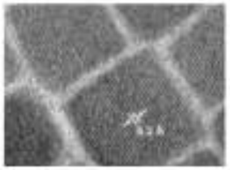
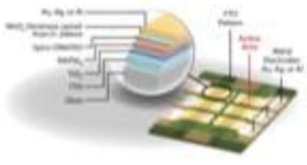
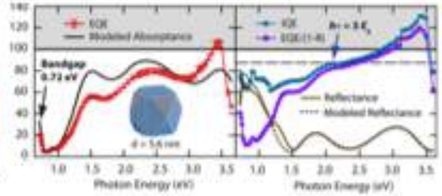




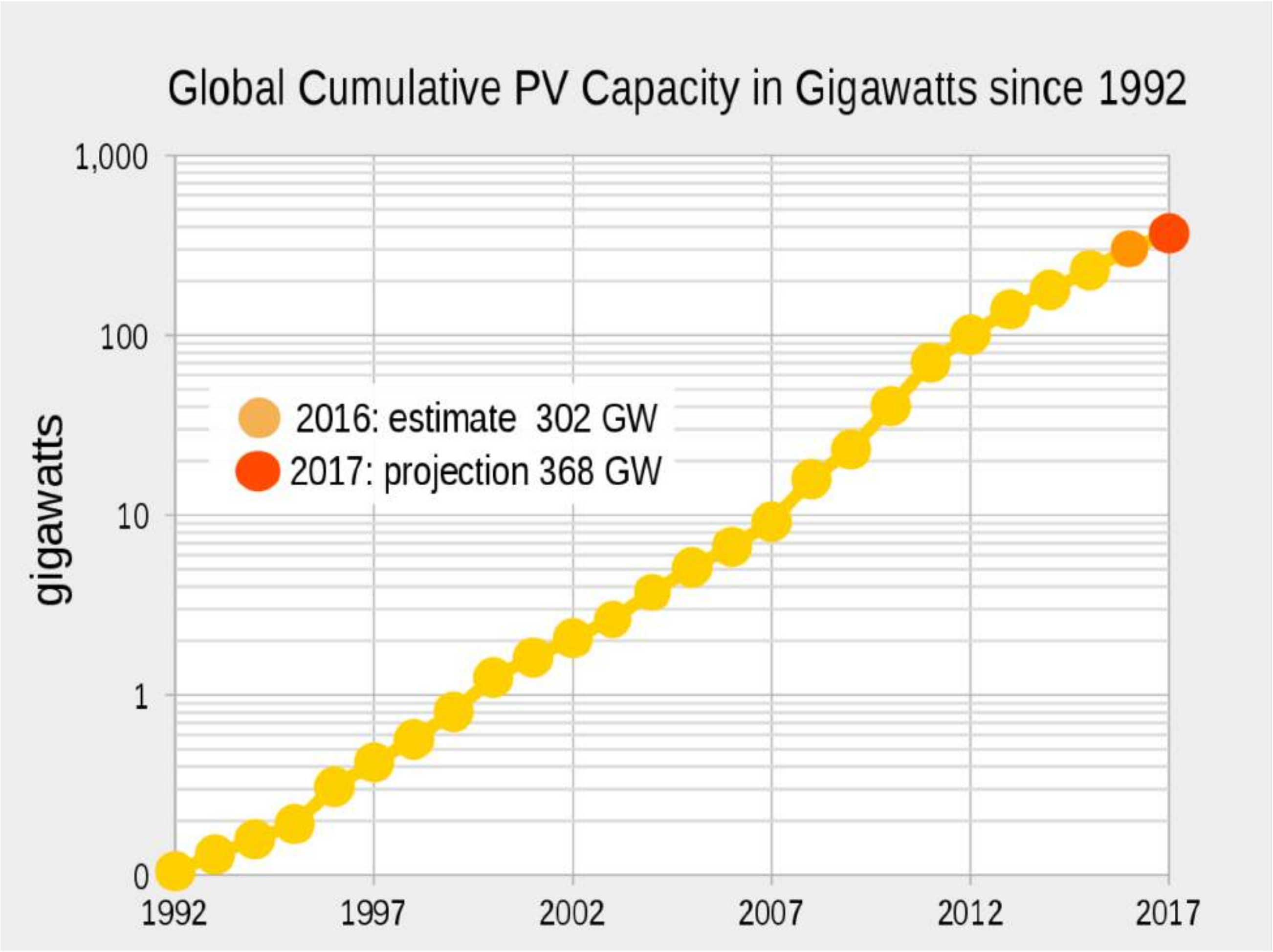



Quantum Dots and Perovskites – Realizing the Best of Both Worlds for Revolutionary Optoelectronic Applications

Joseph M. Luther
National Renewable Energy Laboratory
Golden, Colorado

NREL PV Systems: South Table Mesa Campus

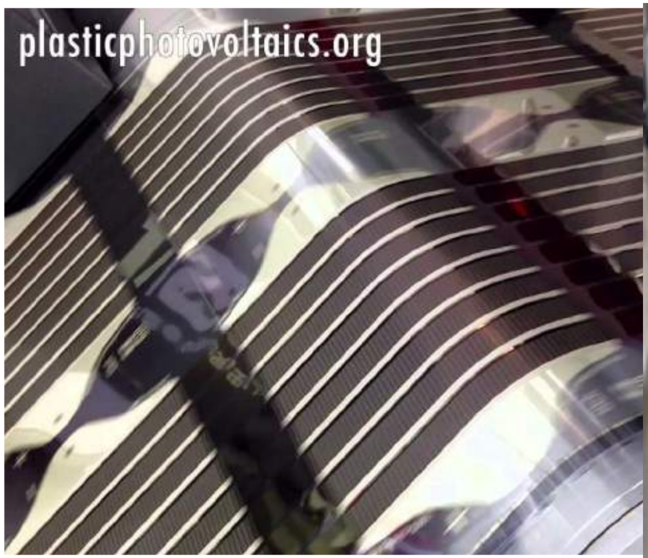
Photovoltaic Panel Production rates



- **2023 before the global cumulative capacity is at 1 TW**
- **At current rates, over 400 years to produce 30 TW**

Grand Vision of Rapidly Manufactured PV

Newspaper



Solar cell

If we can “print” solar cells like we print newspaper, we could cheaply prod electricity we need very rapidly

