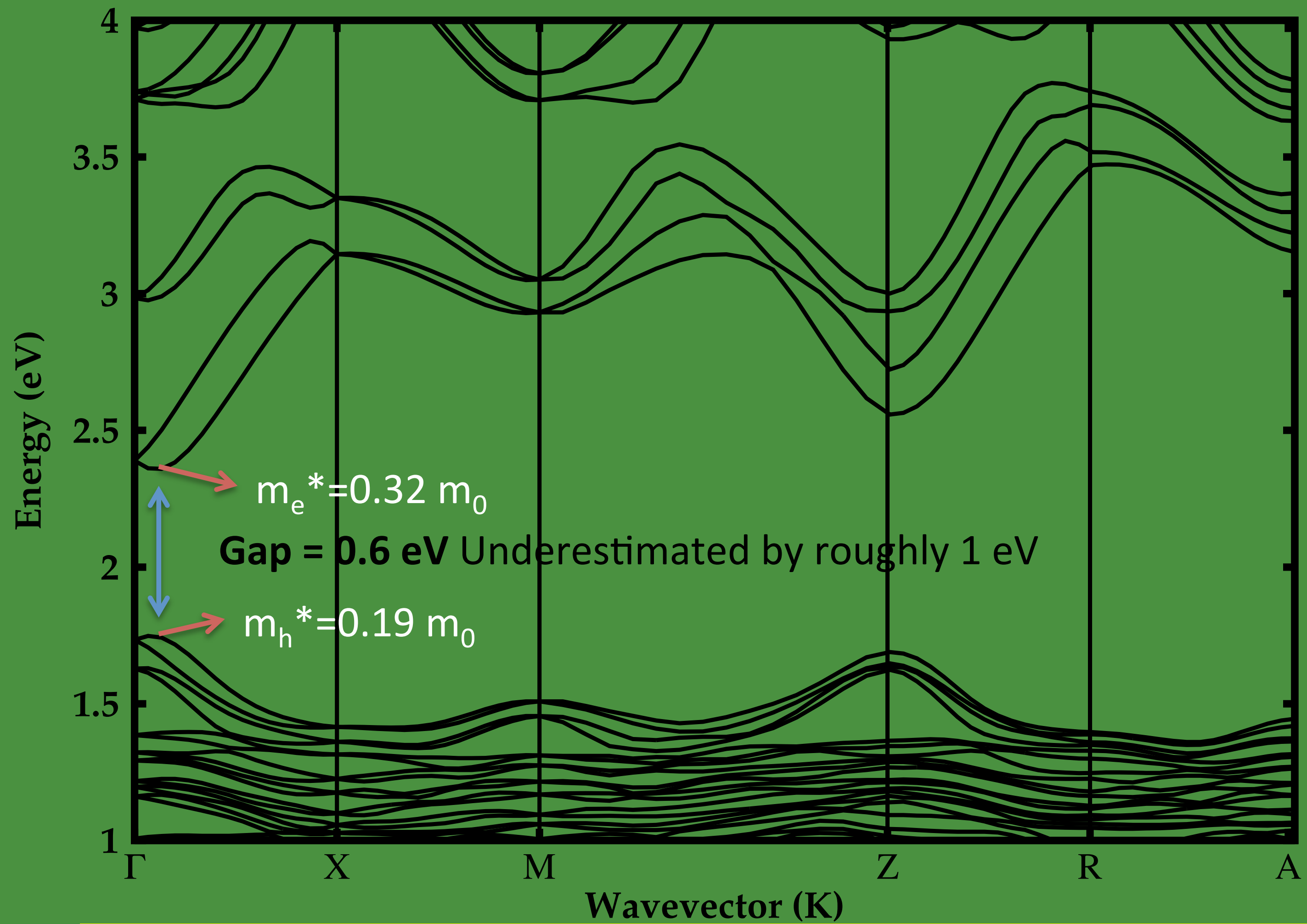


Antibonding orbitals form valence
And conduction band

CB : Pb 6p	**+**	**I 5s**	**electron**
VB : Pb 6s	**+**	**I 5p**	**hole**

Band structure calculations for cubic-$CH_3NH_3PbI_3$

DFT using GGA + **SOC** (correct dispersion shape but gap underestimated by 1eV)



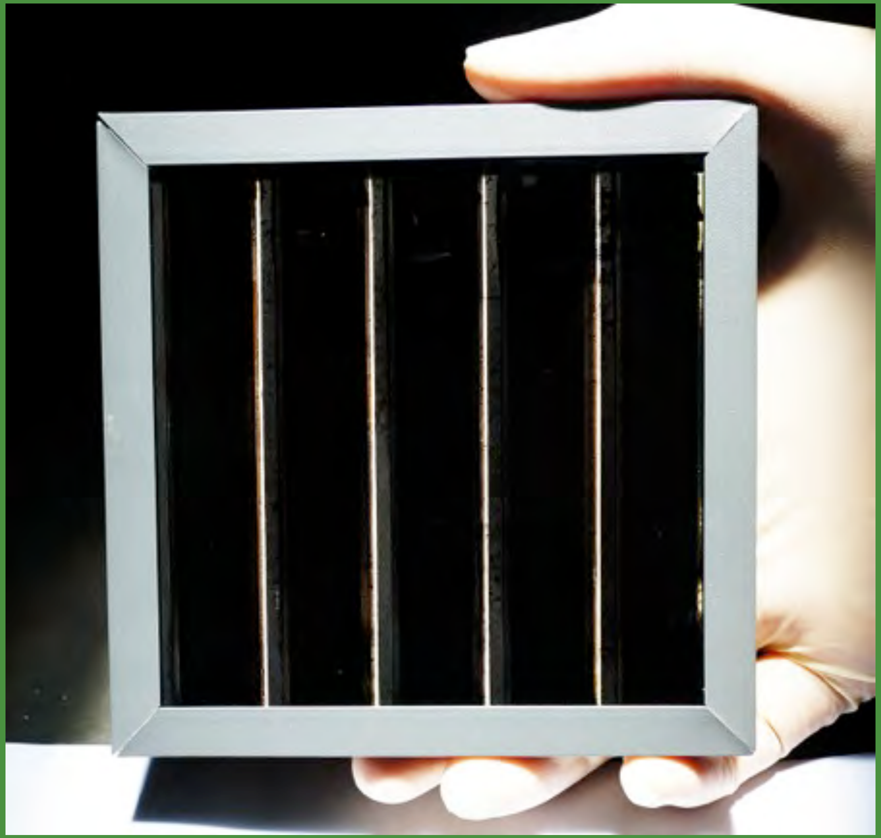
Courtesy: Ashtani Asari Negar, Simone Meloni Ursula Roethlisberger EPFL

Outline

- The advent of perovskite solar cells
- Mixed organic cation/anion formulations, effect of stoichiometric PbI_2 excess on PV performance
- Lithium doping of mesocopic TiO_2 scaffold
- New hole conductors
- Planar configurations
- Tandem cells
- Stability

Perovskite Solar Cells (PSCs) emerged from Dye Sensitized Solar Cells

Dye sensitized solar cell (DSC) → Perovskite solar cell (PSC)



Dye sensitized solar cell
courtesy Sony corporation

Pervovskite solar cell
courtesy Hongwei Han

PSCs evolved from the DSC

The first embodiment of a PSC described by Miyasaka In his 2009 JACS paper was a mesoscopic dye sensitized solar cell using ammonium lead halide perovskites as sensitizer and iodide base liquid electrolyte.

J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

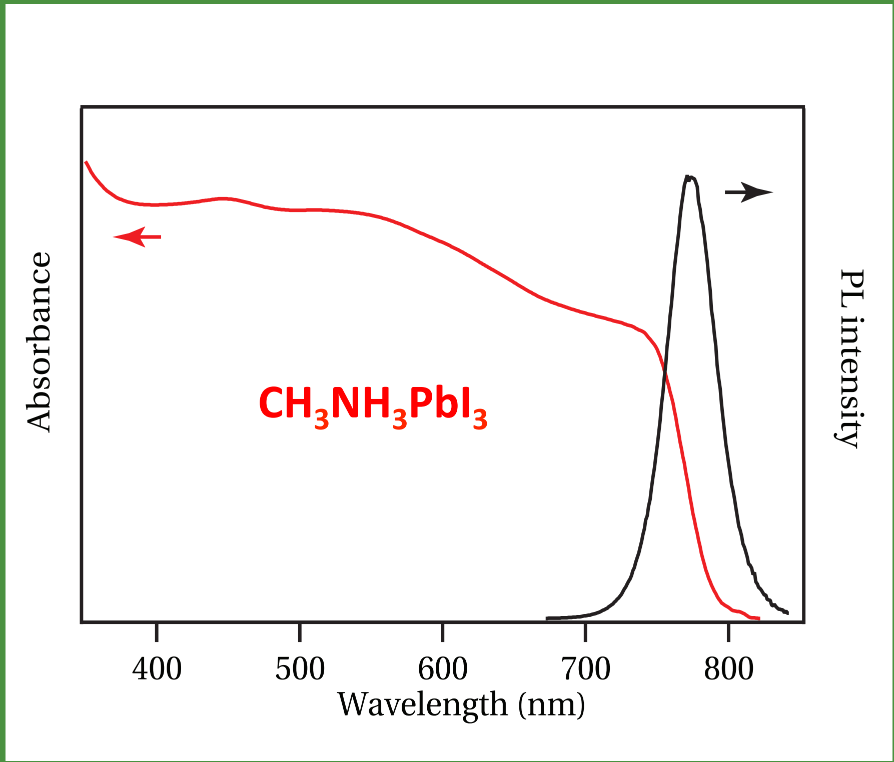
Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*,[†,‡,∥]

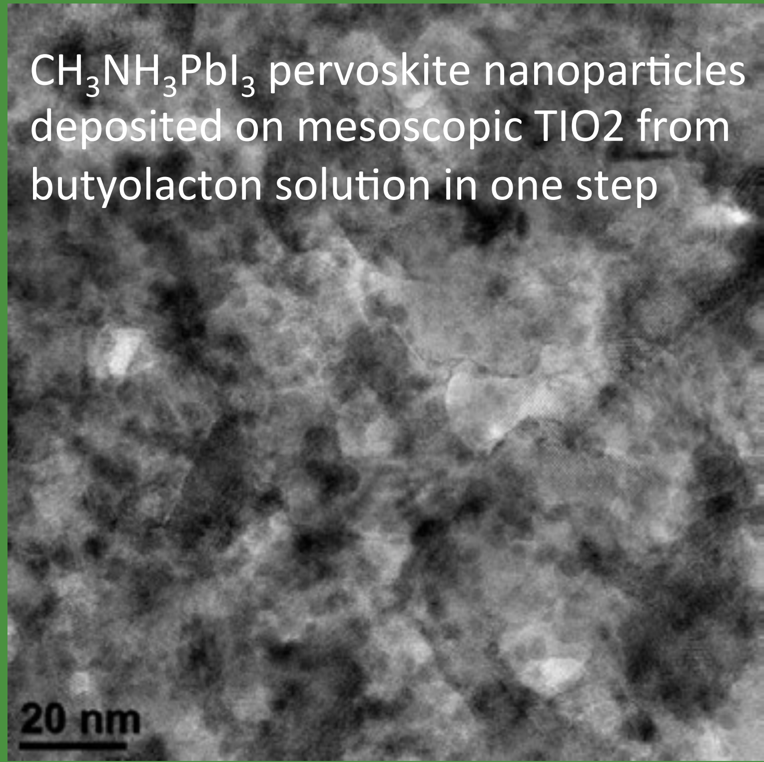
Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan, Graduate School of Engineering, Toin University of Yokohama, and Peccell Technologies, Inc., 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8502, Japan, and Graduate School of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan

Received December 9, 2008; Revised Manuscript Received April 1, 2009; E-mail: miyasaka@cc.toin.ac.jp

Tsutomu (Tom) Miyasaka playing his violin fabricated in 1835 in Torino Italy during the ICES 2014 conference Dinner in Niseto, Hokkaido, Japan on February 06, 2014.

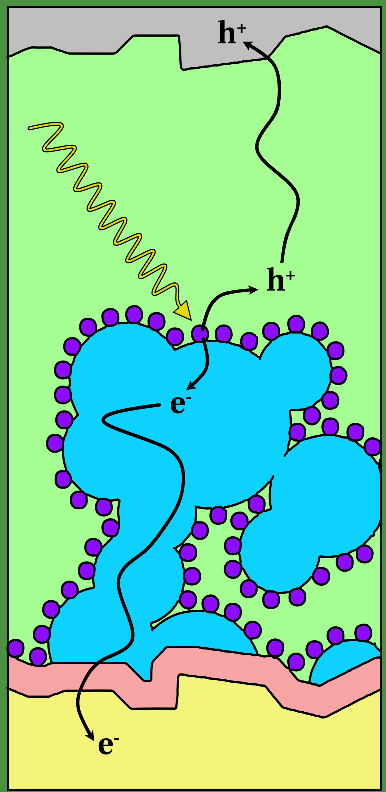
Perovskite solar cells (PSCs) emerged from dye sensitized solar cells

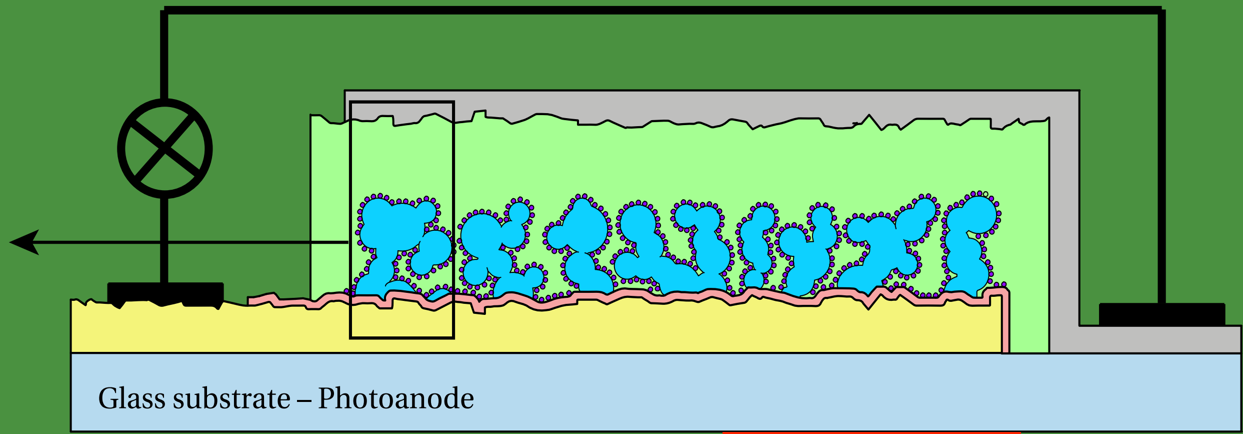


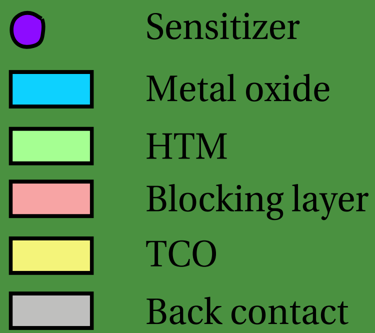


- Perovskite pigment replaces the molecular sesntizer in a dye sensitized solar cells (T.Miyasaka, et al. JACS 2009, 131, 6050–6051, N.G Park et al *Nanoscale 2011,* **3**, 4088-4093)
- unstable in liquid electrolyte based DSSC
- stable and more efficient in solid state hole conductor based DSSC

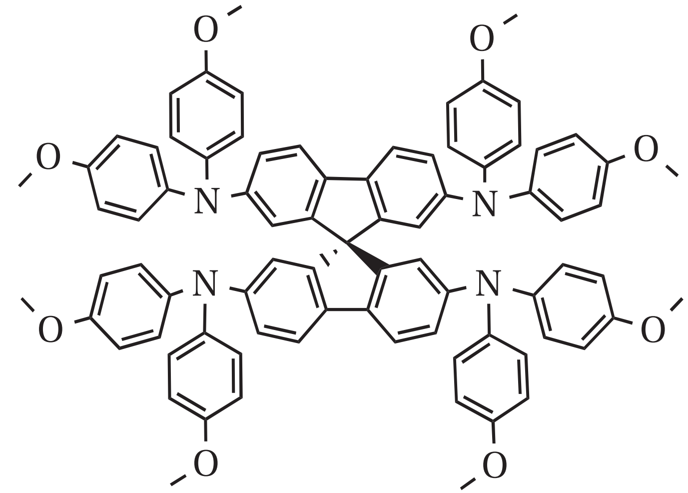
Solid state sensitized DSCs launched PSC’s on their high effiency path







spiro-MeOTAD

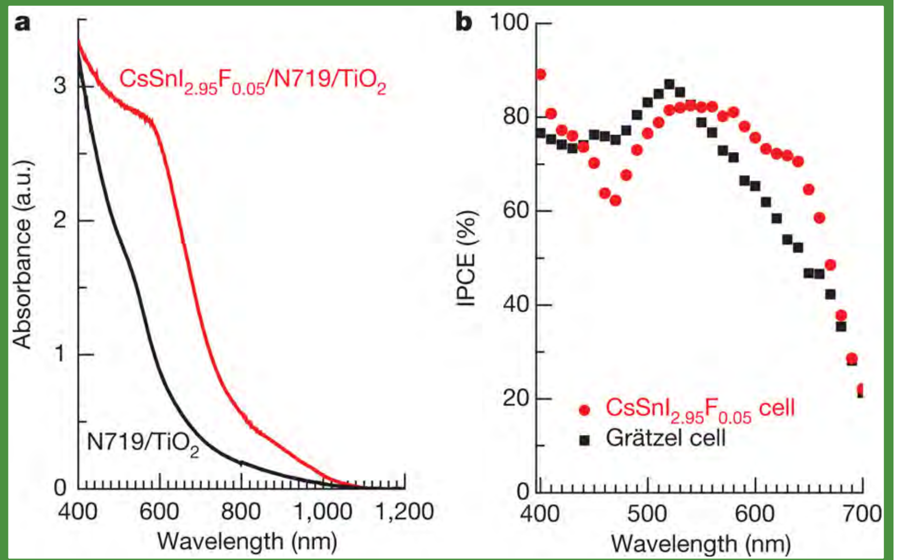


Most widely employed hole conductor remains spiro-MeOTAD

U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer and M. Grätzel "Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to- electron conversion efficiencies” ***Nature*** 1998, *395*, 583–585.

Year 2012 Landmark paper fpr PSCs

Chung, I., Lee, B., He, J., Chang, R. P. H. & Kanatzidis, M. G. **All-solid-state dye-sensitized solar cells with high efficiency** *Nature* **485,** 4478?6?–4?8?9 (2012).

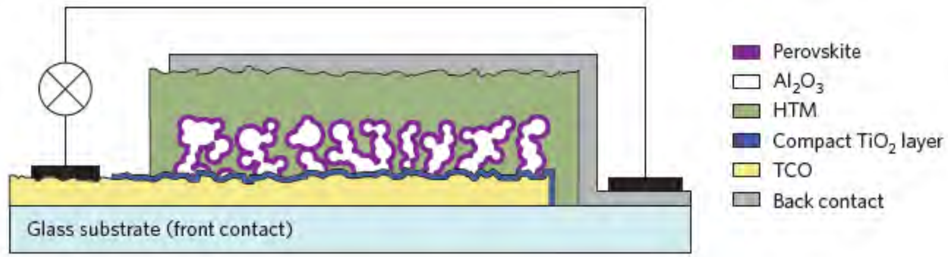


Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Science 2012

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

Electron conduction assumed by $CH_3NH_3PbI_3$ →



H.S.Kim, C.R.Lee, J.H.Im, K.B. Lee, T. Moehl, A. Marchioro, S.J.Moon, R. R.Humphry Baker, J.H.Yum, J.E. Moser, M. Grätzel, N.G. Park,
Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%, Sci.Reports 2, 591 (2012)

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Mesoscopic $CH_3NH_3PbI_3/TiO_2$ Heterojunction Solar Cells

Lioz Etgar,[*,†,§] Peng Gao,[†] Zhaosheng Xue,[‡] Qin Peng,[†] Aravind Kumar Chandiran,[†] Bin Liu,[‡] Md. K. Nazeeruddin,[†] and Michael Grätzel[†]

← Hole conduction assumed by PSC

SCIENTIFIC REPORTS

OPEN

Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%

SUBJECT AREAS:
NANOPHOTONICS
OPTICAL MATERIALS AND DEVICES
INORGANIC CHEMISTRY
APPLIED PHYSICS

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21 August 2012

Hui-Seon Kim[1], Chang-Ryul Lee[1], Jeong-Hyeok Im[1], Ki-Beom Lee[1], Thomas Moehl[2], Arianna Marchioro[2], Soo-Jin Moon[2], Robin Humphry-Baker[2], Jun-Ho Yum[2], Jacques E. Moser[2], Michael Grätzel[2] & Nam-Gyu Park[1]

[1]School of Chemical Engineering and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea, [2]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

Correspondence and requests for materials should be addressed to M.G. (michael.graetzel@epfl.ch) or N.-G.P. (npark@skku.

