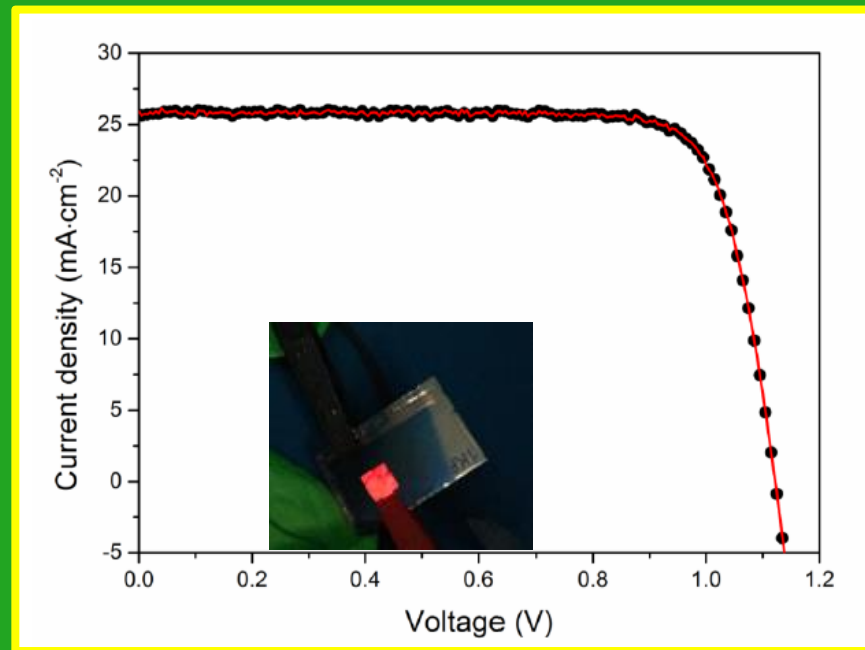
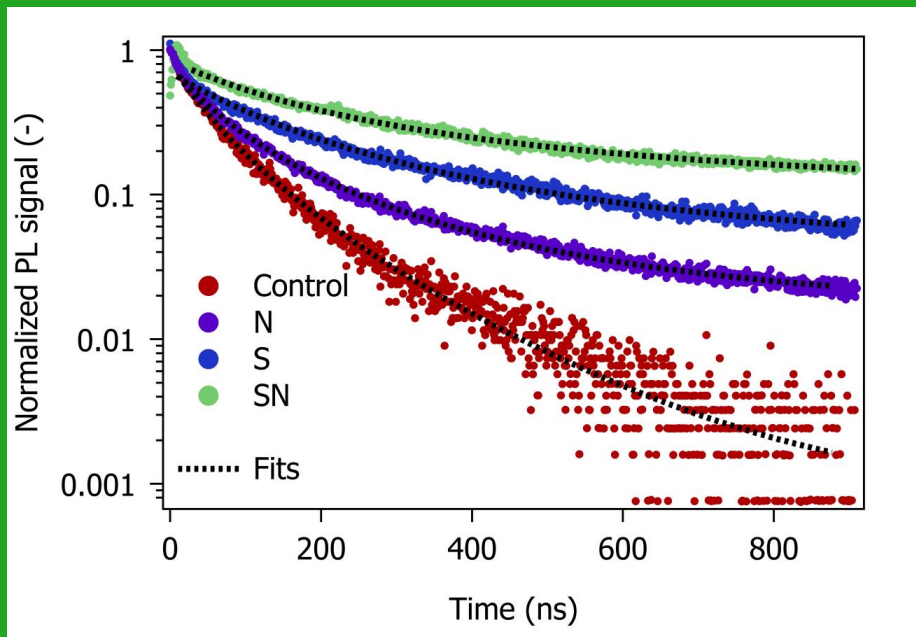


# Molecular Photovoltaics and Perovskite Solar Cells

21<sup>st</sup> Sede Boker Symposium, Negev Israel 2018

The impact of molecular modulators on perovskite charge carrier recombination dynamics



$$-dn/dt = k_1 \times n + k_2 n^2$$

$$dn_{ph}/dt = k_2 n^2$$

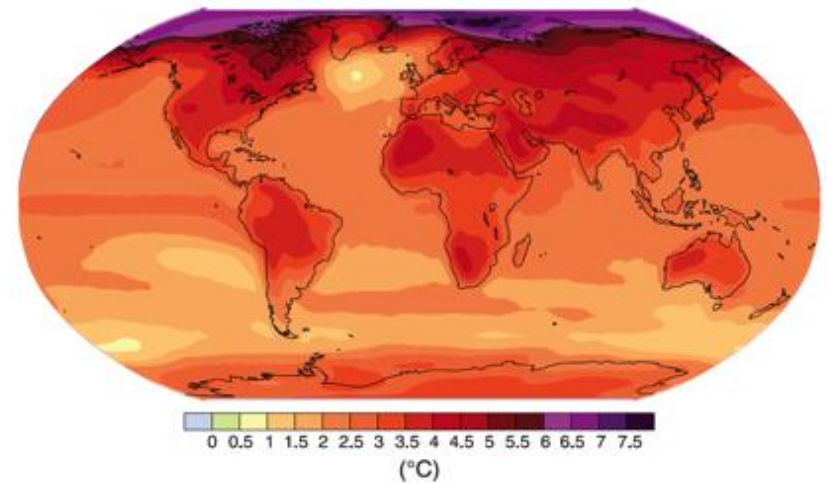
PCE = 23.25 %

# The problem

## pollution

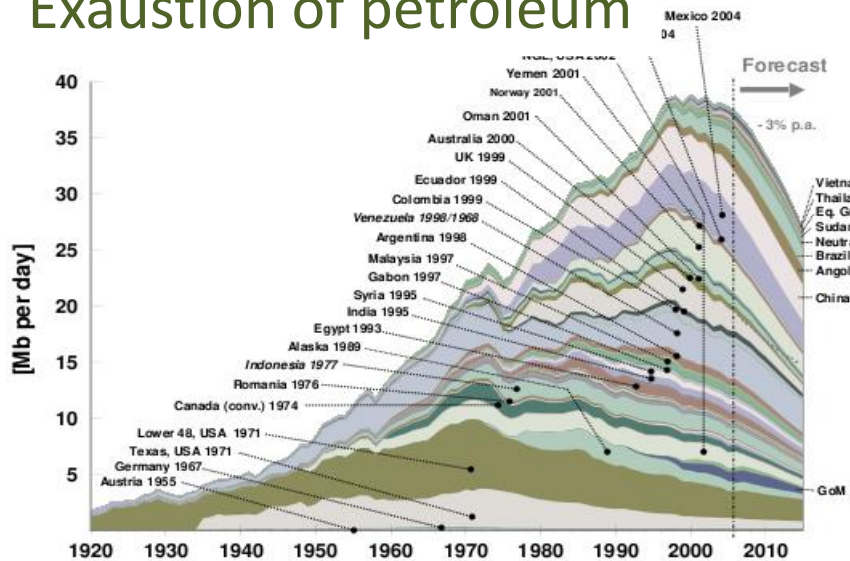


## Global warming



Fi

## Exhaustion of petroleum



Ludwig-Bölkow-Systemtechnik GmbH, 2007  
Source: IHS 2006; PEMEX, petrobras; NPD, DTI, ENS(Dk), NEB, RRC, US-EIA, January 2007  
Forecast: LBST estimate, 25 January 2007

## Nuclear risk



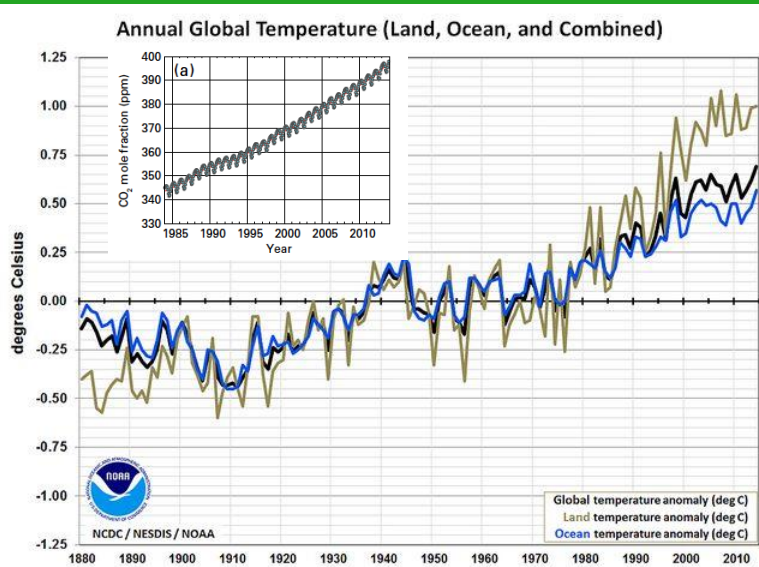


# Oil causes global warming and environmental disasters

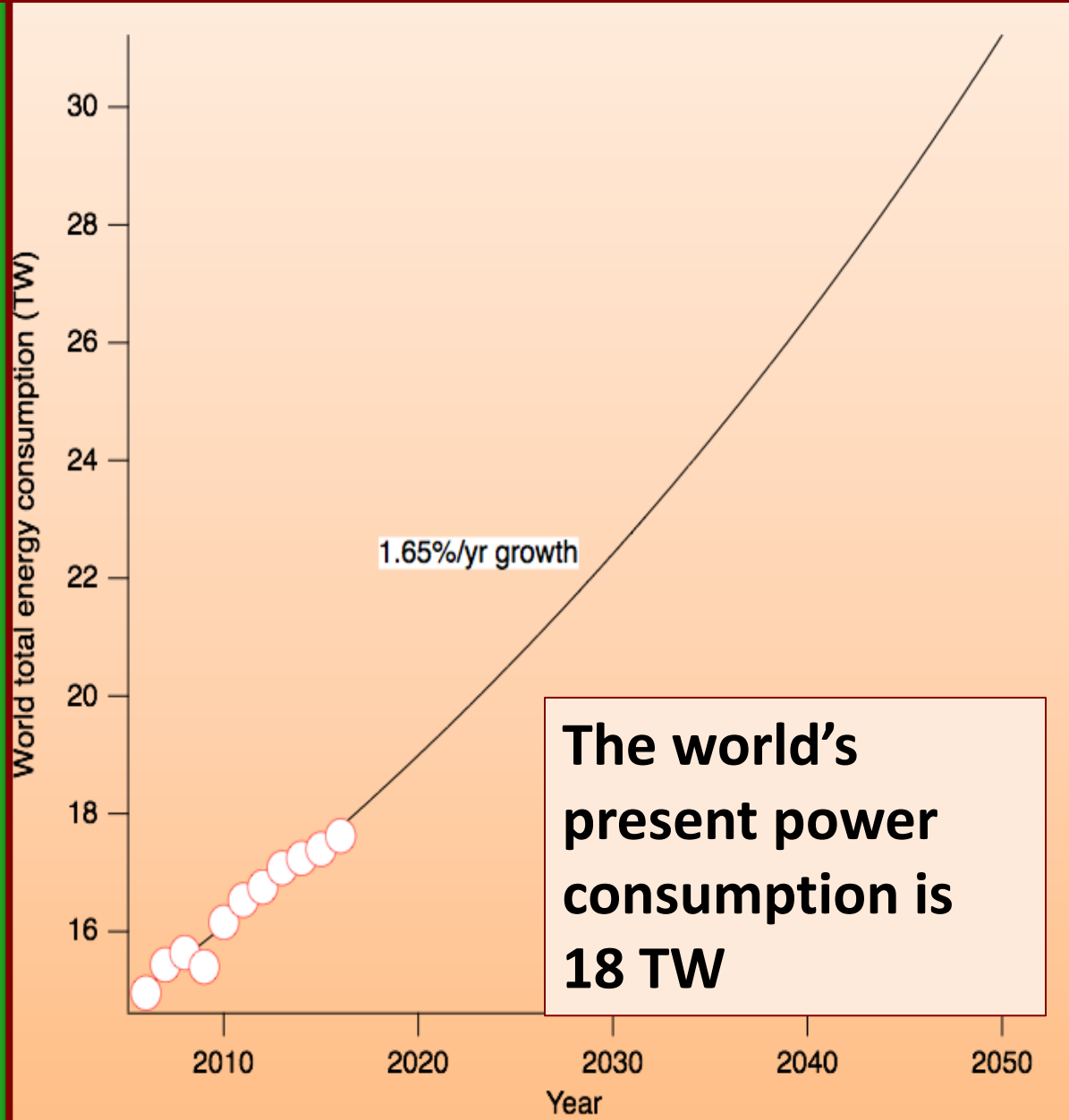


20 April 2010: the BP platform “Deepwater Horizon” explodes in the Gulf of Mexico killing 11 people and causing an unprecedented ecological disaster by spilling at least 1 billion liters of oil in the ocean.

US National Oceanic and Atmospheric Administration (NOAA):  
CO<sub>2</sub> level passed the critical level of 400 ppm !  
in Oct. 2015 !



# The Terrawatt Challenge

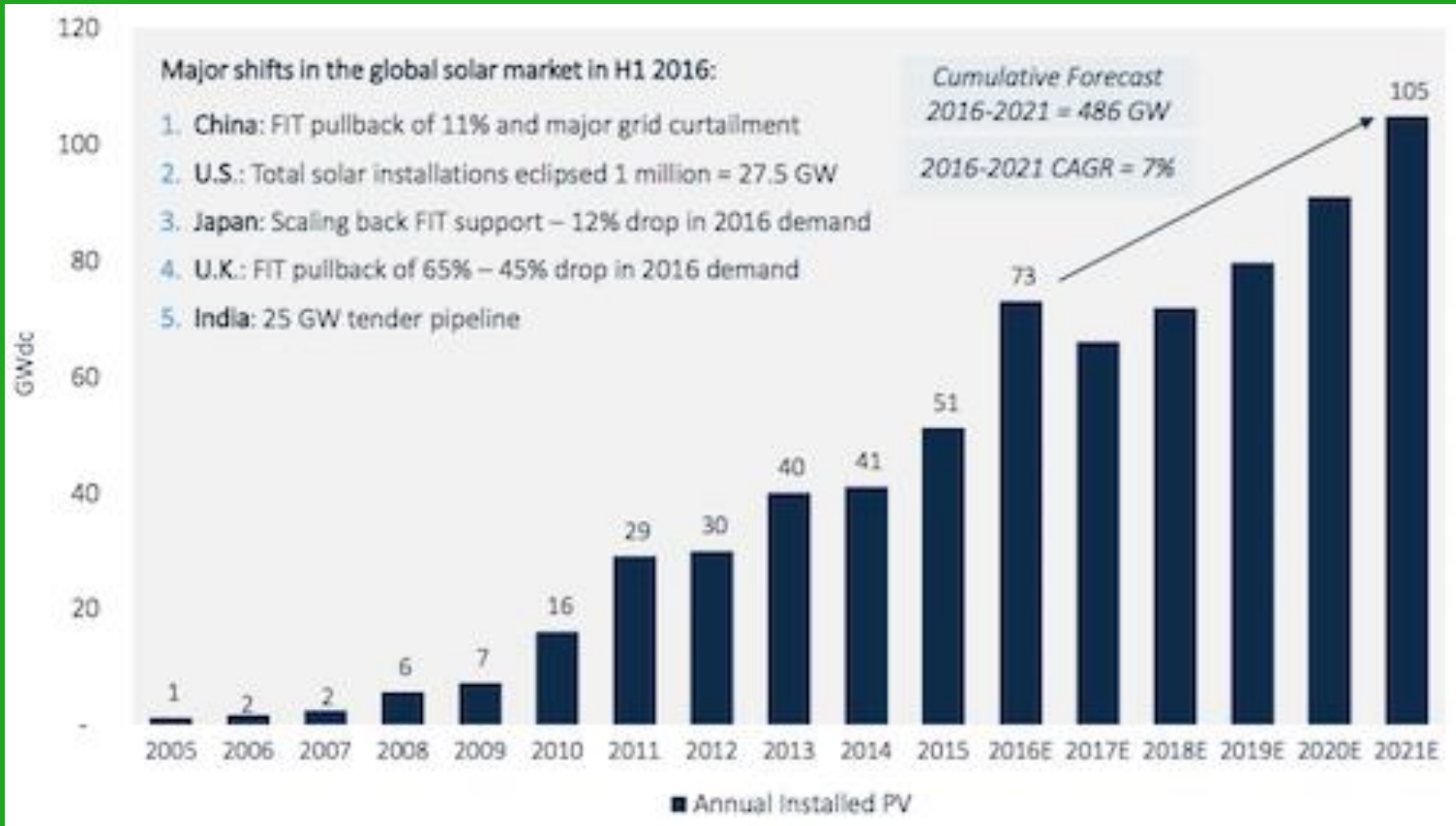


- Another 15 TW needed by 2050
- Only 16% of energy consumption is in electricity generation
- What will be used to 'fuel' this growth?

Courtesy: Jao van de. Lagrmaat  
NREL, USA



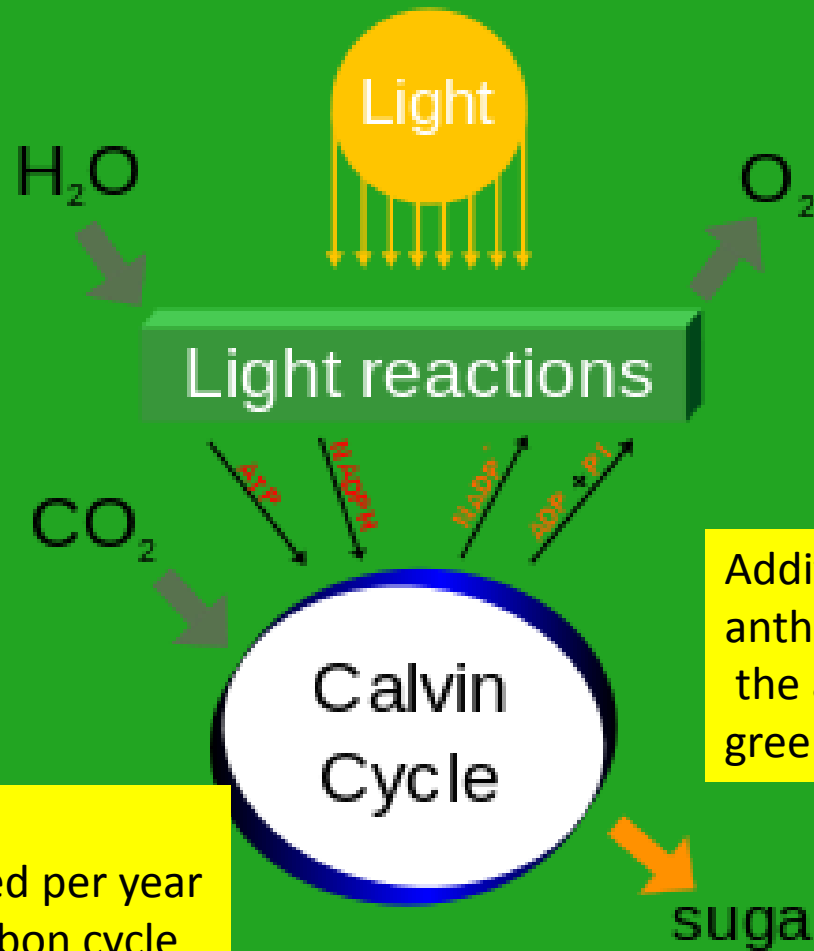
The annual installation of photovoltaics has been growing strongly, but it still contributes only 0.3 % to the world's total energy needs.



Future growth of Si-PV to the TW scale may be compromised by high capex and declining marginal value

# Photosynthesis shows the way

Converts ca 90 terrawatt of the 178'000 terrawatt solar power that strikes the Earth to chemical energy stored in fossile fuels



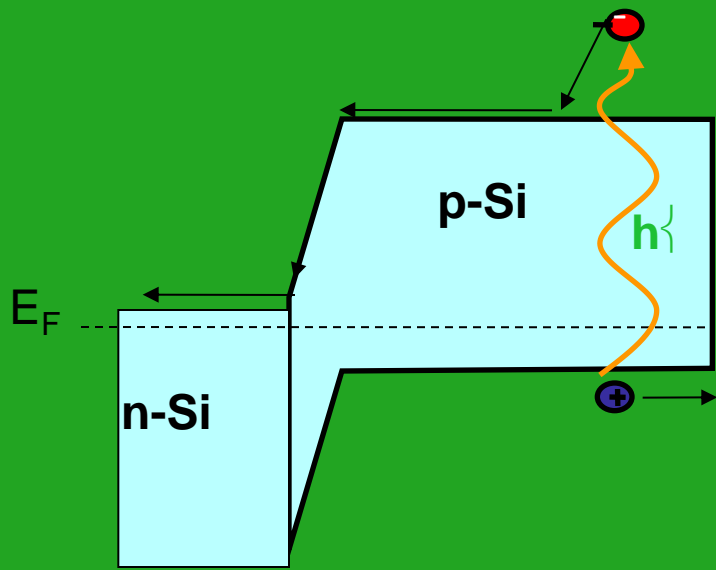
Additional 40 billion tons/year of anthropogenic CO<sub>2</sub> rejected in the atmosphere resulting in green house warming

750 billion tons of CO<sub>2</sub> assimilated and recycled per year through the natural carbon cycle



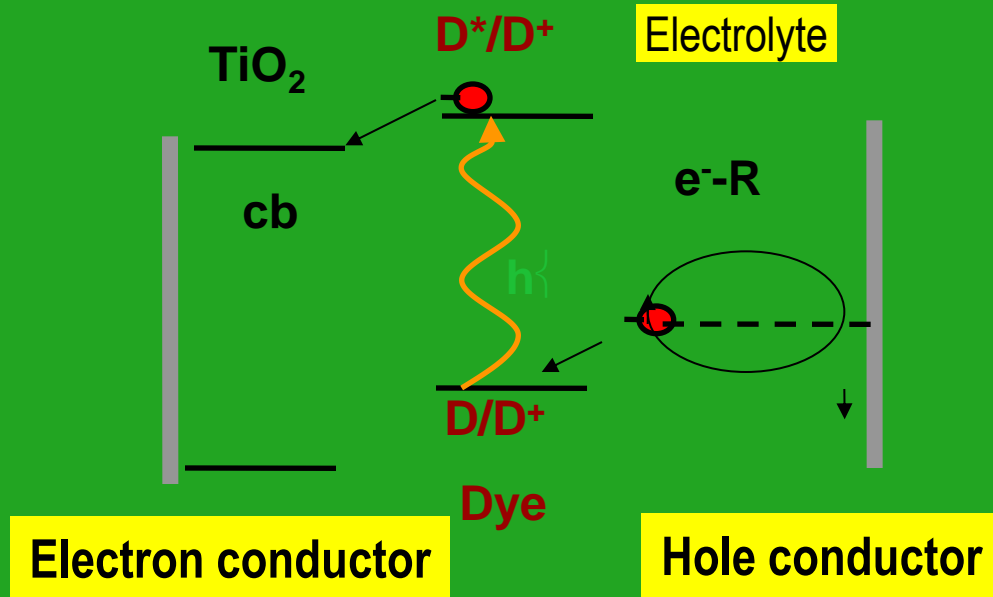
# Photo-induced charge generation in dye sensitized solar cells is different from conventional photovoltaic devices

## p-n junction photovoltaic cells



Charge separation by electric field at the p-n junction minority carrier lifetime is a key issue in photoelectric conversion

## dye sensitized solar cells DSC



Charge separation by kinetic competition as in photosynthesis. No minority charge carrier involved in photoelectric energy conversion