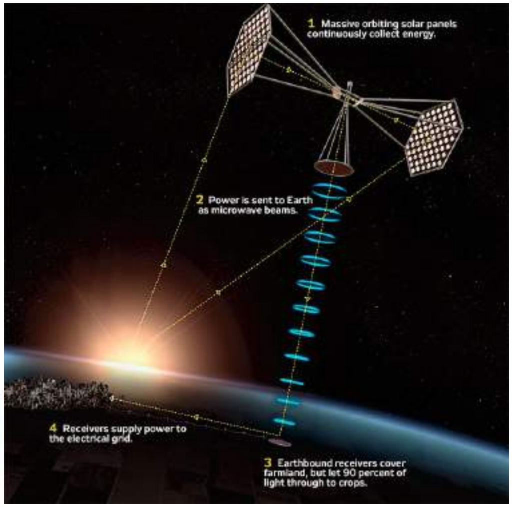
<u>1 “upcycled” newspaper plant</u> could produce a TW/yr

- Printable perovskites offer a revolutionary new PV technology
  - Perovskite stand alone devices
  - Perovskite / perovskite tandems
  - Perovskite / other technologies

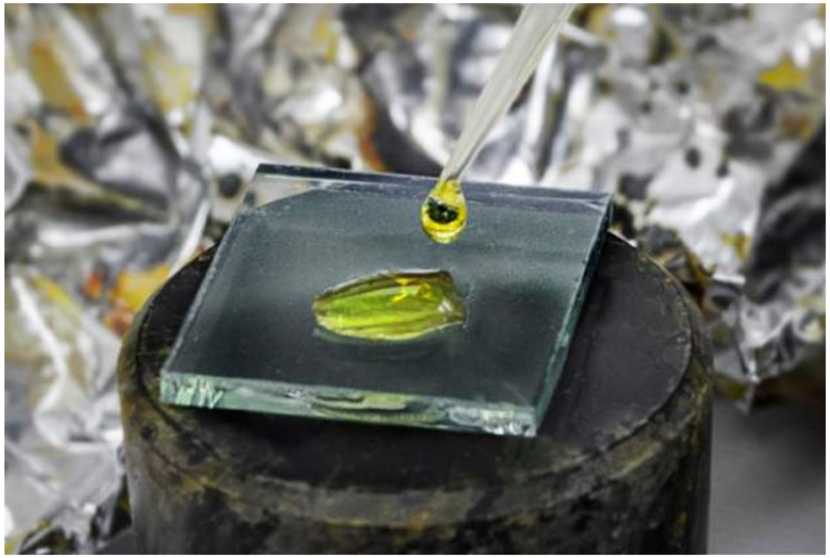
Important new markets for PV

- Building integrated PV
  - Switchable windows
- Wearable PV
- Disaster Relief
- Mobile electricity
  - Self powered drone technologies
  - Car trickle chargers
- Power Beaming

Wheeler et al. *Nat Comms* 2017.

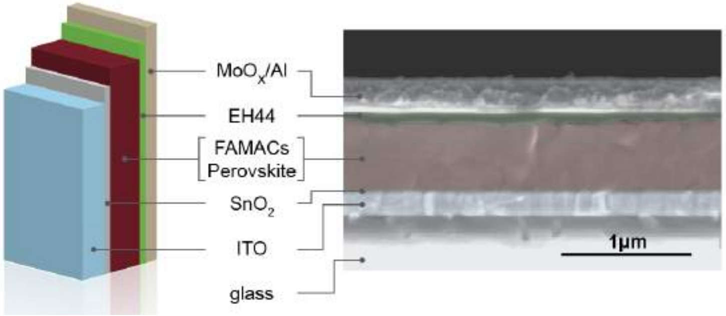


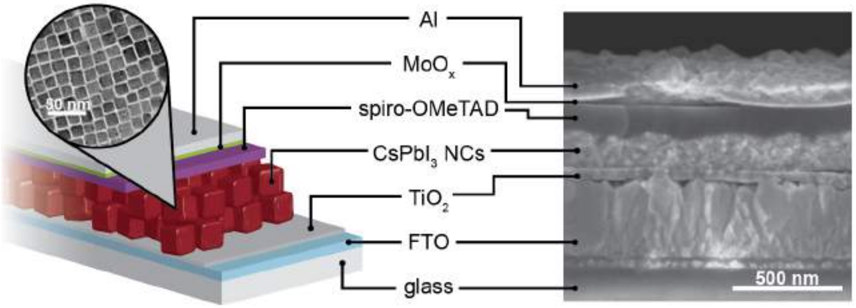
Thin film (bulk) perovskites vs Nanocrystals



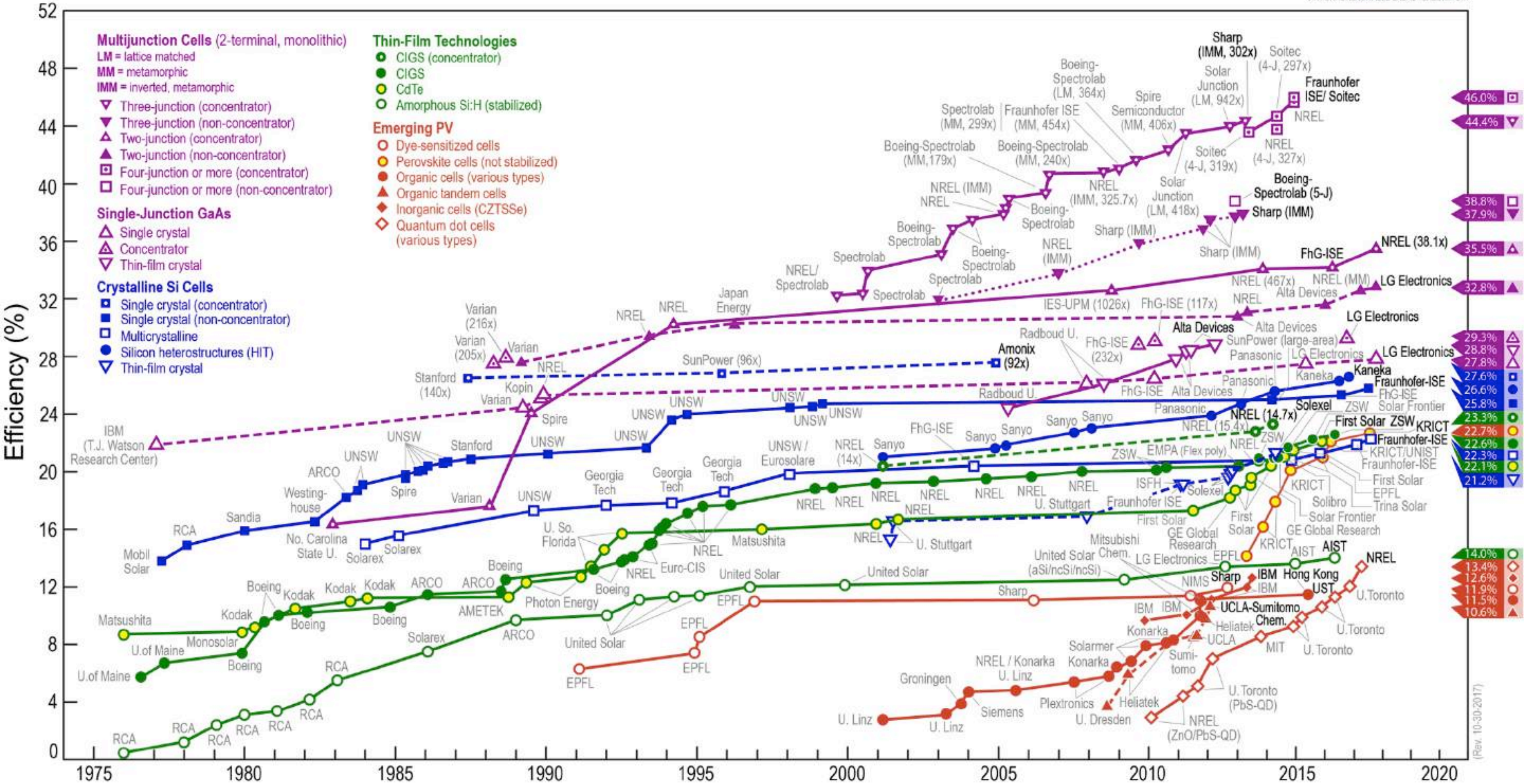
Solvated Perovskite precursor molecules which crystalize as the solvent dries