We report on solid-state mesoscopic heterojunction solar cells empl ammonium lead iodide $(CH_3NH_3)PbI_3$ as light harvesters. The perov methylammonium iodide with PbI_2 and deposited onto a submicro pores were infiltrated with the hole-conductor *spiro*-MeOTAD. Illum generated large photocurrents (J_{SC}) exceeding 17 mA/cm², an open and a fill factor (FF) of 0.62 yielding a power conversion efficiency date for such cells. Femto second laser studies combined with phot showed charge separation to proceed via hole injection from the ex *spiro*-MeOTAD followed by electron transfer to the mesoscopic TiO_2 dramatically improved the device stability compared to $(CH_3NH_3)P$

Sciencexpress

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

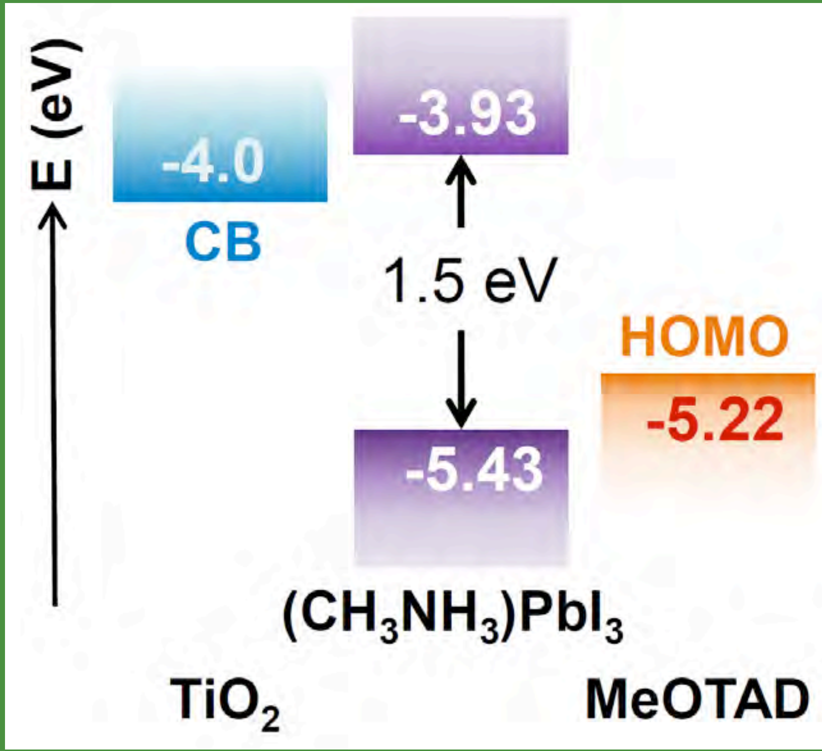
Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1*]

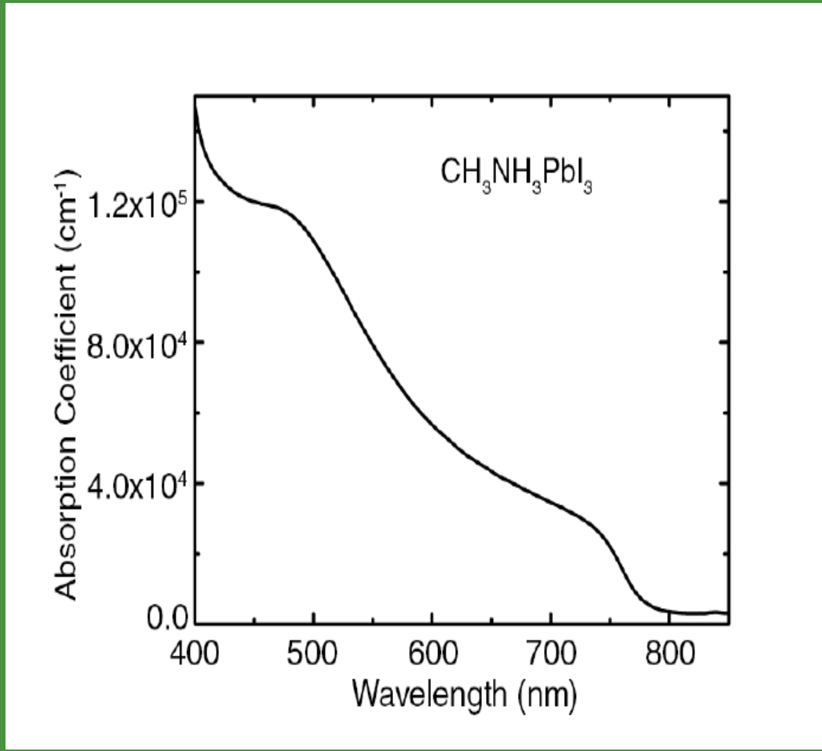
[1]Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, UK. [2]Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane, Aoba, Yokohama 225-8503, Japan. [3]Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

*To whom correspondence should be addressed. E-mail: h.snaith1@physics.ox.ac.uk

The energy cost associated with separating tightly-bound excitons, photo-generated electron-hole pairs, and extracting free charges from highly disordered low mobility networks represent fundamental losses for many low-cost photovoltaic technologies. We report a low-cost, solution-processable solar cell based on a highly crystalline perovskite absorber with intense visible-to-near-infrared absorptivity that has a power conversion efficiency of 10.9% in a single junction device under simulated full sunlight. This "meso-superstructured solar cell" (MSSC) exhibits exceptionally few fundamental energy losses illustrated by generating open-circuit photovoltages of over 1.1 volts, despite the relatively narrow absorber band gap of 1.55 electron volts. The functionality arises from the use of mesoporous alumina as an inert scaffold which structures the absorber and forces electrons to reside in and be transported through the perovskite.

Band alignement of pervoskite/TiO_2/spiro-MeOTAD heterojunction solar cells





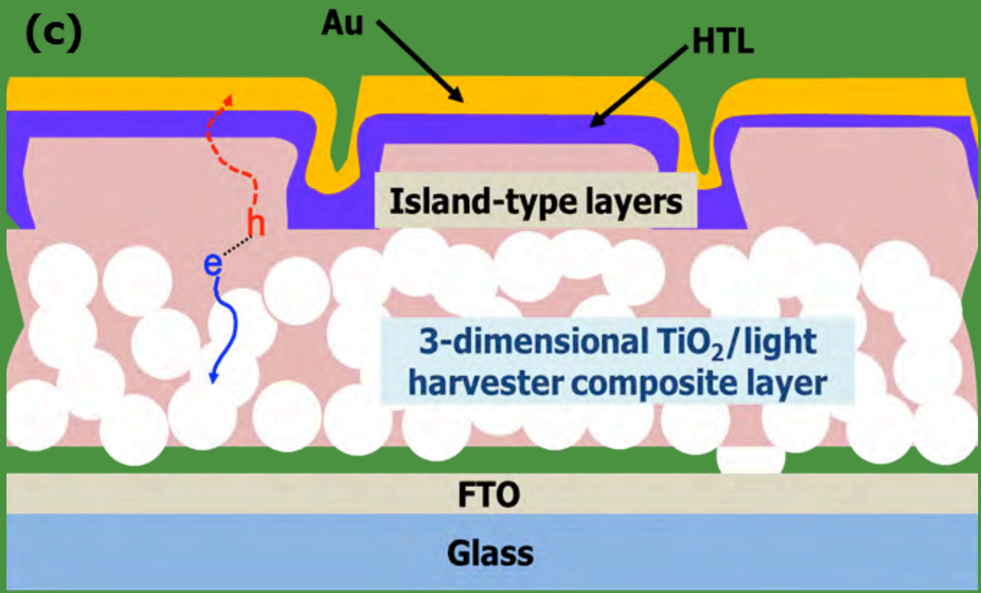
$CH_3NH_3PbI_3$:

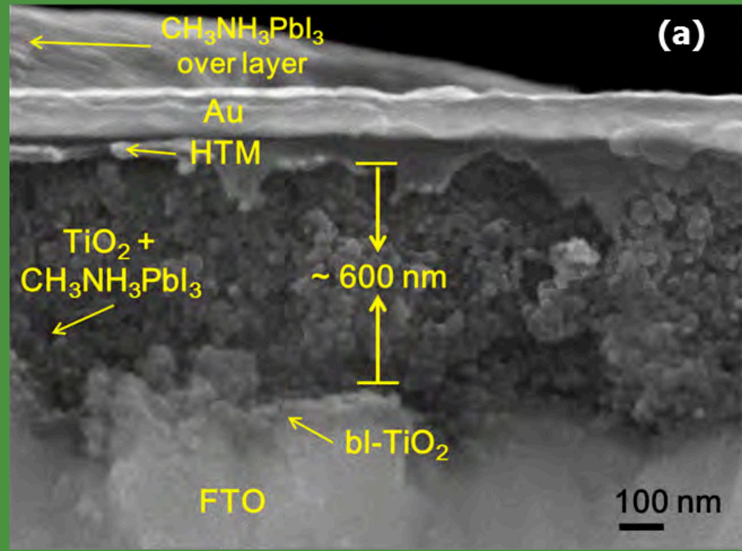
Ambipolar semiconductor band gap 1.55 eV

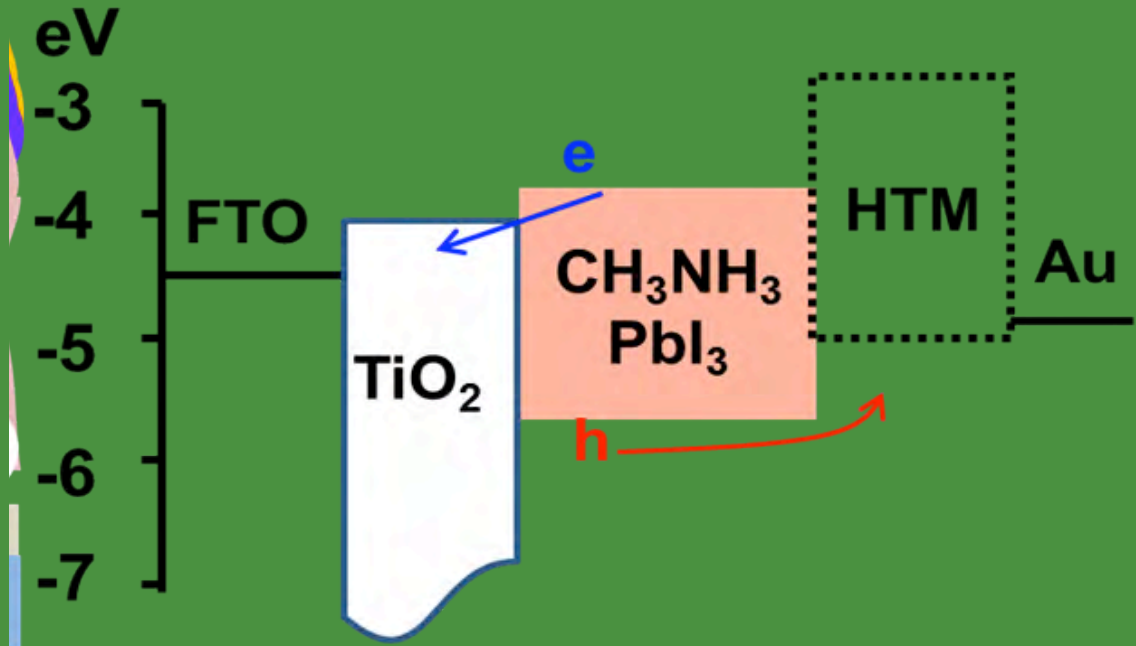
Bohr radius of the first exciton: 2 nm

Exciton binding energy 10 -30 meV, exciton dissociation time 1-2 ps

Infiltration of mesoporous TiO_2 scaffold by perovskite enhances light harvesting







Seok et.al Nature Photonics (2013), 7(6), 486-491.

LETTER

Nature, 499, 316-319 (2013) article
announces leap of conversion efficiency from ca 10% to 15%

Sequential deposition as a route to high-performance perovskite-sensitized solar cells

Julian Burschka[1]*, Norman Pellet[1,2]*, Soo-Jin Moon[1], Robin Humphry-Baker[1], Peng Gao[1], Mohammad K. Nazeeruddin[1] & Michael Grätzel[1]

1300 citations in 2 years !

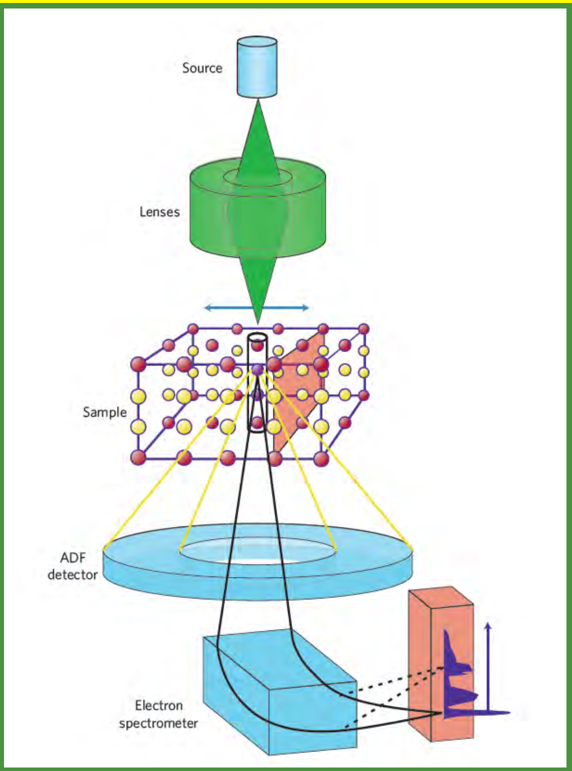
Following pioneering work[1], solution-processable organic–inorganic hybrid perovskites—such as $CH_3NH_3PbX_3$ (X = Cl, Br, I)—have attracted attention as light-harvesting materials for mesoscopic solar cells[2–15]. So far, the perovskite pigment has been deposited in a single step onto mesoporous metal oxide films using a mixture of PbX_2 and CH_3NH_3X in a common solvent. However, the uncontrolled precipitation of the perovskite produces large morphological variations, resulting in a wide spread of photovoltaic performance in the resulting devices, which hampers the prospects for practical applications. Here we describe a sequential deposition method for the formation of the perovskite pigment within the porous metal oxide film. PbI_2 is first introduced from solution into a nanoporous titanium dioxide film and subsequently transformed into the perovskite by exposing it to a solution of CH_3NH_3I. We find that the conversion occurs within the nanoporous host as soon as the two components come into contact, permitting much better control over the perovskite morphology than is possible with the previously employed route. Using this technique for the fabrication of solid-state mesoscopic solar cells greatly increases the reproducibility of their performance and allows u[...] to achieve a power conversion efficiency of approximately 15 pe[...] cent (measured under standard AM1.5G test conditions on sola[...] zenith angle, solar light intensity and cell temperature). This tw[...] step method should provide new opportunities for the fabrication of solution-processed photovoltaic cells with unprecedented power conversion efficiencies and high stability equal to or even greater than those of today's best thin-film photovoltaic devices.

EPFL/LPI Graduate students Norman Pellet (left) and Julian Burschka (right)

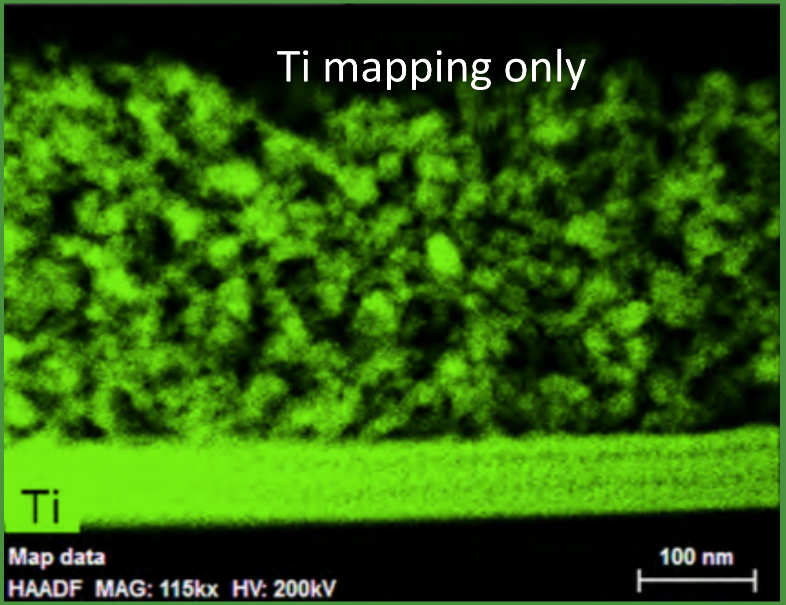
emission and X-ray diffraction (XRD) spectroscopy. Figure 1b shows that the increase over time of the perovskite absorption at 550 nm is

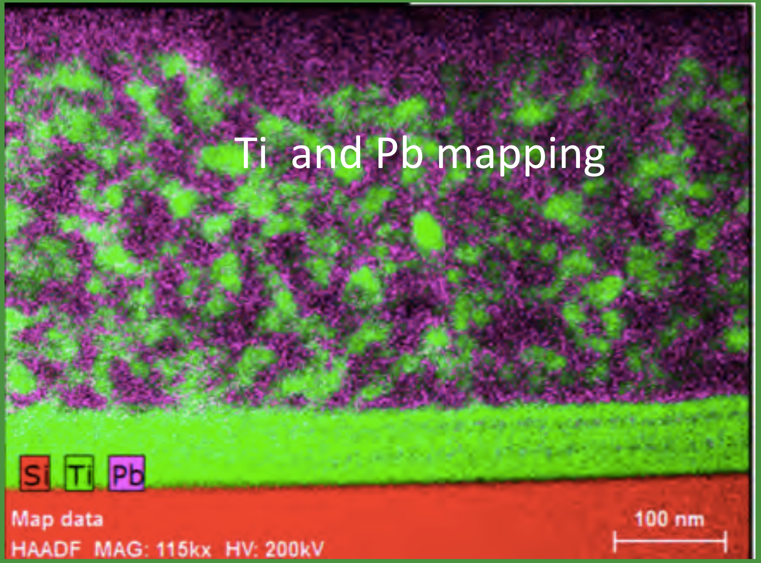
STEM –EDS elemental Mapping shows complete infiltration of mesoporous TiO_2 by perovskite

STEM –EDS images from a a thin slab carved out by ion milling from a mesoporous TiO_2 film infiltrated with $CH_3NH_3PbI_3$ by sequential deposition
Courtesy: Dr. Ibrahim Dar, EPFL, 2015



Scanning transmission electron microscope + energy dispersive X-ray spectroscopy





Outline

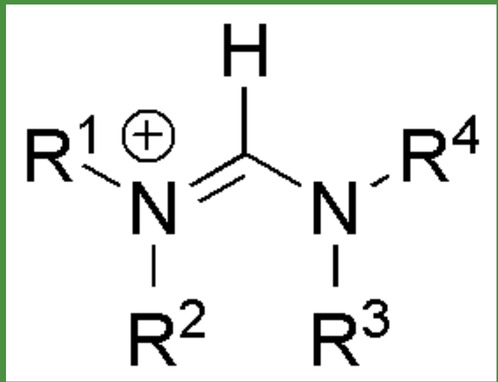
- The advent of perovskite solar cells
- Mixed cation/anion formulations, effect of stoichiometric PbI2 excess on PV performance
- Lithium doping of mesocopic TiO_2 scaffold
- New hole conducots
- Planar configurations
- Tandem cells
- Stability

Today's most efficient pervoskite solar cells employ mixtures of A cations and iodide /bromide as anion

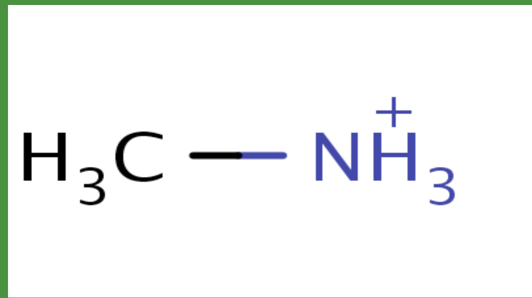
General composition $FA_{1-x}MA_xPb(I_{1-x}Br_x)$

FA =

formamidinium



$R^1 - R^4 = H$



X = 0.15 gives optimal results

MA = methylammonium

N. Pellet *et al.*, Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar -Light Harvesting. *Angew. Chem. Int. Ed.* **53**, 3151-3157 (2014).

N. J. Jeon *et al.*, Compositional engineering of perovskite materials for high-performance solar cells. *Nat.* **517**, 476-480 (2015).