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

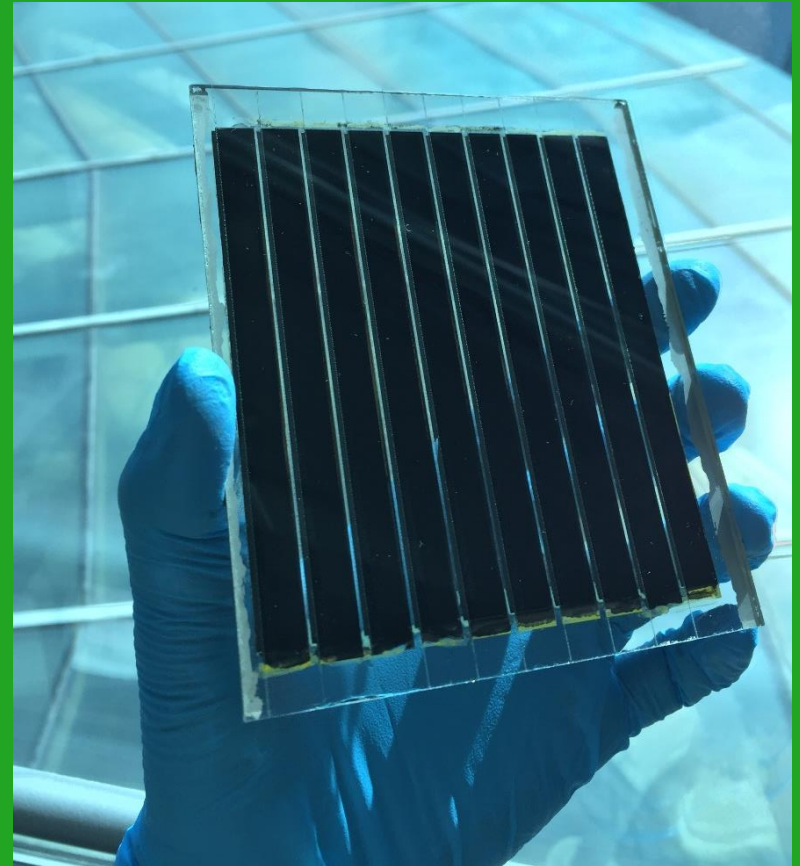
Dye sensitized solar cell (DSC)



Perovskite solar cell (PSC)



Dye sensitized solar cell  
courtesy Sony corporation



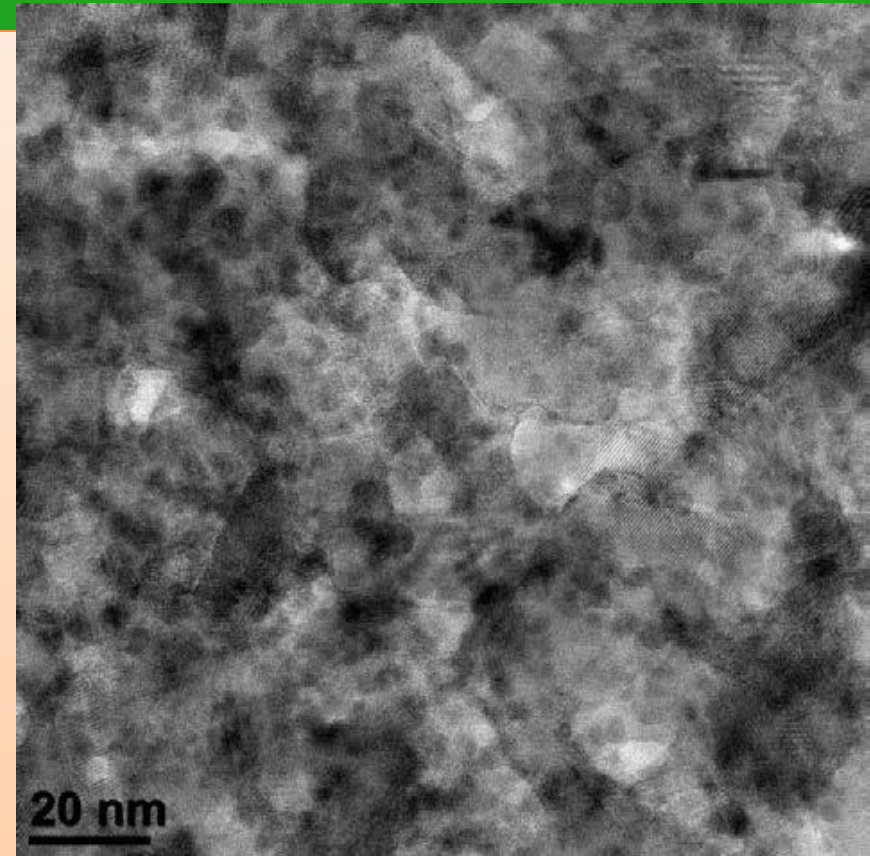
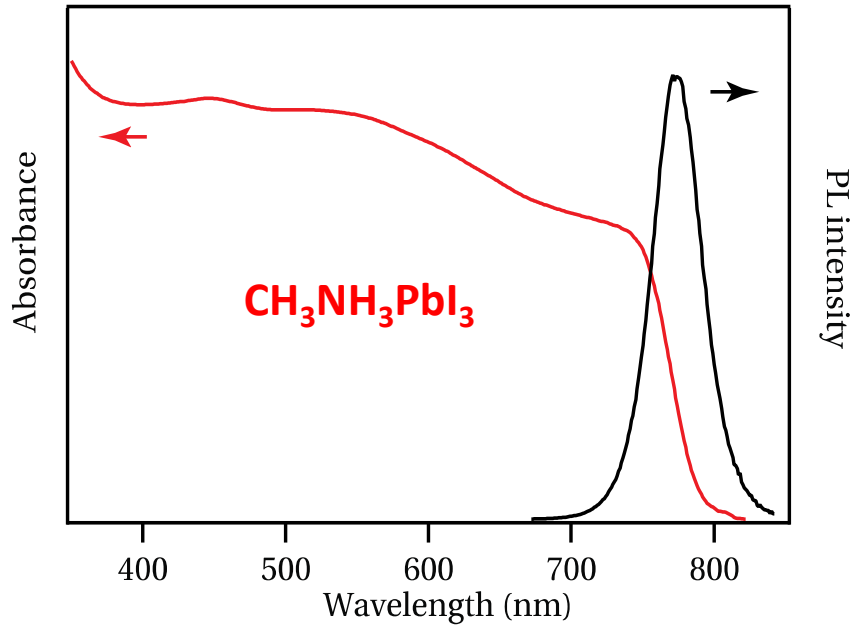
Pervovskite solar cell  
courtesy Subodh Mhalkalsar NTU

# Outline

- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - Multi-cation formulations, the power of solid state NMR analysis.
  - The amazing impact of molecular modulators
  - Boosting the PSC stability.

Applications for solar fuel generation

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

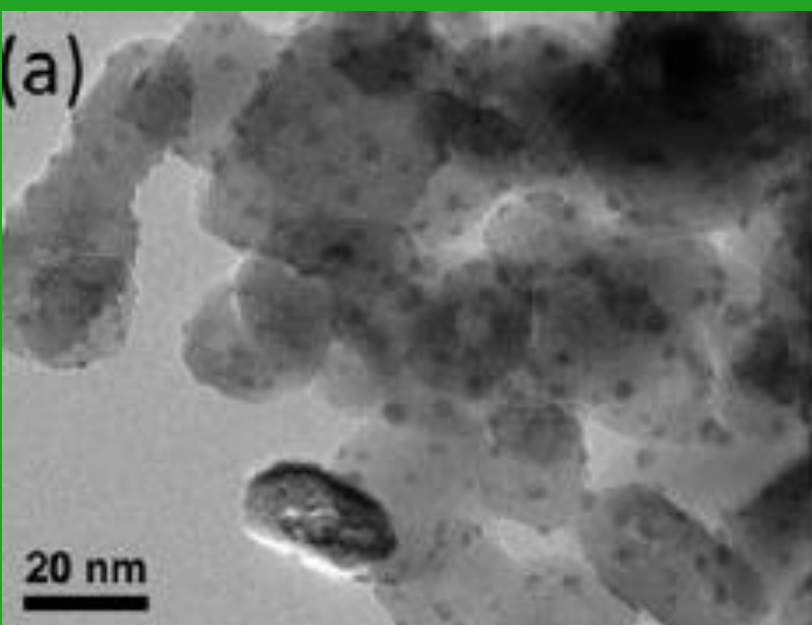


- ◆ Perovskite pigment replaces the molecular sensitizer in a dye sensitized solar cells (T.Miyasaka, et al. JACS 2009, 131, 6050–6051, N.G Park et al *Nanoscale* 2011, 3, 4088-4093)
- ◆ unstable in liquid electrolyte based DSSC
- ◆ stable and more efficient in solid state hole conductor based DSSC



# 6.5% efficient perovskite quantum-dot-sensitized solar cell†

Jeong-Hyeok Im, Chang-Ryul Lee, Jin-Wook Lee, Sang-Won Park and Nam-Gyu Park\*



Mesoscopic  $\text{TiO}_2$  film impregnated with  $\text{MAPbI}_3$  perovskite quantum dots

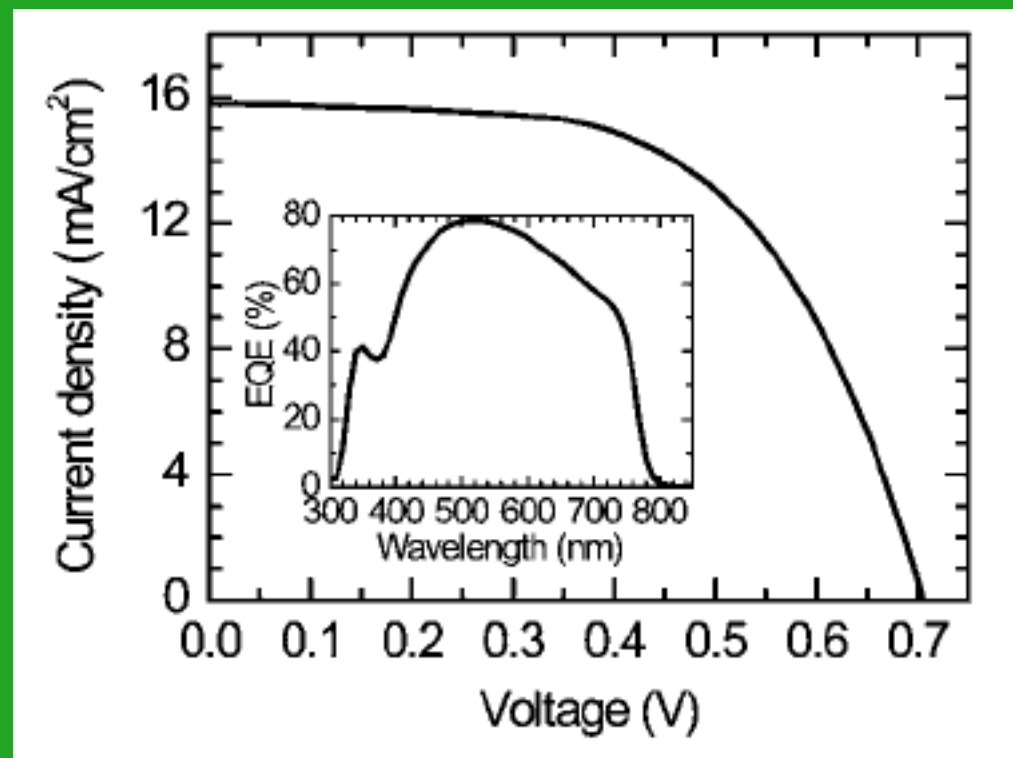


Fig. 5 Photocurrent–voltage curve and EQE for the perovskite  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$  QD-sensitized  $\text{TiO}_2$  film whose surface was modified with  $\text{Pb}(\text{NO}_3)_2$ . Thickness of  $\text{TiO}_2$  film was  $3.6\ \mu\text{m}$  and the redox electrolyte used was composed of 0.9 M LiI, 0.45 M  $\text{I}_2$ , 0.5 M *tert*-butylpyridine and 0.05 M urea in ethyl acetate.

*Nanoscale*, 2011, **3**, 4088



# 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

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

Received  
5 July 2012

Accepted  
6 August 2012

Published  
21 August 2012

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

We report on solid-state mesoscopic heterojunction solar cells employing ammonium lead iodide ( $(\text{CH}_3\text{NH}_3)\text{PbI}_2$ ) as light harvesters. The perovskite methylammonium iodide with  $\text{PbI}_2$  and deposited onto a submicron porous were infiltrated with the hole-conductor *spiro*-MeOTAD. Illumination generated large photocurrents ( $J_{\text{sc}}$ ) exceeding 17 mA/cm<sup>2</sup>, 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 photo showed charge separation to proceed via hole injection from the *spiro*-MeOTAD followed by electron transfer to the mesoscopic  $\text{TiO}_2$  dramatically improved the device stability compared to  $(\text{CH}_3\text{NH}_3)\text{P}$



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

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

Michael M. Lee,<sup>1</sup> Joël Teuscher,<sup>1</sup> Tsutomu Miyasaka,<sup>2</sup> Takuro N. Murakami,<sup>2,3</sup> Henry J. Snaith<sup>1\*</sup>

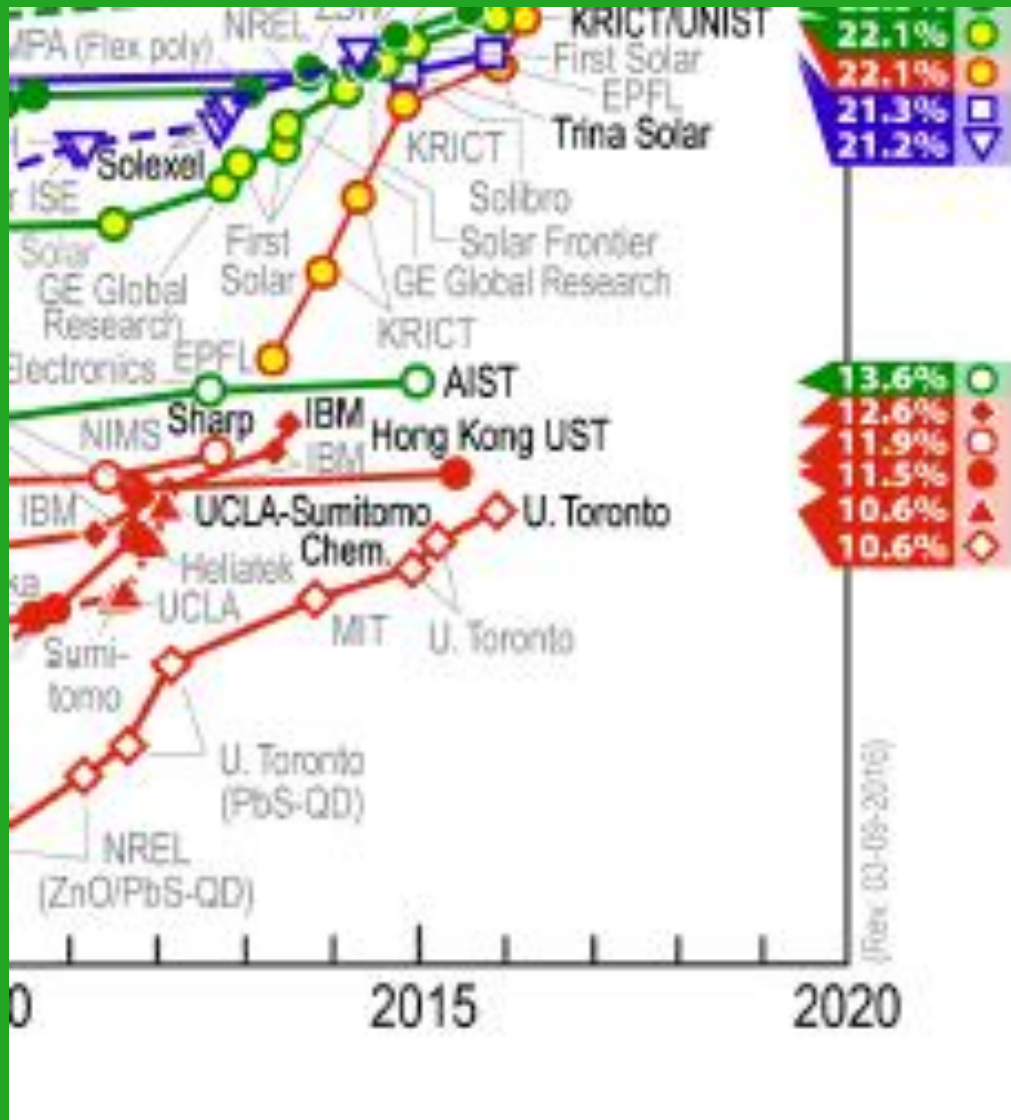
<sup>1</sup>Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, UK. <sup>2</sup>Graduate School of Engineering, Tooin University of Yokohama, 1614 Kurogane, Aoba, Yokohama 225-8503, Japan.

<sup>3</sup>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.

# Power conversion efficiency (PCE) of PSCs reached 22.1 % surpassing PCE of polycrystalline silicon cells



Dr. Dongqin Bi, LPI, EPFL



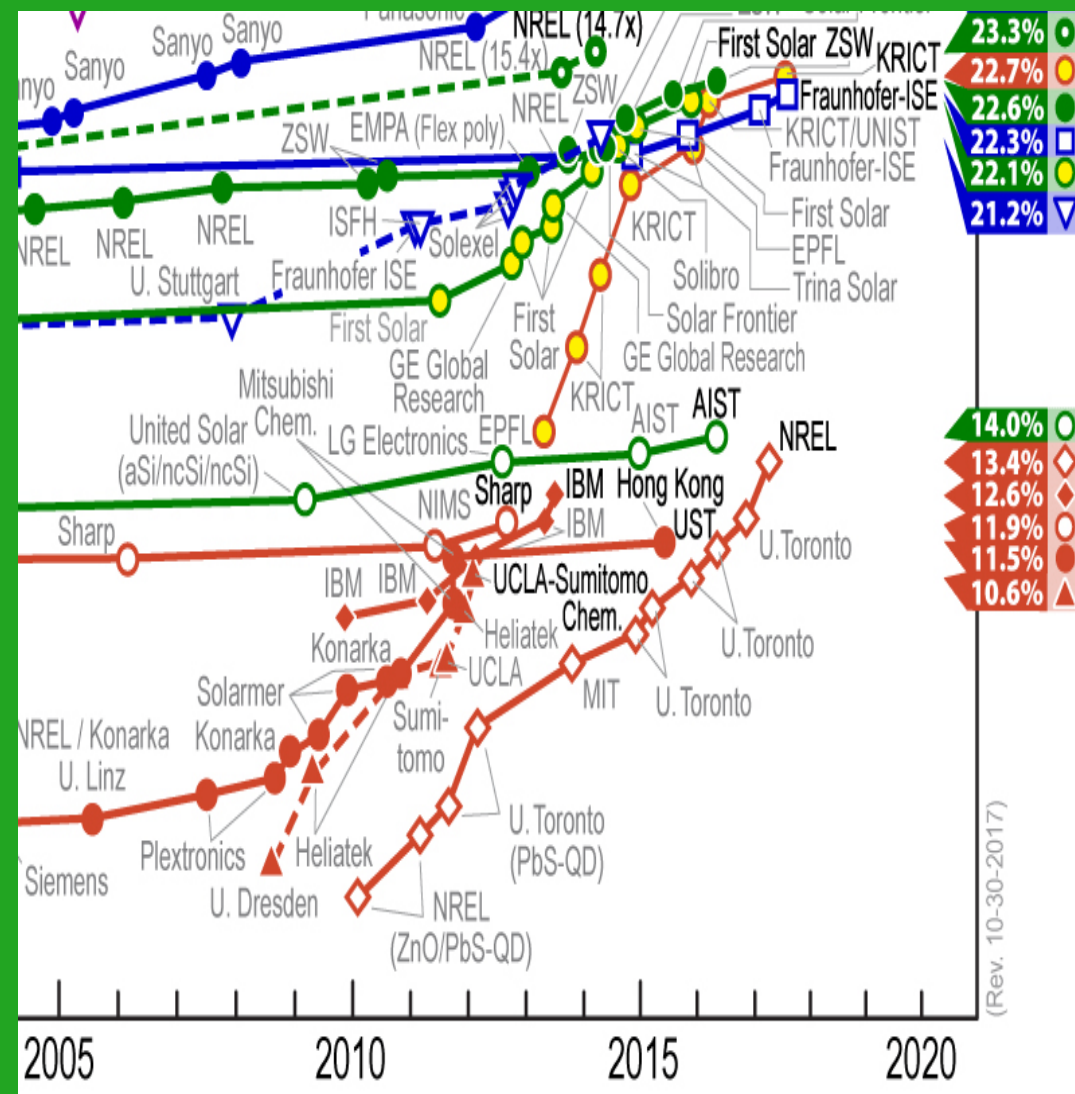
Prof. Anders Hagfeldt.  
Director LSPM, EPFL

NREL chart showing certified efficiencies of best laboratory cells



# Best Research-Cell Efficiencies

ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE



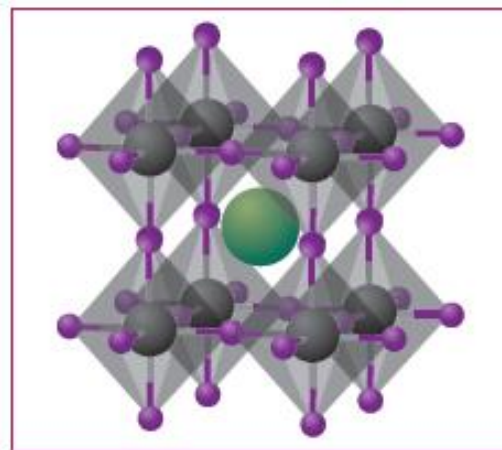
Prof. Anders Hagfeldt.  
Director LSPM, EPFL



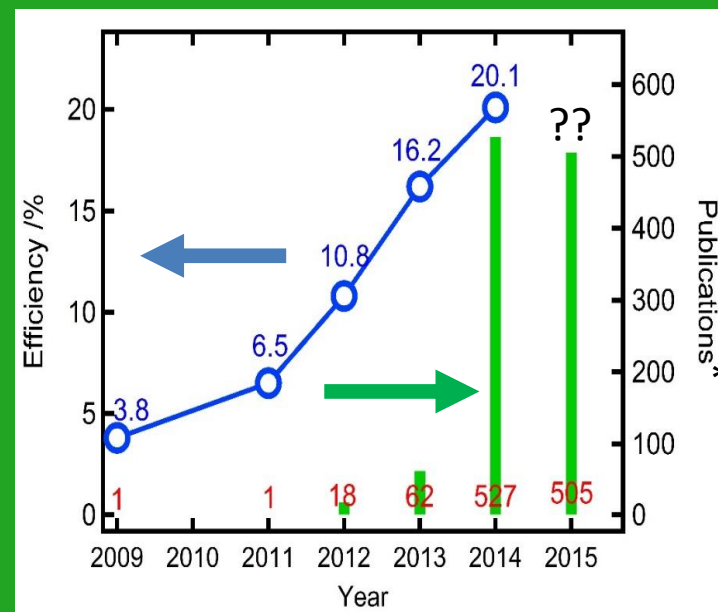
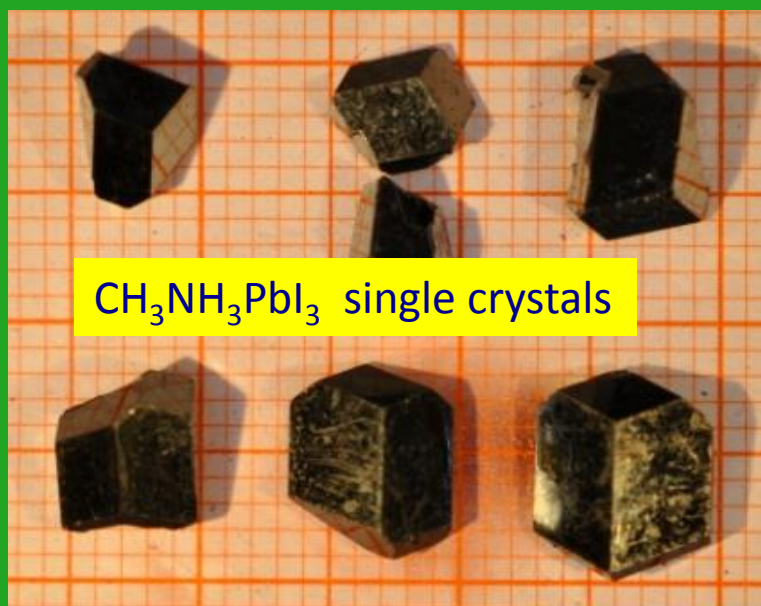
Dr. Dongqin Bi, LPI, EPFL

# The light and shade of perovskite solar cells

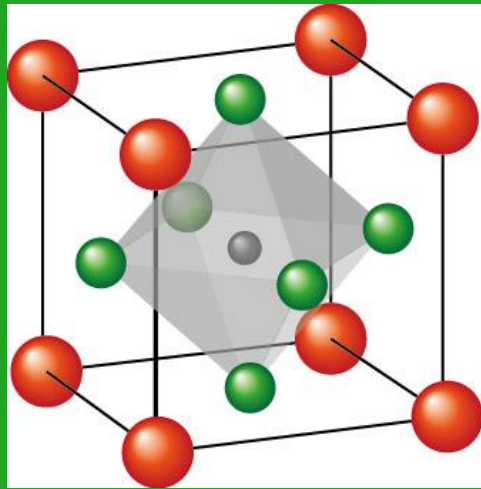
Michael Grätzel



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 are powerful solar light harvesters