Perovskite nanocrystals in solution

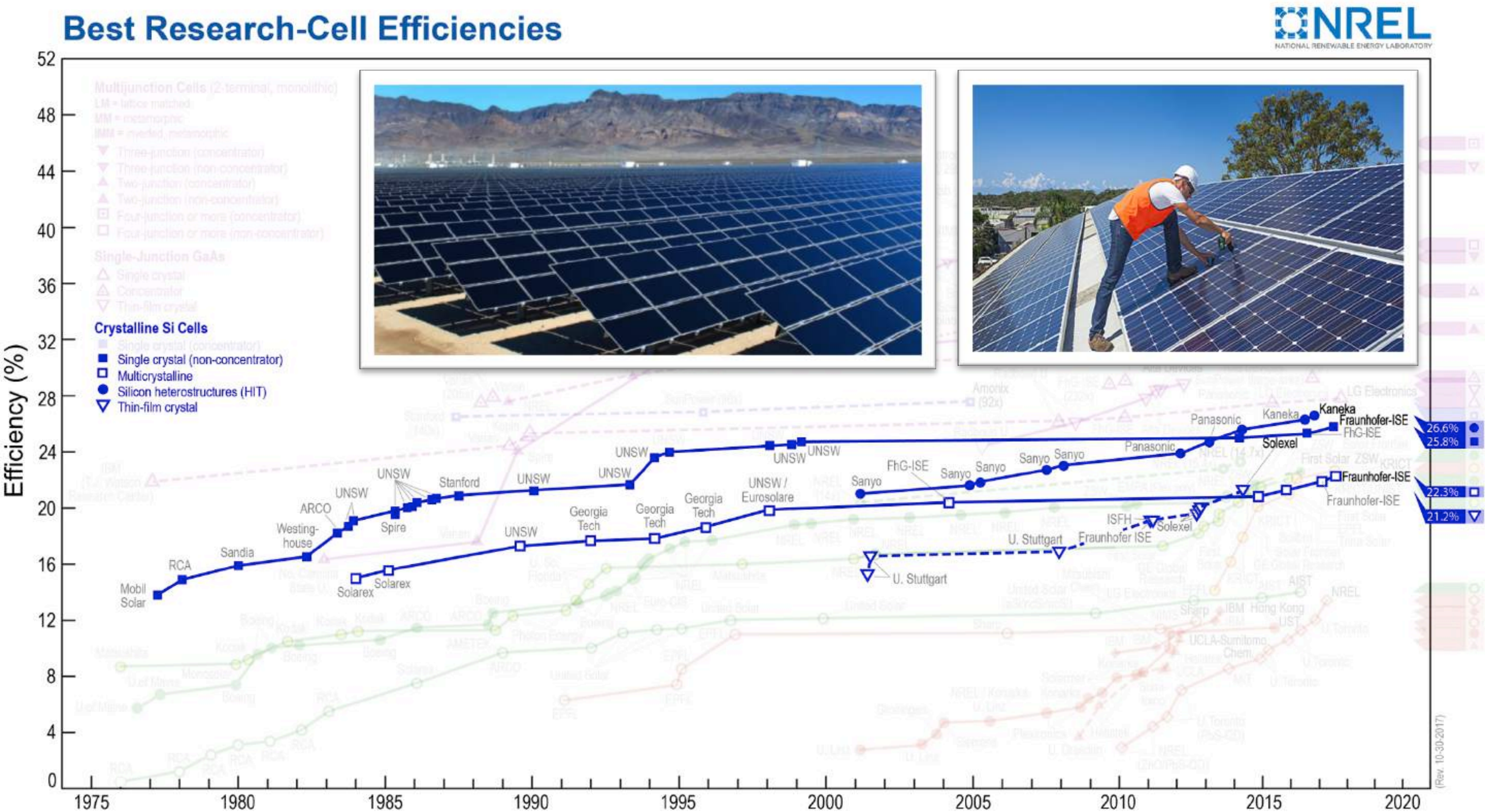




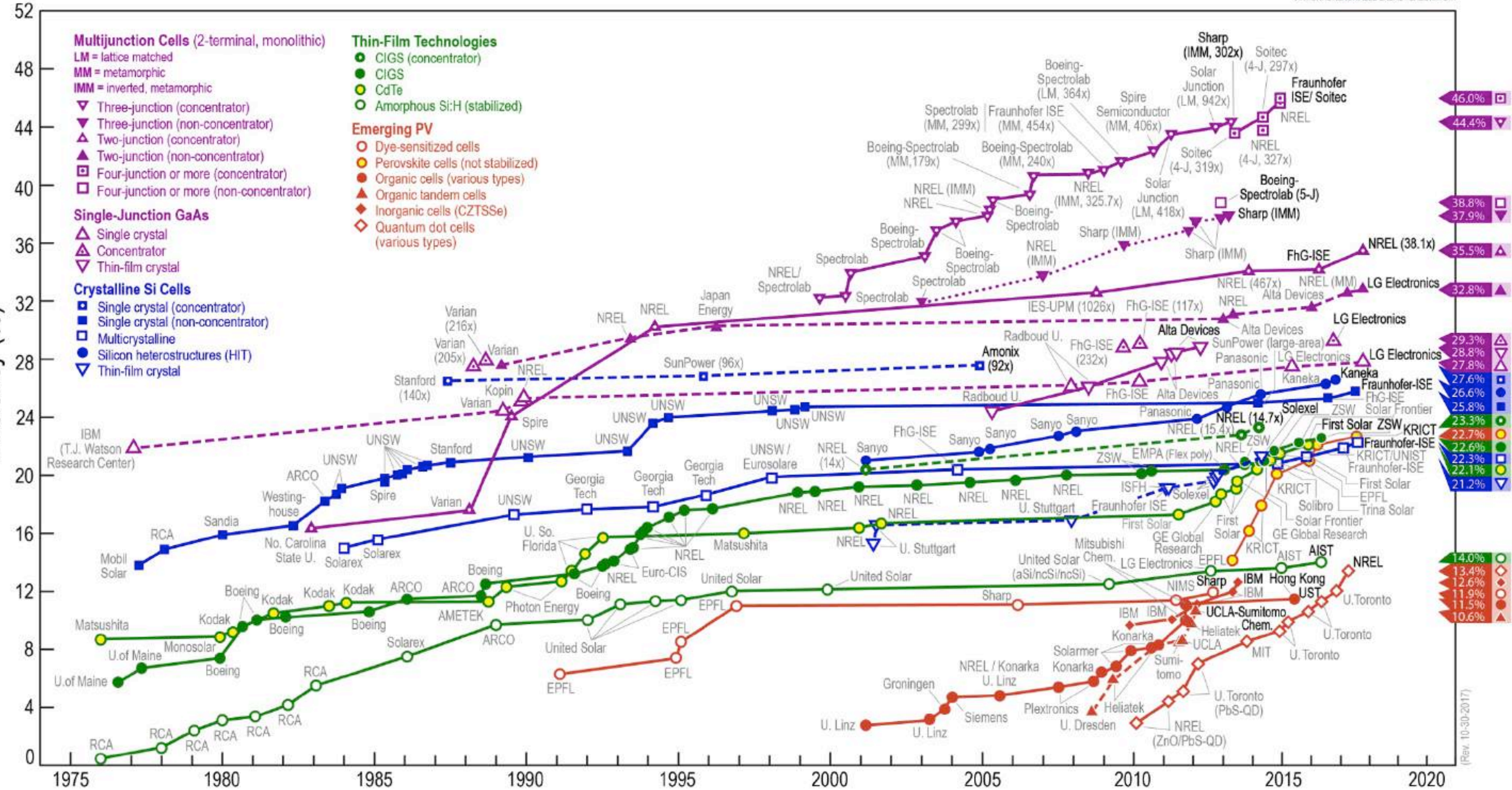