Angew.Chem: Int. Ed. 2014

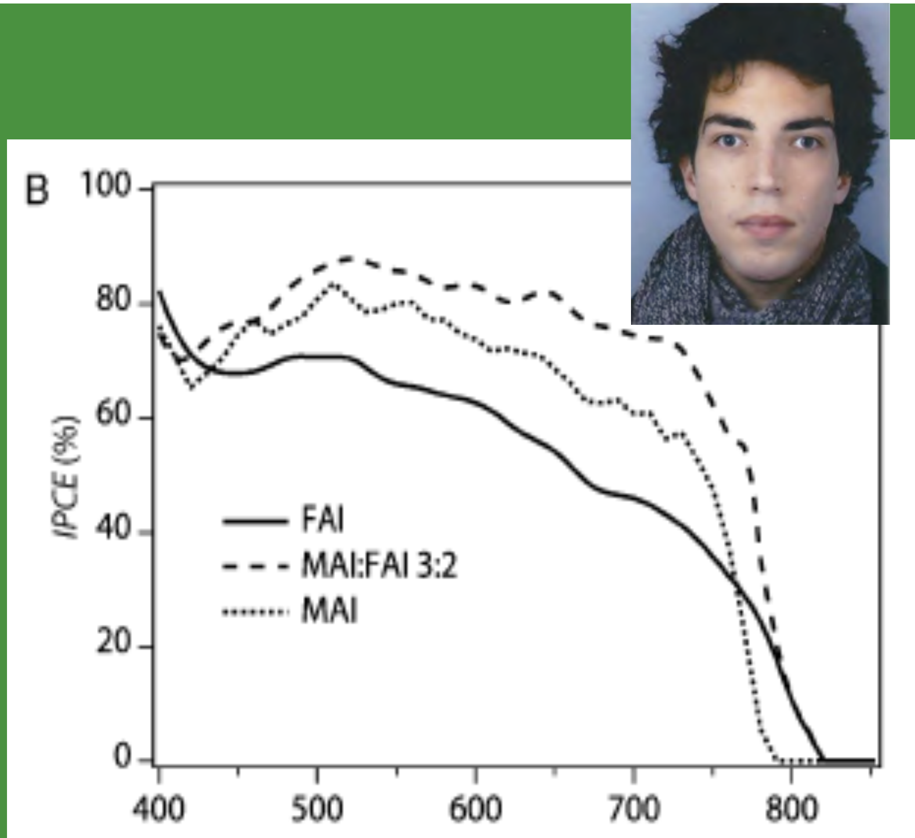
Perovskite Solar Cells

DOI: 10.1002/anie.201309361

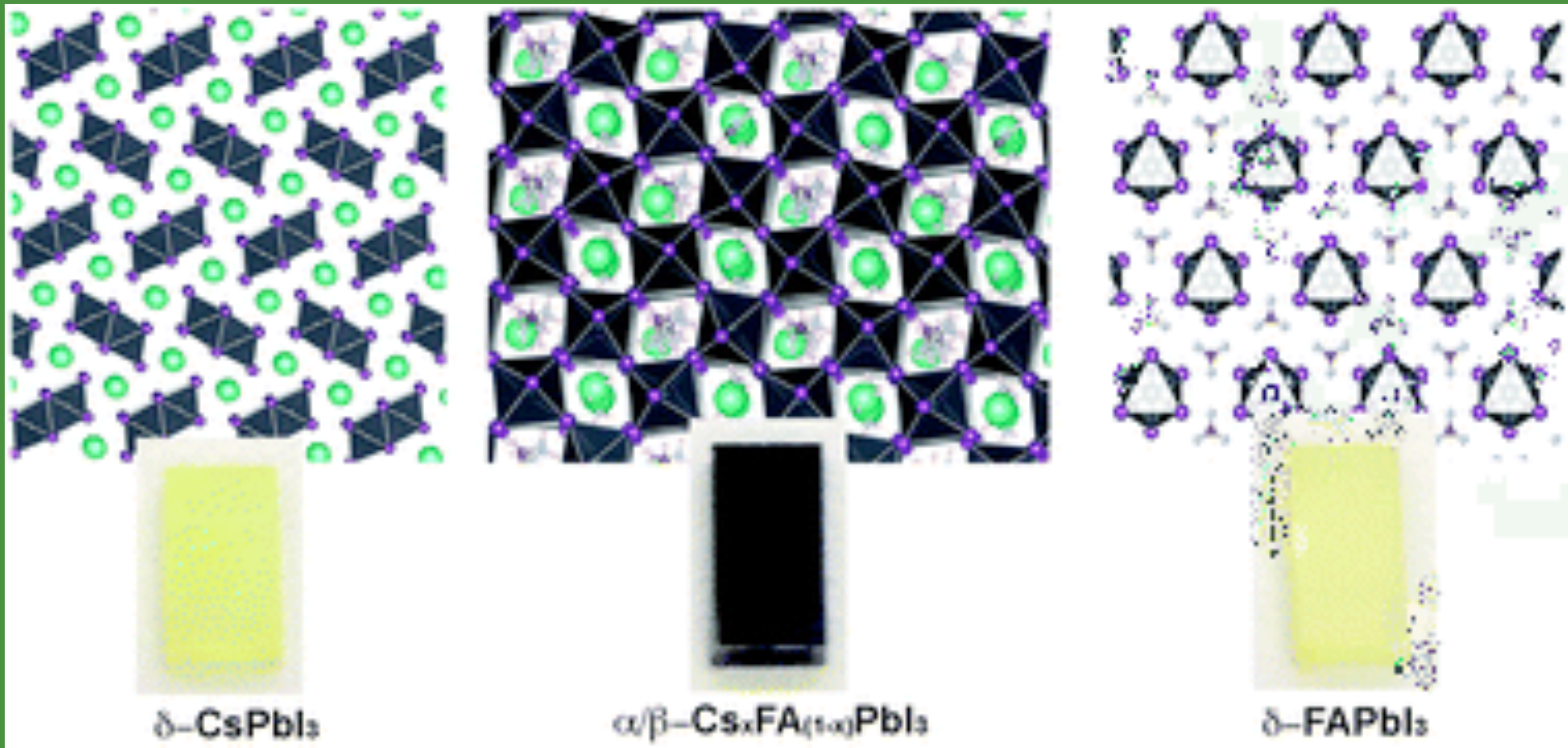
Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting**

*Norman Pellet, Peng Gao, Giuliano Gregori, Tae-Youl Yang, Mohammad K. Nazeeruddin, Joachim Maier, and Michael Grätzel**

Abstract: *Hybrid organic–inorganic lead halide perovskite $APbX_3$ pigments, such as methylammonium lead iodide, have recently emerged as excellent light harvesters in solid-state mesoscopic solar cells. An important target for the further improvement of the performance of perovskite-based photovoltaics is to extend their optical-absorption onset further into the red to enhance solar-light harvesting. Herein, we show that this goal can be reached by using a mixture of formamidinium ($HN{=}CHNH_3^+$, FA) and methylammonium ($CH_3NH_3^+$, MA) cations in the A position of the $APbI_3$ perovskite structure. This combination leads to an enhanced short-circuit current and thus superior devices to those based on only $CH_3NH_3^+$. This concept has not been applied previously in perovskite-based solar cells. It shows great potential as a versatile tool to tune the structural, electrical, and optoelectronic properties of the light-harvesting materials.*



Entropic stabilisation of mixed Cs+ /formamidinium cation perovskites



The stable fprms pf $CsPbI_3$ and $FaPbI_3$ are non –perovskite delta phases at room temperature
Amazingly, upon mixing a stable peroxide structure forms spontaneously

Energy & Environmental Science

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5ee03255e

Entropic stabilization of mixed A-cation ABX_3 metal halide perovskites for high performance perovskite solar cells†

Chenyi Yi,[a] Jingshan Luo,[a] Simone Meloni,[b] Ariadni Boziki,[b] Negar Ashari-Astani,[b] Carole Grätzel,[a] Shaik M. Zakeeruddin,[a] Ursula Röthlisberger*[b] and Michael Grätzel*[a]

ABX_3-type organic lead halide perovskites currently attract broad attention as light harvesters for solar cells due to their high power conversion efficiency (PCE). Mixtures of formamidinium (FA) with methylammonium (MA) as A-cations show currently the best performance. Apart from offering better solar light harvesting in the near IR the addition of methylammonium stabilizes the perovskite phase of $FAPbI_3$ which in pure form at room temperature converts to the yellow photovoltaically inactive δ-phase. We observe a similar phenomenon upon adding Cs^+ cations to $FAPbI_3$. $CsPbI_3$ and $FAPbI_3$ both form the undesirable yellow phase under ambient condition while the mixture forms the desired black pervoskite. Solar cells employing the composition $Cs_{0.2}FA_{0.8}PbI_{2.84}Br_{0.16}$ yield high average PCEs of over 17% exhibiting negligible hysteresis and excellent long term stability in ambient air. We elucidate here this remarkable behavior using first principle computations. These show that the remarkable stabilization of the perovskite phase by mixing the A-cations stems from entropic gains and the small internal energy input required for the formation of their solid solution. By contrast, the energy of formation of the delta-phase containing mixed cations is too large to be compensated by this configurational entropy increase. Our calculations reveal for the first time the optoelectronic properties of such mixed A-cation perovskites and the underlying reasons for their excellent performance and high stability.

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Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency†

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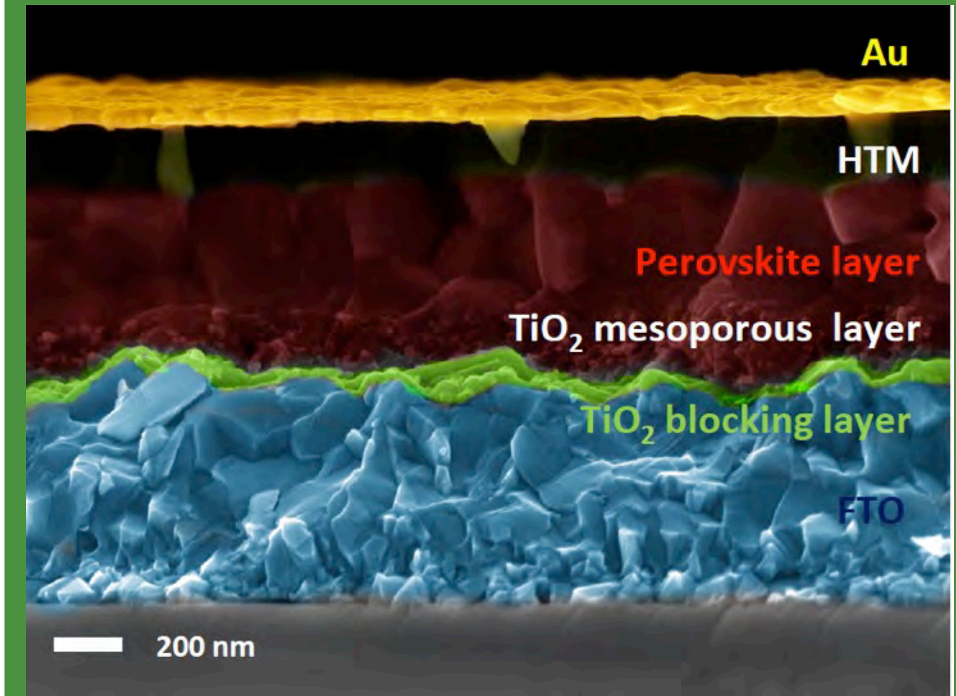
Today's best perovskite solar cells use a mixture of formamidinium and methylammonium as the monovalent cations. With the addition of inorganic cesium, the resulting triple cation perovskite compositions are thermally more stable, contain less phase impurities and are less sensitive to processing conditions. This enables more reproducible device performances to reach a stabilized power output of 21.1% and ~18% after 250 hours under operational conditions. These properties are key for the industrialization of perovskite photovoltaics.

Broader context

Due to their enormous potential for use in the future of photovoltaics, perovskite solar cells have attracted much attention recently. However, achieving stable and reproducible high efficiency results is a major concern towards industrialization. To date, the best perovskite solar cells use mixed organic cations (methylammonium (MA) and formamidinium (FA)) and mixed halides. Unfortunately, MA/FA compositions are sensitive to processing conditions because of their intrinsic structural and thermal instability. The films frequently contain detrimental impurities and tend

Electroluminescent PSCs based on tailored mixed cation perovskites use stochiometric excess of PbI_2

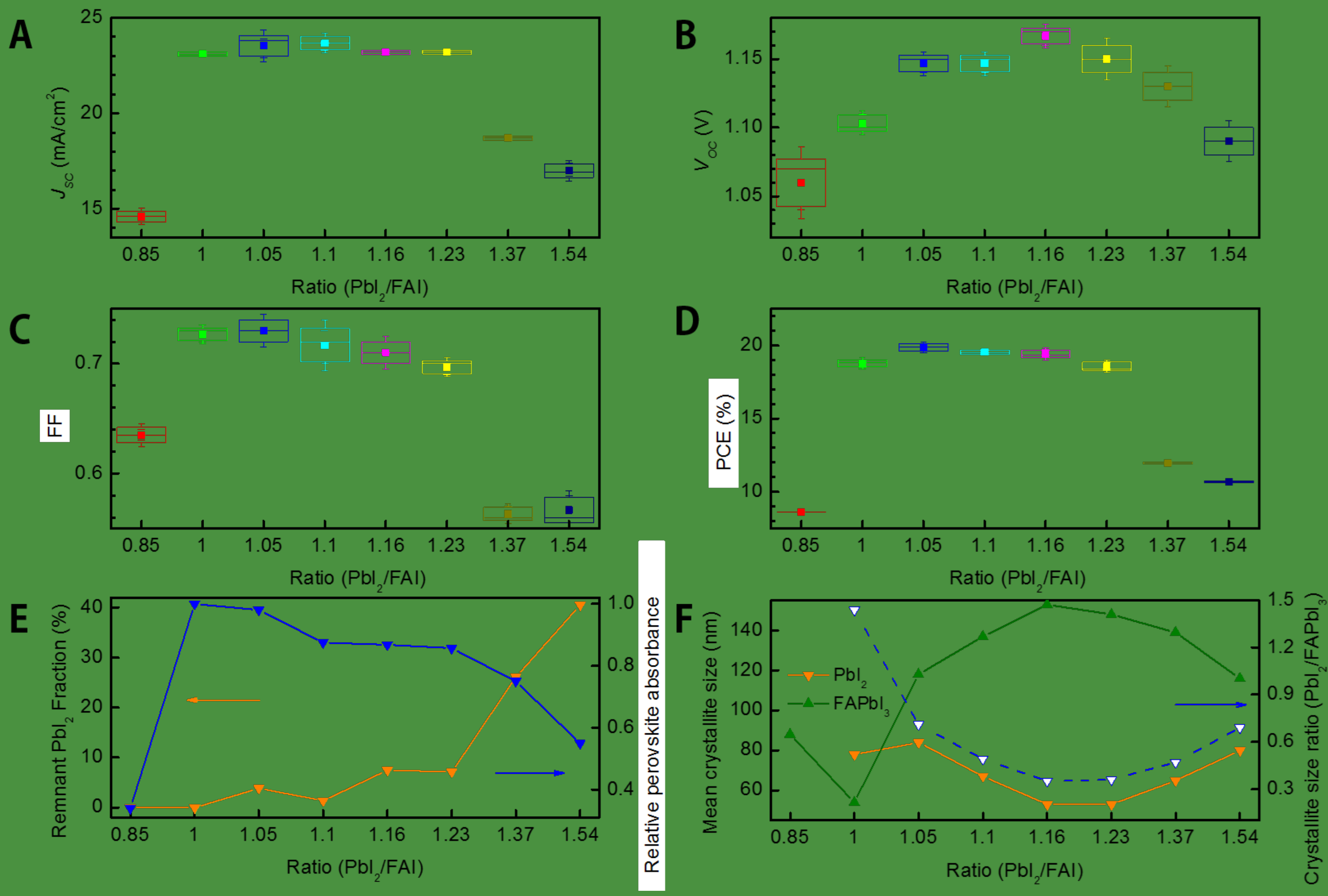
Dongqin Bi, Wolfgang Tress, M. Ibrahim Dar, Peng Gao, Jingshan Luo, Clémentine Renevier, Kurt Schenk, Antonio Abate, Fabrizio Giordano, Juan-Pablo Correa Beana, Jean- David Decoppet, Shaik M. Zakeeruddin, M.Khaja Nazeeruddin, Michael Grätzel and Anders Hagfeldt



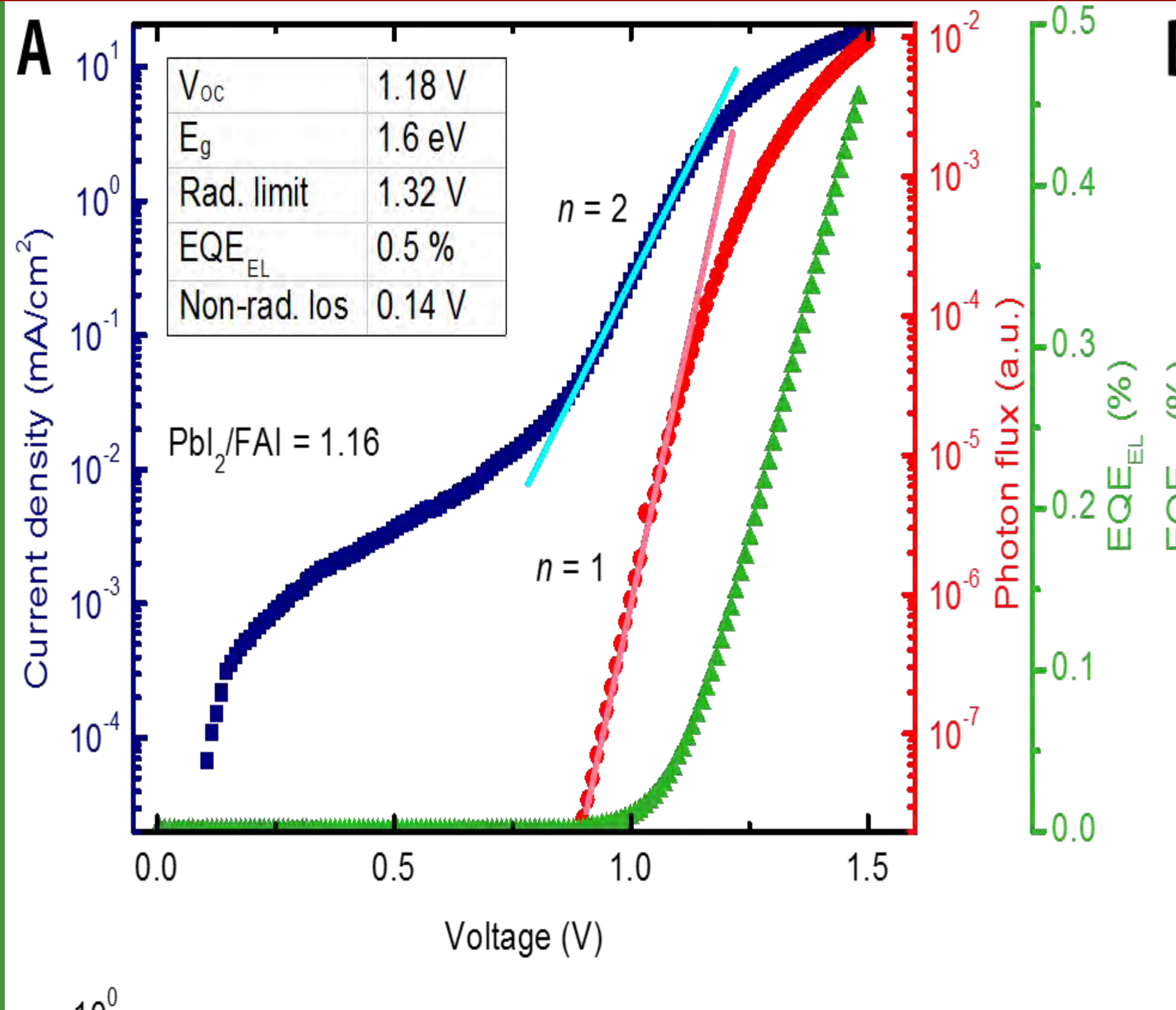
Bi et al. Sci. Adv. 2016;2:e1501170 1 January 2016

- Single step from a solution containing a mixture of FAI, PbI2, MABr and PbBr2
- Mesoporous TiO2 and spiro-MeOTAD
- Molar ratio of PbI2/FAI of 1.05 in the precursor solution.
- Excess PbI2 content is about 3 weight %.
- Excess of PbI2 suppresses non-radiative charge carrier recombination.
- External electroluminescence quantum efficiency 0.5 % at a voltage of 1.5 V

Effect of excess stochiometric PbI_2 on the photovoltaic metrics of mixed cation PSCs



Electroluminescence of pervoskite solar cell



The open circuit photo-voltage of a photovoltaic cell is linked to its external emission quantum yield at open circuit

$$V_{oc} = V_{oc\text{-}ideal} + (kT/q)\ln\phi_{ext}$$

$$V_{oc\text{-}ideal} \simeq E_g - 0.3\ \text{V} \quad \text{(for silcon)}$$

E_g = band gap energy expressed in electron volt
ϕ_{ext} = external quantum yield of light emission by the PV cell under open circuit condition

Ross, R. T. *J. Chem. Phys.* **46,** 4590 (1967).