● A =  $\text{CH}_3\text{NH}_3^+$ ,  $\text{HC}(\text{NH}_2)_2^+$ ,  $\text{Cs}^+$

● B =  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$

● X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$

General formular  
 **$\text{ABX}_3$**

**$\text{CH}_3\text{NH}_3\text{PbX}_3$ , ein Pb(II)-System mit kubischer Perowskitstruktur**

$\text{CH}_3\text{NH}_3\text{PbX}_3$ , a Pb(II)-System with Cubic Perovskite Structure

Dieter Weber

Institut für Anorganische Chemie der Universität Stuttgart

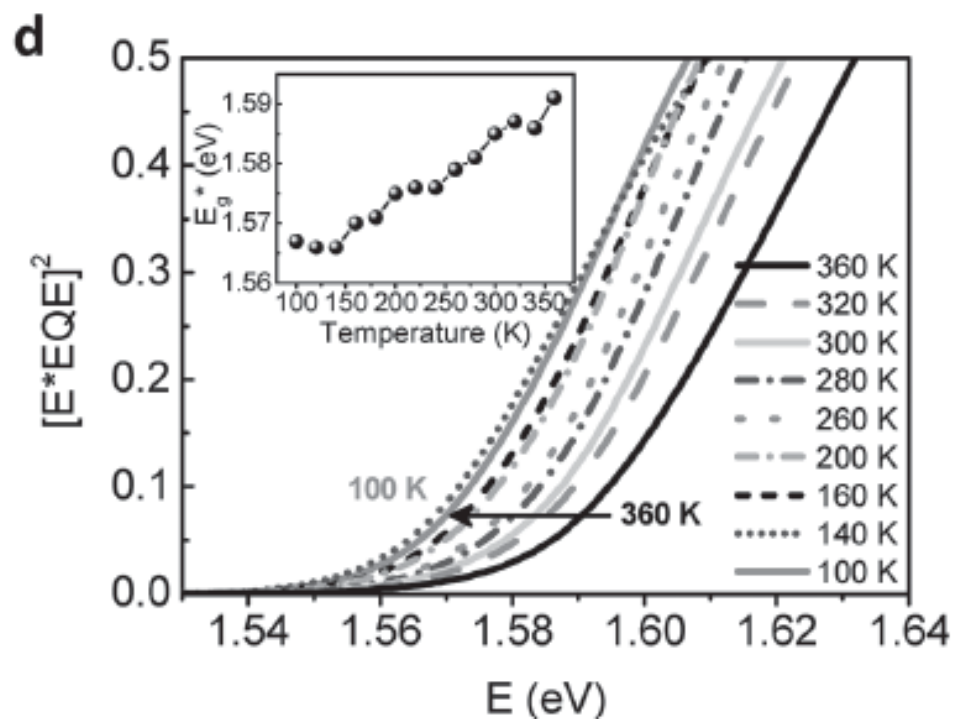
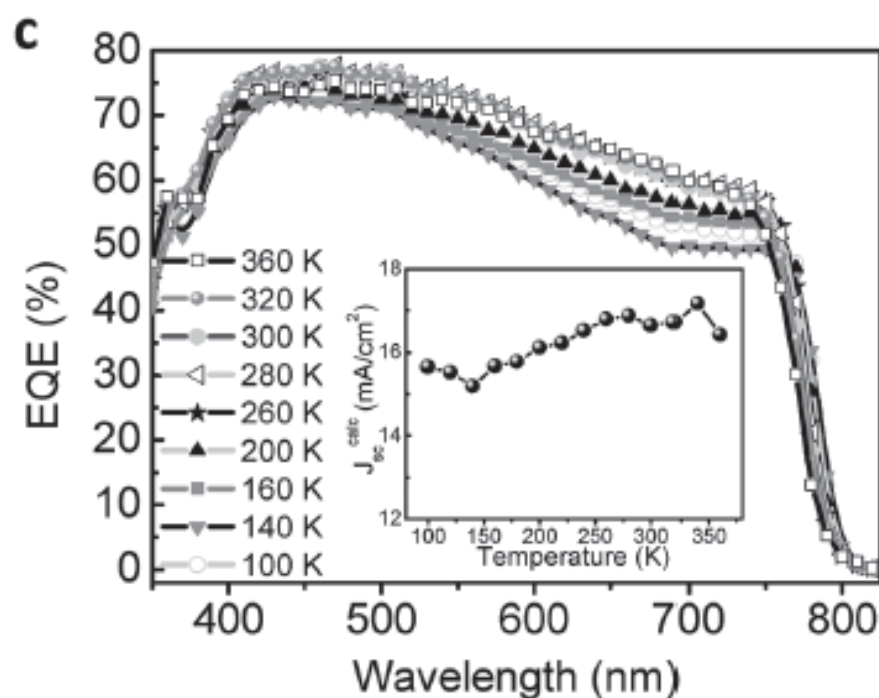
Z. Naturforsch. **33b**, 1443–1445 (1978); eingegangen am 21. August 1978

- 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



# Identifying Fundamental Limitations in Halide Perovskite Solar Cells

Wei Lin Leong,\* Zi-En Ooi, Dharani Sabba, Chenyi Yi, Shaik M. Zakeeruddin, Michael Graetzel, Jeffrey M. Gordon, Eugene A. Katz, and Nripan Mathews



# Outline

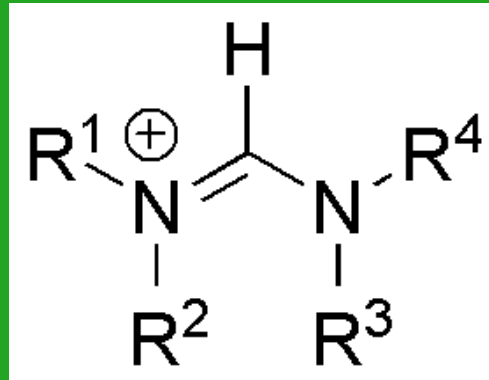
- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - **Multi-cation formulations, the power of solid state NMR analysis**
  - The amazing impact of molecular modulators
  - Boosting the PSC stability

Applications for solar fuel generation

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

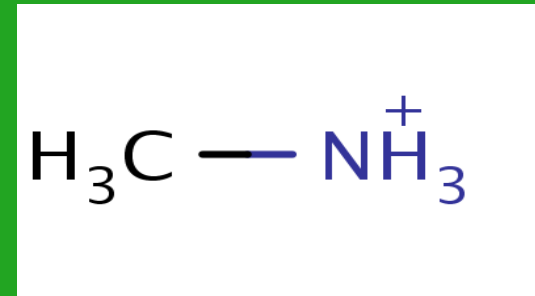
General composition  $\text{FA}_{1-x}\text{MA}_x\text{Pb}(\text{I}_{1-x}\text{Br}_x)$

FA =  
formamidinium



$\text{R}^1 - \text{R}^4 = \text{H}$

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).

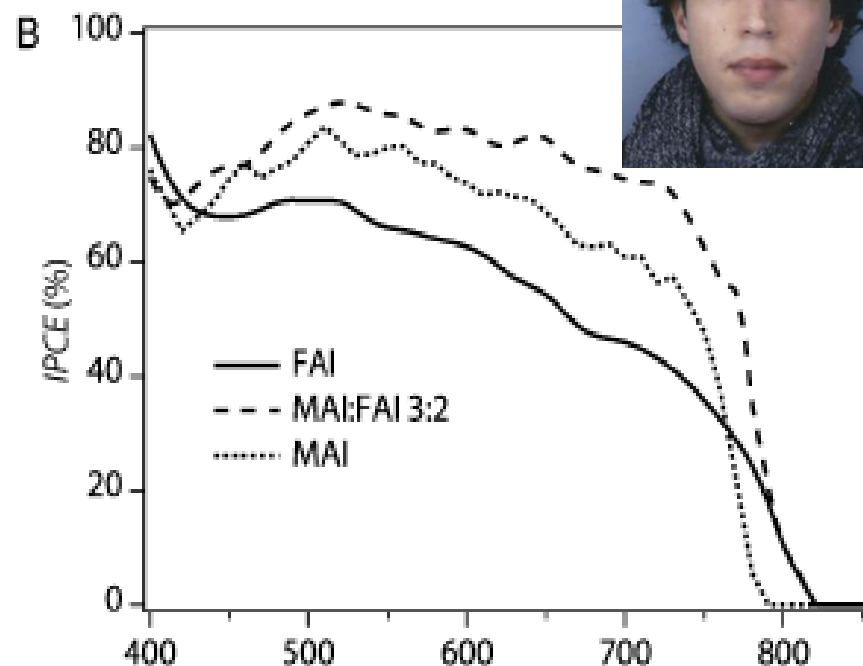
N. J. Jeon *et al.*, Compositional engineering of perovskite materials for high-performance solar cells. *Nat.* **517**, 476-480 (2015).

## Perovskite Solar Cells

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

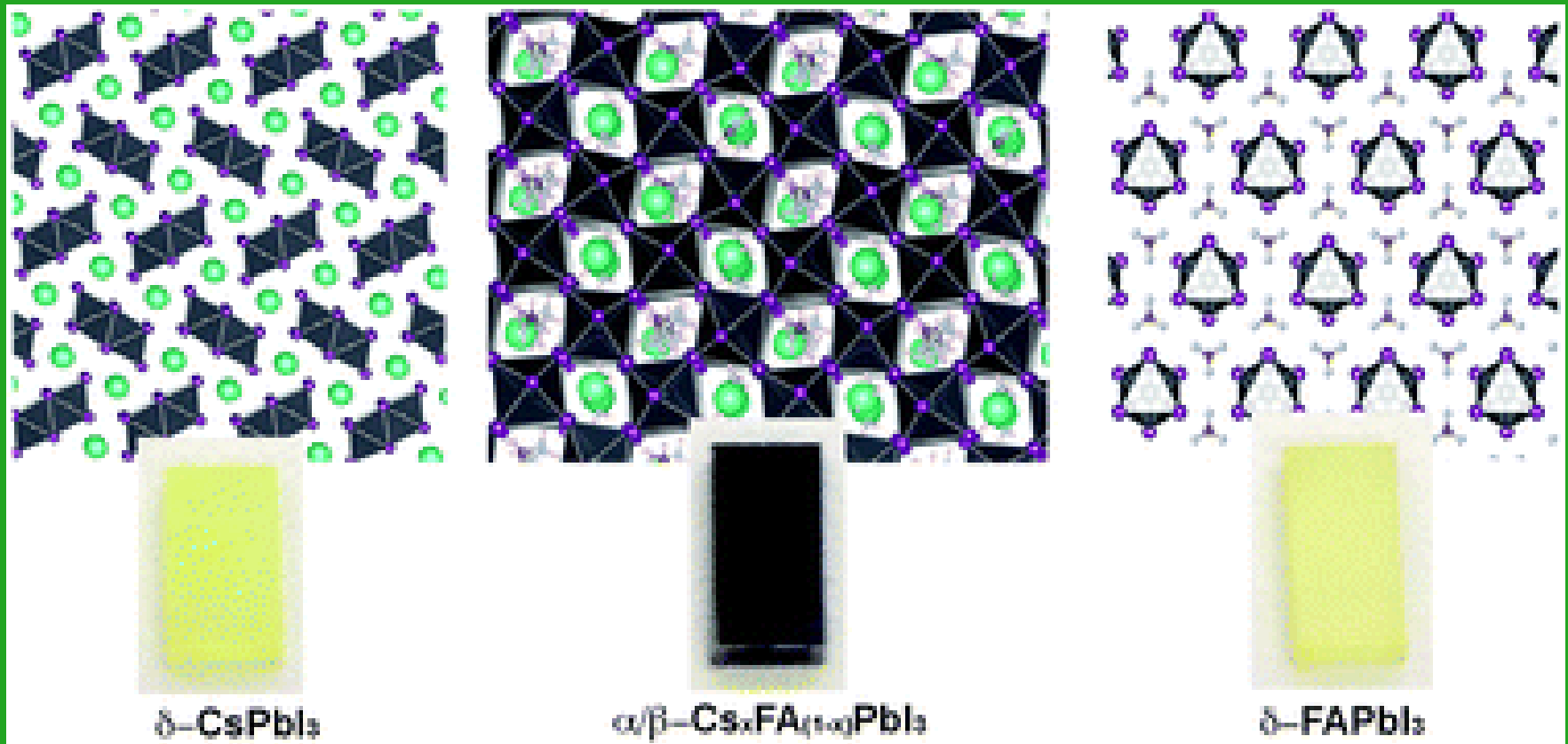
*Norman Pellet, Peng Gao, Giuliano Gregori, Tae-Youl Yang, Mohammad K. Nazeeruddin, Joachim Maier, and Michael Grätzel\**

**Abstract:** Hybrid organic–inorganic lead halide perovskite  $\text{APbX}_3$  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 ( $\text{HN}=\text{CHNH}_3^+$ , FA) and methylammonium ( $\text{CH}_3\text{NH}_3^+$ , MA) cations in the A position of the  $\text{APbI}_3$  perovskite structure. This combination leads to an enhanced short-circuit current and thus superior devices to those based on only  $\text{CH}_3\text{NH}_3^+$ . 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.





# Stabilisation of mixed $\text{Cs}^+$ /formamidinium A-cation perovskites



The stable forms of  $\text{CsPbI}_3$  and  $\text{FAPbI}_3$  are non-perovskite delta phases at room temperature. Amazingly, upon mixing a stable perovskite structure forms spontaneously.

J.-W. Lee, D.-H. Kim, H.-S. Kim, S.-W. Seo, S.M. Cho and N.-G. Park,  
Formamidinium + Cesium Hybridization for Photo+ Moisture Stable Perovskite Solar Cell  
Adv. Energy Mater., 2015, 5, 1501310.

## COMMUNICATION

[View Article Online](#)

[View Journal](#)



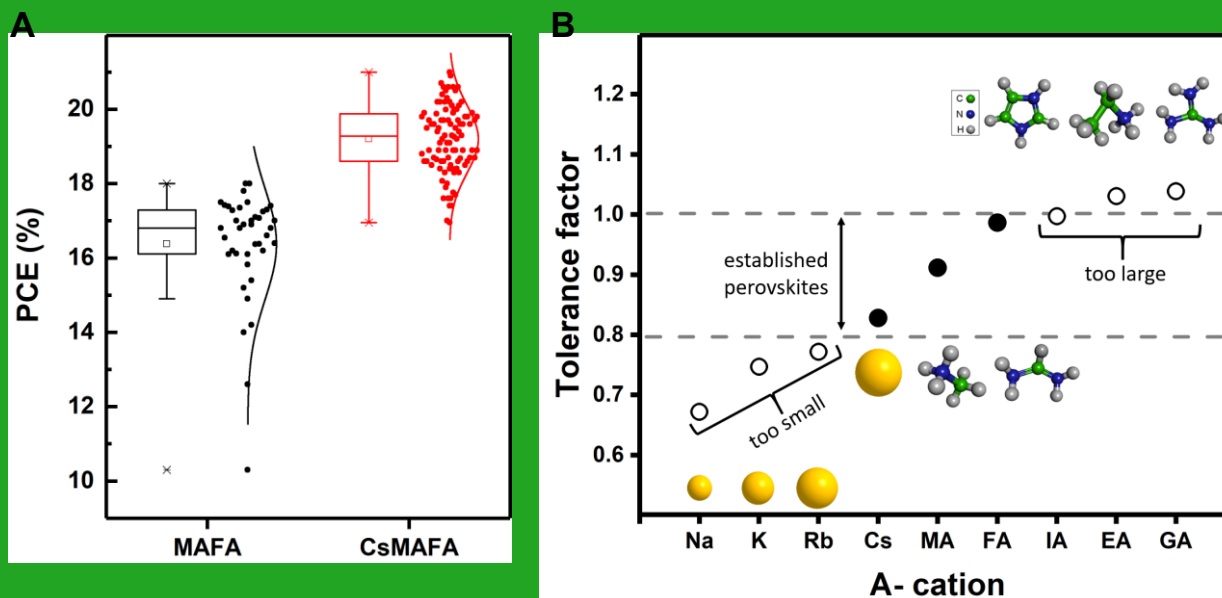
Cite this: DOI: 10.1039/c5ee03874j

Received 24th December 2015,  
Accepted 14th March 2016

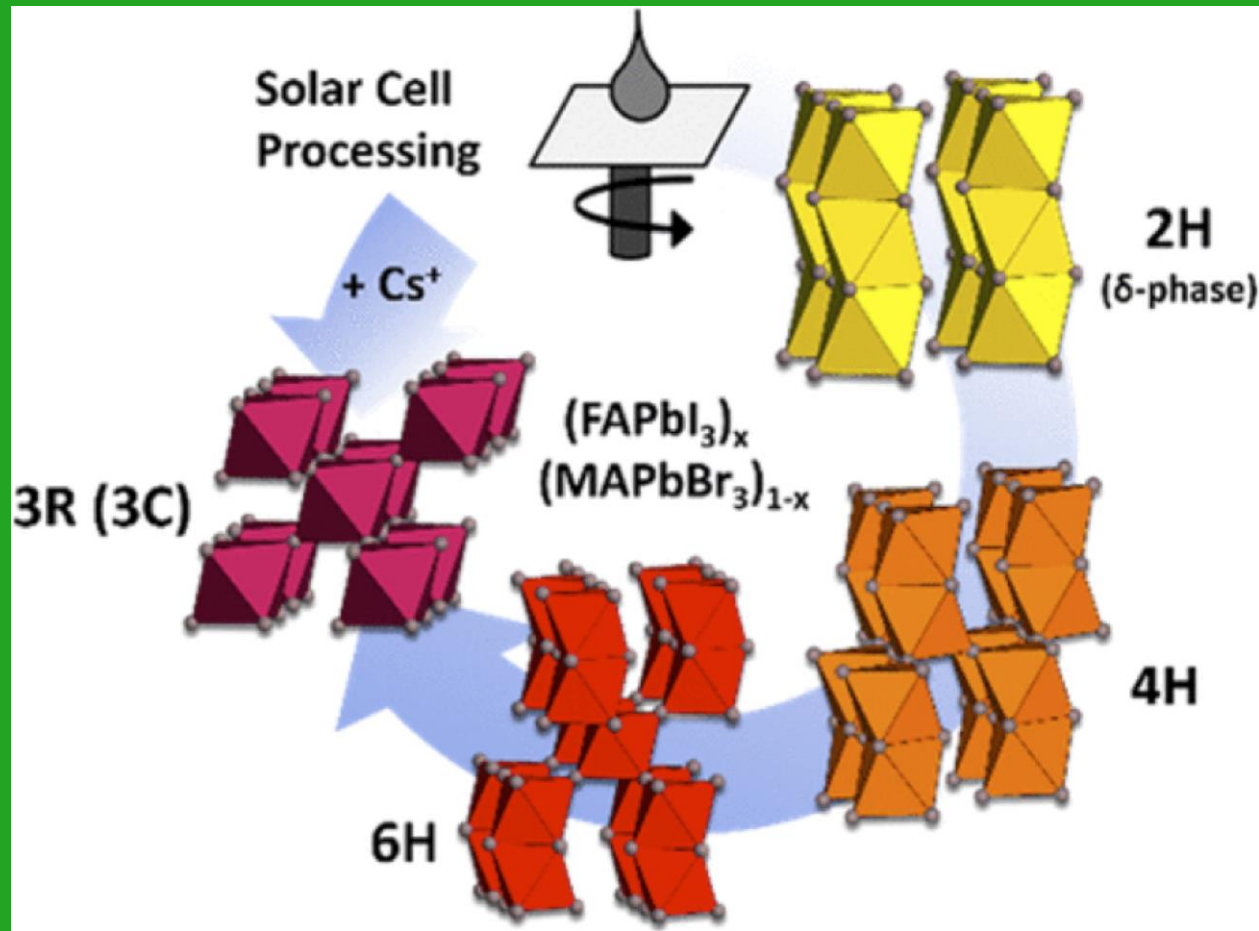
DOI: 10.1039/c5ee03874j

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

Michael Saliba,<sup>‡,\*ab</sup> Taisuke Matsui,<sup>‡,c</sup> Ji-Youn Seo,<sup>a</sup> Konrad Domanski,<sup>a</sup> Juan-Pablo Correa-Baena,<sup>d</sup> Mohammad Khaja Nazeeruddin,<sup>b</sup> Shaik M. Zakeeruddin,<sup>a</sup> Wolfgang Tress,<sup>a</sup> Antonio Abate,<sup>a</sup> Anders Hagfeldt<sup>d</sup> and Michael Grätzel<sup>a</sup>



# The many faces of mixed ion perovskites: unraveling and understanding the crystallization process

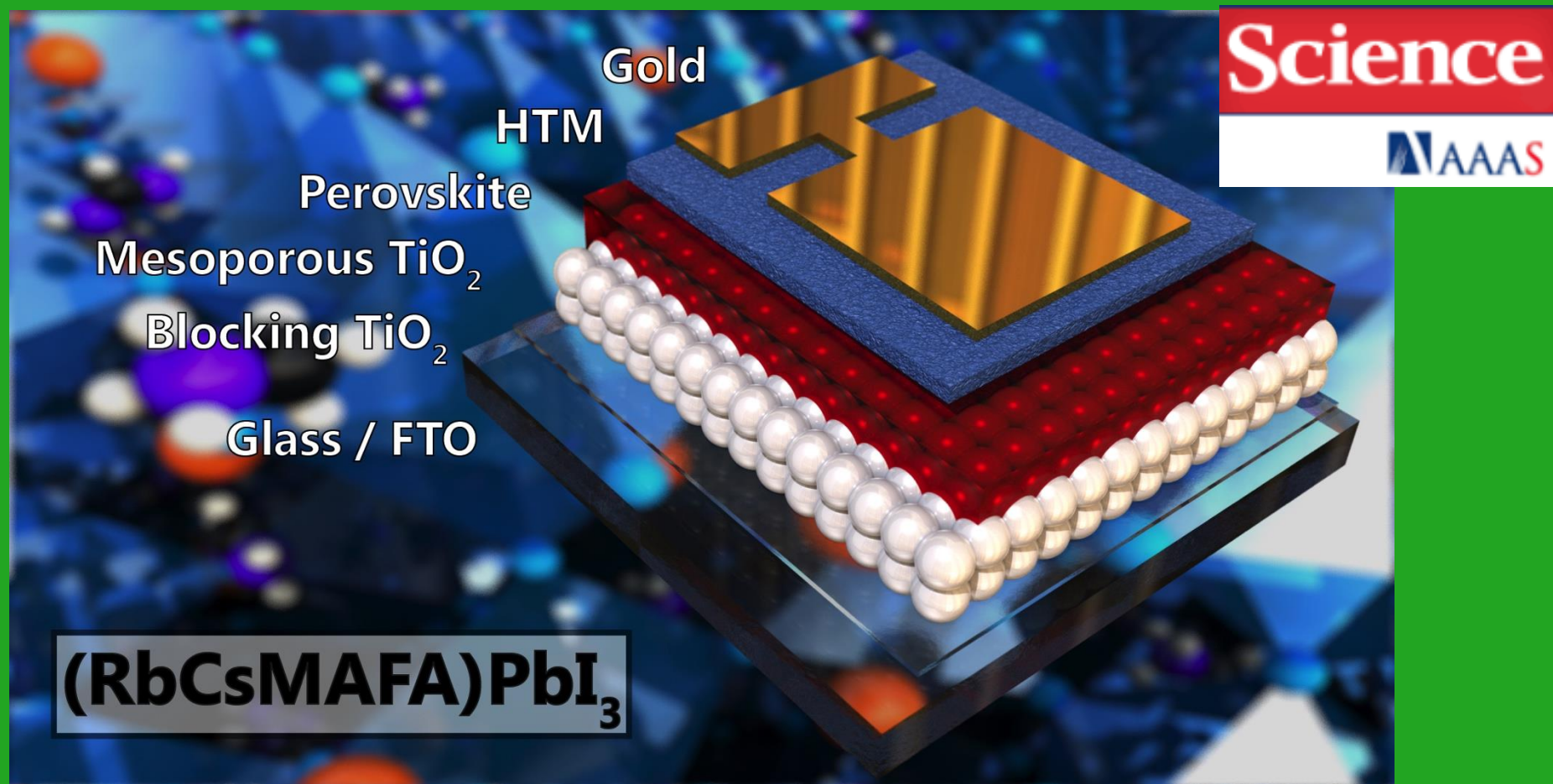


Paul Gratia  
EPFL graduate student

P. Gratia et.al  
*ACS Energy Lett.*, 2017,  
2 (12), pp 2686–2693

The role of Cs ions is to short-cut the formation of perovskite crystals avoiding the intermediate formation of 2H, 4H and 6H hexagonal phases which are detrimental to PSC performance.