Best Research-Cell Efficiencies



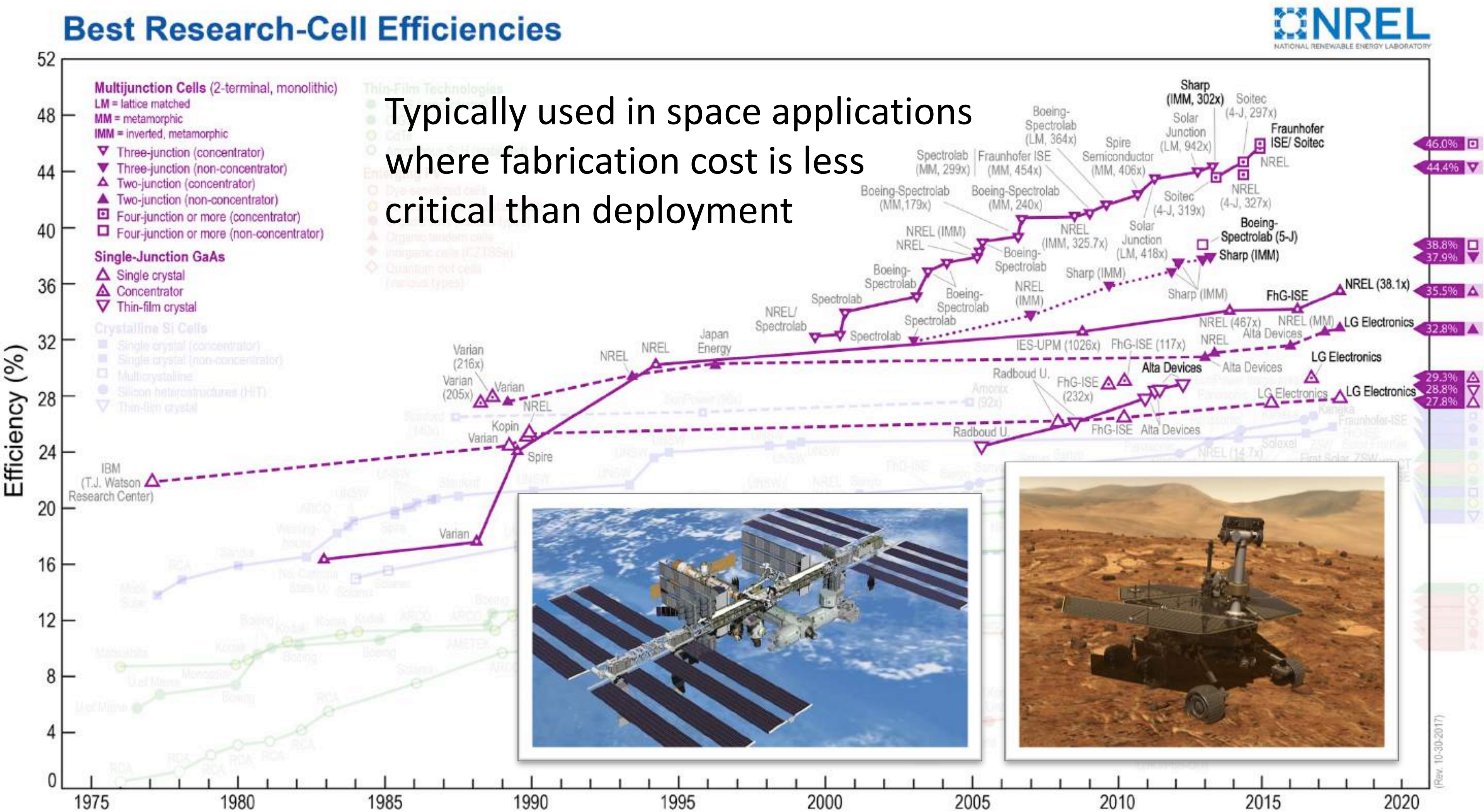
Silicon – industry leader for utility/residential PV