Materials Views — *Adv. Energy Mater.* **2014**, 1400812 — ADVANCED ENERGY MATERIALS

www.MaterialsViews.com www.advenergymat.de

Predicting the Open-Circuit Voltage of $CH_3NH_3PbI_3$ Perovskite Solar Cells Using Electroluminescence and Photovoltaic Quantum Efficiency Spectra: the Role of Radiative and Non-Radiative Recombination

Wolfgang Tress, Nevena Marinova, Olle Inganäs, Mohammad. K. Nazeeruddin, Shaik M. Zakeeruddin, and Michael Graetzel*

The maximum open circuit photovoltage of a $CH_3NH_3PbI_3$ based photovoltaic under standard AM 1.5 illumination is 1.55 – 0.23 = 1.32 V

Urbach energy reflects degree of disorder

- Characteristic of the structural disorder
- $EQE(E) = F_0 e^{(E-E_1)/E_0}$ where Eo is the Urbach energy
- Urbach energy around 15meV: low disorder
- Urbach energy is smaller for cells with the highest Voc

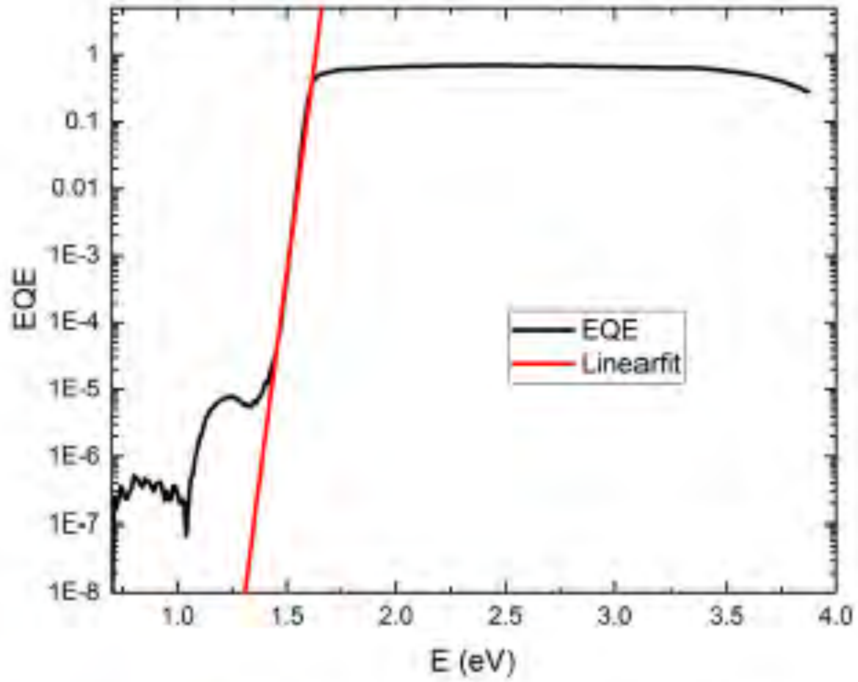


Figure 11: *Logarithmic EQE (from FTPS measurement) fitted with a line. The inverse of the slope is the Urbach energy.*

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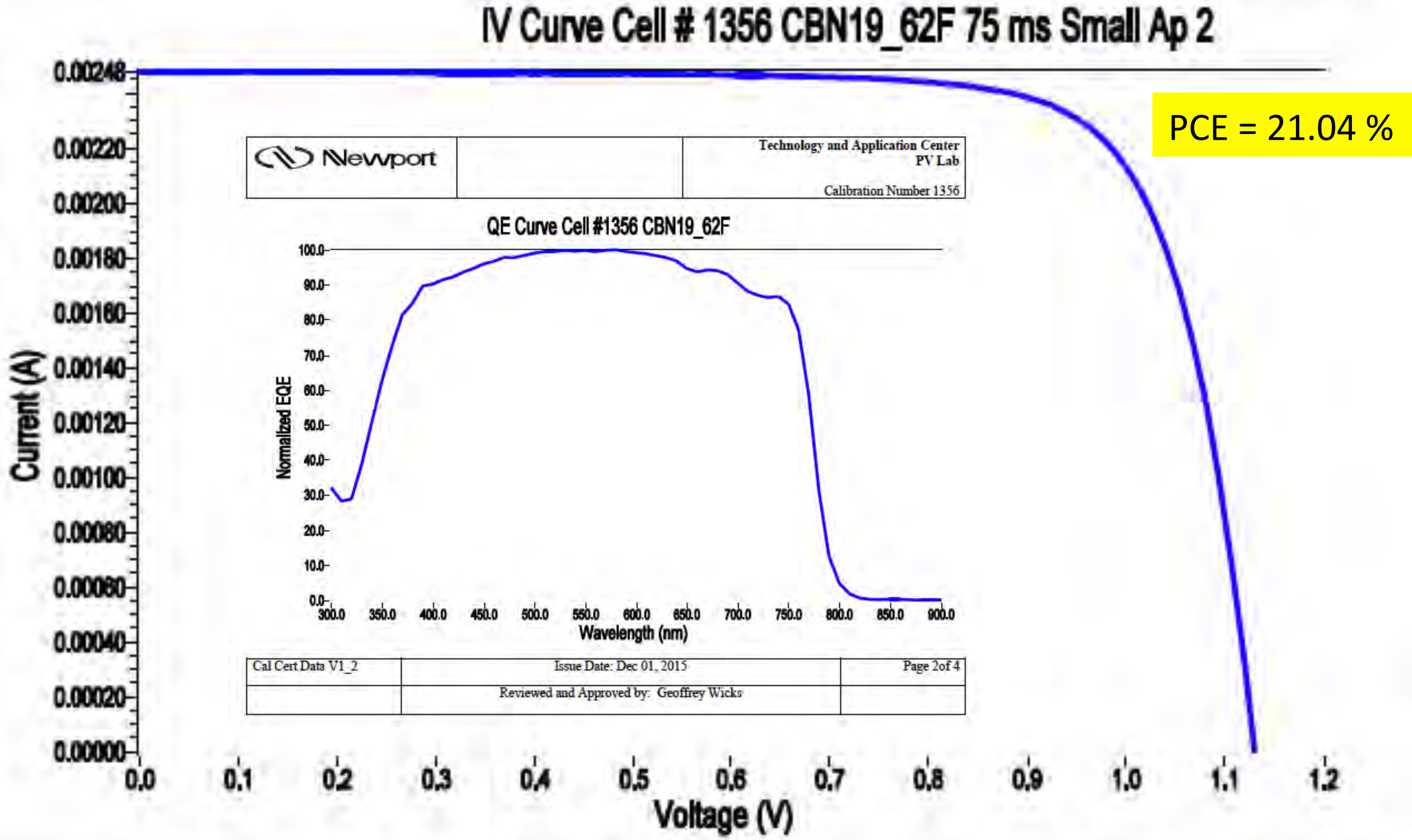
PV Lab

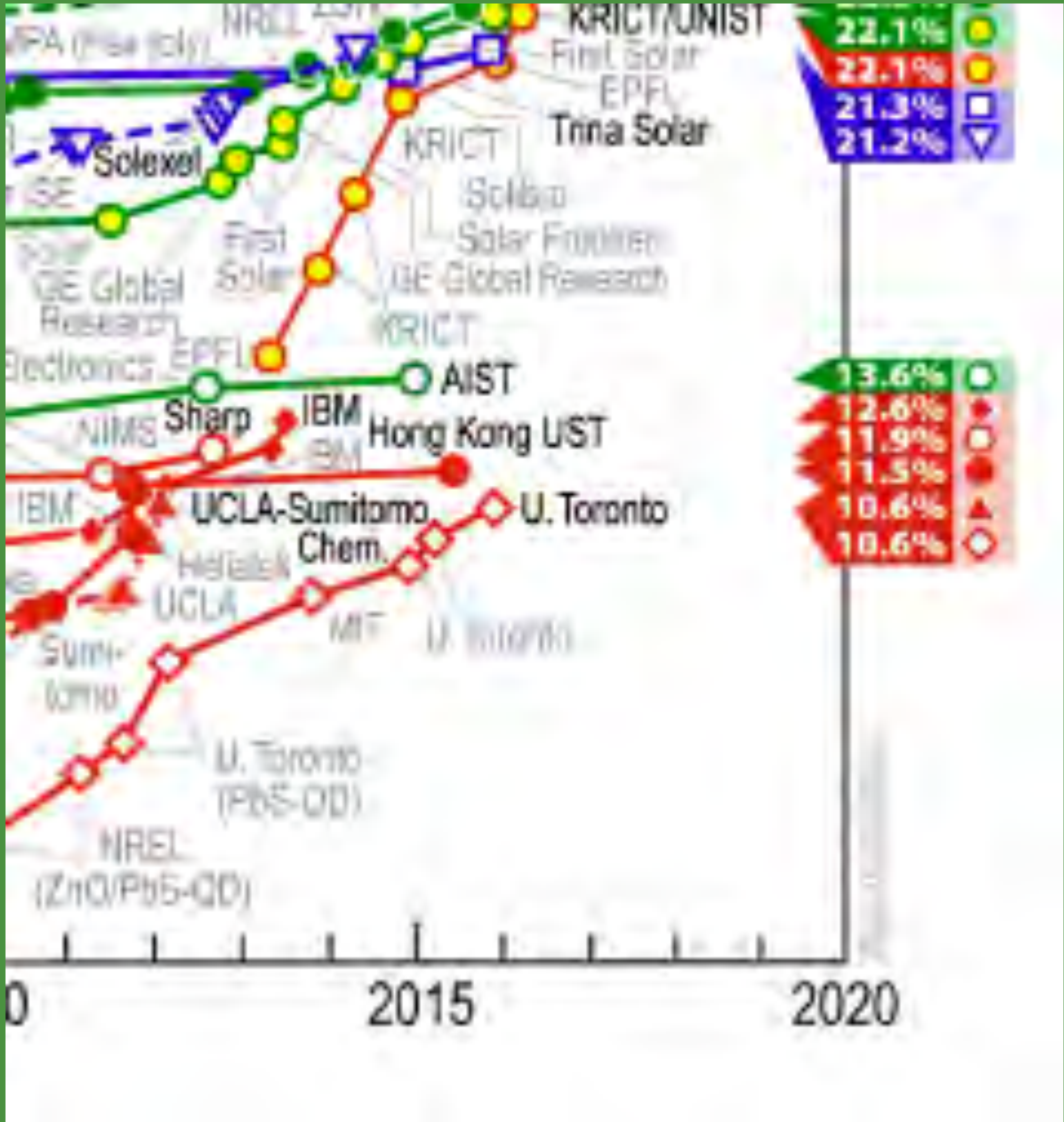
Calibration Number 1356

Certification of 21 % efficient pervoskite solar cell made by EPFL



Cal Cert Data V1_2	Issue Date: Dec 01, 2015	Page 1of 4
	Reviewed and Approved by: Geoffrey Wicks	

Presently PSC record efficiency stands at 22.1 % surpassing polycrystalline silicon cells

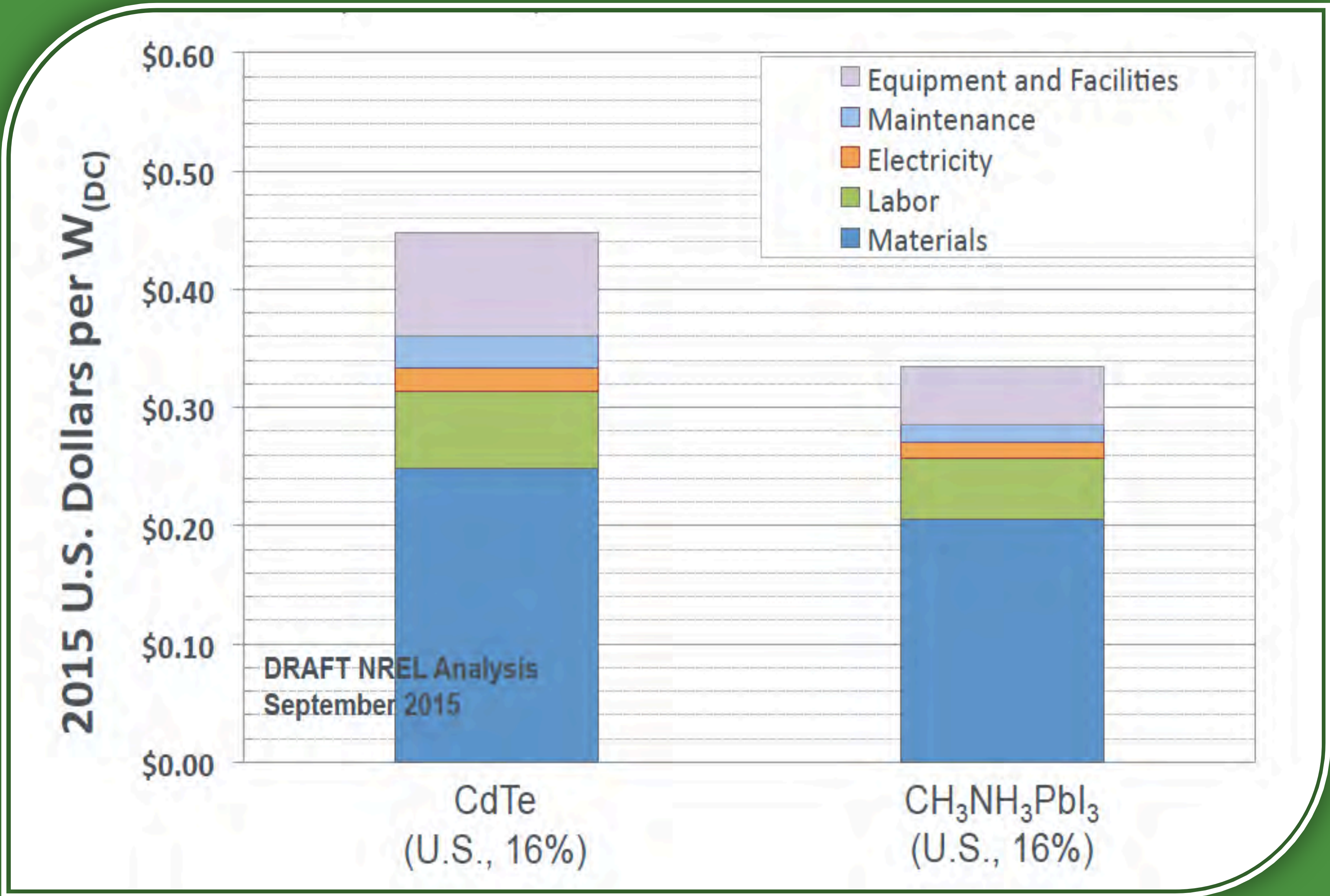


NREL chart showing certified efficiencies of best laboratory cells

Dr. Dongqin Bi, LSPM, EPFL

Prof. Anders Hagfeldt.
Director LSPM. EPFL

Perovskite solar cells offer lowest cost of all photovoltaic technologies



Courtesy Martin Green

Outline

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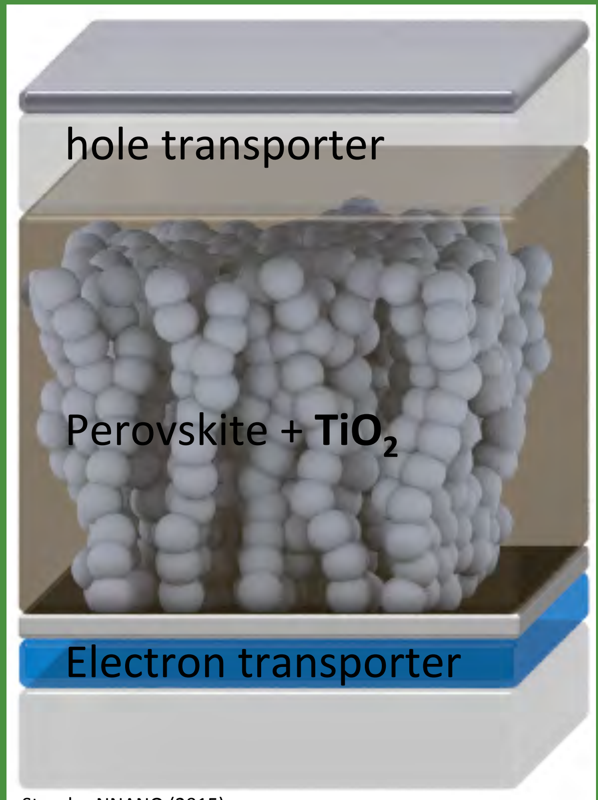
- New hole conductors
- Planar configurations
- Tandem cells
- Stability

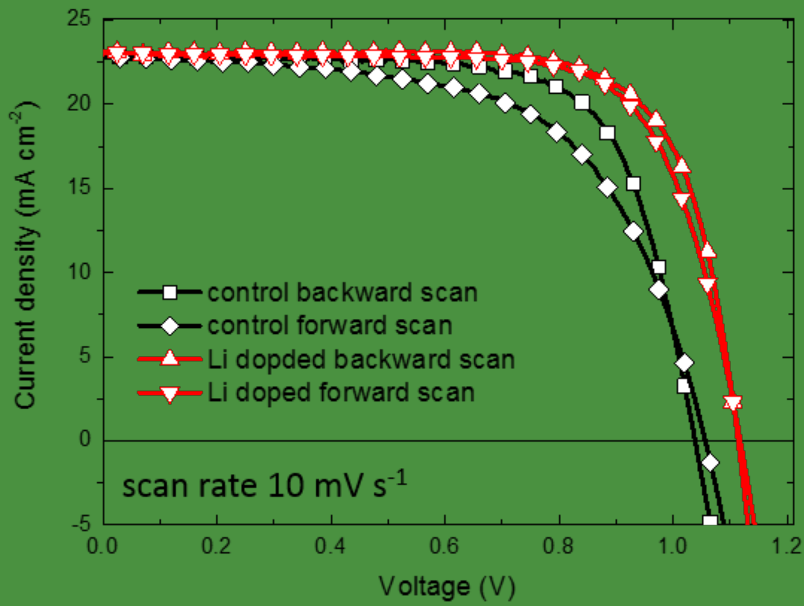
Lithium Doping of Mesoporous TiO_2

Dr. Fabrizio Giordano

Mr. Taisuke Matsui



Stranks, NNANO (2015)

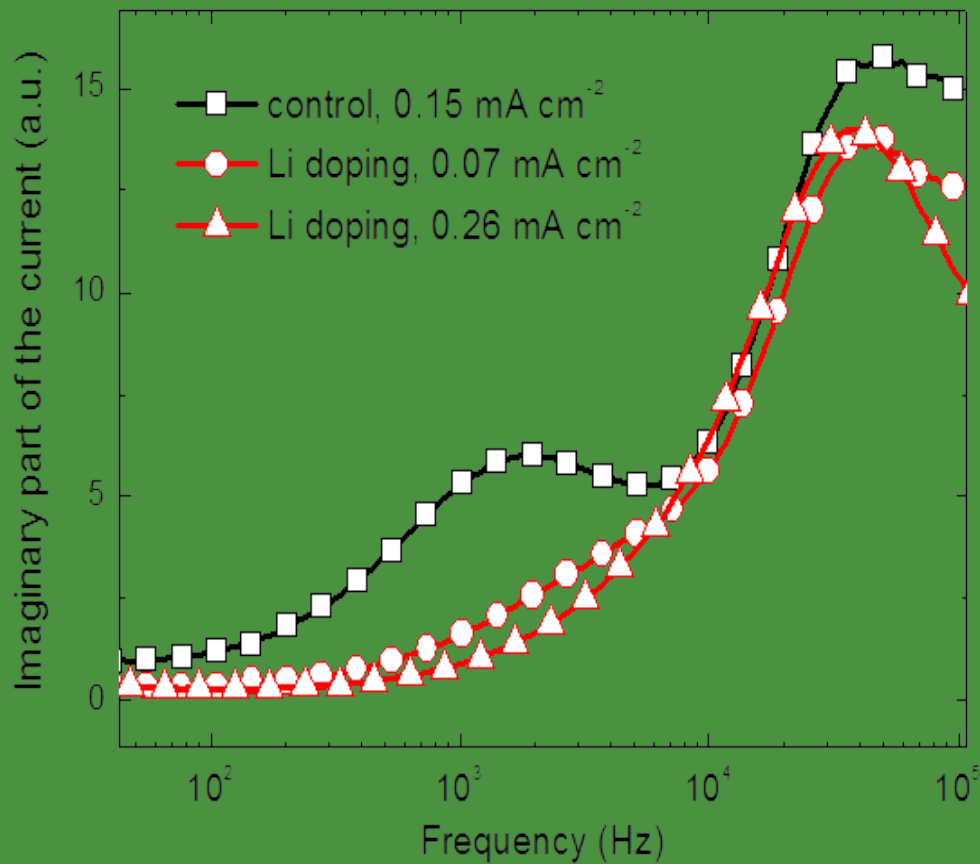


	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	Eff (%)
Li doped	23.0	1.11	0.74	**19.3**
control	22.7	1.04	0.72	**17.1**

Li treatment improves electron transport in TiO_2

F. Giordano, A. Abate, J.-P. Correa Baena, M. Saliba, T. Matsui, S. M. Zakeeruddin, M. K. Nazeeruddin, A. Hagfeldt, M. Graetzel, *Enhanced Electronic Properties in Mesoporous TiO2 via Lithium Doping for High Efficiency Perovskite Solar Cells* (submitted)

Intensity modulated photocurrent spectroscopy shows faster electron transport by Li^+ doping of TiO_2 scaffold



Imaginary component of the intensity-modulated photocurrent spectra collected for the PSCs prepared with Li doped and bare mesoporous TiO_2.