Top-performing perovskite formulation uses A cation cascade with Rb

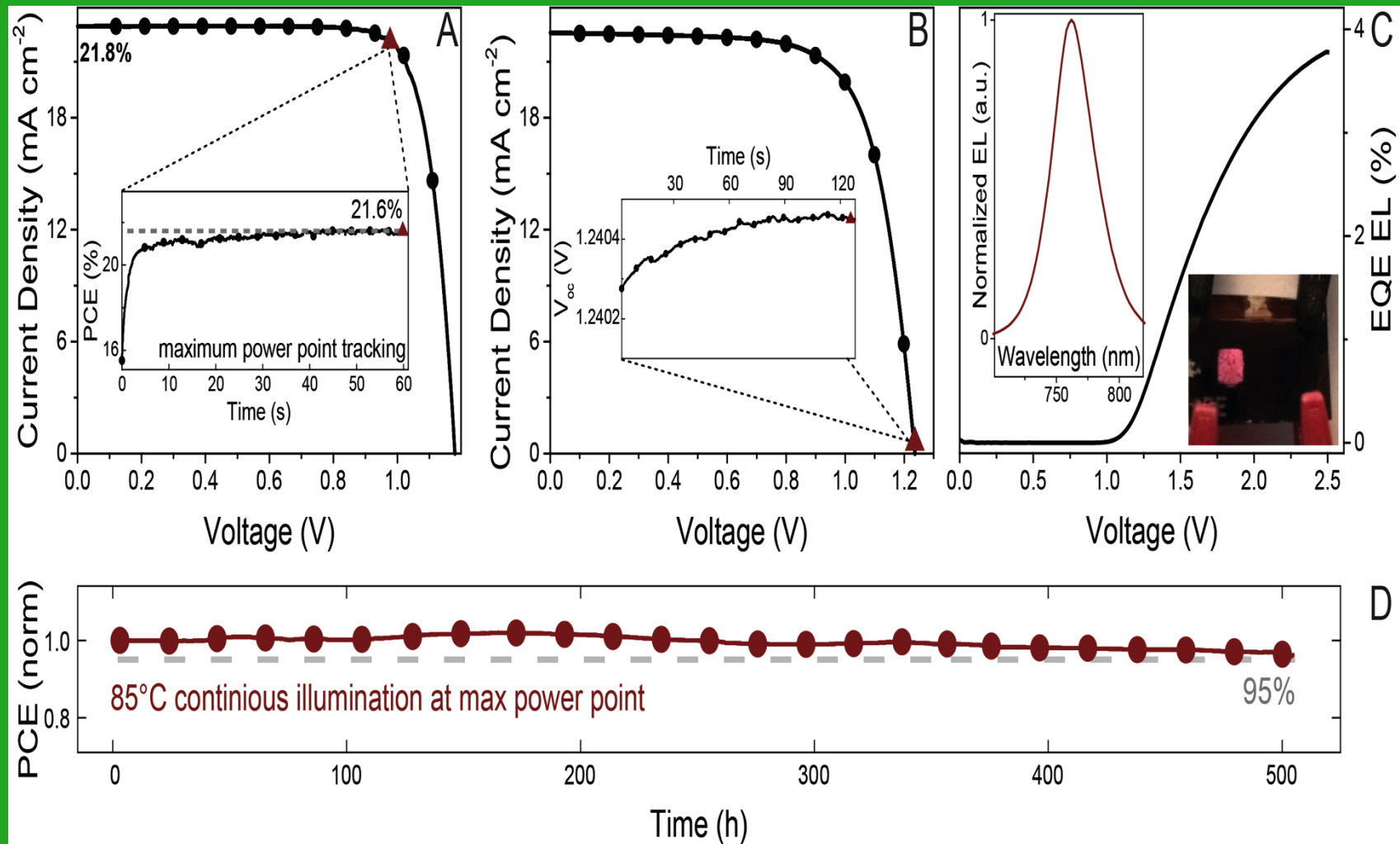


## Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance

Michael Saliba,<sup>1\*†</sup> Taisuke Matsui,<sup>1,2\*</sup> Konrad Domanski,<sup>1\*</sup> Ji-Youn Seo,<sup>1</sup> Amita Ummadisingu,<sup>1</sup> Shaik M. Zakeeruddin,<sup>1</sup> Juan-Pablo Correa-Baena,<sup>3</sup> Wolfgang R. Tress,<sup>1</sup> Antonio Abate,<sup>1</sup> Anders Hagfeldt,<sup>3</sup> Michael Grätzel<sup>1†</sup> 10.1126/science.aah5557 (2016).



Quadruple A cation perovskite sets new records for solar power conversion efficiency, open-circuit voltage and electroluminescence quantum yield along with extraordinary high temperature stability.



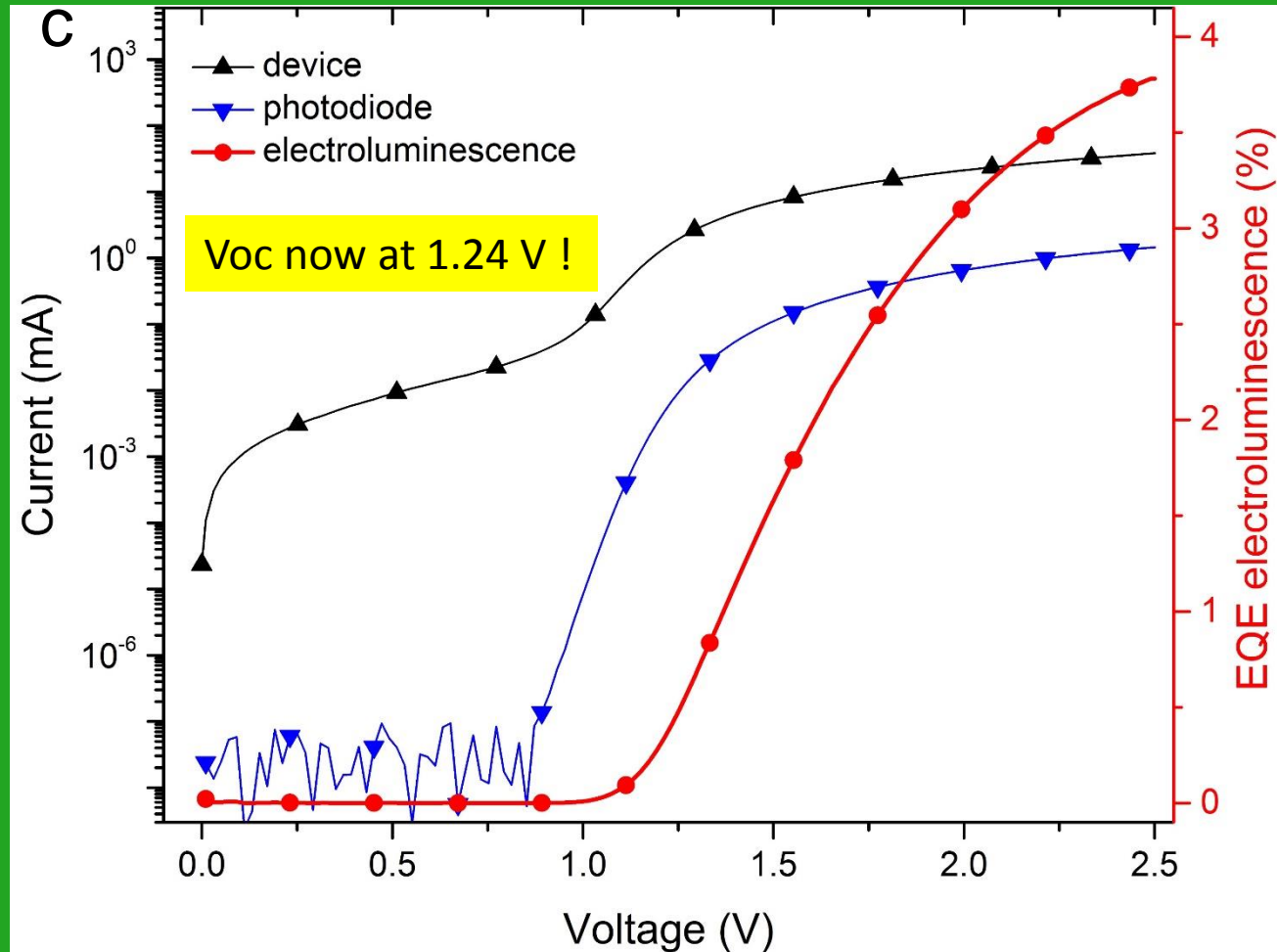
# A good solar cell that is a good LED



LED



solar cell or  
photodetector



Science, 354, 206-209 (2016)

Wolfgang Tress,  
Konrad Domanski  
Michael Saliba  
Taisuke MATsui

# Electro-luminescence offers a powerful tool to probe the level of radiation- less recombination in perovskite solar cells

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

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

$$V_{oc\text{-ideal}} \simeq E_g - 0.23 \text{ V}$$

$E_g$  = band gap energy expressed in electron volt

$\phi_{ext}$  = external quantum yield of electroluminescence  
at an applied forward bias voltage where  $J = J_{sc}$

$$V_{oc} = \frac{k_B T}{e} \ln \left( EQE_{EL} \frac{J_{ph}}{J_{em,0}} + 1 \right)$$

$$J_{ph} = e \int EQE_{PV}(E) \Phi_{AM1.5g}(E) dE$$

$$J_{em,0} = e \int EQE_{PV}(E) \Phi_{BB}(E) dE$$

The maximum open circuit photovoltage of a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  based photovoltaic under standard AM 1.5 illumination is  $1.55 - 0.23 = 1.32 \text{ V}$

# Magic angle spinning (MAS) solid-state NMR a powerful tool to probe the lattice structure, composition and dynamics of metal halide perovskites

## Structure

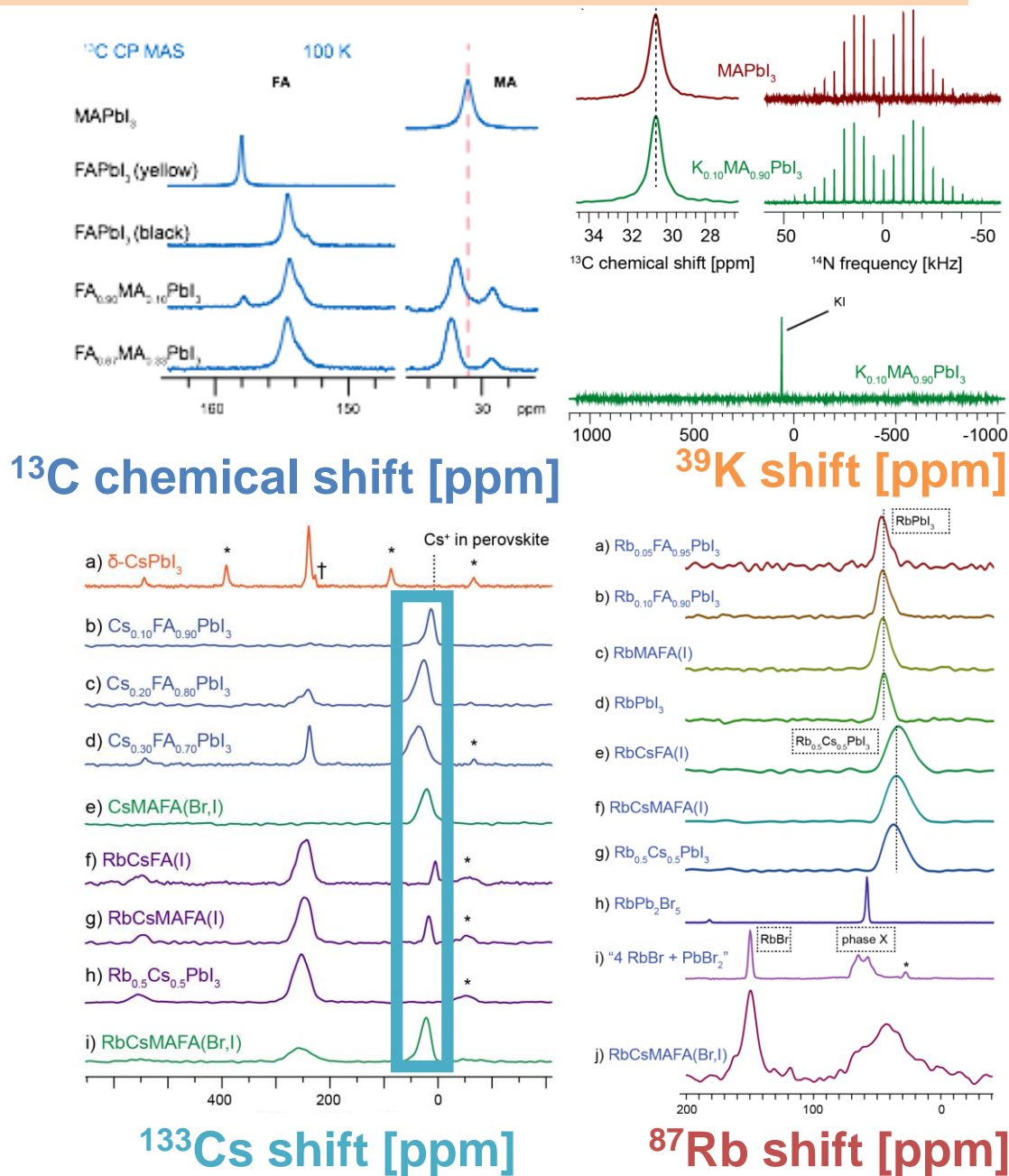
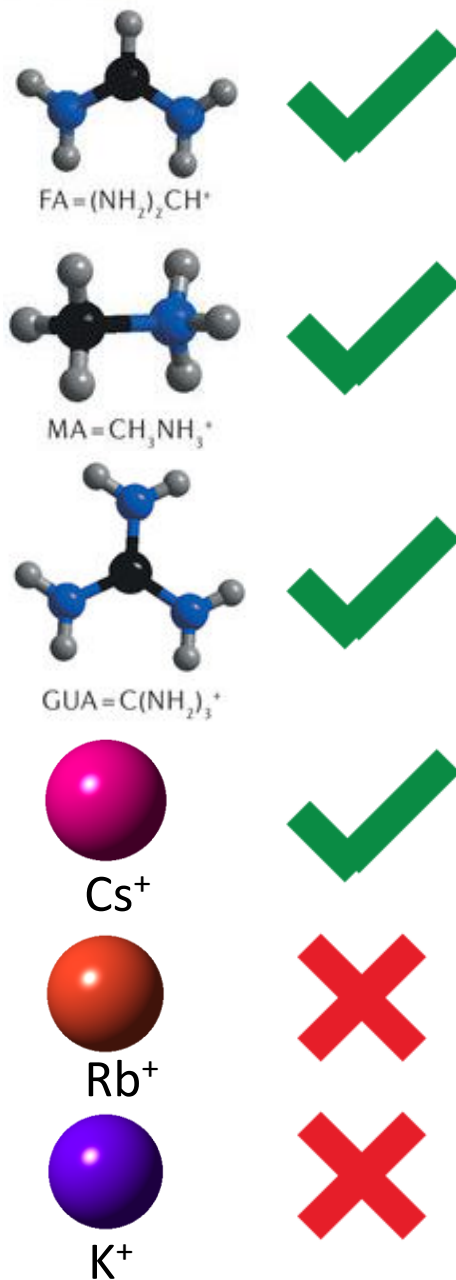
D.J. Kubicki, D. Prochowicz, A. Hofstetter, S.M. Zakeeruddin, M. Grätzel, L.Emsley  
"Phase Segregation in Cs-, Rb- and K-Doped Mixed-Cation (MA)<sub>x</sub>(FA)<sub>1-x</sub>PbI<sub>3</sub> Hybrid Perovskites from Solid-State NMR"  
J.Am.Chem.Spc, 139, 14173-14180 (2017)

## Dynamics

D.J. Kubicki, D. Prochowicz, A. Hofstetter, P. Pechy, S.M. Zakeeruddin, M. Grätzel, L. Emsley  
"Cation Dynamics in Mixed-Cation (MA)<sub>x</sub>(FA)<sub>1-x</sub>PbI<sub>3</sub> Hybrid Perovskites from Solid-State NMR"  
J. Am. Chem. Soc., 139, 10055-10061 (2017)

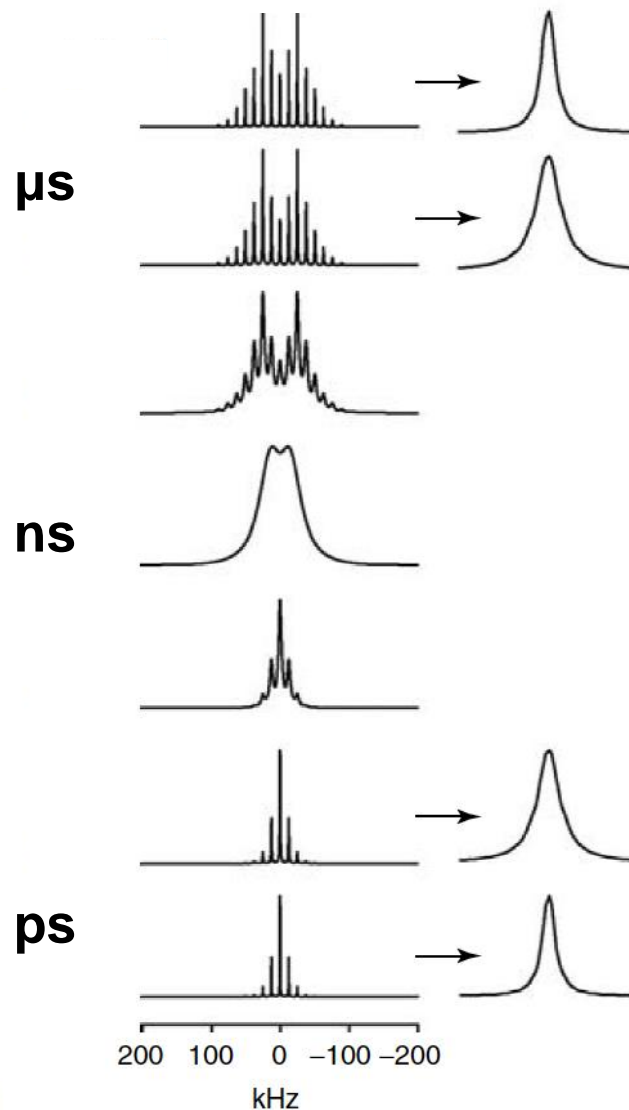


# Structure: NMR yields local and nucleus-specific information



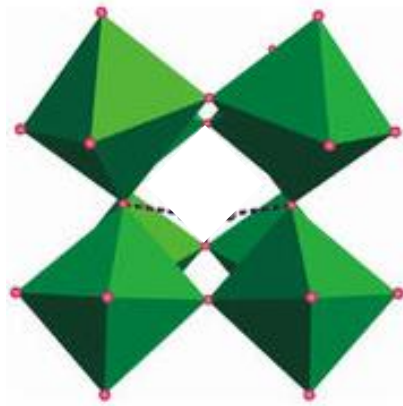
# Dynamics: ps — ns — $\mu$ s — ms — s timescale motions

## $^{14}\text{N}$ MAS NMR

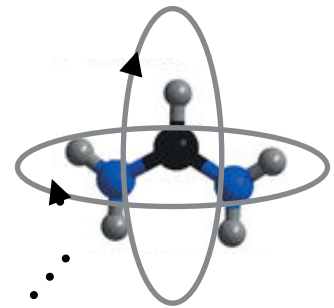
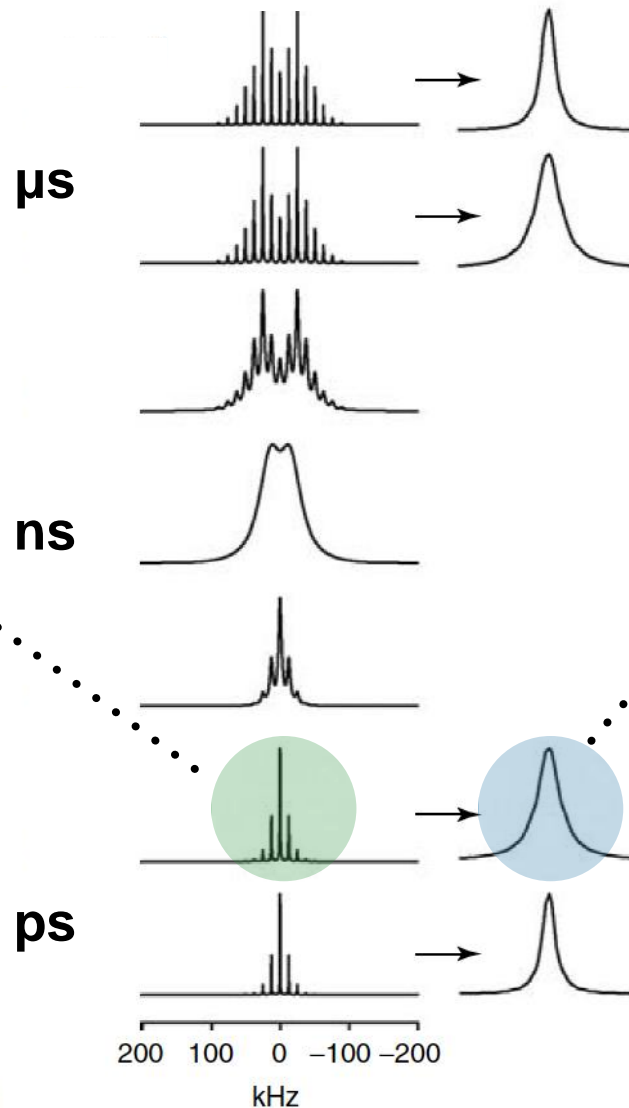


# Dynamics: ps — ns — $\mu$ s — ms — s timescale motions

## $^{14}\text{N}$ MAS NMR



envelope:  
cage symmetry



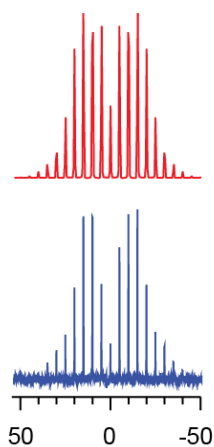
line widths:  
reorientation dynamics

# FA reorients faster than MA

MAPbI<sub>3</sub>

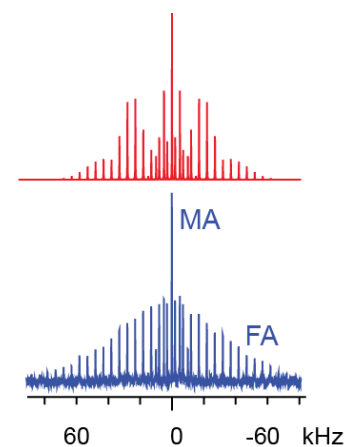
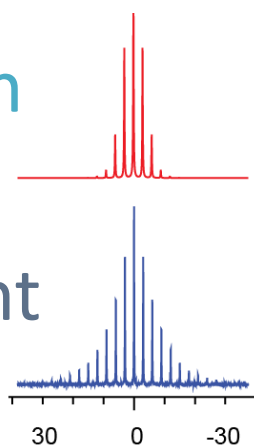
FAPbI<sub>3</sub> (black)