Best Research-Cell Efficiencies



III-V semiconductors – highest efficiency & cost

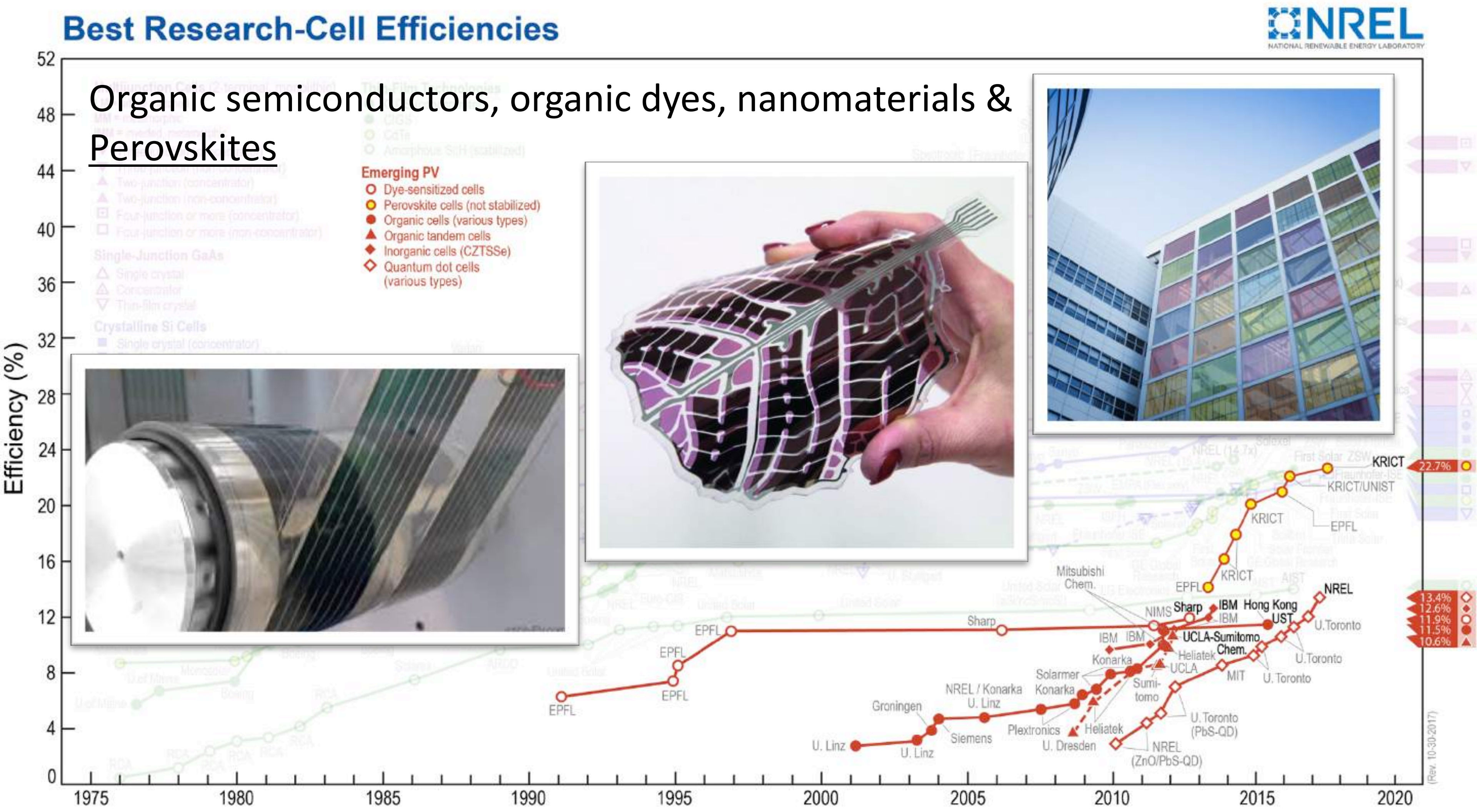


Typically used in space applications where fabrication cost is less critical than deployment