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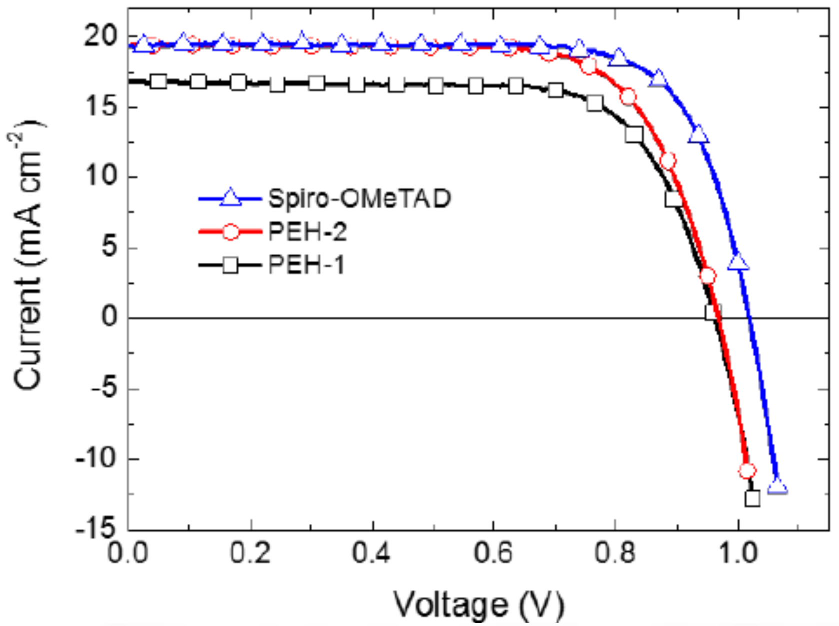
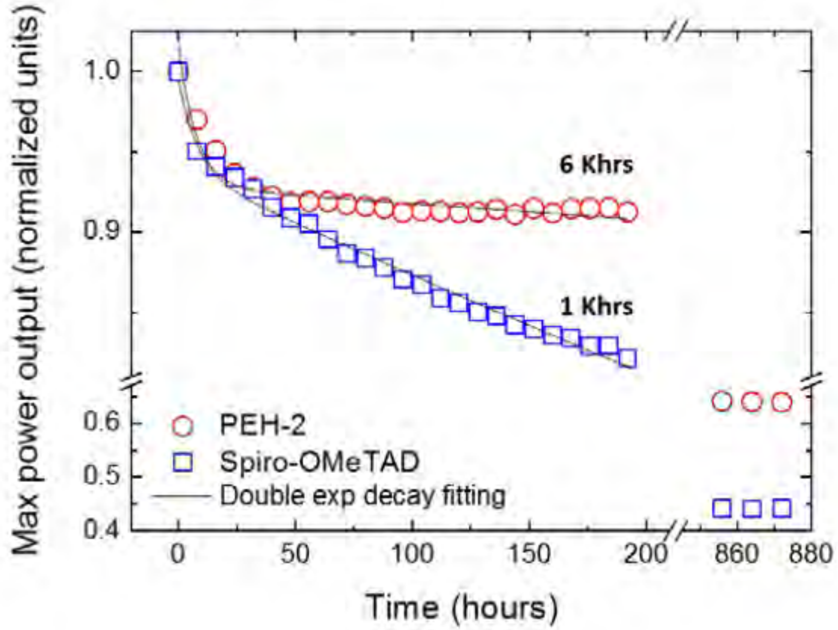
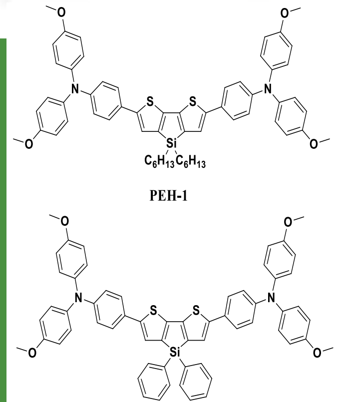
Hole Transporting Materials for Stability

Dr. Antonio Abate





	J_{sc} ($mA\ cm^{-2}$)	V_{oc} (V)	FF	R_s ($Ohm\ cm^{-2}$)	PCE (%)
Spiro-MeTAD	19.4	1.02	0.76	44	15.2
PEH-2	19.4	0.97	0.72	87	13.5
PEH-1	16.8	0.96	0.72	103	11.7



Higher Stability with less efficient materials!

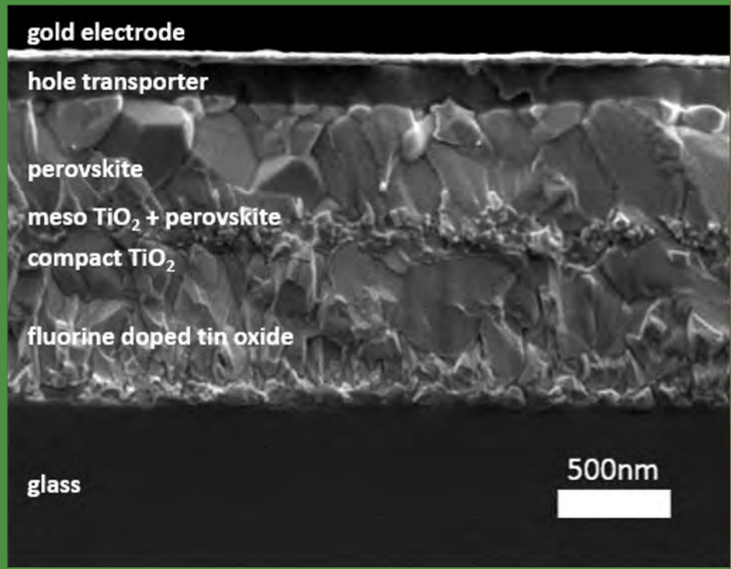
A. Abate, S. Paek, F. Giordano, J.-P. Correa-Baena, M. Saliba, P. Gao, T. Matsui, J. Ko, S. M. Zakeeruddin, K. H. Dahmen, A. Hagfeldt, M. Grätzel, M. K. Nazeeruddin, *Silolothiophene-linked triphenylamines as stable hole transporting materials for high efficiency perovskite solar cells*, **Energy & Environmental Science** (2015)

New Hole Transporting Materials for High Efficiency

Dr. Michael Saliba

Taisuke Matsui

a



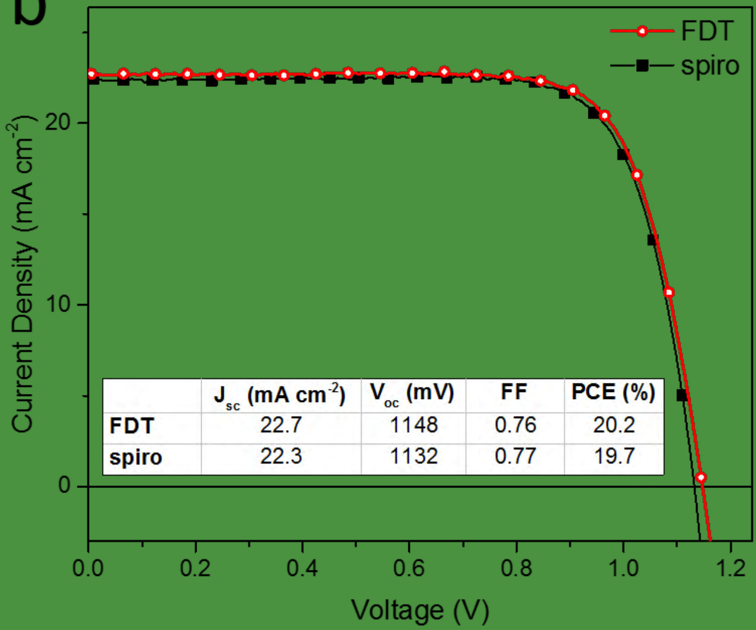
J_{sc} = 22.7 mA/cm^2

V_{oc} = 1.15 V

FF = 0.76

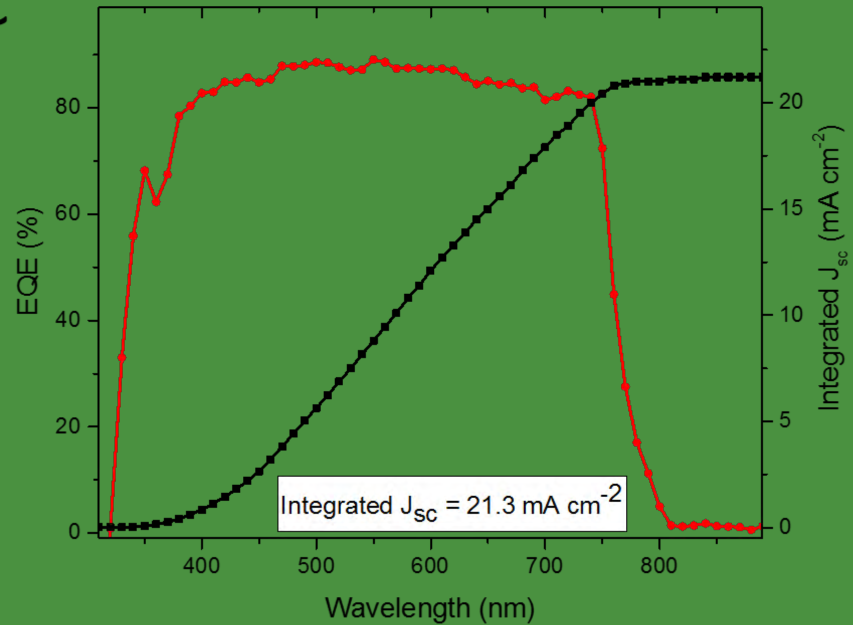
PCE = 20.20 %

b



	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	PCE (%)
FDT	22.7	1148	0.76	20.2
spiro	22.3	1132	0.77	19.7

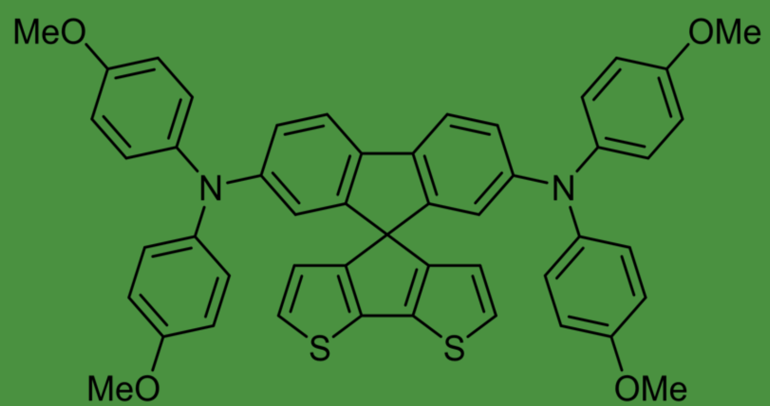
c



Molecular structure of 2',7'-Bis(bis(4-methoxyphenyl)amino)spiro[cyclopenta[2,1-b:3,4-b']dithiophene-4,9'-fluorene, refered to as **FDT**

Simonetta Orlandi

a



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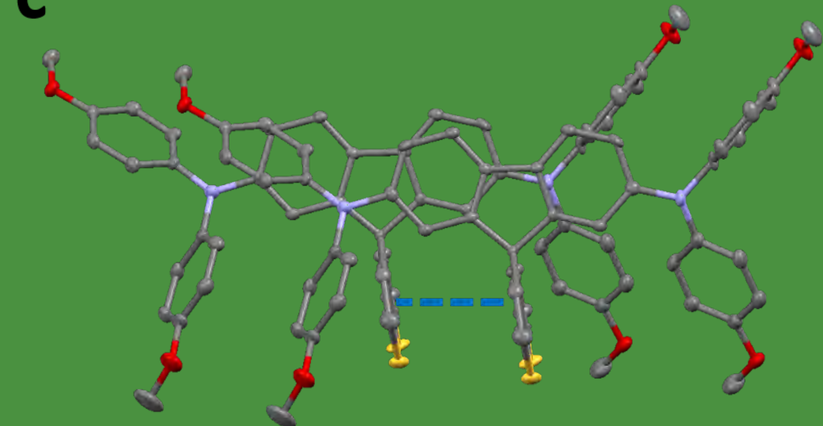

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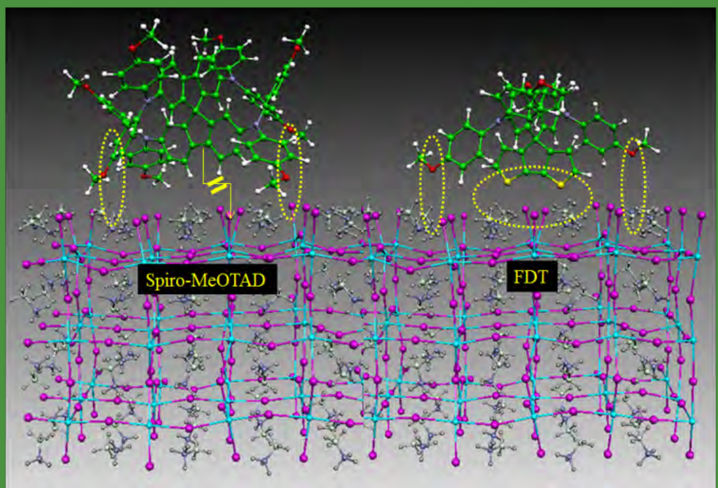
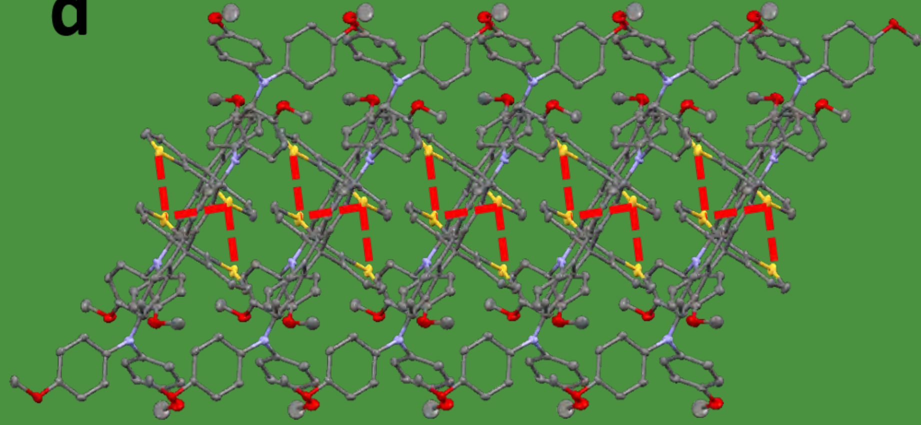


d



M. Saliba, S. Orlandi, T. Matsui, A. Sadig, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K. H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel and M. K. Nazeeruddin, *A Low-cost Molecularly Engineered Hole Transporting Material for 20% Perovskite Solar Cells* (submitted to **Nature Energy**)

Outline

- The advent of perovskite solar cells
- Mixed organic cation/anion formulations, effect of stoichiometric PbI_2 excess on PV performance
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- New hole conductors
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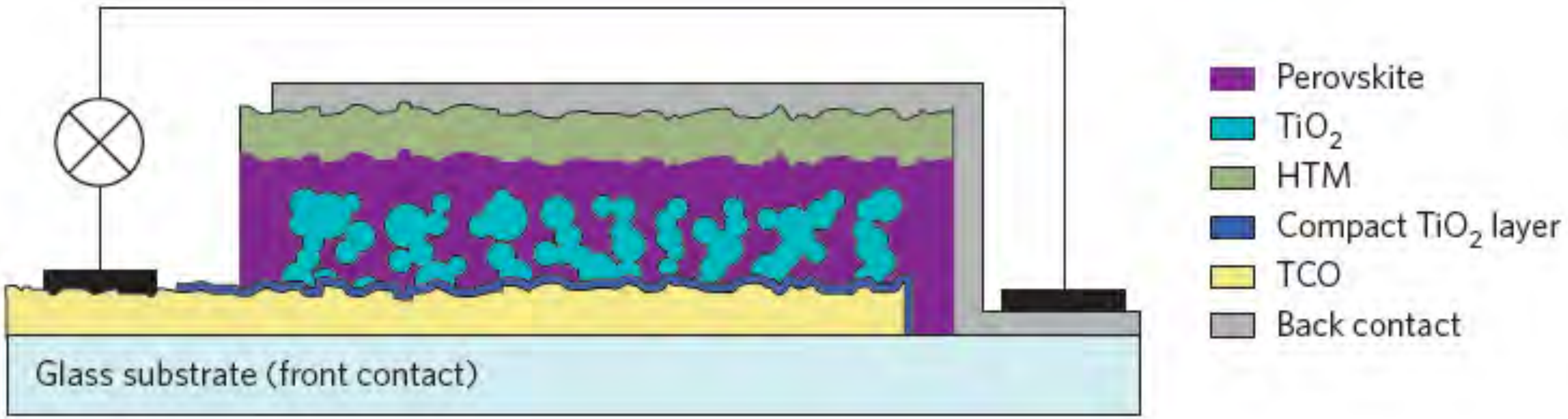
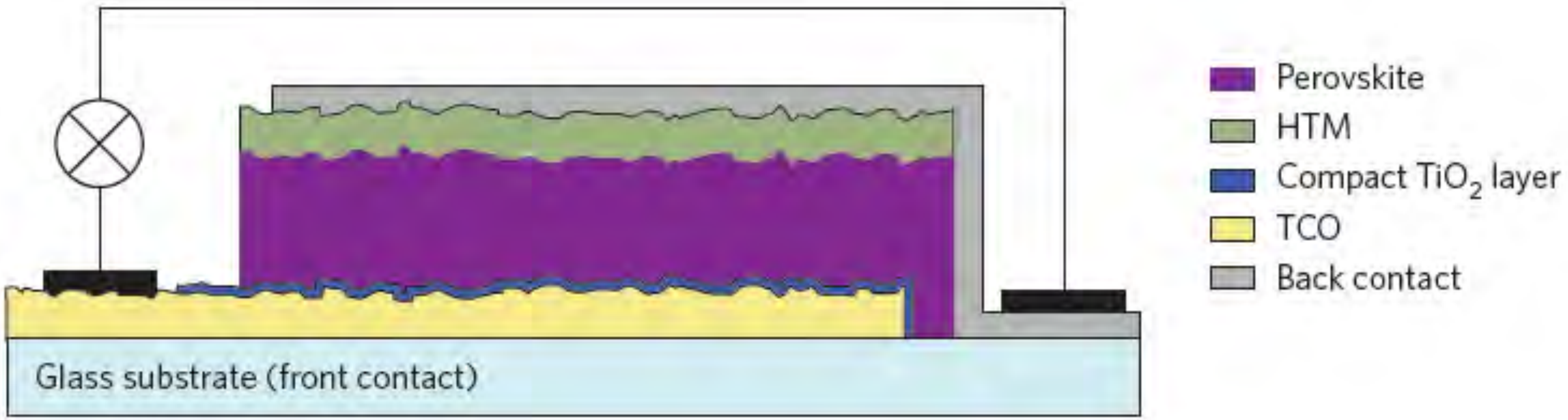
- Tandem cells
- Stability

Mesoscopic vs planar perovskite cell configuration



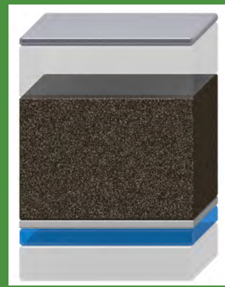


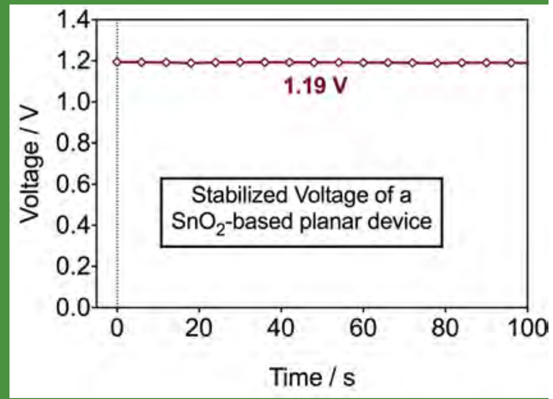
Band Alignment Engineering

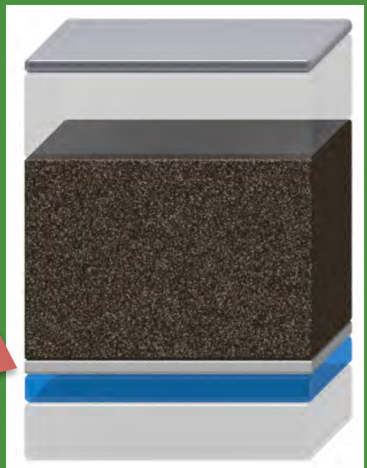
Dr. Juan-Pablo Correa-Baena

Ms. Ludmilla Steier

Planar devices!