FA<sub>0.67</sub>MA<sub>0.33</sub>PbI<sub>3</sub>



simulation

experiment



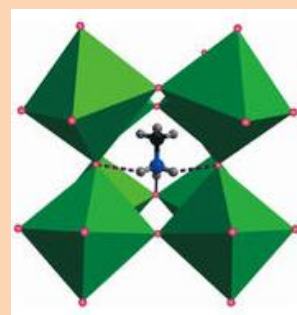
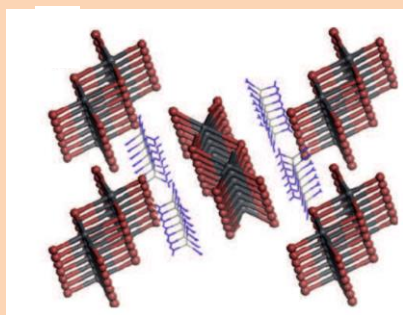
$$\tau = (108 \pm 18) \text{ ps}$$

$$\tau = (8.7 \pm 0.5) \text{ ps}$$

$$\tau^{\text{MA}} = (133 \pm 46) \text{ ps}$$

$$\tau^{\text{FA}} = (12 \pm 5) \text{ ps}$$

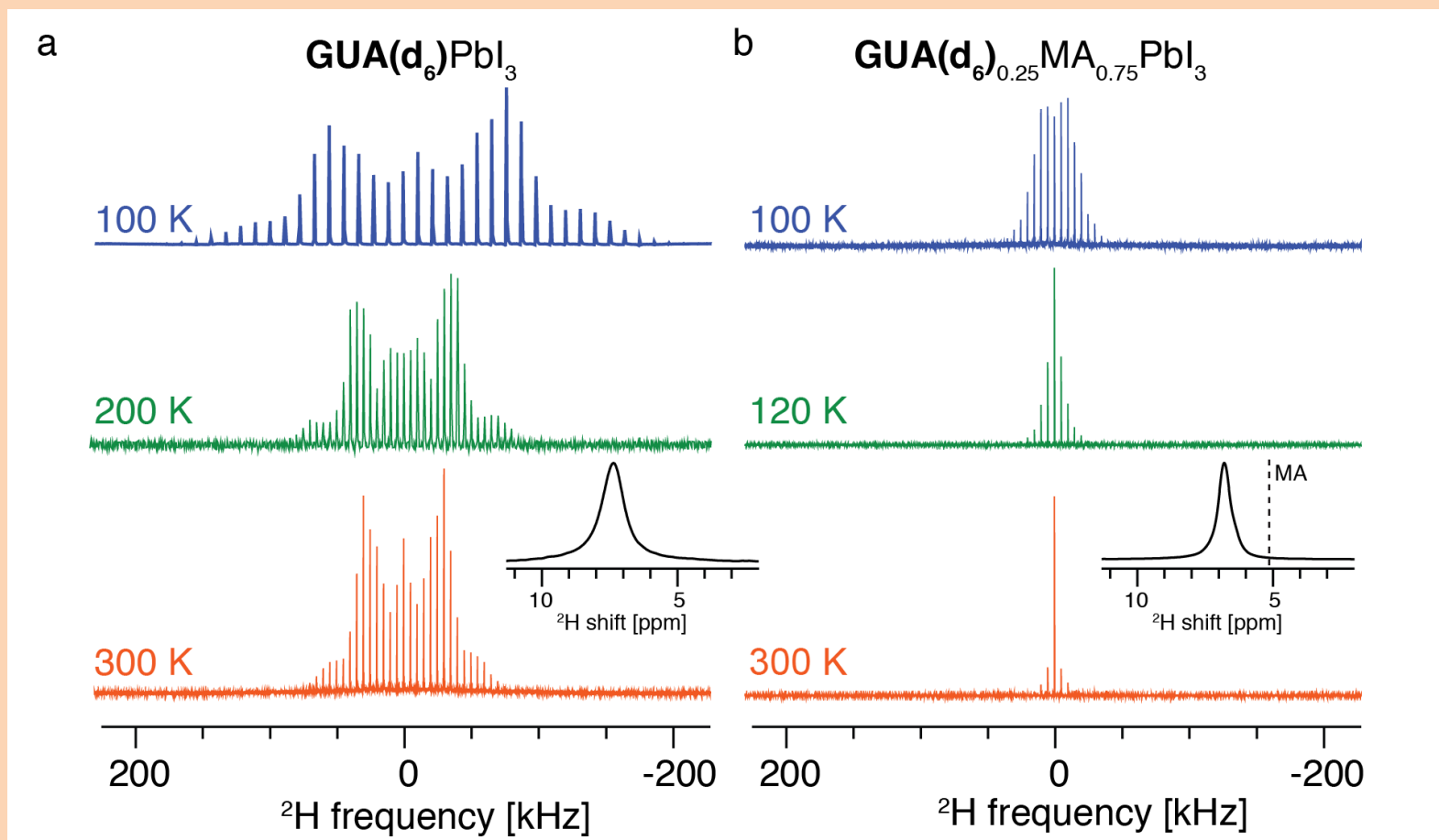


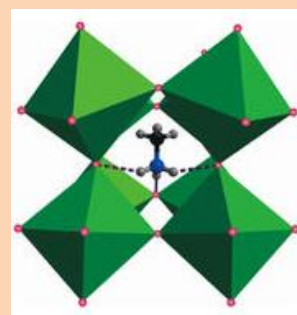
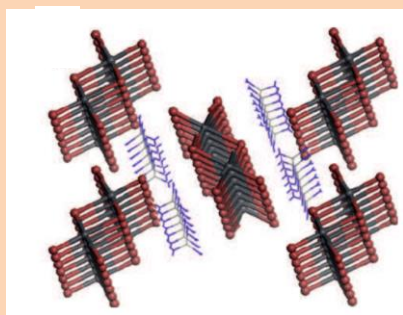


Angew Chem Int Ed Engl. **2016**, 55, 14972

1D

3D

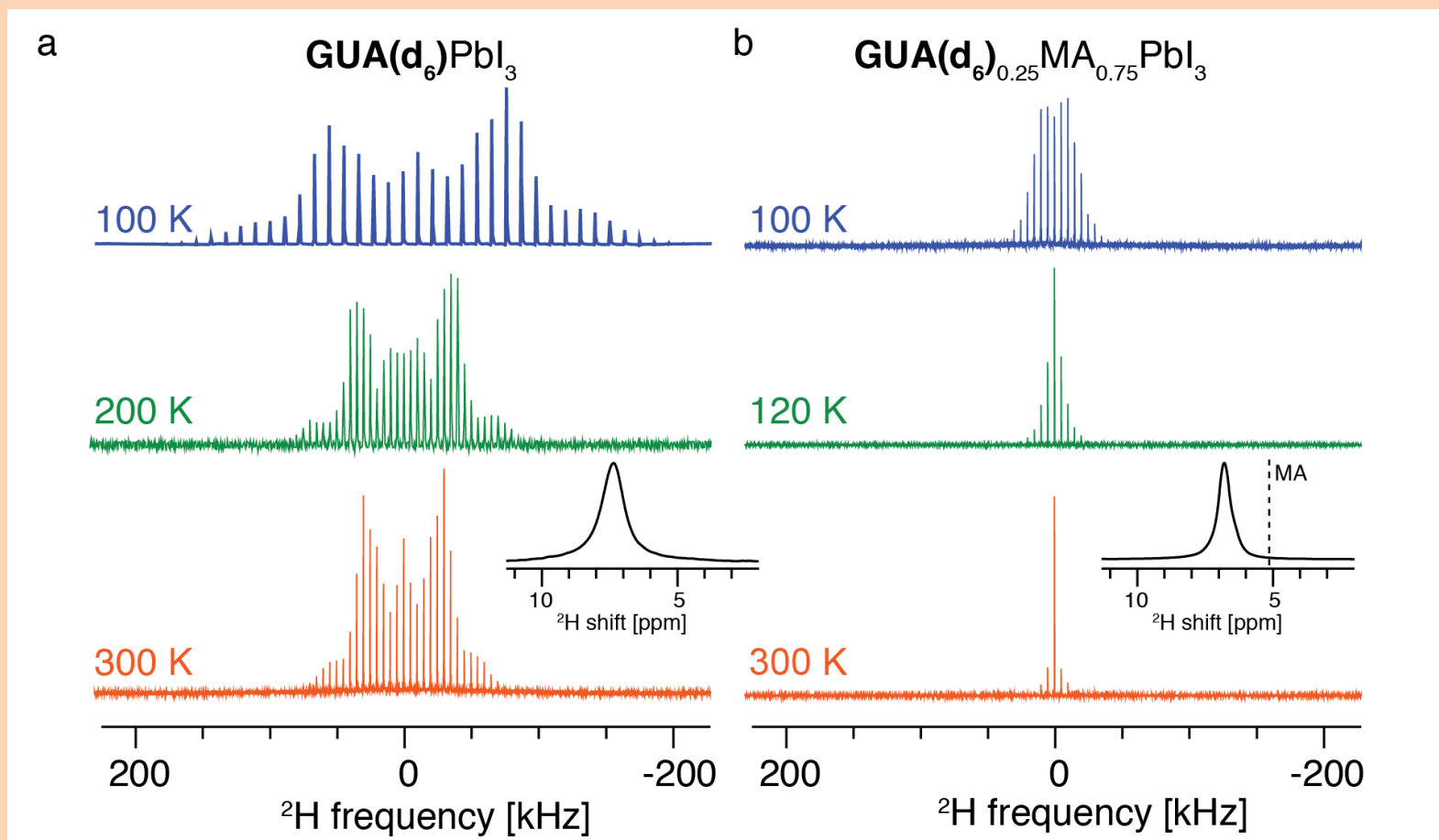




Angew Chem Int Ed Engl. **2016**, 55, 14972

1D

3D



# Outline

- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - Multi-cation formulations, the power of solid state NMR analysis
  - **The advent of molecular modulators**
  - Boosting the PSC stability

Applications for solar fuel generation

# A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells

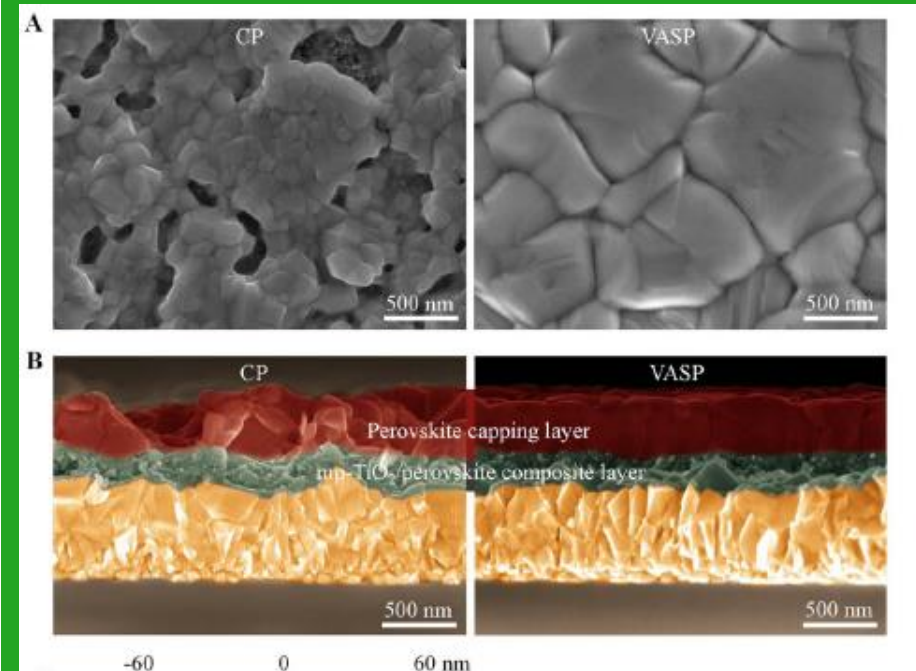
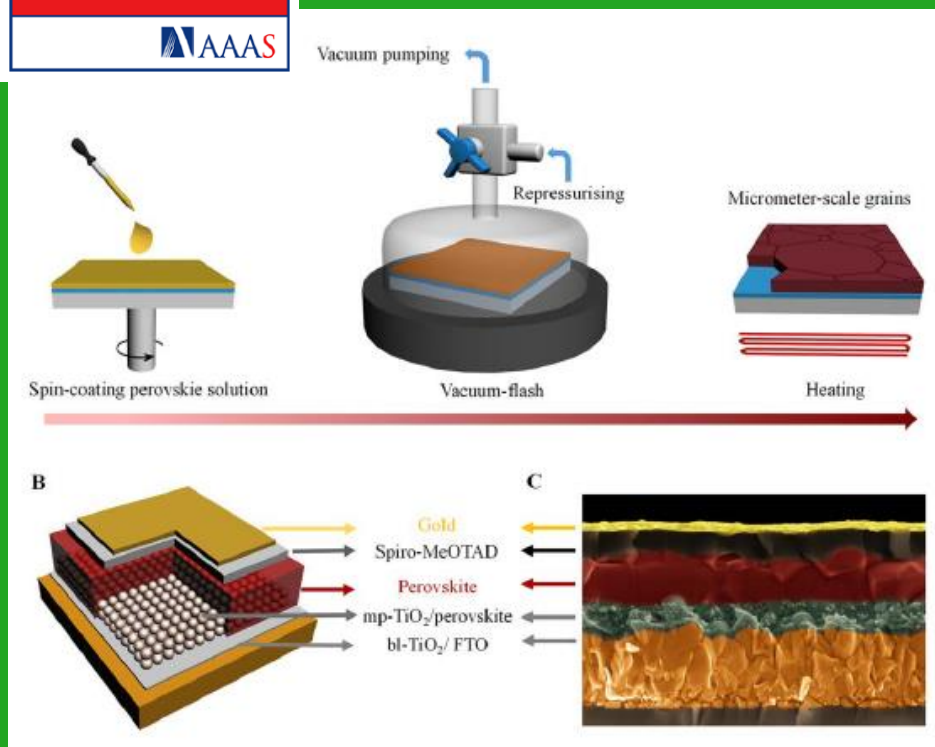
Xiong Li,<sup>1\*</sup> Dongqin Bi,<sup>2\*</sup> Chenyi Yi,<sup>1\*</sup> Jean-David Décoppet,<sup>1</sup> Jingshan Luo,<sup>1</sup> Shaik Mohammed Zakeeruddin,<sup>1</sup> Anders Hagfeldt,<sup>2</sup> Michael Grätzel<sup>1†</sup>



Dr. Xiong Li



Li *et al.* *Science*, 10.1126/science aaf8060 (2016)



Vacuum flash treatment produces smooth and shiny perovskite films of high quality yielding a PCE of 19.6% for 1cm<sup>2</sup> device size



# Molecular Engineering of Scalable Perovskite Solar Cells with over 20% Efficiency and High Operational Stability

Perovskite composition

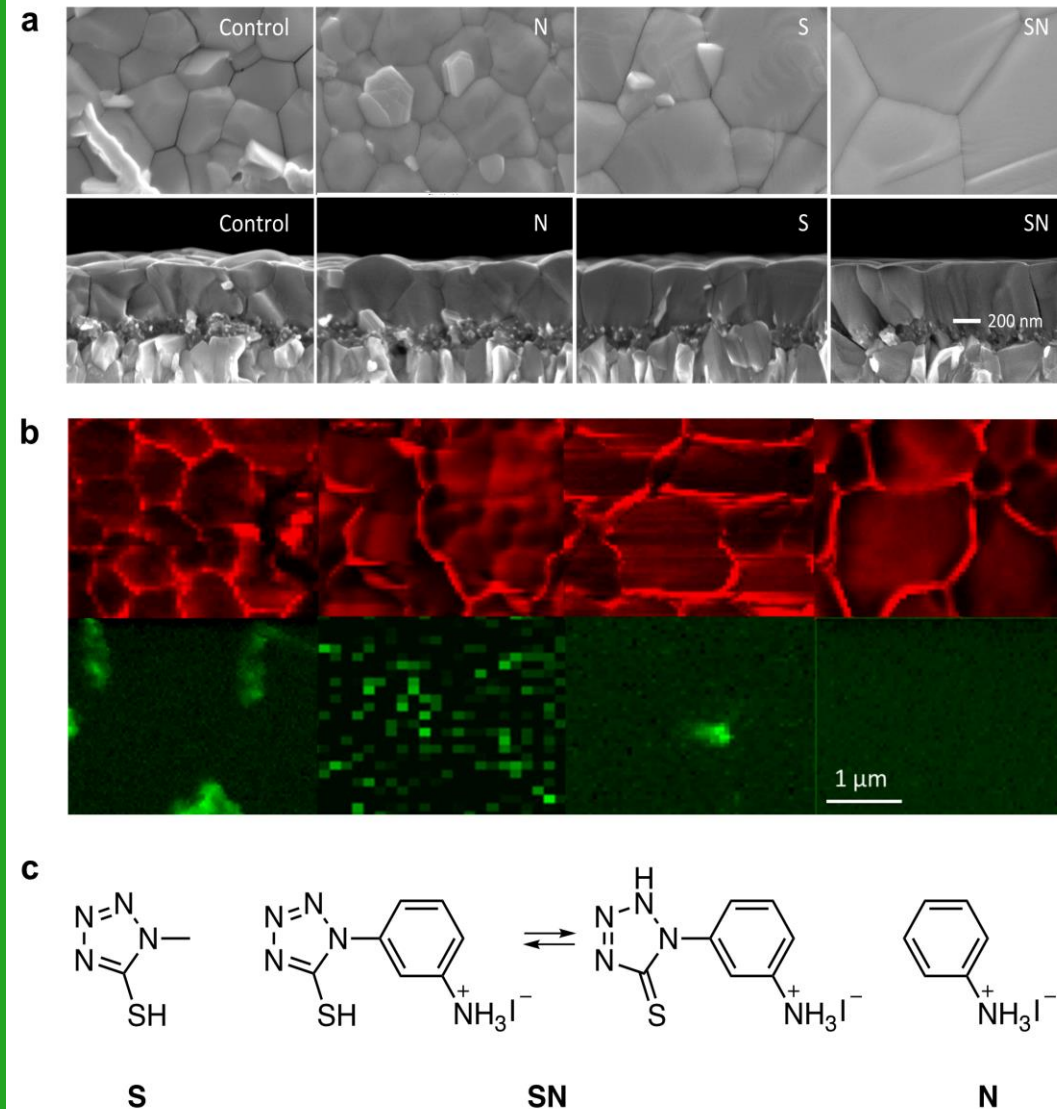


Dr. Xiong Li

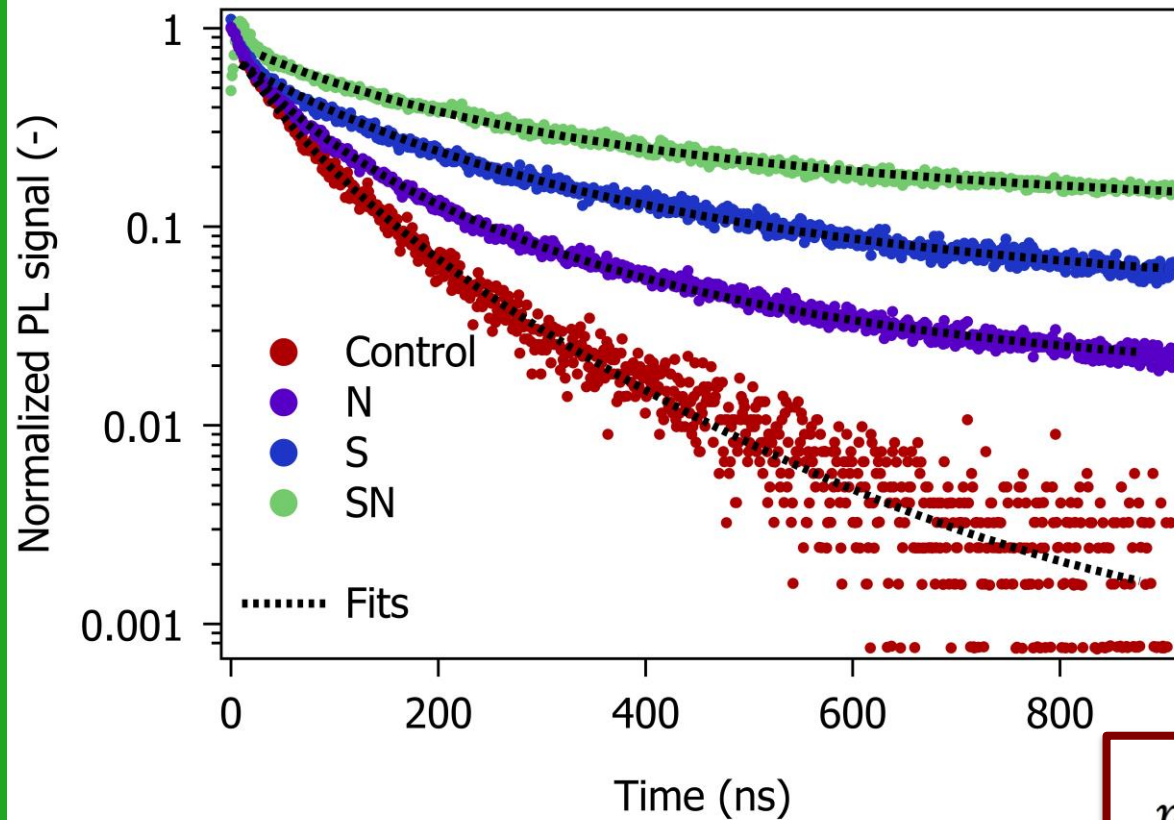


Dr. Dongqin Bi,

D. Bi, X. Li, J. Milic et.al, submitted



# Time resolved photoluminescence decay reveals effective suppression of radiationless carrier recombination by molecular modulators



	$\tau_1$ (ns)
Control	380
N	1690
S	2020
SN	2770

$$I_{PL} \approx dn_{ph}/dt = k_2 n^2$$

$$-dn/dt = k_1 \times n + k_2 n^2$$

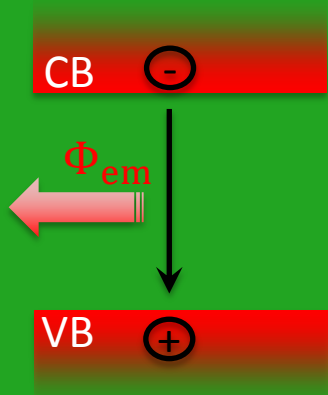
$$n(t) = \frac{k_1}{k_2} \cdot \frac{1}{e^{k_1 t} \cdot \left(1 + \frac{k_1}{n^0 k_2}\right) - 1}$$

$$I_{PL}(t) \sim \frac{dn_{hv}}{dt} = k_2 n^2 = \frac{k_1^2}{k_2} \cdot \frac{1}{\left[e^{k_1 t} \cdot \left(1 + \frac{k_1}{n^0 k_2}\right) - 1\right]^2}$$

# Carrier recombination dynamics in a semiconductor device

$$R_r \cdot n \cdot p$$

**radiative**  
electron-hole

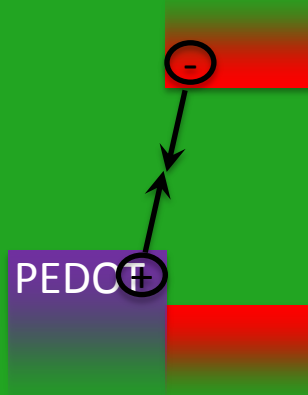


→ enters  
thermodynamic  
limit

unavoidable  
in absorber

$$\beta_{nr} \cdot n \cdot p$$

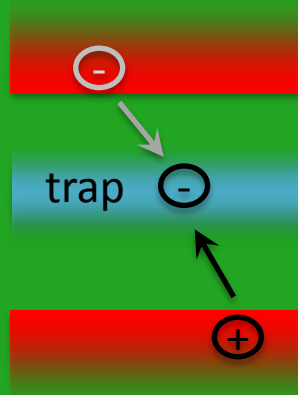
**non-rad. direct**  
electron-hole



→ replace HTM,  
add passivation  
layer

$$k_{tr} n$$

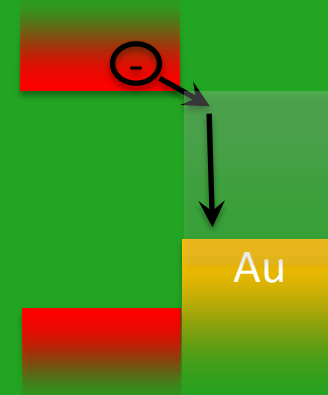
via bulk **defects**  
(SRH type)



→ pure, defect-  
free/tolerant  
material

$$v_{srec} n$$

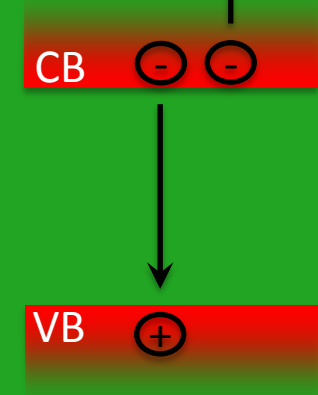
at **surfaces** (wrong  
electrode)