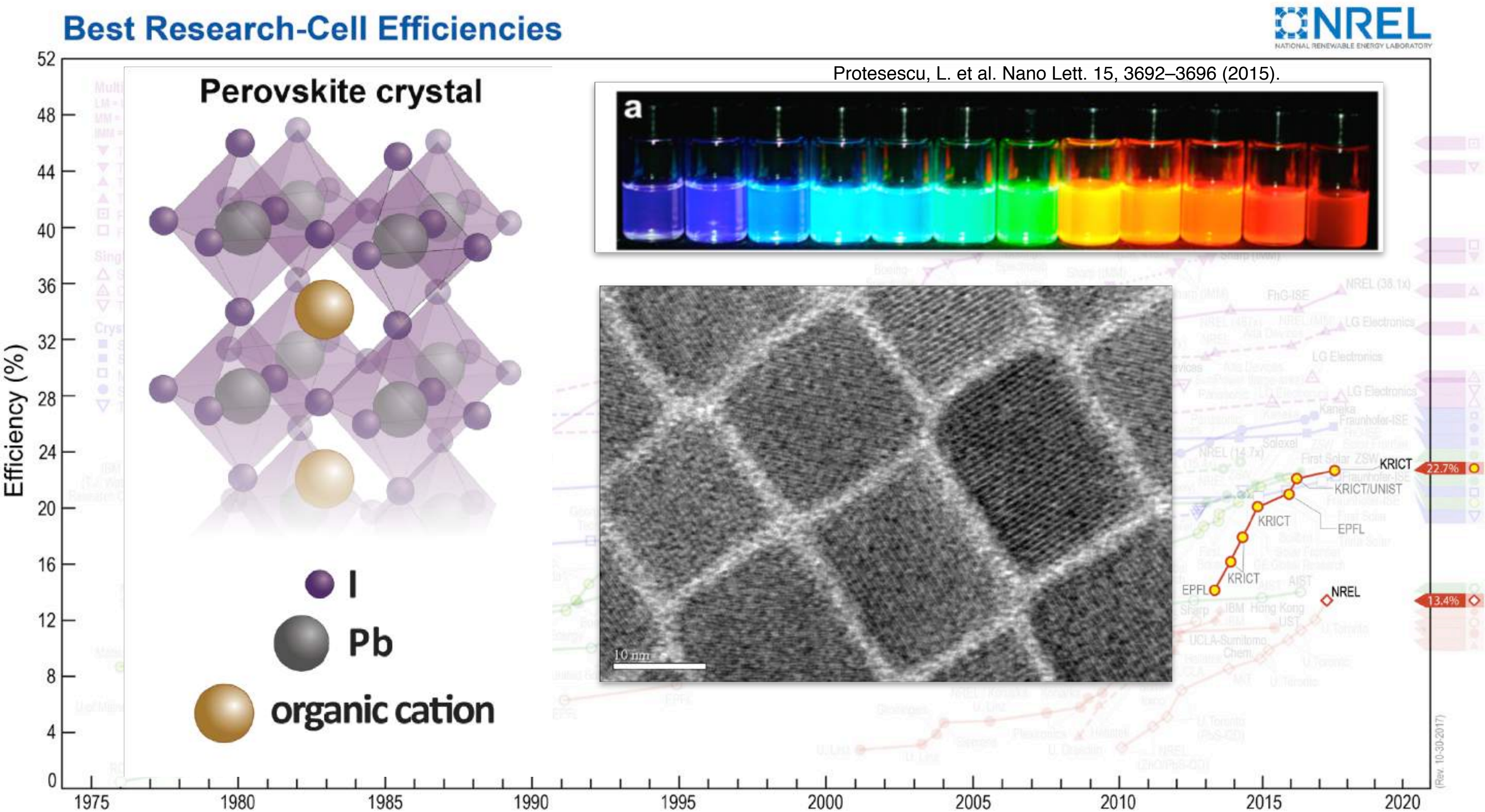
$25,000 to lift a pound into space

Emerging PV offers potential – but still emerging

Organic semiconductors, organic dyes, nanomaterials & <u>Perovskites</u>



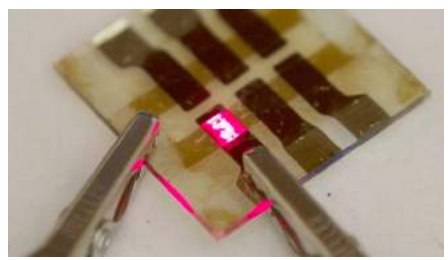
Pb-halide Perovskite semiconductors

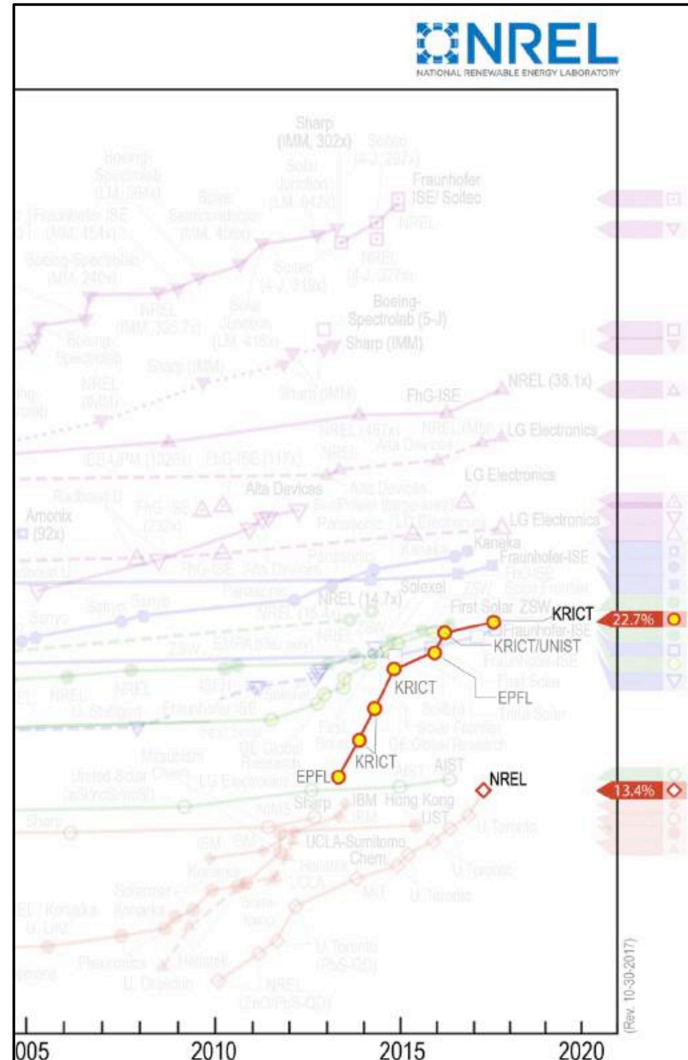


Perovskites: Efficient, inexpensive, flexible, radiation hard, tunable (composition, size)…

How did Pb-halide Perovskite PVs get to where they are?

- Incredible rise in efficiency (<4 to 23% short time)
- As <u>tolerant to defects</u> as any other electronic material we know.
- Solution or vapor-deposited material
- New Semiconductor system poised to greatly reform optoelectronics:
  - Solar Cells
  - LED / Solid State Lighting
  - TV / Display technology
  - Quantum Computation, spin devices/memory
  - Lasers, photodetectors, sensors, Gamma detectors
- Stability and Phase Transitions are critical to understand before deployment.





Perovskite stability

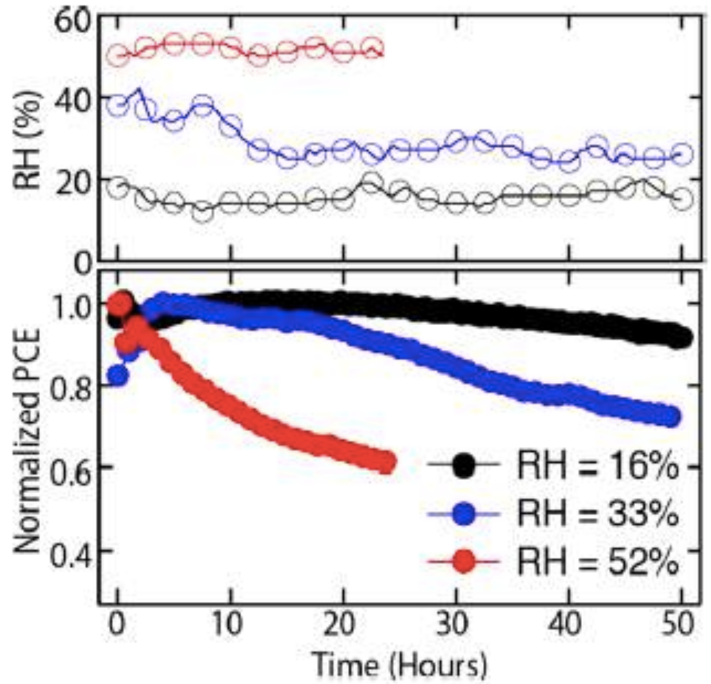
- Identify the unstable part of perovskite solar cells and fix it
  - Why is this so challenging?
    - Ion migration (Li, A-site cation, halides, metals)
    - Moisture ingress
    - Low formation energy for crystallization