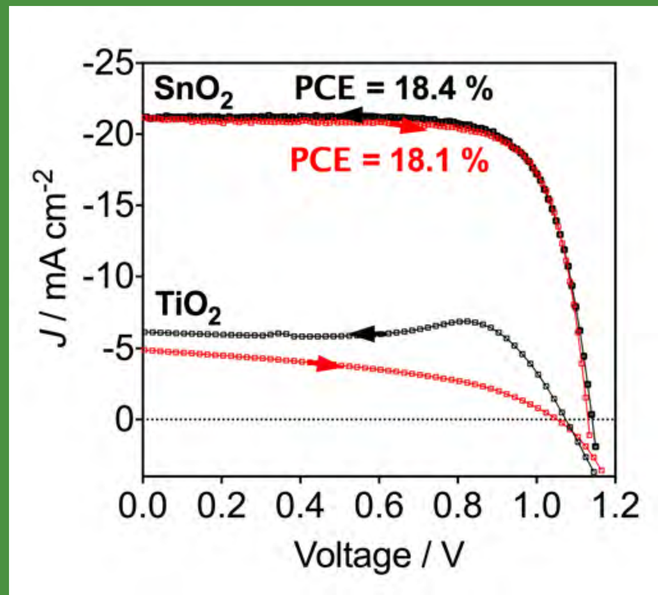


Stranks, NNANO (2015)

hole transporter

Perovskite

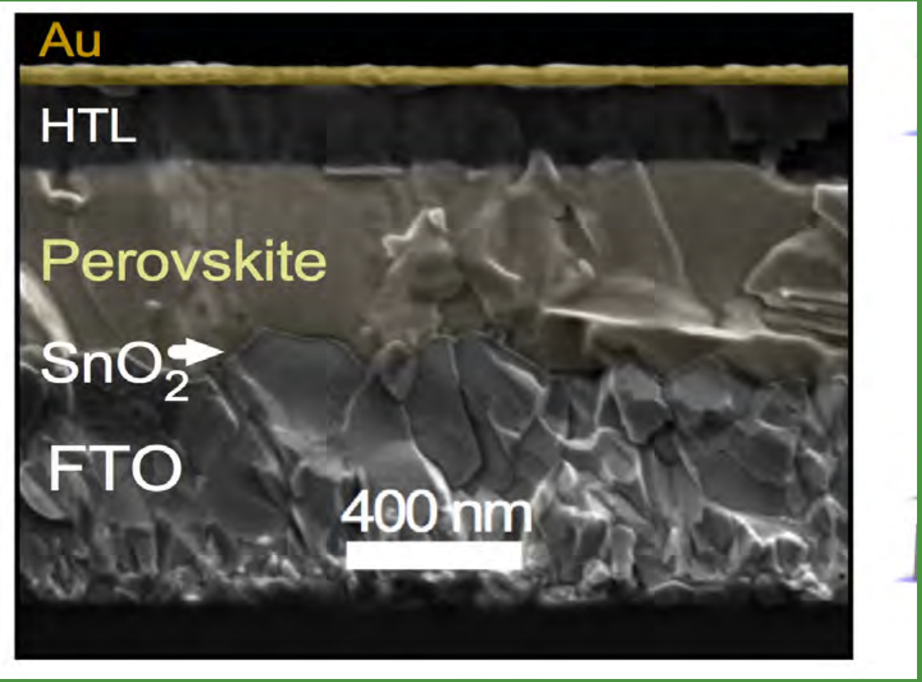
electron transporter

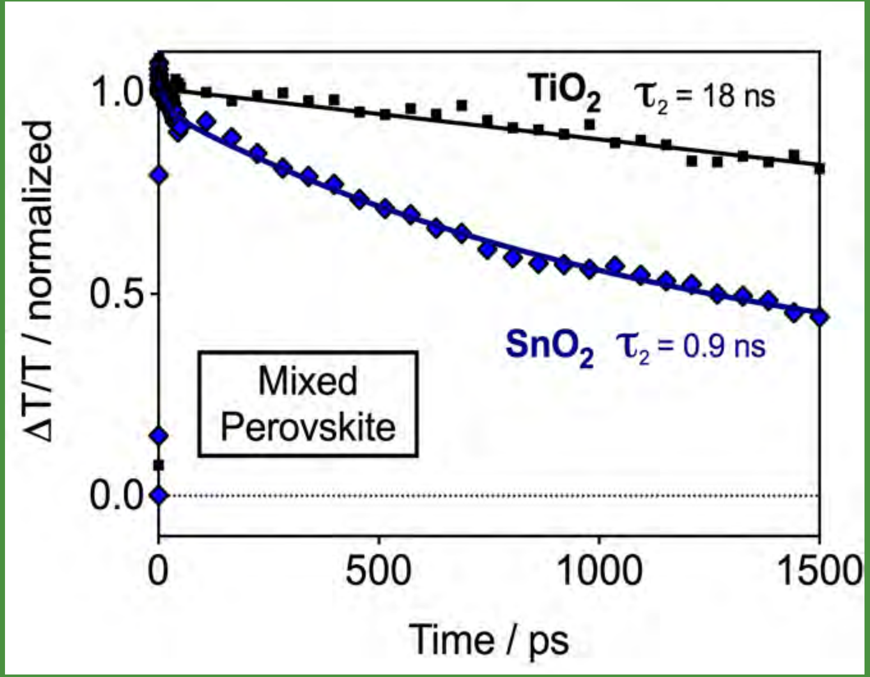


Flat SnO_2 ALD layer works better than flat TiO_2 ALD Layer

J.-P. Correa Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. S. Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, M. Graetzel, A. Hagfeldt, *Highly efficient planar perovskite solar cells through band alignment engineering*, **Energy & Environmental Science** (2015)

Electron extraction from the photo-excited cation/anion mixed perovskite is 20 times faster with SnO2 compared to TiO2 compact layer





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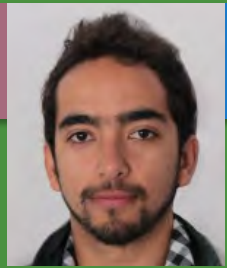
Monolithic Perovskite/Silicon Tandem

Dr. Steve Albrecht

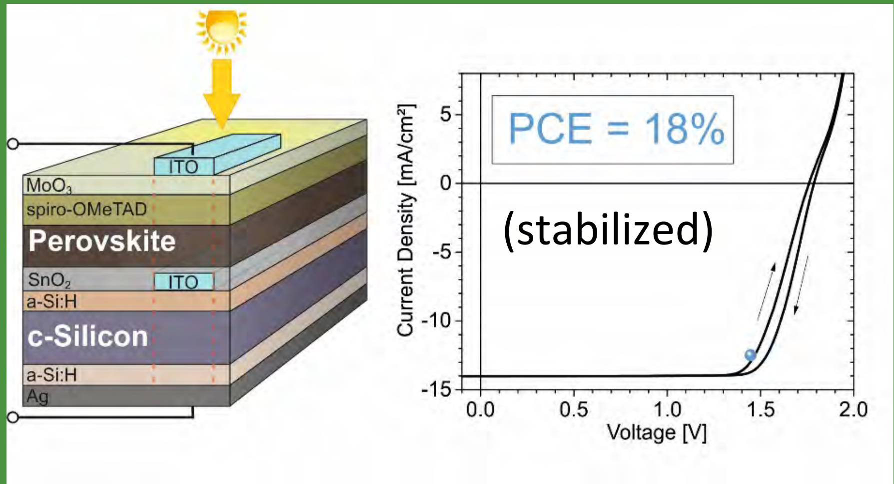
Dr. Michael Saliba

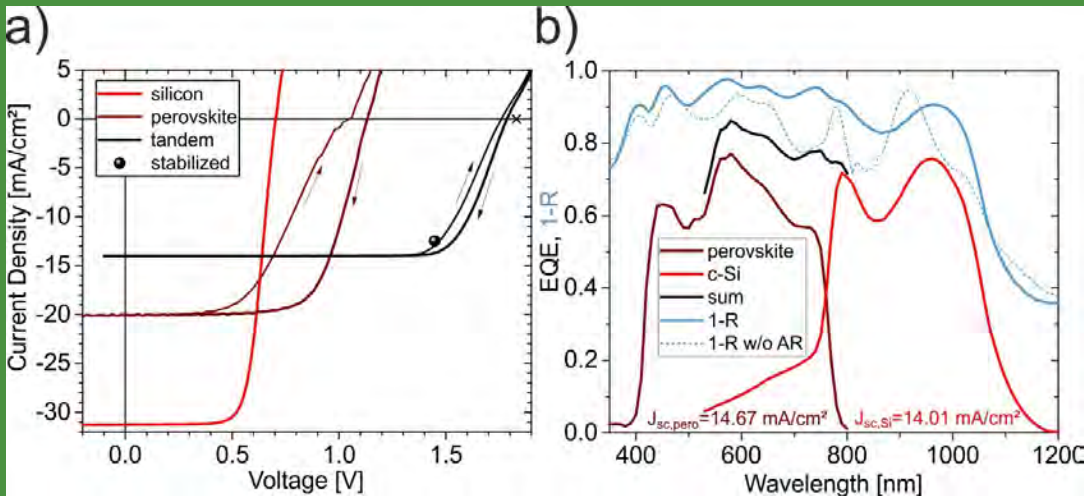


Dr. Juan-Pablo Correa-Baena

Collaboration with Helmholtz Zentrum Berlin

Low temperature SnO_2 useful for tandems!





S. Albrecht, M. Saliba, J.-P. Correa Baena, F. Lang, L. Kegelmann, M. Mews, L. Steier, L. Korte, A. Abate, R. Schlatmann, M. K. Nazeeruddin, A. Hagfeldt, M. Graetzel, and Bernd Rech, *Monolithic Perovskite/Silicon-Heterojunction Tandem Solar Cells Processed at Low Temperature* (submitted)

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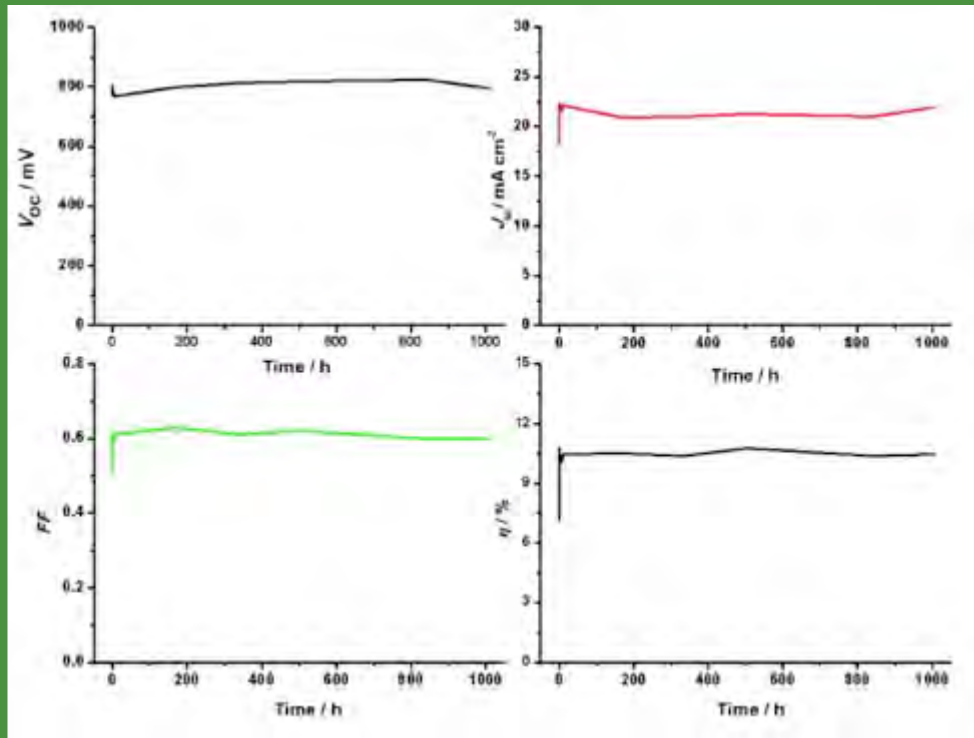
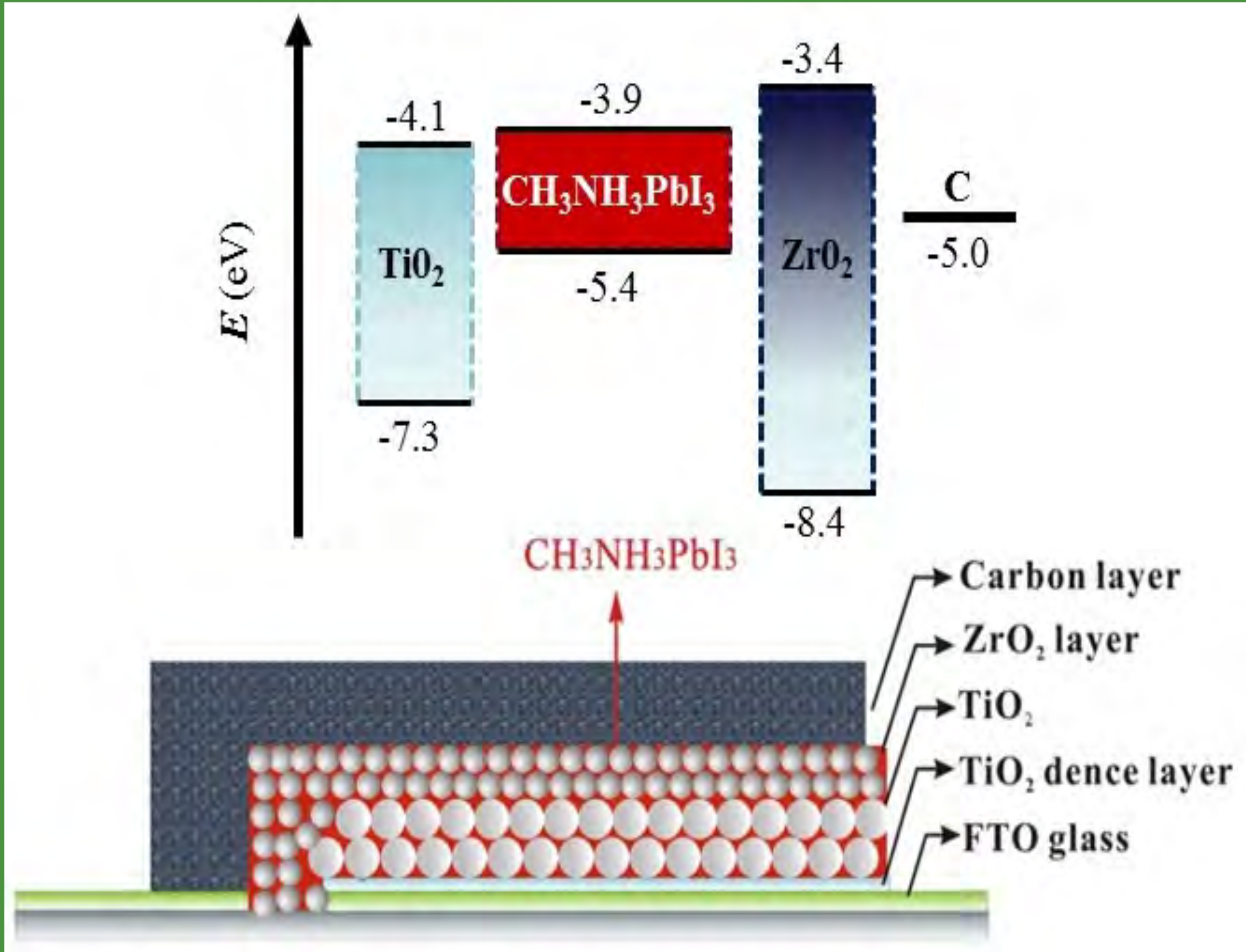
Science 345, 295 (2014)

Anyi Mei,[1*] Xiong Li,[1*] Linfeng Liu,[1] Zhiliang Ku,[1] Tongfa Liu,[1] Yaoguang Rong,[1] Mi Xu,[1] Min Hu,[1] Jiangzhao Chen,[1] Ying Yang,[1] Michael Grätzel,[2] Hongwei Han[1]†

A hole-conductor–free, fully printable mesoscopic perovskite solar cell with high stability



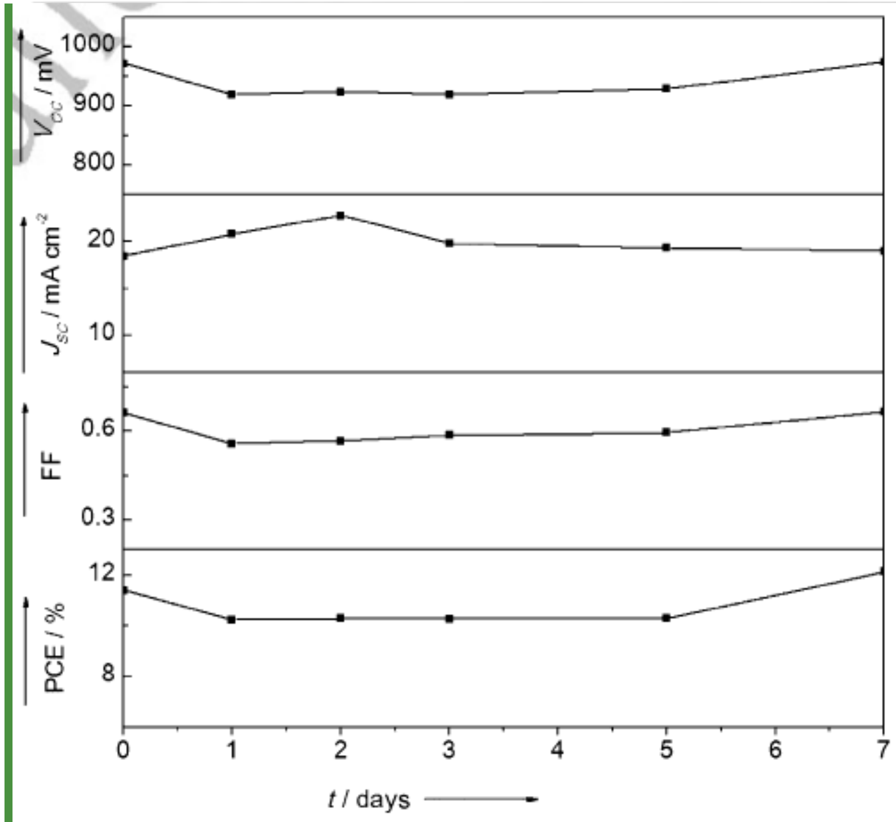
Cross section and energy level diagram of a fully printable triple layer perovskite cell



DOI: 10.1002/ente.201500045

Outdoor Performance and Stability under Elevated Temperatures and Long-Term Light Soaking of Triple-Layer Mesoporous Perovskite Photovoltaics