→ passivation,  
reduction of  
contact area

$$A n^2 p$$

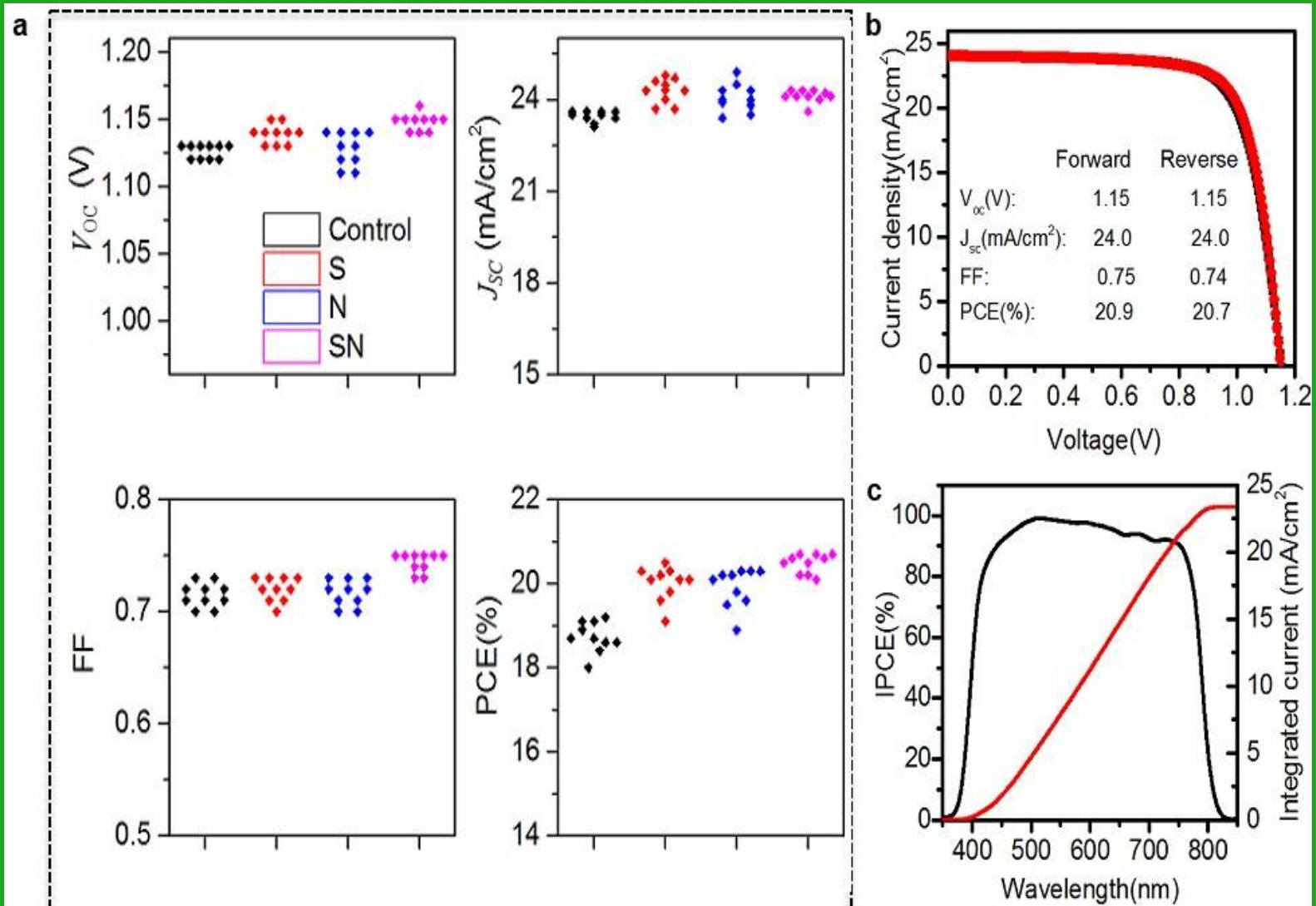
Auger  
recombination



→ material property  
(avoid indirect  
semiconductor)

Should be avoided

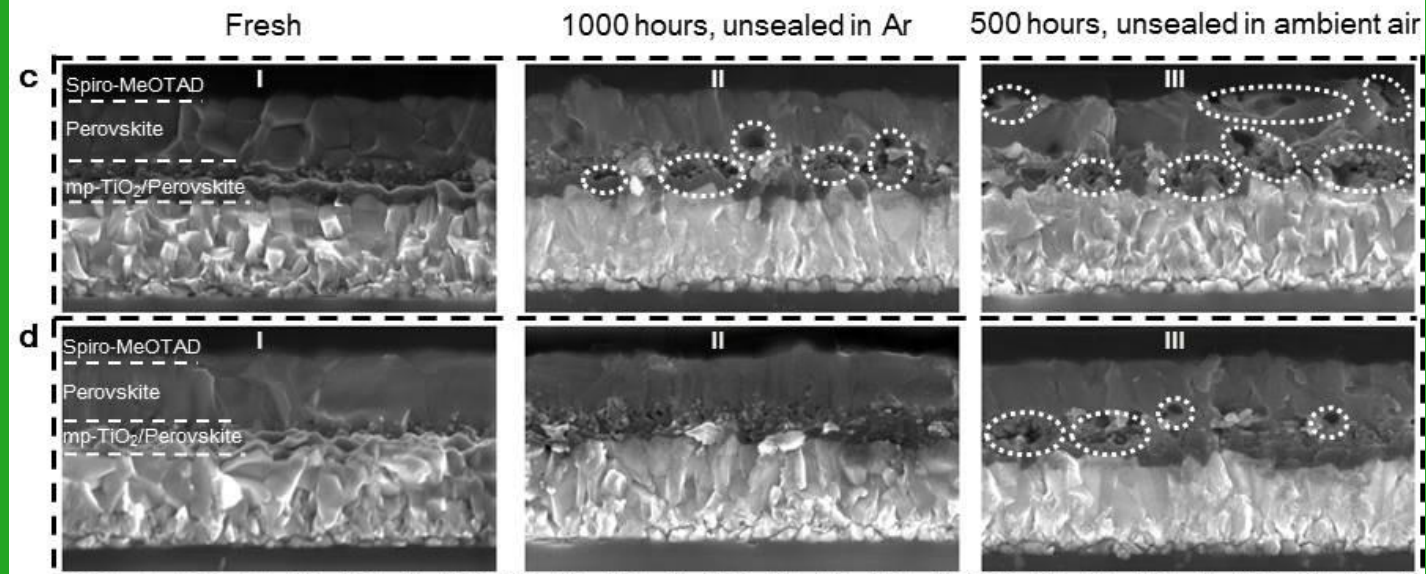
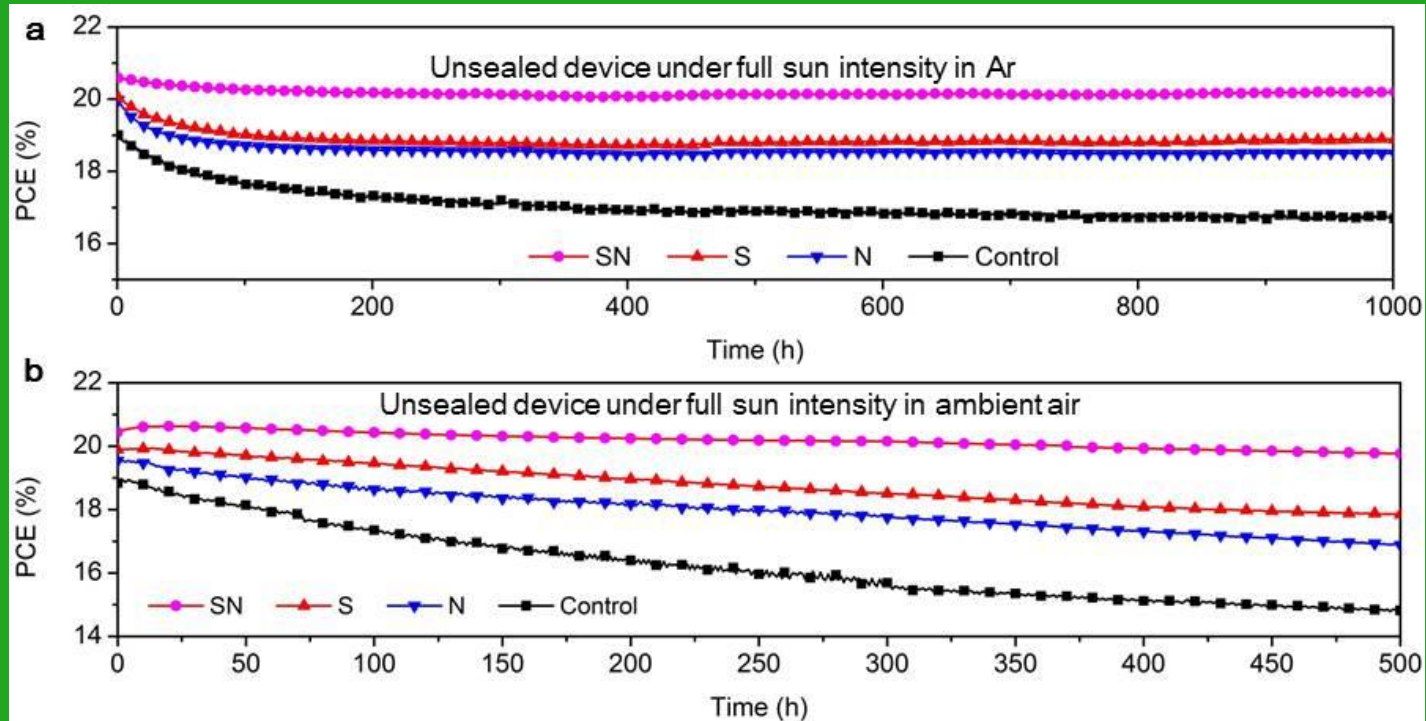
# The positive impact of our new bifunctional modulator on PV performance



a) .PV metrics of perovskite solar cells with different additives. **b**,  $J$ - $V$  curves of the champion cell under standard AM 1.5 solar radiation. **c**, IPCE spectrum (black curve) and projected photocurrent (red curve).

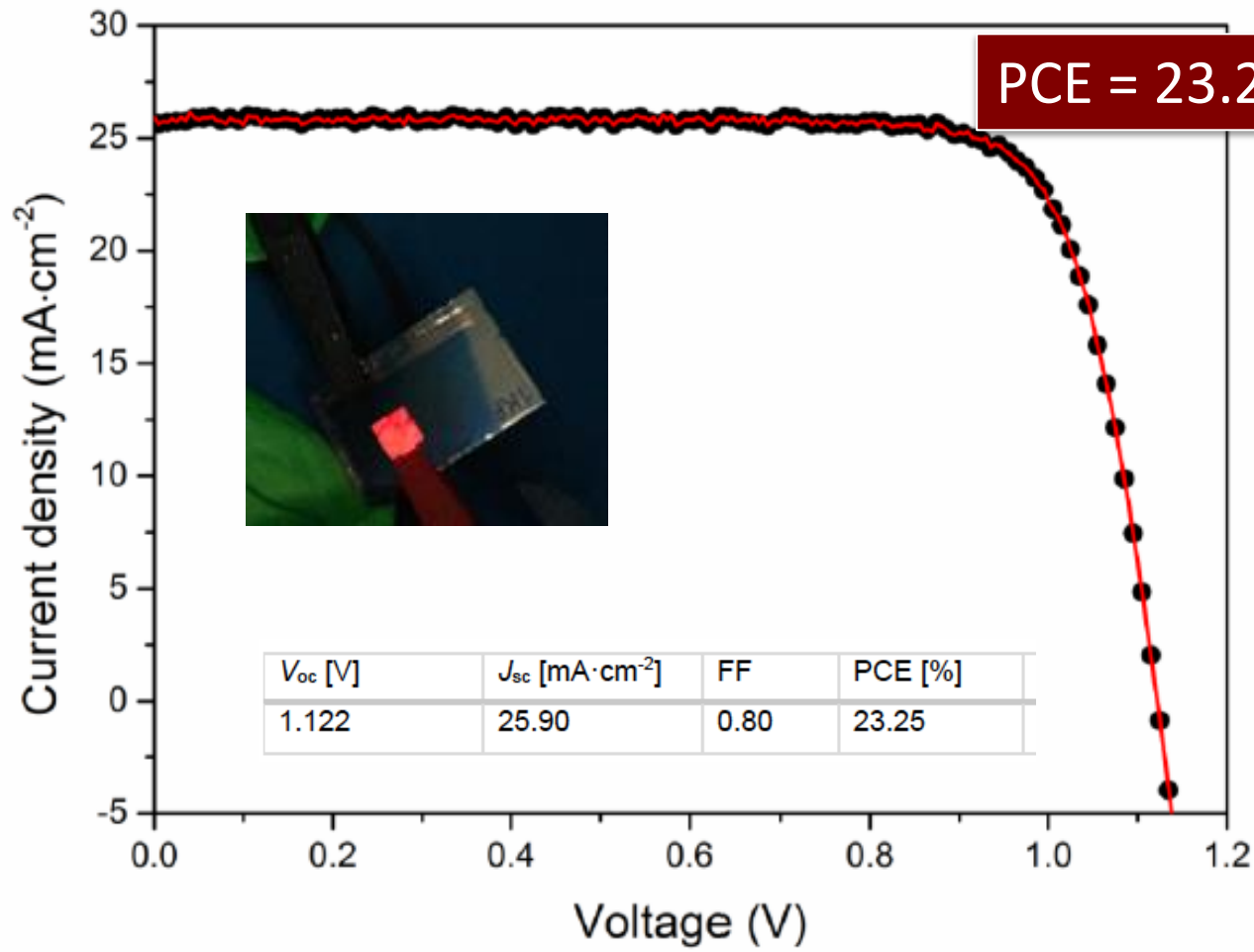


# The impact of the molecular mpdulators on operational stability of PSCs

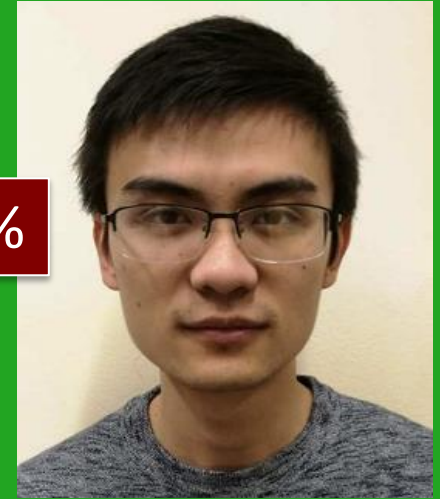




Our present power conversion efficiency record is (PCE) is 23.25 %



PCE = 23.25 %



Dr. Yuhang Liu



Lichen Zhao

# Outline

- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - Multi-cation formulations, the power of solid state NMR analysis
  - The amazing impact of molecular modulators
  - **Boosting the PSC stability**

Applications for solar fuel generation

# The quest for operational stability of perovskite solar cells

K. Domanski et.al. Nature Energy 2018,  
<https://doi.org/10.1038/s41560-017-0060-5>



Konrad Domanski

nature  
energy

ARTICLES

<https://doi.org/10.1038/s41560-017-0060-5>

## Systematic investigation of the impact of operation conditions on the degradation behaviour of perovskite solar cells

Konrad Domanski <sup>1\*</sup>, Essa A. Alharbi<sup>1</sup>, Anders Hagfeldt<sup>2</sup>, Michael Grätzel<sup>1</sup> and Wolfgang Tress <sup>1,2\*</sup>

Perovskite solar cells have achieved power-conversion efficiency values approaching those of established photovoltaic technologies, making the reliable assessment of their operational stability the next essential step towards commercialization. Although studies increasingly often involve a form of stability characterization, they are conducted in non-standardized ways, which yields data that are effectively incomparable. Furthermore, stability assessment of a novel material system with its own peculiarities might require an adjustment of common standards. Here, we investigate the effects of different environmental factors and electrical load on the ageing behaviour of perovskite solar cells. On this basis, we comment on our perceived relevance of the different ways these are currently aged. We also demonstrate how the results of the experiments can be distorted and how to avoid the common pitfalls. We hope this work will initiate discussion on how to age perovskite solar cells and facilitate the development of consensus stability measurement protocols.

One year long stable operation under full sunlight corresponding to 11 years outdoors achieved with carbon based PSCs featuring a 2D/3D perovskite architecture

## ARTICLE

Received 19 Aug 2016 | Accepted 20 Apr 2017 | Published 1 Jun 2017

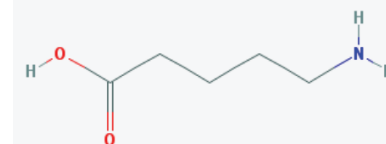
DOI: 10.1038/ncomms15684

OPEN

# One-Year stable perovskite solar cells by 2D/3D interface engineering

G. Grancini<sup>1</sup>, C. Roldán-Carmona<sup>1</sup>, I. Zimmermann<sup>1</sup>, E. Mosconi<sup>2,3</sup>, X. Lee<sup>4</sup>, D. Martineau<sup>5</sup>, S. Narbey<sup>5</sup>, F. Oswald<sup>5</sup>, F. De Angelis<sup>2,3</sup>, M. Graetzel<sup>4</sup> & Mohammad Khaja Nazeeruddin<sup>1</sup>

Despite the impressive photovoltaic performances with power conversion efficiency beyond 22%, perovskite solar cells are poorly stable under operation, failing by far the market requirements. Various technological approaches have been proposed to overcome the instability problem, which, while delivering appreciable incremental improvements, are still far from a market-proof solution. Here we show one-year stable perovskite devices by engineering an ultra-stable 2D/3D  $(\text{HOOC}(\text{CH}_2)_4\text{NH}_3)_2\text{PbI}_4/\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite junction. The 2D/3D forms an exceptional gradually-organized multi-dimensional interface that yields up to 12.9% efficiency in a carbon-based architecture, and 14.6% in standard mesoporous solar cells. To demonstrate the up-scale potential of our technology, we fabricate  $10 \times 10 \text{ cm}^2$  solar modules by a fully printable industrial-scale process, delivering 11.2% efficiency stable for  $>10,000 \text{ h}$  with zero loss in performances measured under controlled standard conditions. This innovative stable and low-cost architecture will enable the timely commercialization of perovskite solar cells.



Amino-valeric acid AVA

Cite as: N. Arora *et al.*, *Science*  
10.1126/science.aam5655 (2017).

# Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%

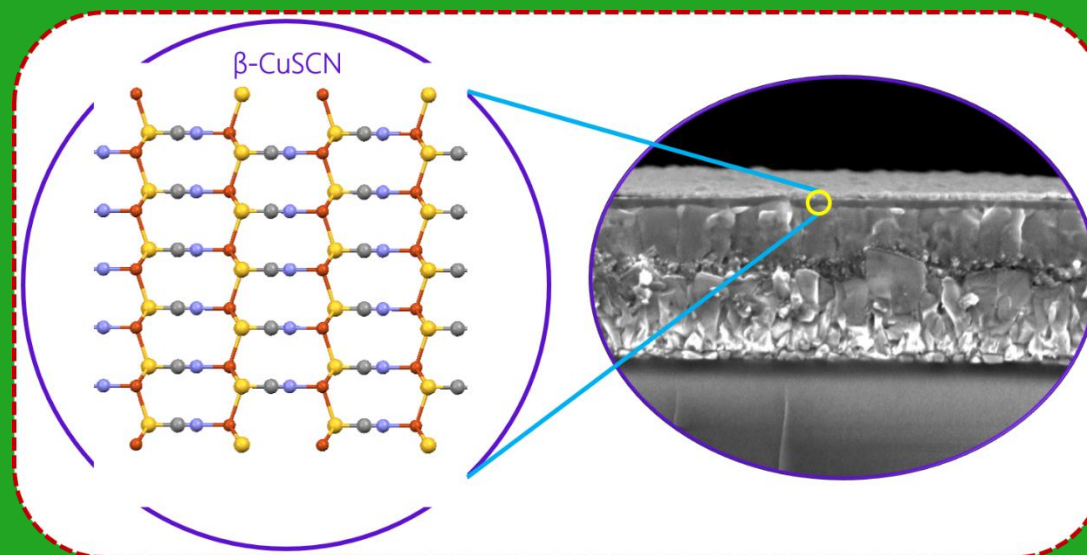
Neha Arora,<sup>1\*</sup> M. Ibrahim Dar,<sup>1\*†</sup> Alexander Hinderhofer,<sup>2</sup> Norman Pellet,<sup>1</sup> Frank Schreiber,<sup>2</sup> Shaik Mohammed Zakeeruddin,<sup>1</sup> Michael Grätzel<sup>1†</sup>

<sup>1</sup>Laboratory of Photonics and Interfaces, Department of Chemistry and Chemical Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland.

<sup>2</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany.

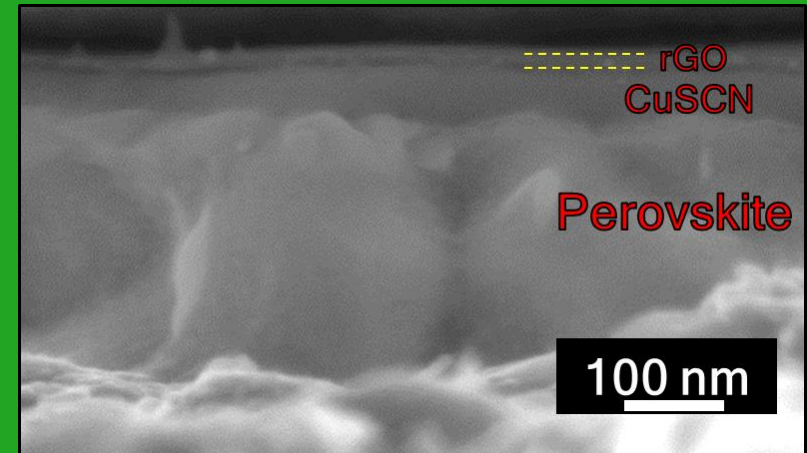
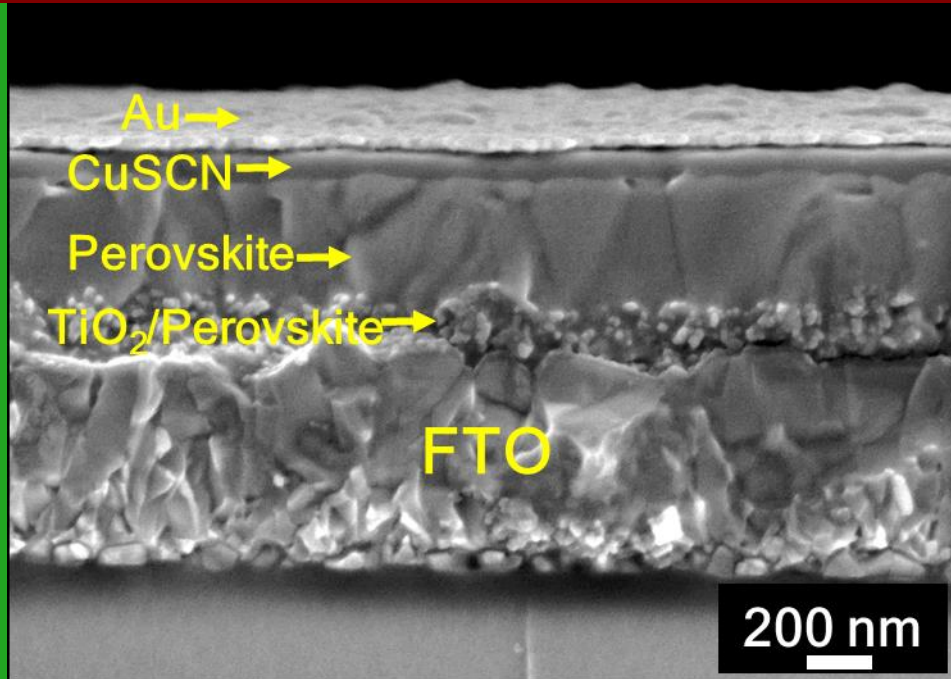
\*These authors contributed equally to this work.

†Corresponding author. Email: [ibrahim.dar@epfl.ch](mailto:ibrahim.dar@epfl.ch) (M.I.D.); [michael.gratzel@epfl.ch](mailto:michael.gratzel@epfl.ch) (M.G.)