Constant need for studies providing greater insight into degradation
As a function of:

- Atmosphere (temperature, humidity, …)
- Device configuration (absorber chemistry, ETL, HTL, additives (Li^+, *etc.*) & concentration, electrodes, polarity)
- Substrate

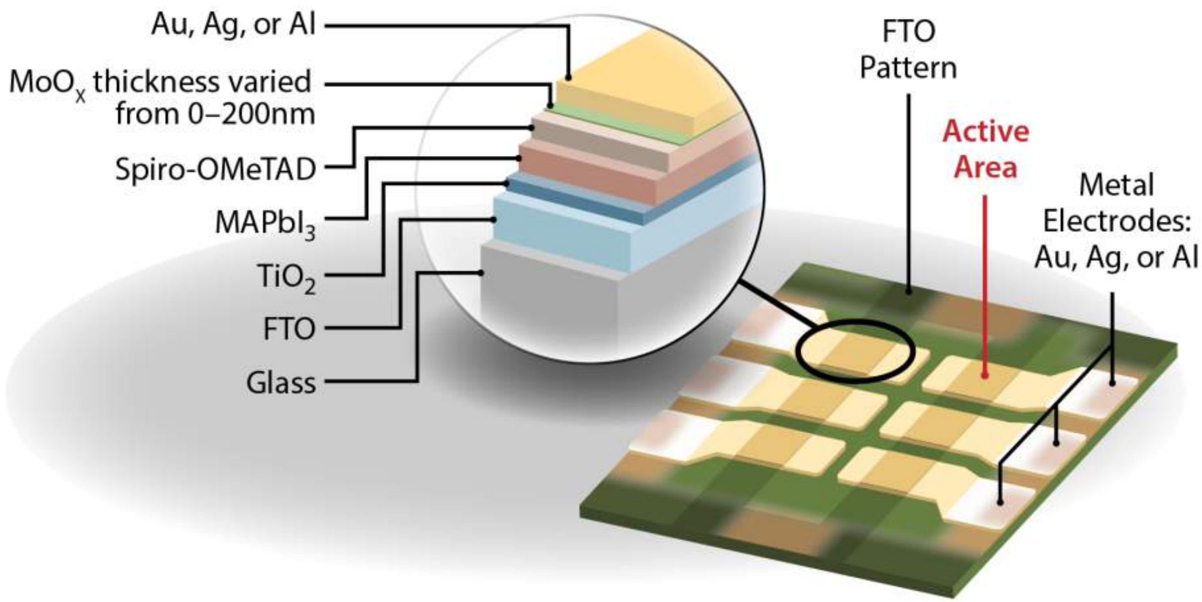
All while tracking output under standardized measurement conditions

Stability *vs.* humidity



Influence of electrode interfaces on the stability of perovskite solar cells: reduced degradation using MoO_x/Al for hole collection. Sanehira, Tremolet de Villers, Schulz, Reese, Ferrere, Zhu, Lin, Berry, Luther, *ACS Energy Letters* 2016.

Components to a Perovskite solar cell



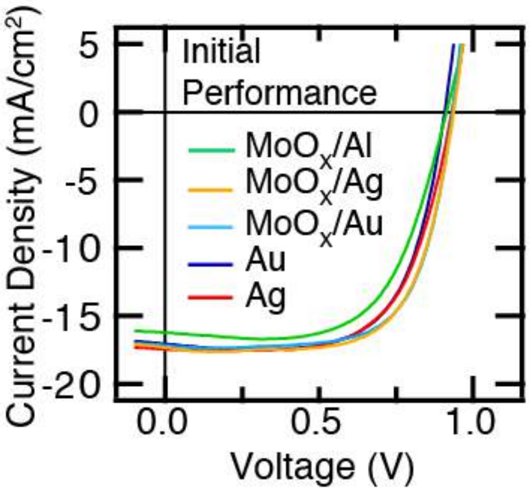
Perovskite Active Layer: Phase segregation, phase stability, ion migration, thermal decomposition…

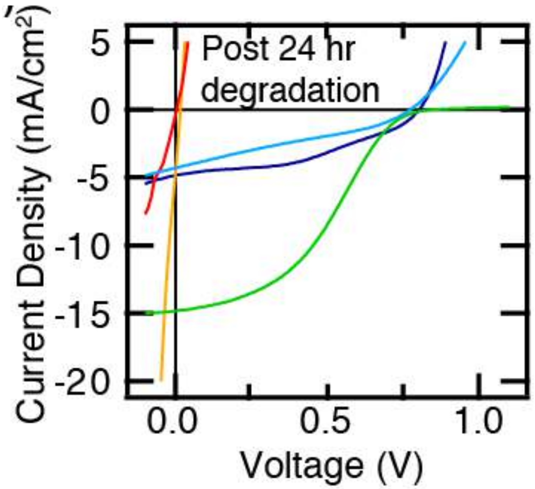
Interfaces: Band alignment, trapped charges, catalysis, water ingress…

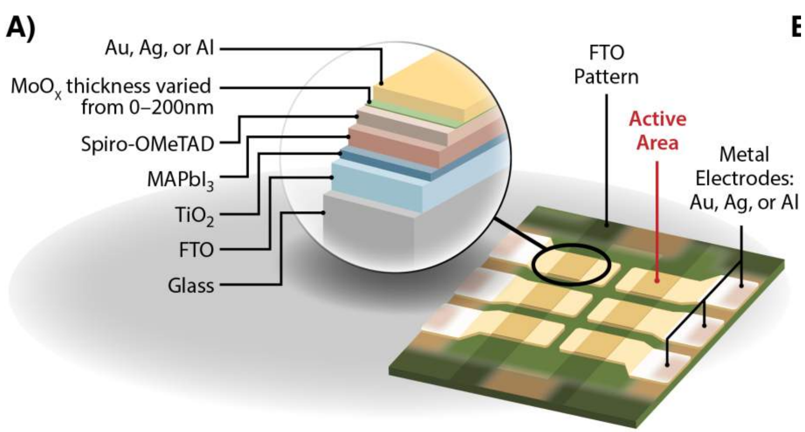
Contact Layers: doping, redox, thermal stability…