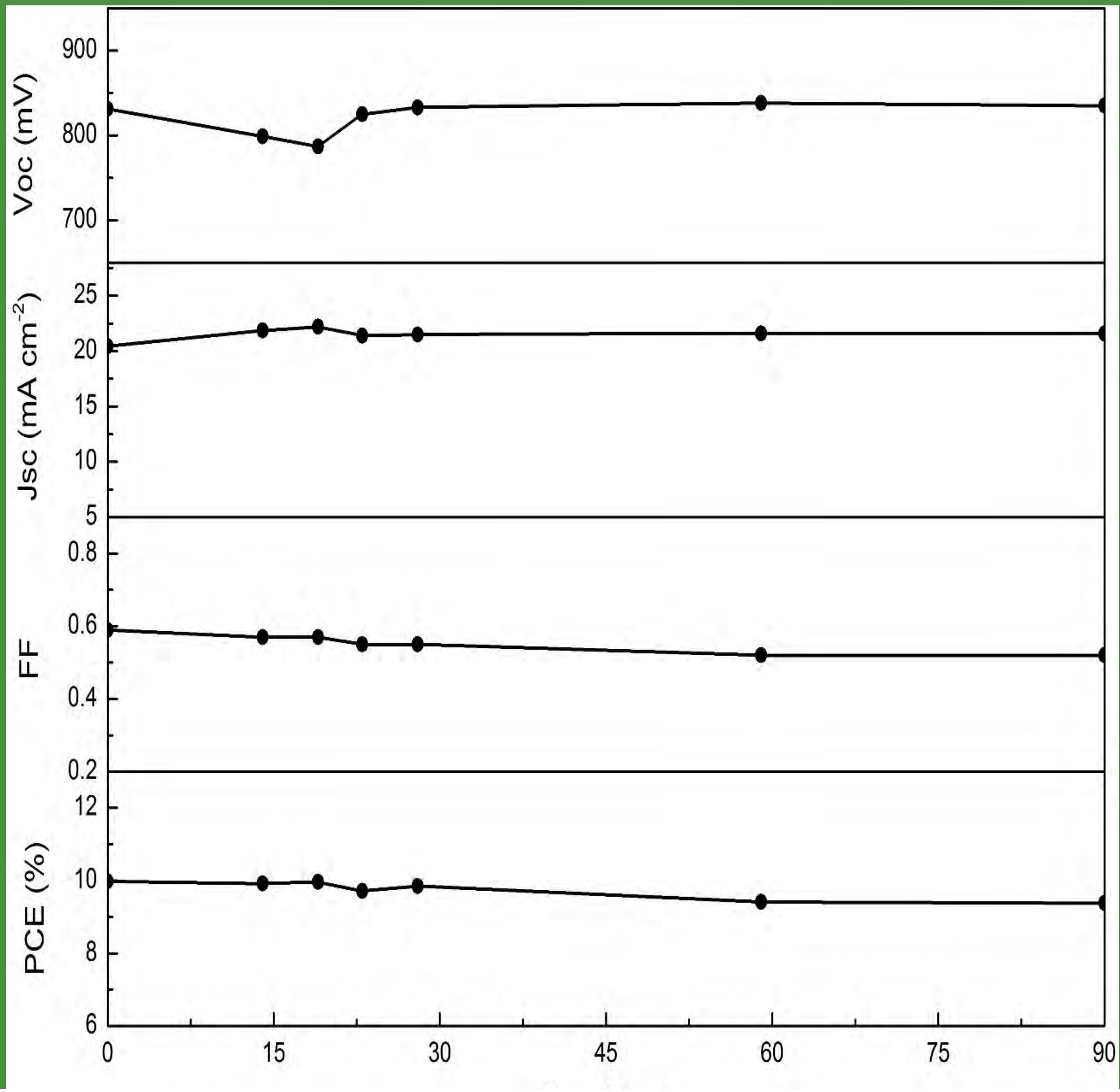
Xiong Li,[a] Manuel Tschumi,[a] Hongwei Han,[e] Saeed Salem Babkair,[c] Raysah Ali Alzubaydi,[c] Azhar Ahmad Ansari,[c] Sami S. Habib,[d] Mohammad Khaja Nazeeruddin,[a] Shaik M. Zakeeruddin,[a] and Michael Grätzel*[a, b]



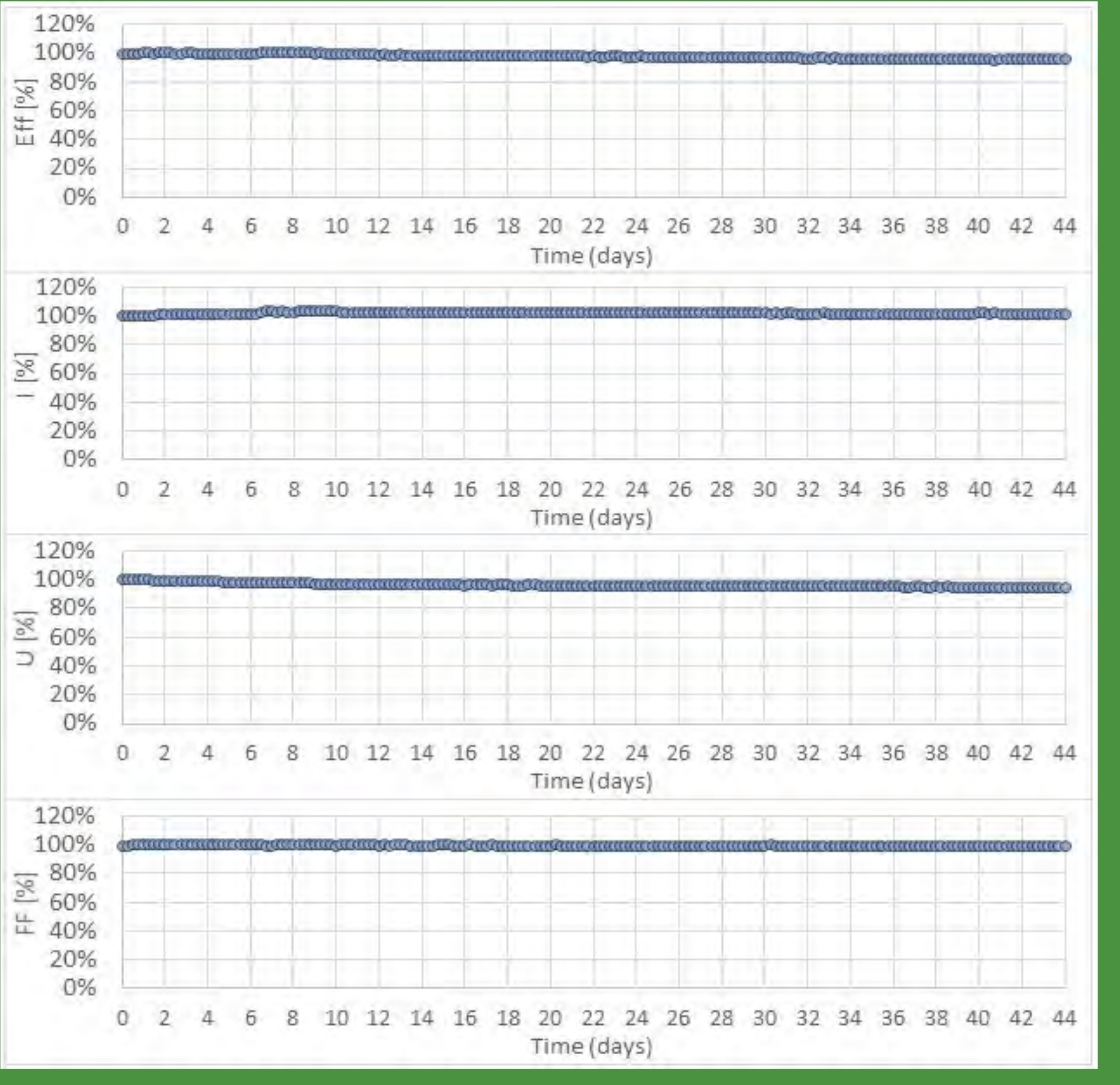
Prof. Saeed S. Babkair, KAU, Jeddah

Figure 4. Time evolution of the encapsulated PSC solar cell metrics during outdoor aging in Jeddah, Saudi Arabia.

Heat stress test of a triple layer PSC. The device was kept in an oven at 80-85 C for 90 days. It was removed at several intervals from the oven and cooled overnight to equilibrate at ambient temperature before recording the PV device performance metrics. Measurements employed simulated full solar AM 1.5 light at room temperature.



Stability pf a carbon based PSC led at the maximum power point under prolonged light soaking at 45 °C and 1000 W/m2 LED white light



Our new world record efficiency for scaled up perovskite cells 19.6 %

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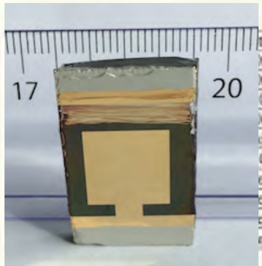
Photovoltaic Cell Performance Certificate

Calibration Conducted For:
Institut des Sciences et Ingenierie Chimique (ISIC)
Faculte des Sciences de Bases (FSB)
Ecole Polytechnique Federale de Lausanne
CH-1015 Lausanne, Switzerland

Calibration Conducted By:
Newport Corporation
PV Lab
31950 Frontage Rd.
Bozeman, MT 59715



...turer	Model	Due Date
...riel ®	QE-PV-SI	Apr 2016
...riel ®	Sol3A	Apr 2016
Oriel	10510-0054 KG5	Sep 2017
...riel ®	Spectroradiometer	Apr 2016
...ope	XT-D8126-XY	Apr 2016
Corp	IQE-SAMPLE-SI	Jun 2017
...ey	2700	Apr 2016
...ey	2440	Apr 2016
...ey	2440	Apr 2016
...ey	2400	Apr 2016

Approved by: [signature] Date: 02-26-2016
Name: Geoffrey Wicks
Title: Laboratory Manager

Verified by: [signature] Date: 2016-02-26
Name: Charlie Keith
Title: Test Engineer

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	Reviewed and Approved by: Geoffrey Wicks	

Newport | Calibration Cert. # 2893.01 | Technology and Application Center **PV Lab** Newport Calibration Cert # 1420

DUT S/N: T2
Newport Calibration #: 1420
Manufacturer: Ecole Polytechnique Federale de Lausanne
Material: Perovskite
Temperature Sensor: None
Environmental conditions at the time of calibration: Temperature: 24 ± 3 °C; Humidity: 40 ± 10 %

The above DUT has been tested using the following methods to meet the ISO 17025 Standard by the PV Lab at Newport Corporation. Quoted uncertainties are expanded using a coverage factor of k = 2 and expressed with an approximately 95% level of confidence. Measurement of total irradiance is traceable to the World Radiometric Reference (WRR) and all other measurements and uncertainties are traceable to either NIST or CNRC and the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test, and do not imply future performance.

Efficiency [%]	19.56 ± 0.43	V_oc [V]	1.1428 ± 0.0159	I_sc [A]	0.022601 ± 0.000414
P_max [mW]	19.56 ± 0.42	V_max [V]	0.9534 ± 0.0105	I_max [A]	0.020518 ± 0.000249
FF [%]	75.7 ± 1.1	Area [cm^2]	1.0003 ± 0.0036	M	0.999 ± 0.004

Methods:
I-V: ASTM E948-15 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *Standard Test Method for Spectral Responsivity Measurements of Photovoltaic Devices*

Standard Reporting Conditions:
Spectrum: AM1.5-G (ASTM G173-03/IEC 60904-3 ed. 2)
1000.0 W/m² at 25.0°C

Secondary Reference Cell:
Device S/N: 10510-0054 KG5
Device Material: mono-Si
Window Material: KG5
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 1830
Certified short circuit current (I_{sc}) under standard reporting conditions (SRC): 47.76mA
Calibration due date: 15-Sep-17

Solar Simulator:
Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0179.xls*
Total irradiance: 1000 W/m² based on I_{sc} of the above Secondary Reference Cell

Quantum Efficiency for DUT:
Newport Corporation filename *QE 1420 T2 97 R) W1.0.lsg*
Spectral mismatch correction factor: M = 0.999 ± 0.004

DUT Calibration Procedures:
Newport Corporation document WI1 (IQE).docx
Newport Corporation document Area Measurement WI3 (Area).docx
Newport Corporation document WI3 (IV Sweep).docx

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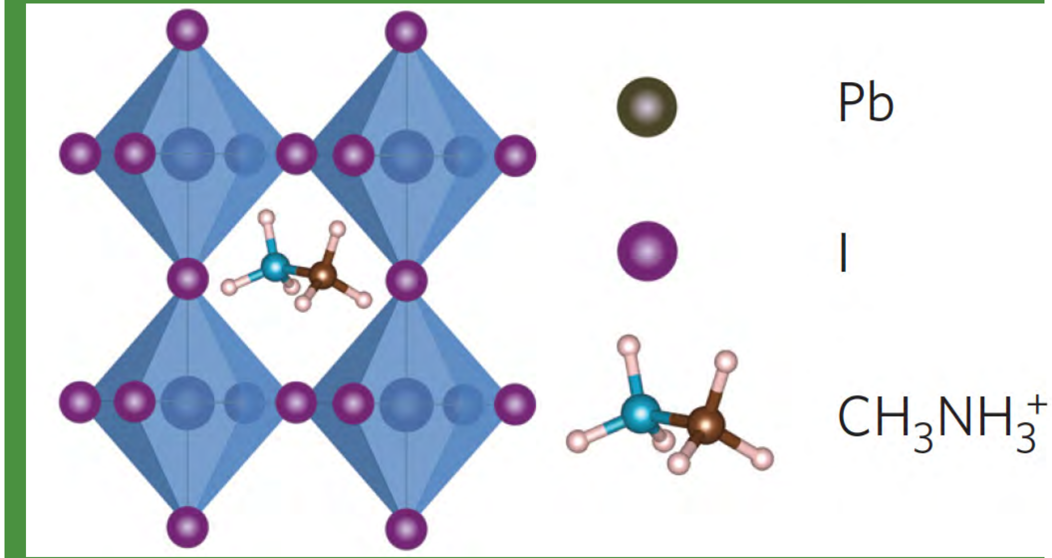
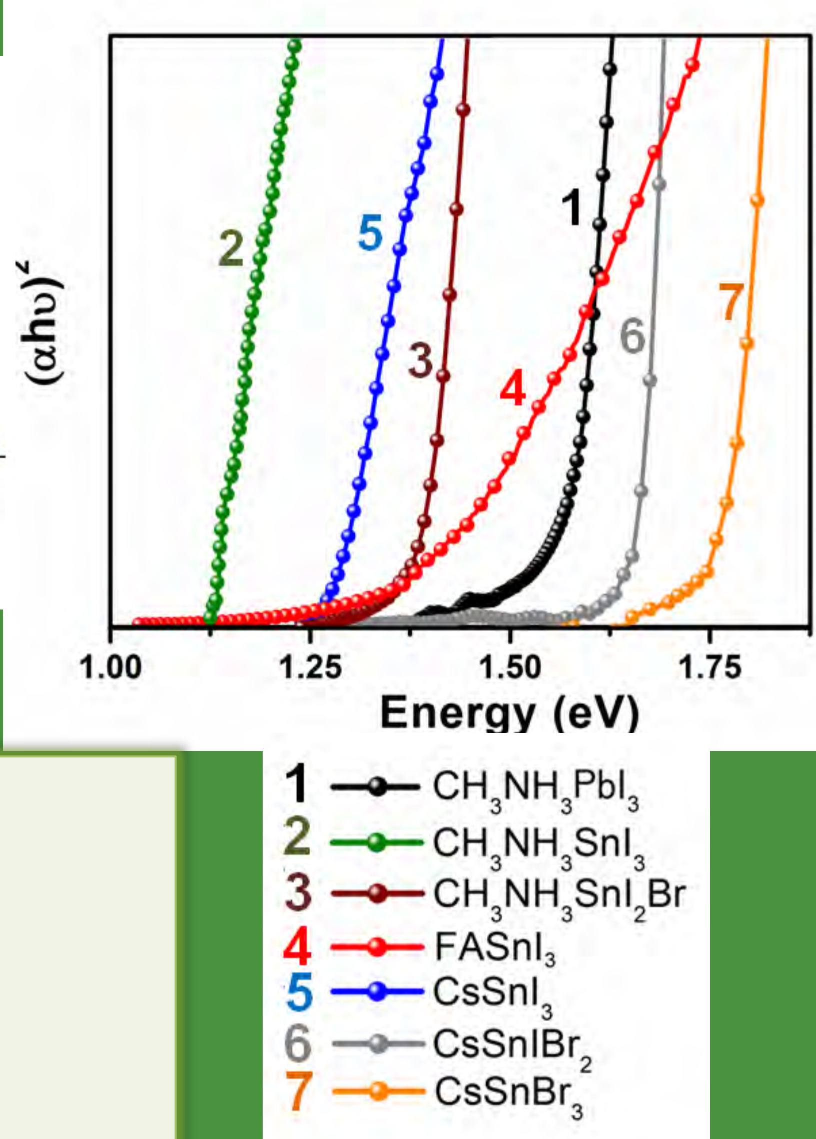
Outline

- The advent of perovskite solar cells
- Mixed organic cation/anion formulations, effect of stoichiometric PbI_2 excess on PV performance
- Lithium doping of mesocopic TiO_2 scaffold
- New hole conductors
- Planar configurations with ALD films of SnO_2 as electron selective layer
- Tandem cells
- Stability
- Lead-free perovskites

Lead-free perovskites beyond $CH_3NH_3PbI_3$





AMX_3

- Halides: I, Br, Cl
- Cation (divalent): Sn, Cu, Ge?
- Cation (monovalent): $(HC(NH_2)_2PbI_3$; Cs, …?

Beyond AMX_3

- Multidimensional : 0D – 2D perovskites

$CsGeI_3$, $MAGeI_3$
$MA_2CuCl_2Br_2$

Towards Pb-free perovskite solar cells

Boix, Agarwala, Koh, Mathews, Mhaisalkar. *J. Phys. Chem. Lett.* **6**, 898–907 (2015)

- Substitution of Pb by Sn slightly increases the Urbach tails
- Low Urbach energies suggest low inherent structural disorder.

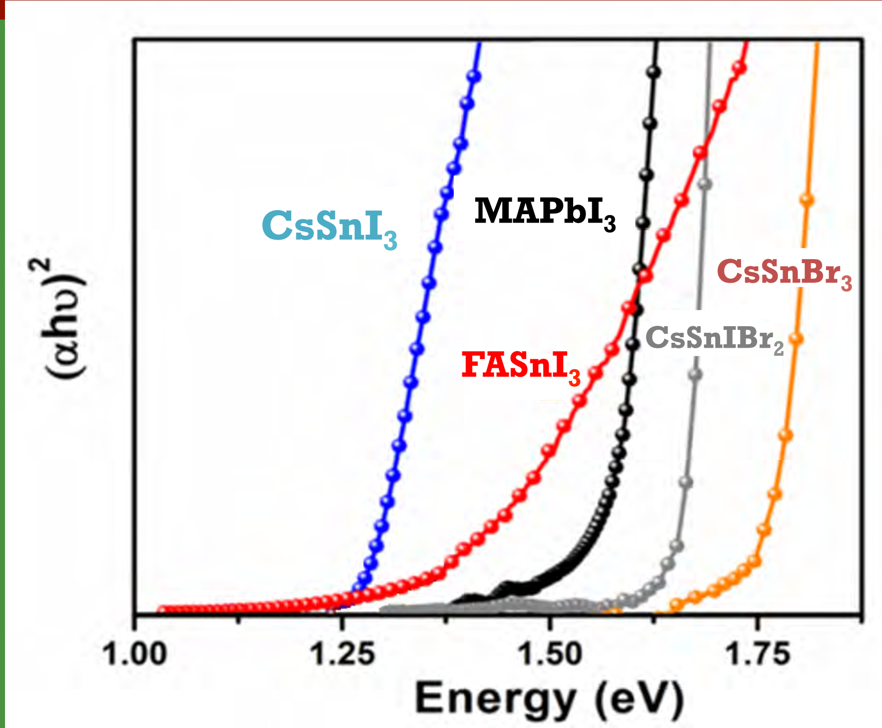
	Eg (eV)	E_e (meV)
$CsSnBr_3$	1.76	32.6
$CsSnIBr_2$	1.65	39.0
$CsSnI_2Br$	1.37	32.0
$CsSnI_3$	1.27	16.8
c-Si	1.12	11
$CH_3NH_3PbI_3$	1.57	15
GaAs	1.42	7.5

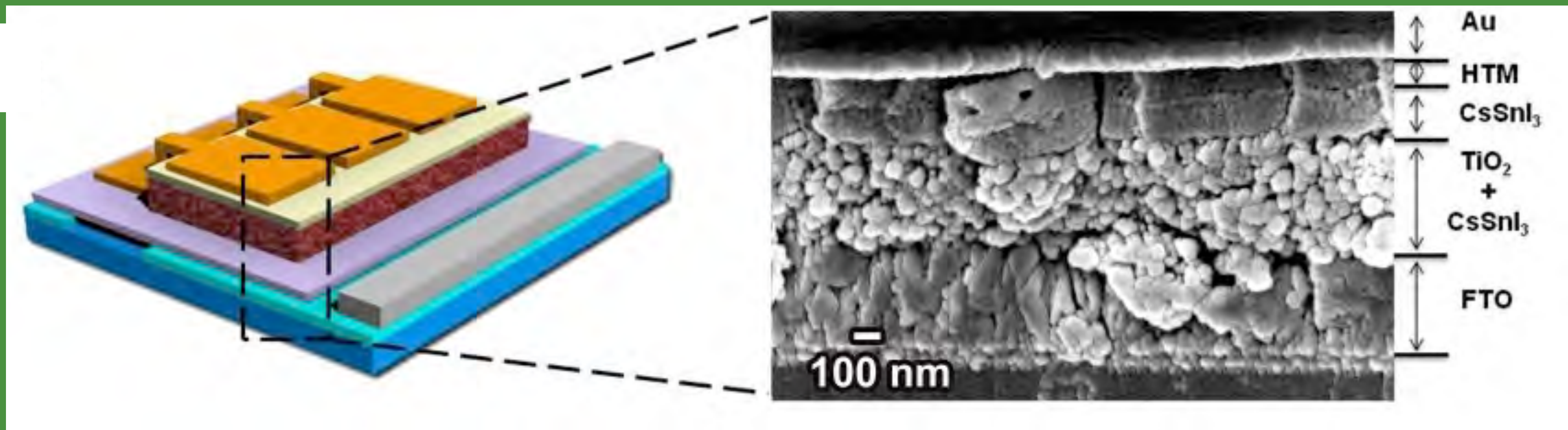
Pb-Free Perovskite Solar Cells: $CsSnI_xBr_{3-x}$