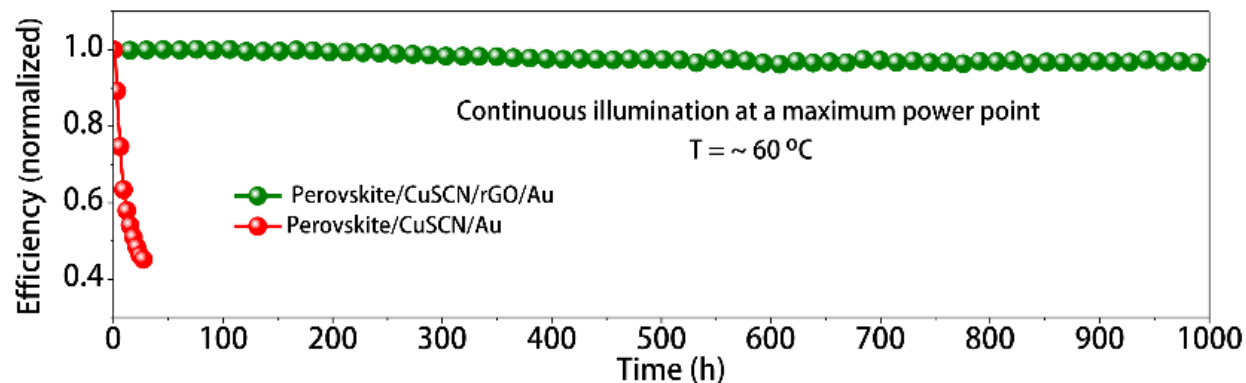




Operational stability of un-encapsulated CuSCN based device and un-encapsulated CuSCN based device containing a thin layer of rGO (as a spacer layer between CuSCN and gold layers), examined at a maximum-power-point under continuous full-sun illumination at 60 °C in nitrogen atmosphere.

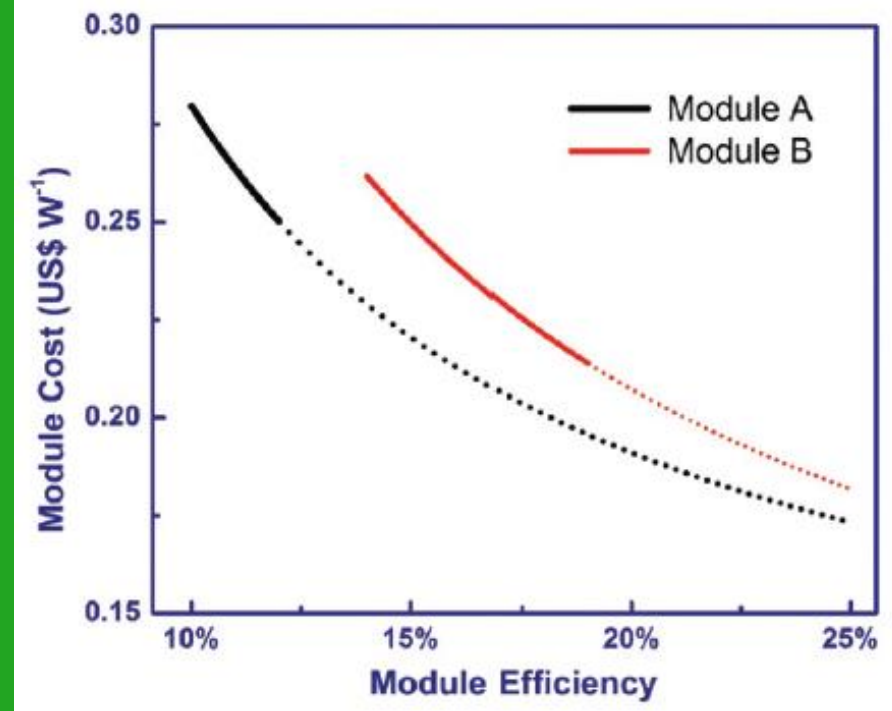
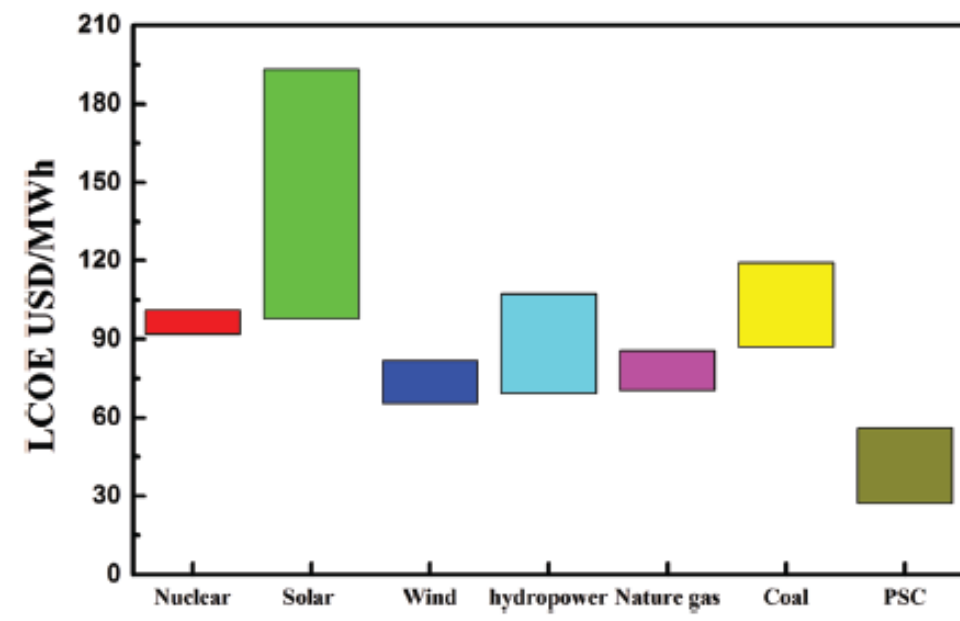


Morphological characterization of CuSCN/rGO/Au sample



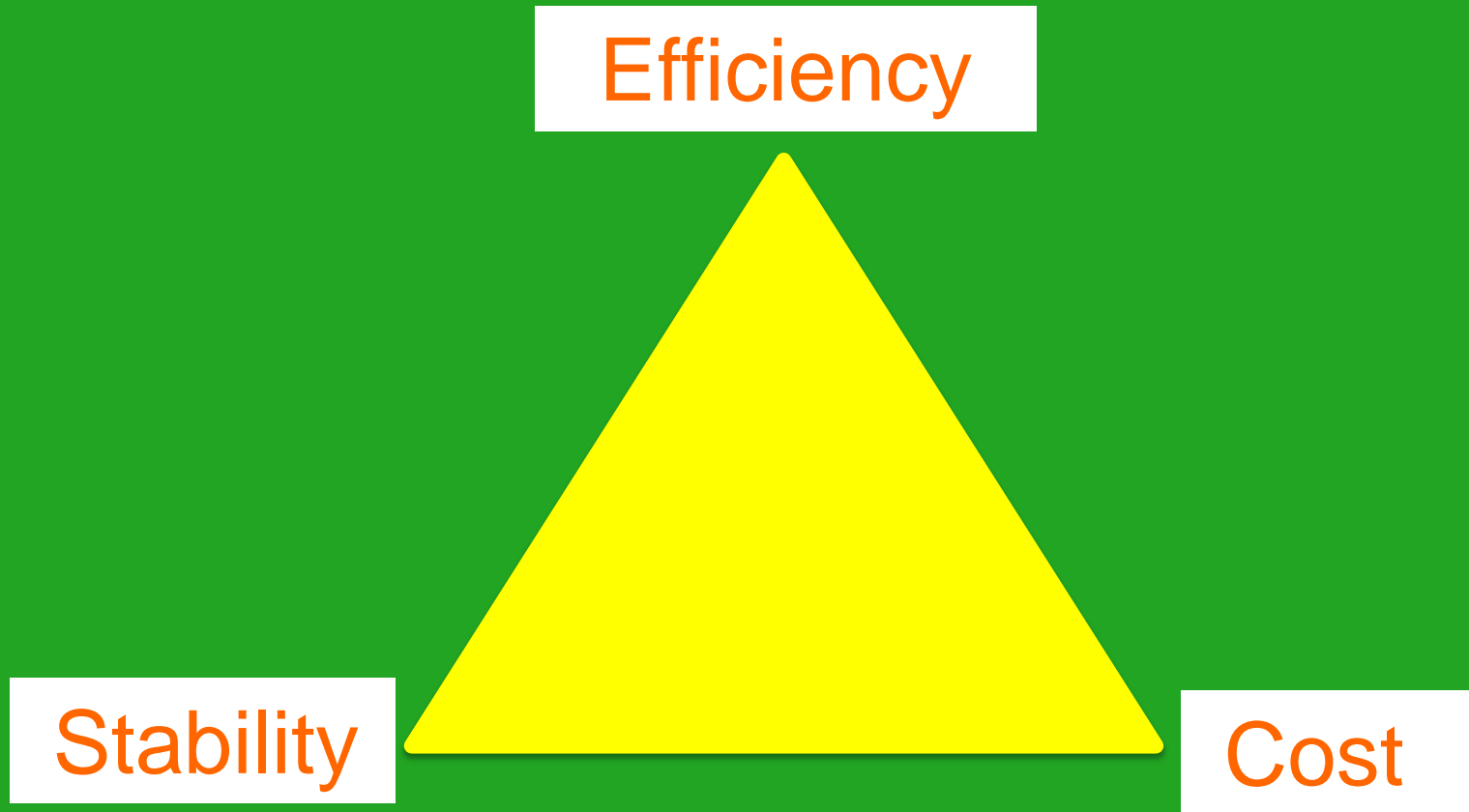
# Cost-Performance Analysis of Perovskite Solar Modules

Molang Cai, Yongzhen Wu, Han Chen, Xudong Yang, Yinghuai Qiang, and Liyuan Han\*



Perovskite solar cells (PSC) offer lowest cost of all energy producing technologies

# The “Golden Triangle” of photovoltaics



# Science

2014

AAAS

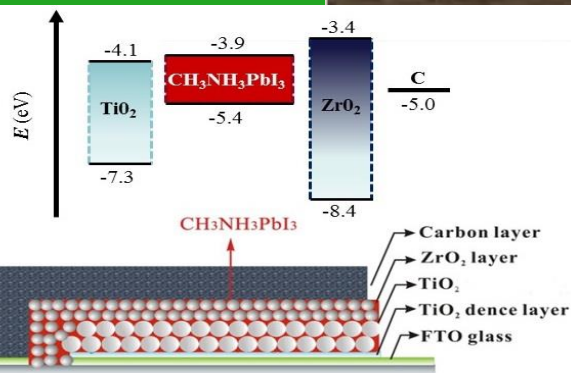
Anyi Mei,<sup>1\*</sup> Xiong Li,<sup>1\*</sup> Linfeng Liu,<sup>1</sup> Zhiliang Ku,<sup>1</sup> Tongfa Liu,<sup>1</sup> Yaoguang Rong,<sup>1</sup> Mi Xu,<sup>1</sup> Min Hu,<sup>1</sup> Jiangzhao Chen,<sup>1</sup> Ying Yang,<sup>1</sup> Michael Grätzel,<sup>2</sup> Hongwei Han<sup>1†</sup>

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



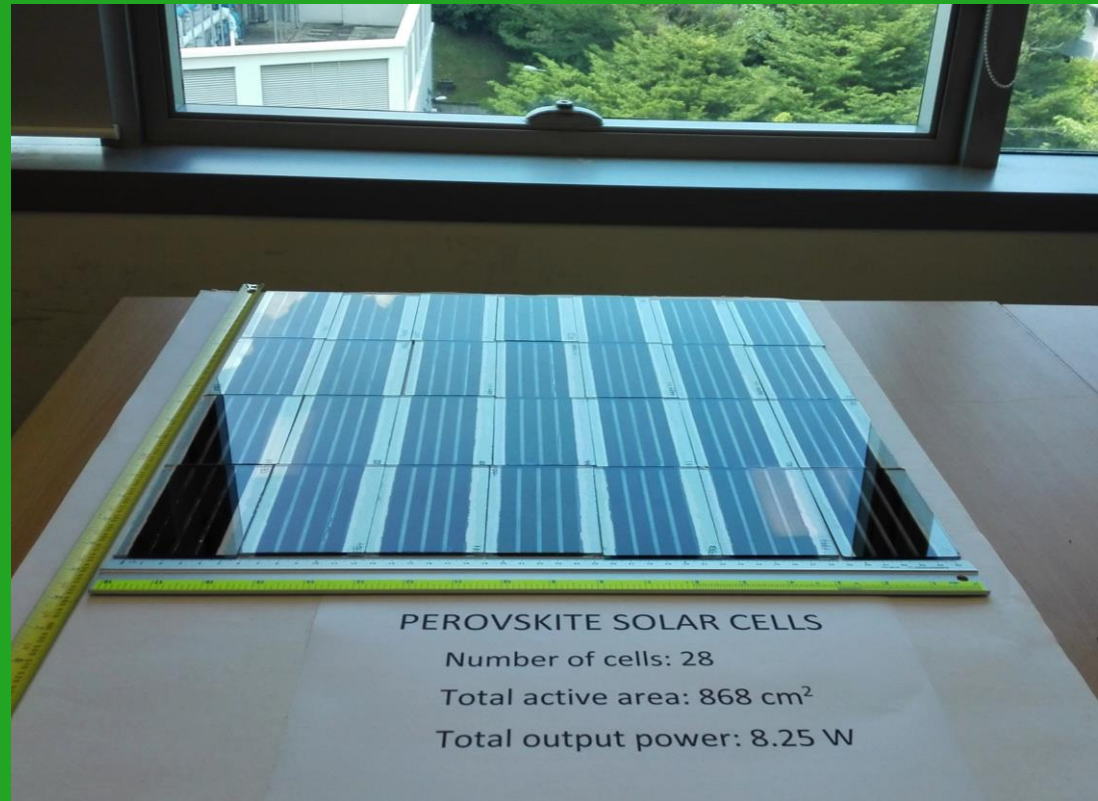
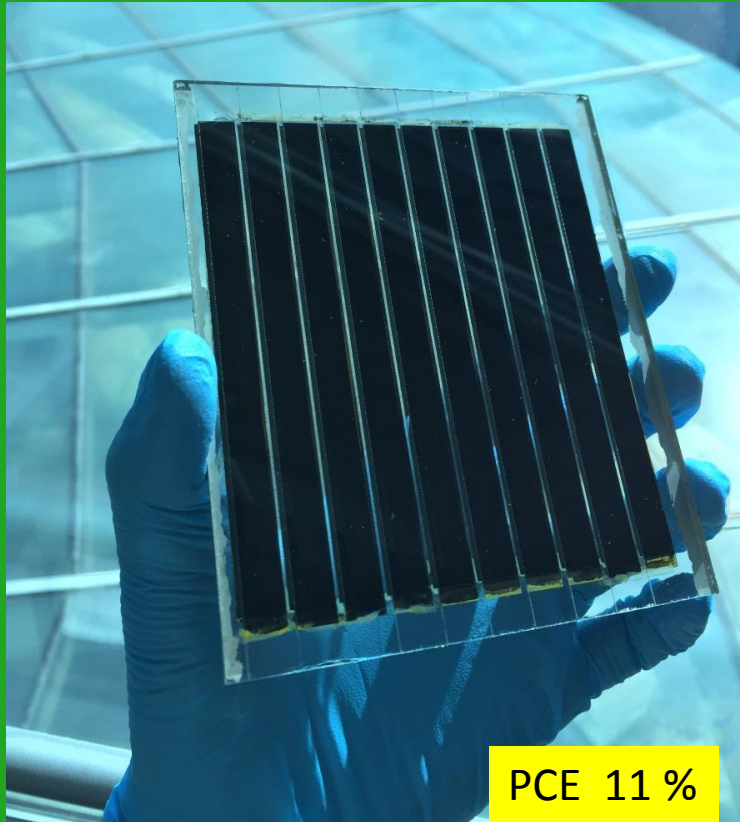
格兰泽尔介观太阳能电池研究中心  
Michael Grätzel Center for Mesoscopic Solar Cells

June 2016





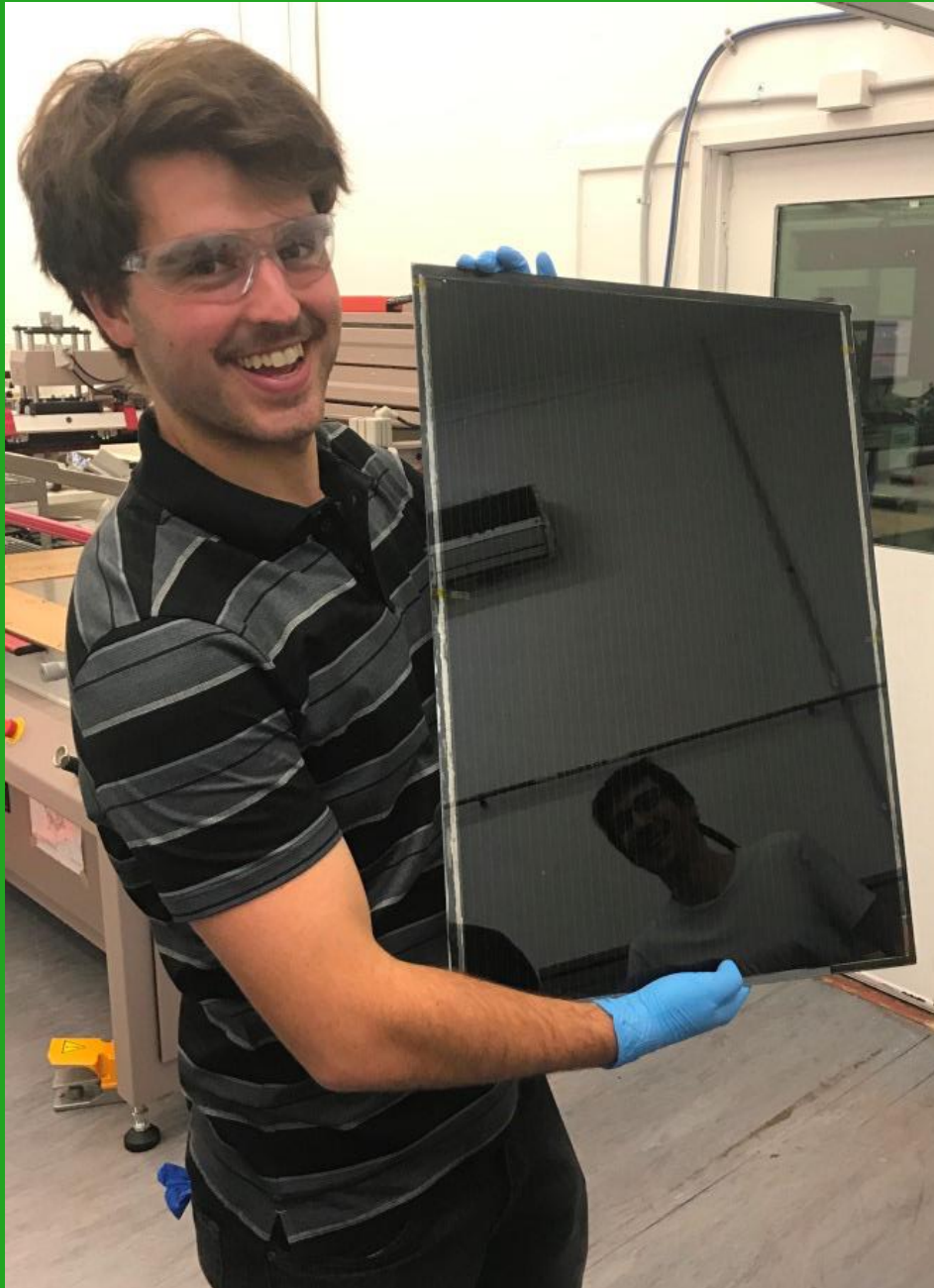
# Pervoskite solar cell modules produced at NTU Singapore



Courtesy Prof. Subodh Mhaikalsar, Nripan Matthew NTU Singapore



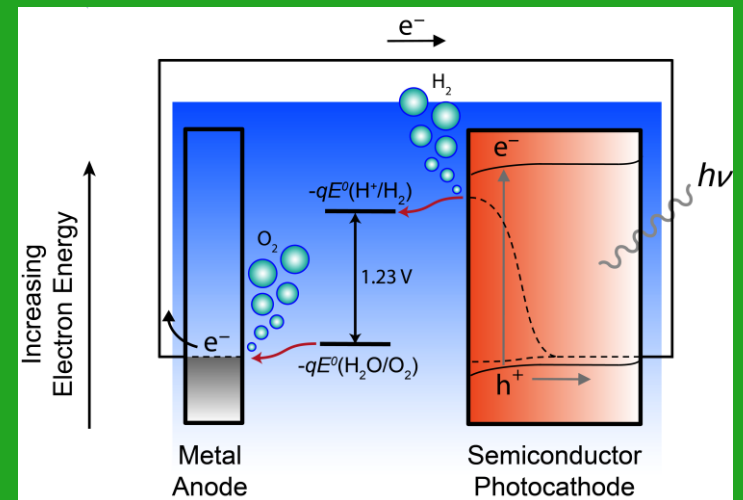
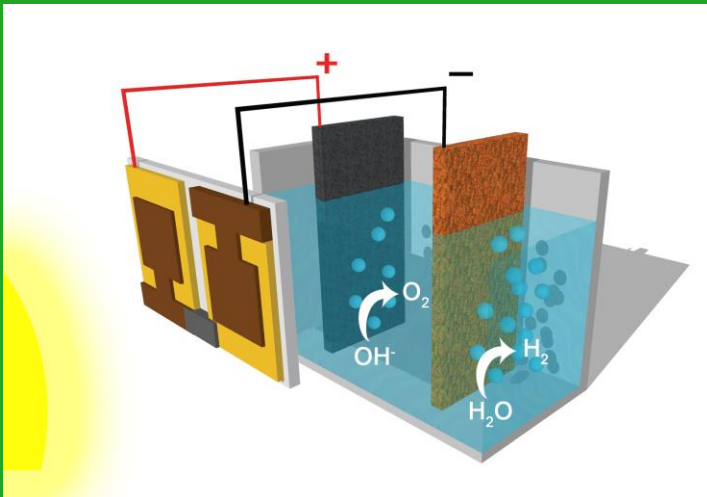
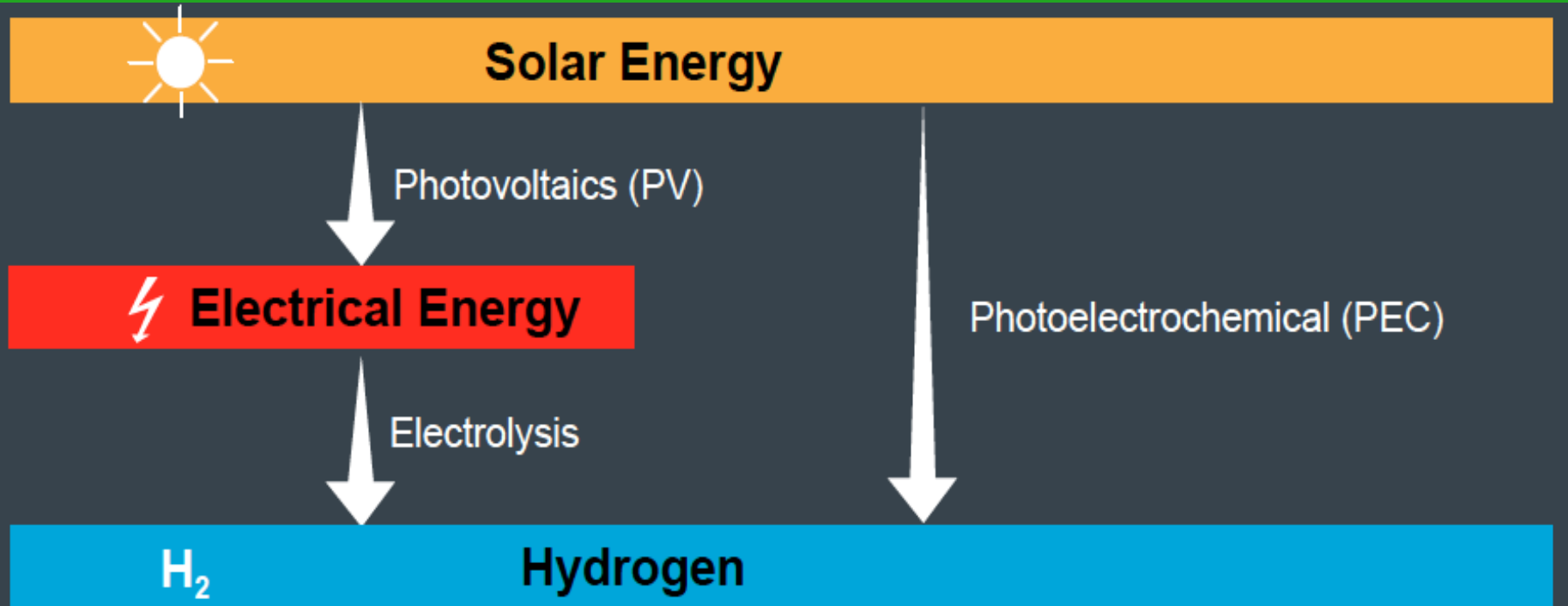
# Dyesol Perovskite solar cell prototype



# Outline

- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - Multi-cation formulations, the power of solid state NMR analysis
  - The amazing impact of molecular modulators
  - Boosting the PSC stability
  - **solar fuel generation**
  - Applications

# Solar fuel research in LPI



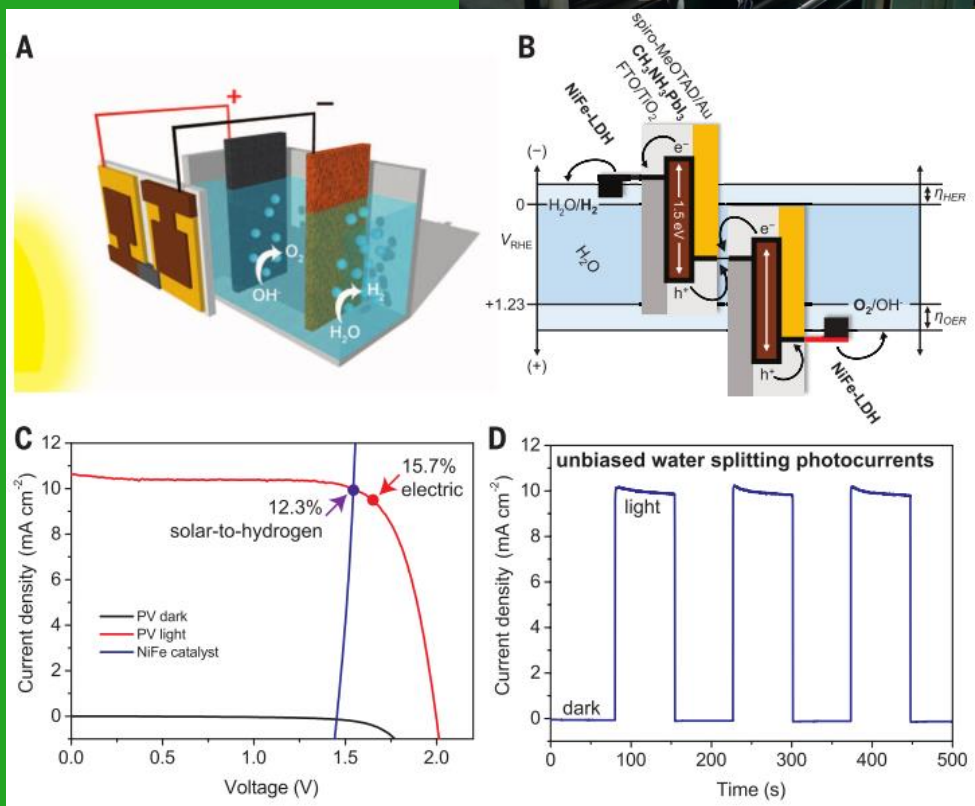
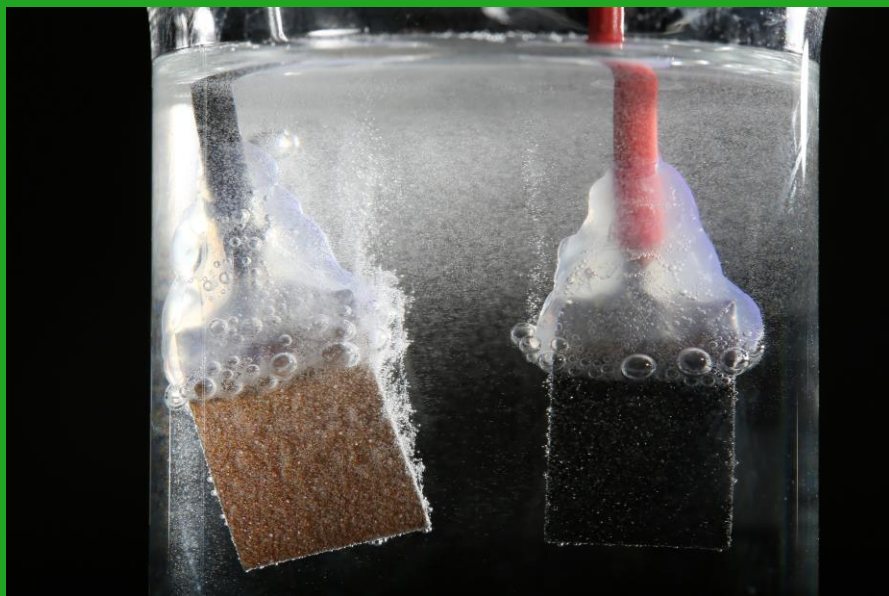
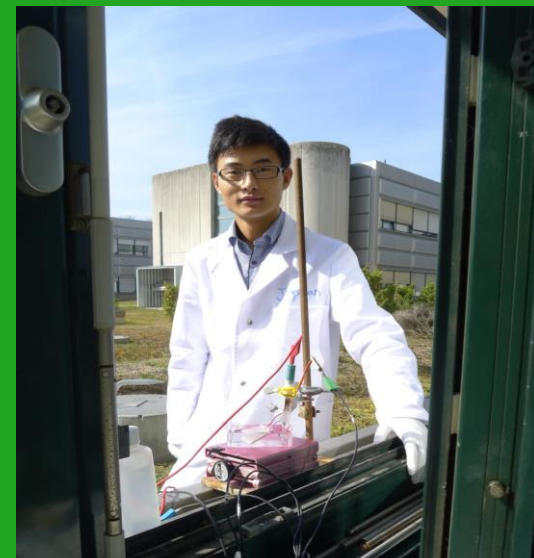
## WATER SPLITTING

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

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



Jingshan Luo



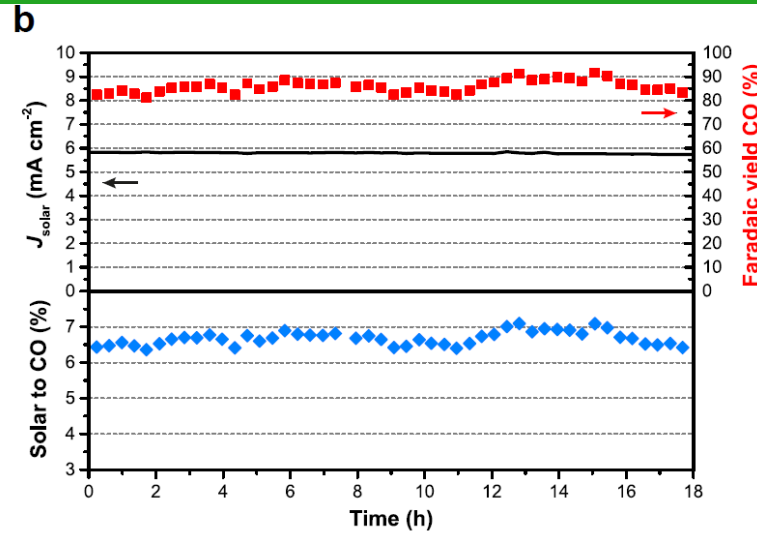
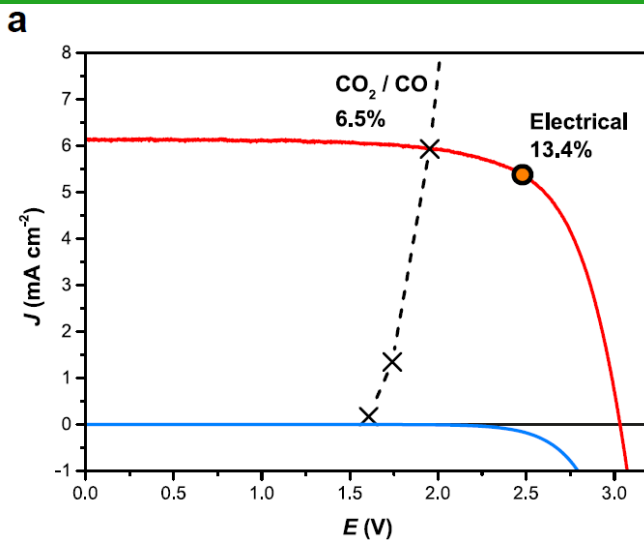
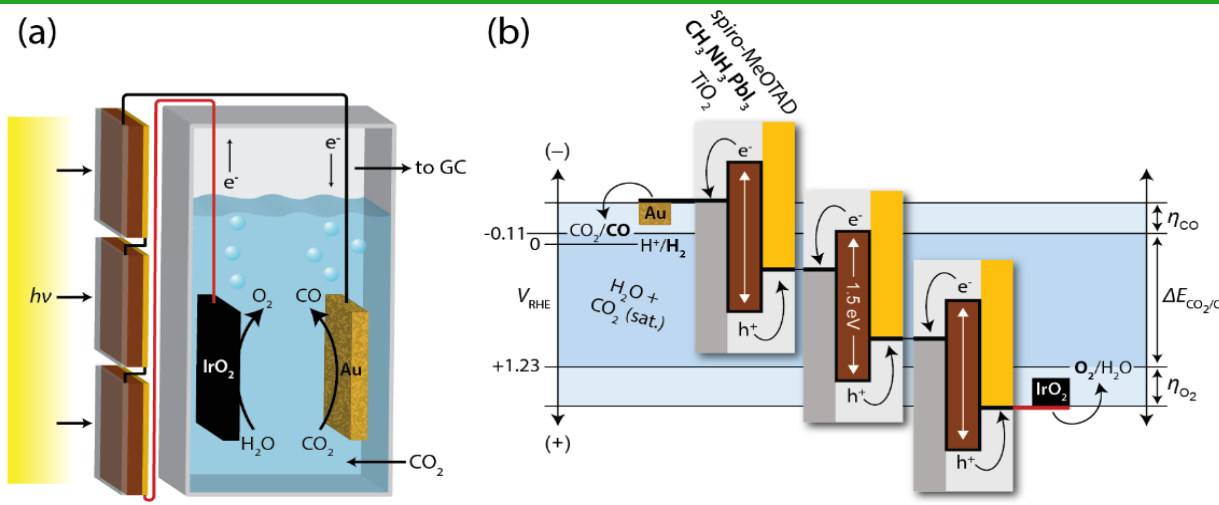
Luo, J... Grätzel, M. et al. *Science* **2014**, *345*, 1593.

Triple junction mesoscopic pervoskite cells achieve the reduction of  $\text{CO}_2$  to CO with 6.5 % solar to CO (STCO) conversion efficiency using water as electron source



Marcel Schreier

6.5 % Solar to CO





# Breakthrough Energy Ventures to invest > 1 billion in energy research



Beating Nature at  
Its Own Game

Bill Gates on Linked in  
March 14 , 2017

We need thousands of scientists following all paths that might lead us to a clean energy future. That's why a group of investors and I recently launched Breakthrough Energy Ventures, a fund that will invest more than \$1 billion in scientific discoveries that have the potential to deliver cheap and reliable clean energy to the world.

Hyundai NEXO fuel cell car

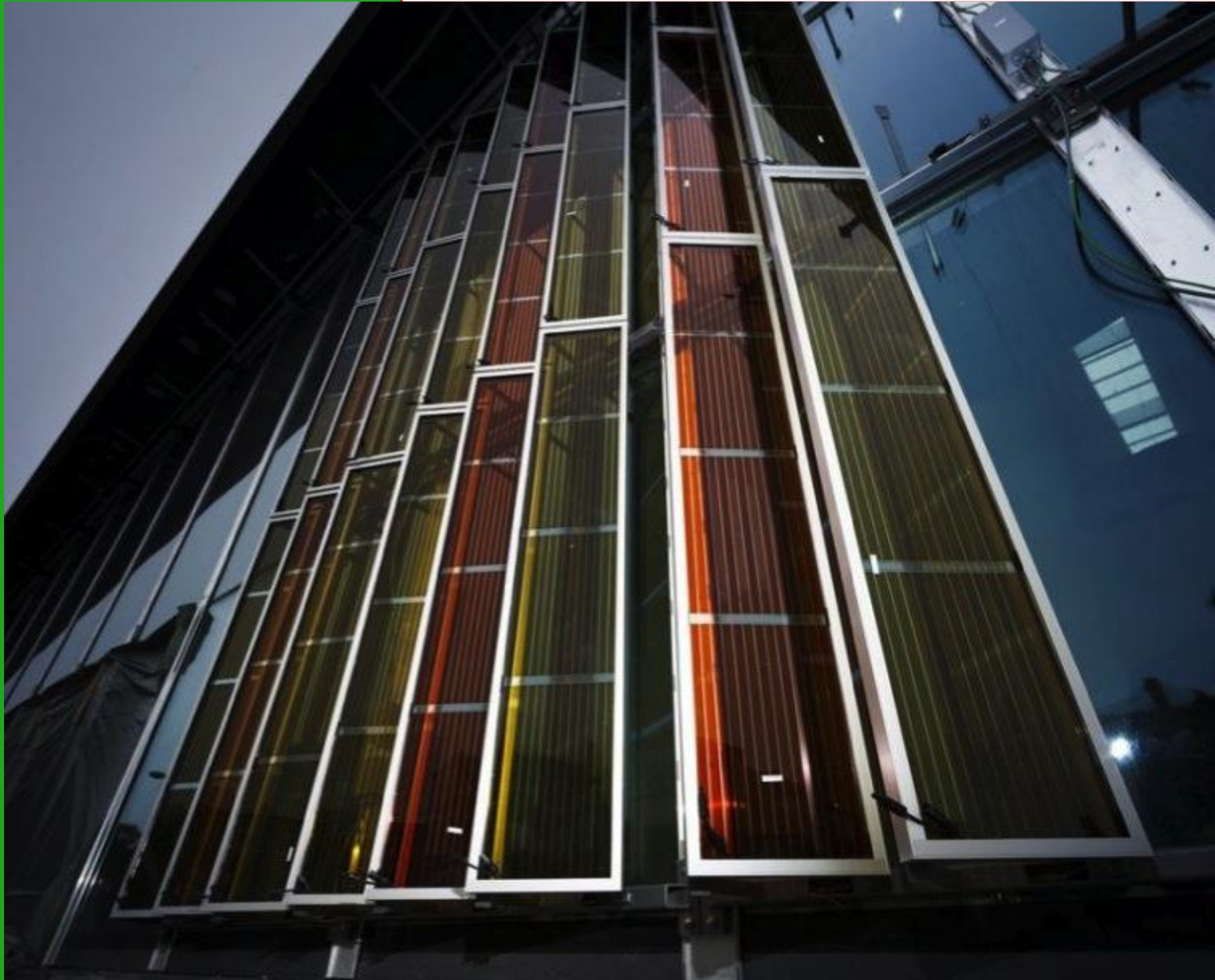


# Outline

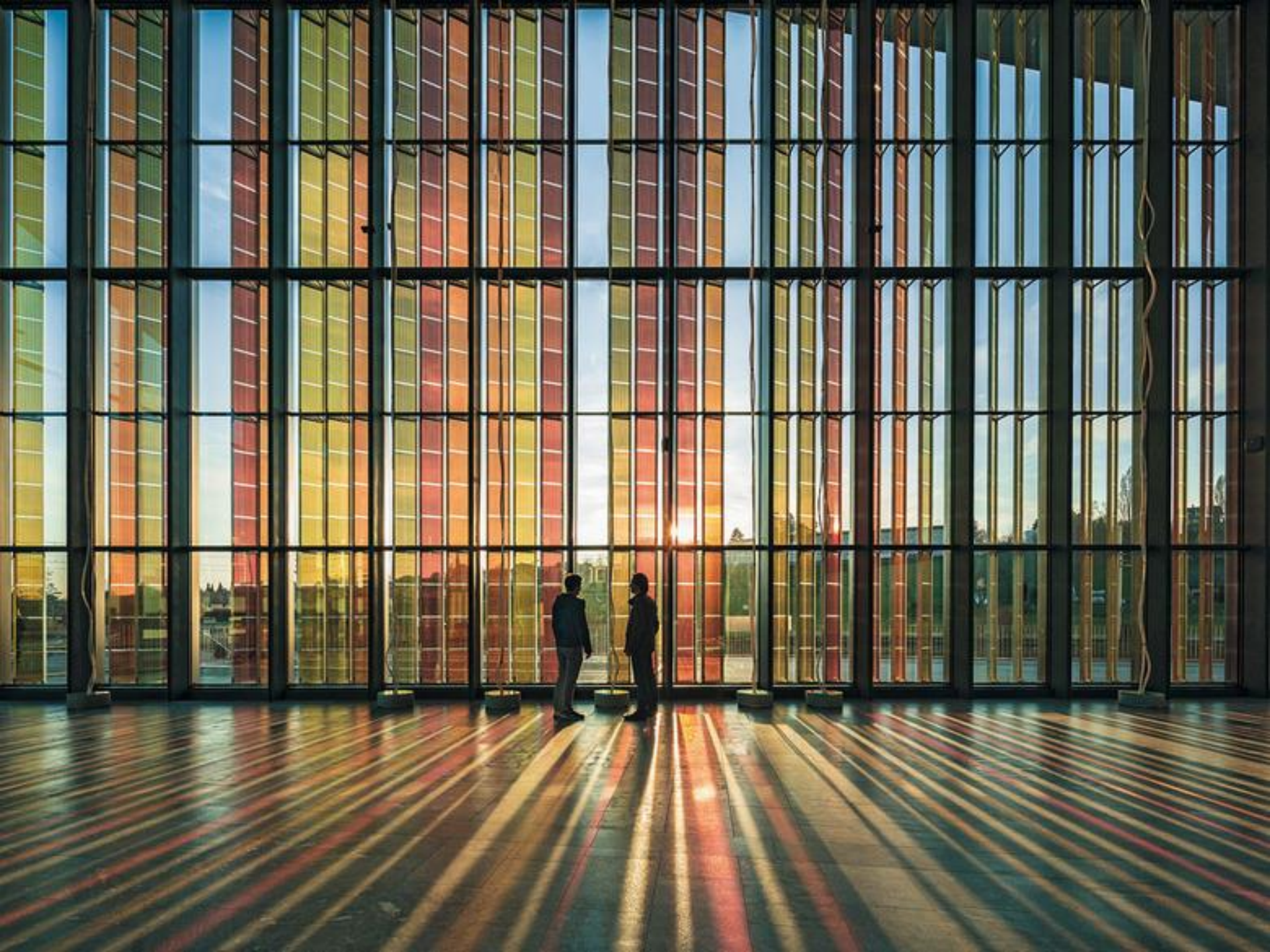
- The stunning rise of perovskite solar cells
- Recent research advances to increase their efficiency and stability
  - Multi-cation formulations, the power of solid state NMR analysis
  - The amazing impact of molecular modulators
  - Boosting the PSC stability
  - solar fuel generation
  - **Applications**

**TODAY**

# Swiss Tech Convention Center













# Electric car charging station powered by H.Glass panels







**The first Energy Noise Barrier made with H.Glasss panels. Energy yield: 1'012.5 kWh / year**

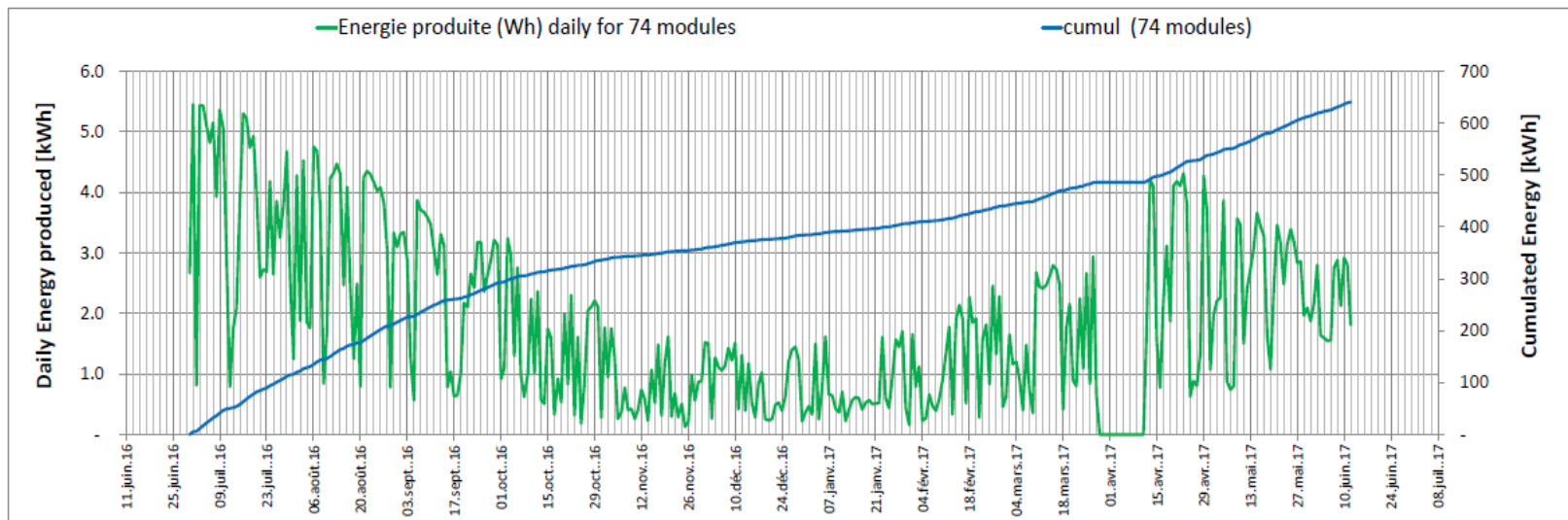


# Tracking energy output of H.Glass modules as sound barriers at the Bern-Zurich motorway

Swisscom  
Bern



- Commissioned in May, 2016
- PV Fence
- 74 Mod 32 cells, green color,
- Follow on projects: Yes



# Green H..Glass panels in Lausanne Ouchy





# DSC energy glass modules entering now the private market

**Fam. Reinhard Basel**



- Commissioned in June, 2016
- PV Railing
- 16 Mod 54 cells, green color, 9.6 m<sup>2</sup>
- Follow on projects: Yes







Graz Science Tower featuring  
1000 m<sup>2</sup> DSC panels produced  
by HGlass (formerly G2E)  
inaugurated on Sept.21 2017



# DSC powered E-reader from EXEGER with eternal battery life



<http://www.exeger.com/>

E-reader with eternal life.

EXEGER has developed the prototype pictured here through seamless integration of the world's best indoor solar cell. The product has eternal life in standard indoor illumination alone.

# Job creation in Sweden through production of dye-sensitized solar cells

EXEGER

APPLICATIONS INNOVATION ABOUT US NEWS CONTACT

View factory



EXEGER manufactures dye-sensitized solar cells

<http://www.exeget.com/>

# Focus-induced photoresponse (FIP)

A revolutionaty new application of Dye sensitized technology



3d -distance  
measurement  
And imaging

Technologies. The solution to your sensing challenge: XperYenZ™ sensor systems. Paving the way for sensing applications that have never been possible before.

World premier presentation  
at SPIEX San Diego on 8.8.2017  
room 16a at 2:10 p.m

Christoph  
Lungenschmied  
from trinamiX  
will present  
"Focus-induced  
photoresponse:  
a  
fundamentally  
novel approach

Join our presentation on  
August 8, 2017, 2:10  
PM

# Market share of PV panels by Technology Group 2014-2030

**Table 7** Market share of PV panels by technology groups (2014-2030)

Technology		2014	2020	2030
Silicon-based (c-Si)	Monocrystalline	92%	73.3%	44.8%
	Poly- or multicrystalline			
	Ribbon			
	a-Si (amorph/micromorph)			
Thin-film based	Copper indium gallium (di)selenide (CIGS)	2%	5.2%	6.4%
	Cadmium telluride (CdTe)	5%	5.2%	4.7%
Other	Concentrating solar PV (CPV)	1%	1.2%	0.6%
	Organic PV/dye-sensitised cells (OPV)		5.8%	8.7%
	Crystalline silicon (advanced c-Si)		8.7%	25.6%
	CIGS alternatives, heavy metals (e.g. perovskite), advanced III-V		0.6%	9.3%

Based on Fraunhofer Institute for Solar Energy Systems (ISE) (2014), Lux Research (2013) and author research

IRENA: End-of-Life Management of Solar Photovoltaic Panels, 2016



# We are very grateful for financial support from



- Swiss CTI , CCEM-CH
- Swiss National Science Foundation, Swiss Energy Office
- Horizon 2020 European Joule Projects: GOTSOLAR
- European Research Council: Adv. Research Grant MESOLIGHT
- The Balzan Prize Foundation
- Marie Curie Actions
- Industrial Partners



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



*Technology for humanity*



# Anzère, Valais Switzerland our skiing day