Adv. Mater., 2014, 26 (41):7122-7127.Jp.Phys.Chem.C., 2015, 119

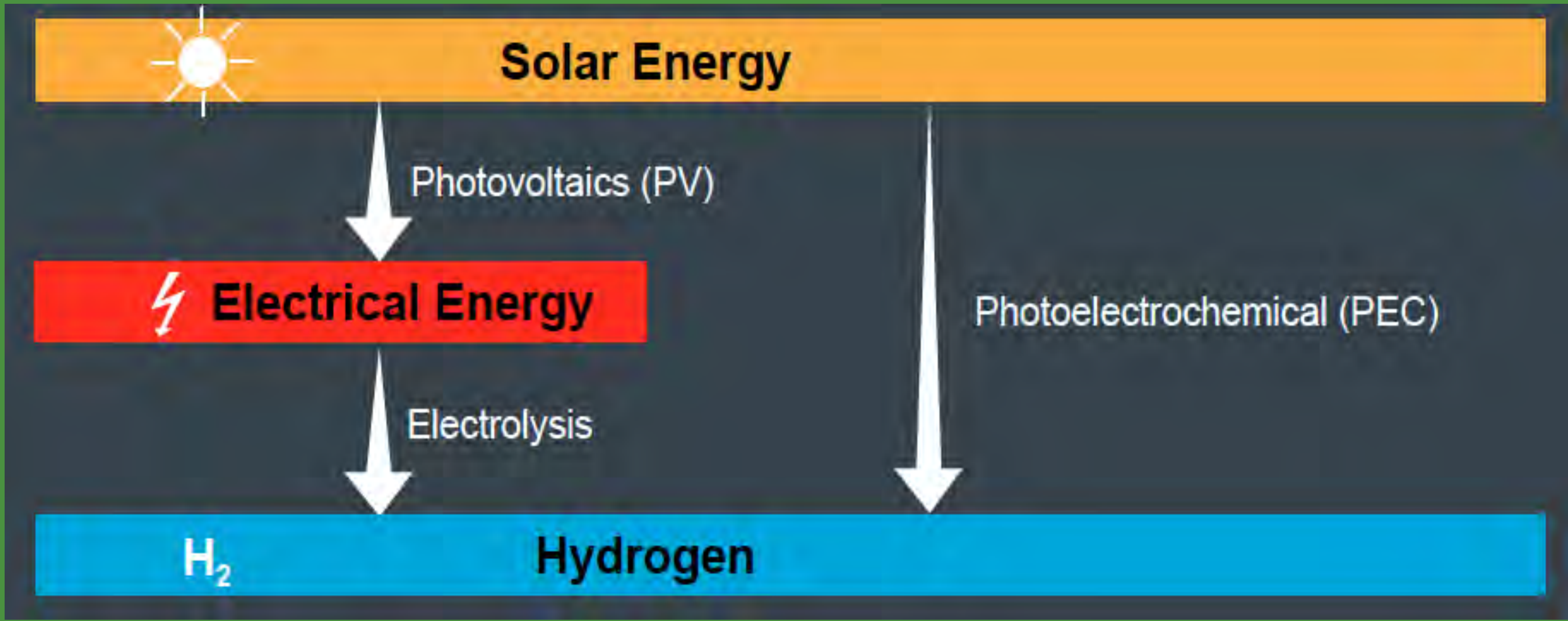
$CsSnI_xBr_{3-x}$

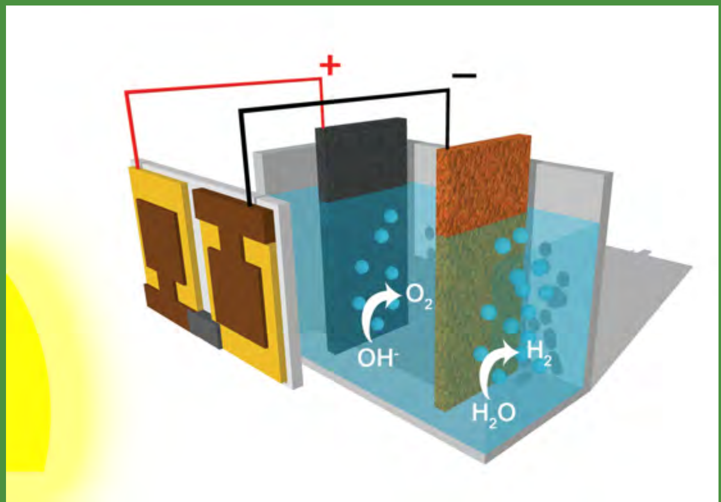
- Solution process, excellent Eg (1.3 – 1.8 eV)
- $CsSnI_3$: $J_{sc\text{-}max}$: 34 $mAcm^{-2}$ ($CH_3NH_3PbI_3$: 24 $mAcm^{-2}$)

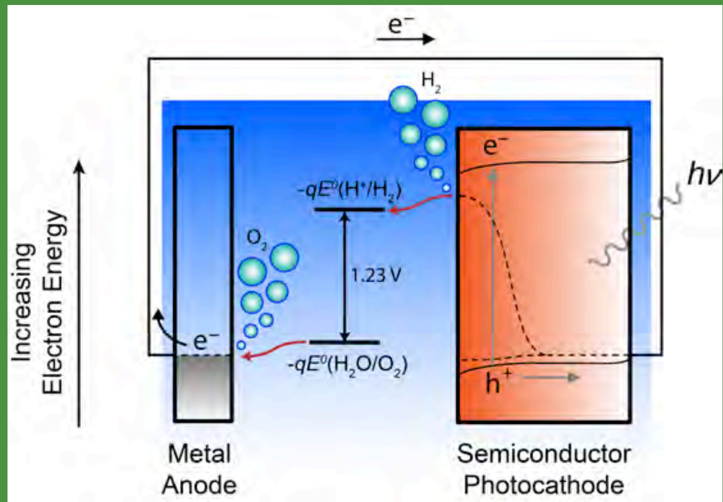




Solar fuel research in LPI





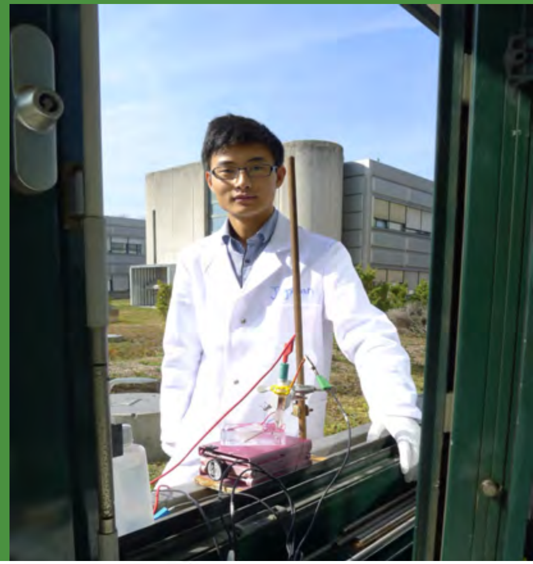


WATER SPLITTING

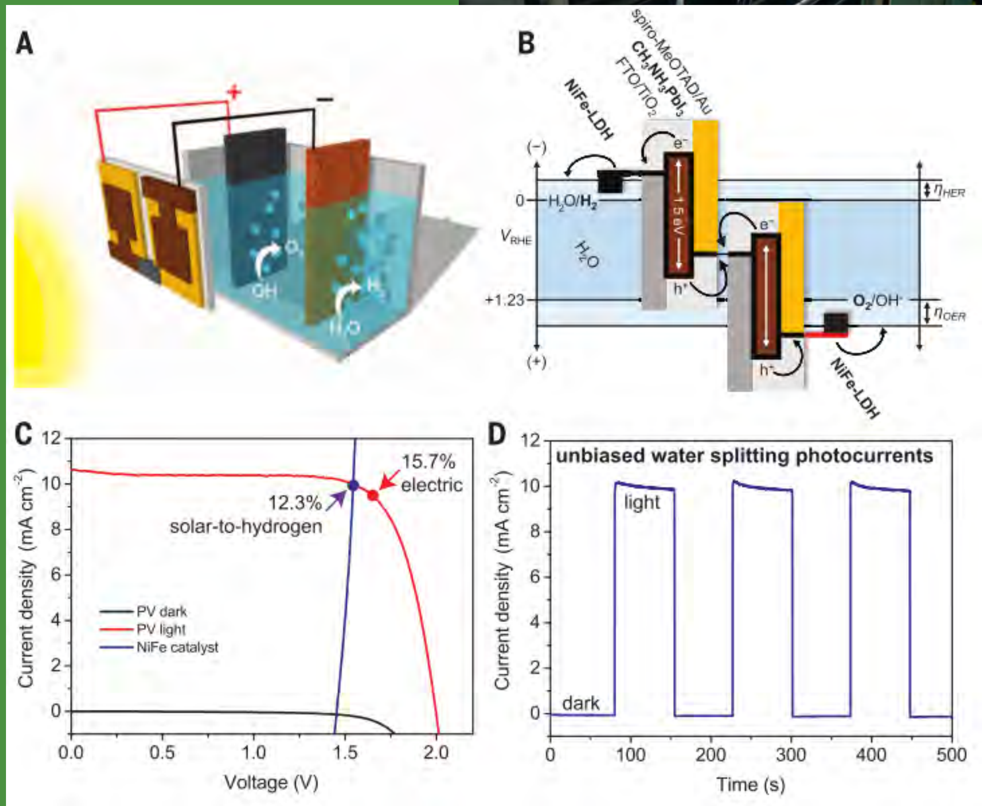
Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts

Jingshan Luo,[1,2] Jeong-Hyeok Im,[1,3] Matthew T. Mayer,[1] Marcel Schreier,[1] Mohammad Khaja Nazeeruddin,[1] Nam-Gyu Park,[3] S. David Tilley,[1] Hong Jin Fan,[2] Michael Grätzel[1*]

Science AAAS



- $CH_3NH_3PbI_3$ perovskite photovoltaics
  - High V_{oc} (≥1.0 V)
  - High PV efficiencies >15%
- 2 in series for electrolysis
  - Doubled V_{oc} (2.0 V)
  - Halved J_{sc} (>10 mA/cm^2)
  - Unbiased water splitting at >12% efficiency
- Perovskites open opportunity for high-performance devices with cheap and easy processing



Luo, J... Grätzel, M. et al. *Science* **2014**, *345*, 1593.

EPFL leads the solar hydrogen fuel generation race

13.4% solar to hydrogen conversion efficiency, highest in standard AM 1.5G

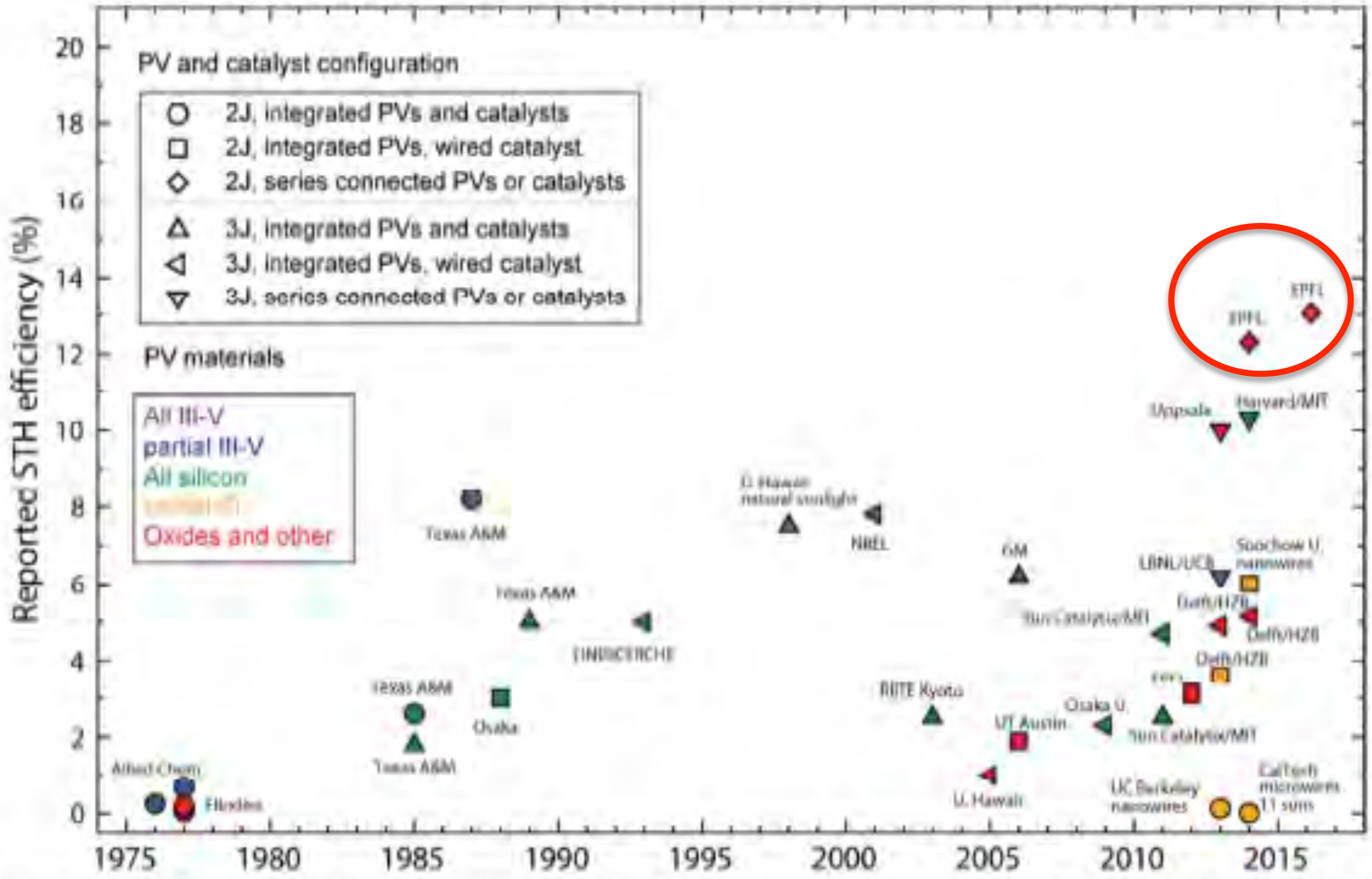
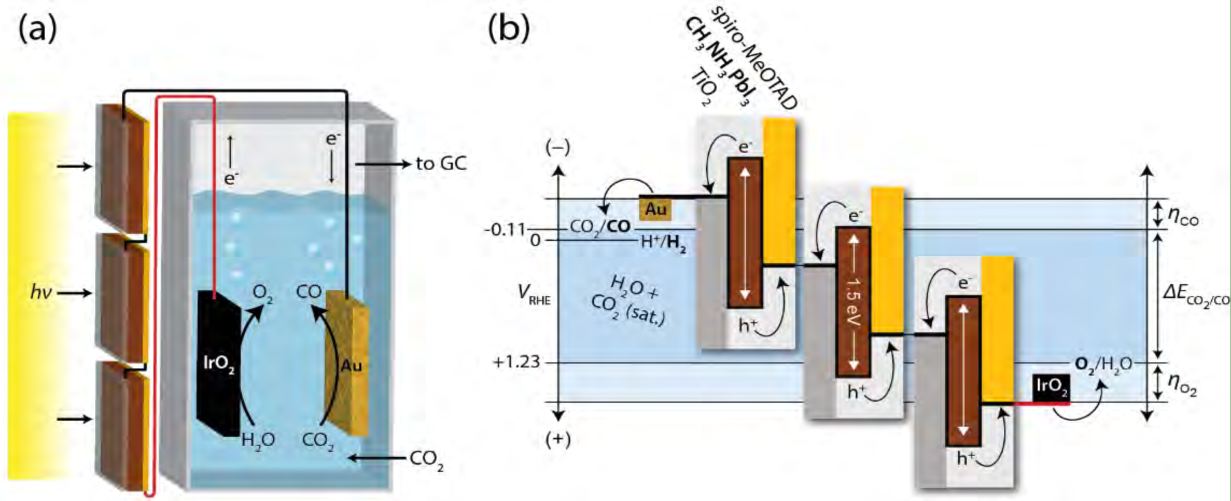


Fig. 3. Reported solar to hydrogen (STH) conversion efficiencies as a function of year and sorted by the number of tandem photovoltaic junctions used (2 or 3). The degree of integration of photovoltaic and catalyst elements is also distinguished, see Fig. 2. The fill colour represents the semiconductor materials used in the photovoltaic portion of the device. All STH conversion efficiencies are as reported in the original publications (see Tables 2 – 5).

J. W. Ager et.al Energy & Env. .Science 2015, DOI: 10.1039/x0xx00000x

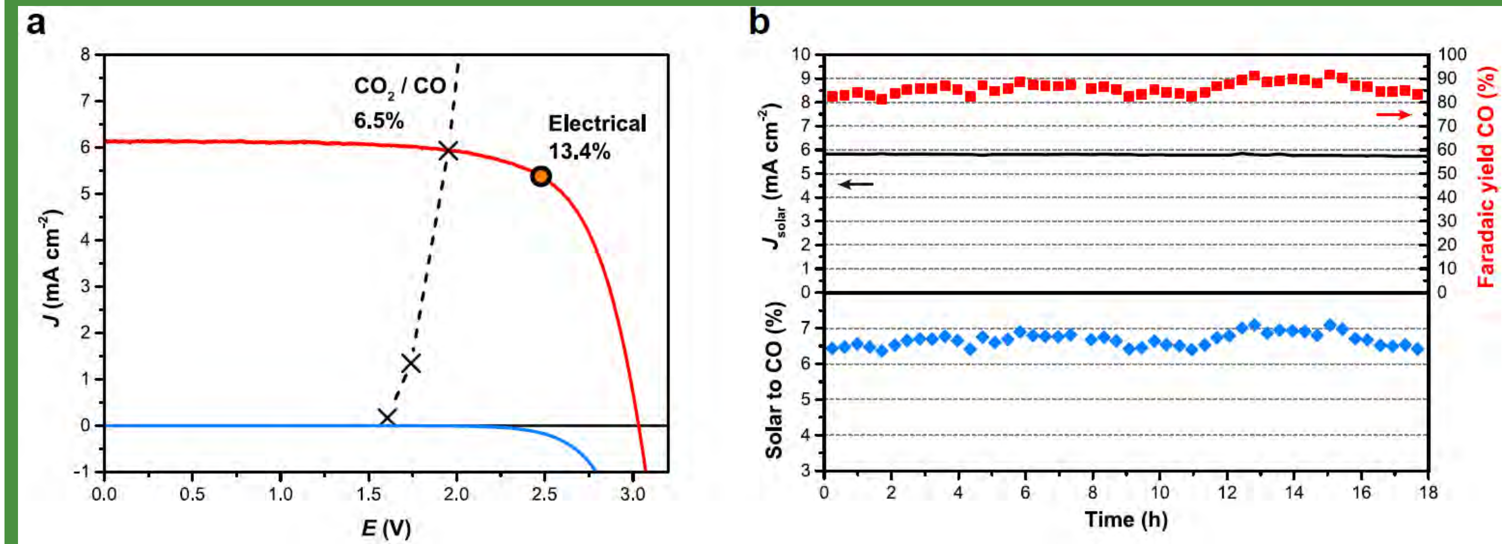
Triple junction mesoscopic pervoskite cells achieve the reduction of CO_2 to CO with 6.5 % solar to CO (STCO) conversion efficiency using water as electron source

$$CO_2 \rightarrow CO + \tfrac{1}{2} O_2 \;,\; \Delta G^* = +1.34\ eV$$



Marcel Schreier

6.5 % Solar to CO



M. Schreier et al. Nature Communications 6, 7326 (2015)

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- European Research Council: Adv. Research Grant MESOLIGHT
- GRL Korea (with KRICT)
- The Balzan Prize Foundation
- Marie Curie Actions
- Industrial Partners

Eric and Sheila Samson Prime Minister's Prize for Innovation in Alternative Fuels for Transportation

MILLENNIUM TECHNOLOGY PRIZE

Technology for humanity

BALZAN

Fuel Choices Initiative

Prime Minister's Office


Anzère, Valais Switzerland March 1, 2013, LPI skiing day