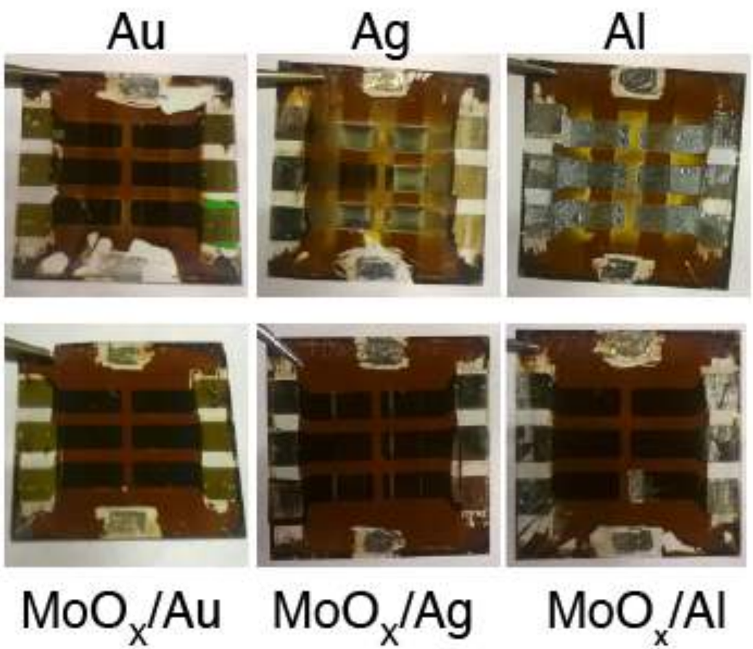
Influence of electrode

If all of these can operate at the same efficiency – optimize based on the most stable!



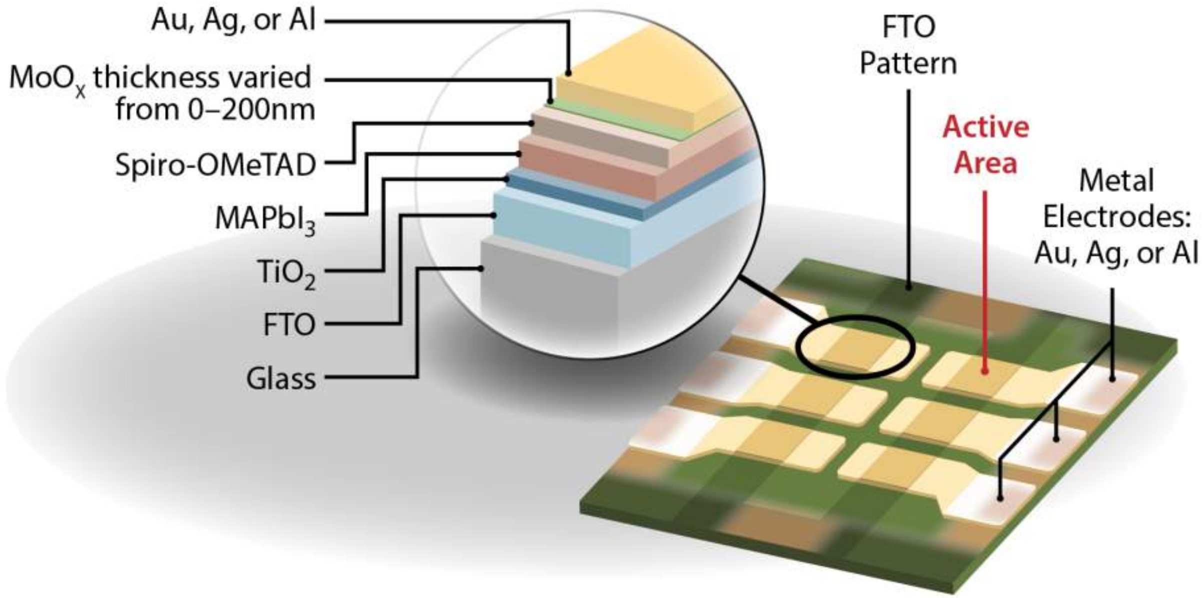






Influence of electrode interfaces on the stability of perovskite solar cells: reduced degradation using MoO_x/Al for hole collection. Sanehira, Tremolet de Villers, Schulz, Reese, Ferrere, Zhu, Lin, Berry, Luther, *ACS Energy Letters* 2016.

Where are the weak links in the device stack?



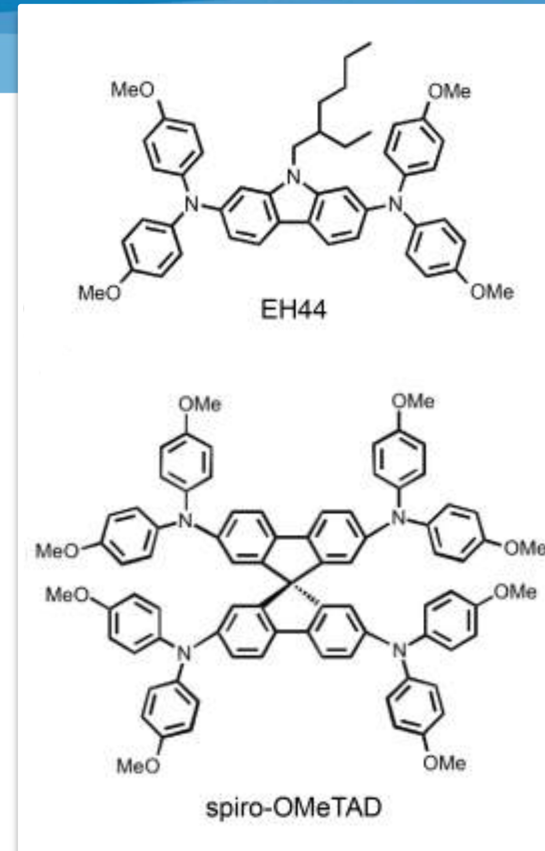
Perovskite Active Layer: Phase segregation, phase stability, ion migration, thermal decomposition… $MAPbI_3$ replaced with FAMACsPbIBr

Interfaces: Band alignment, trapped charges, catalysis, water ingress…

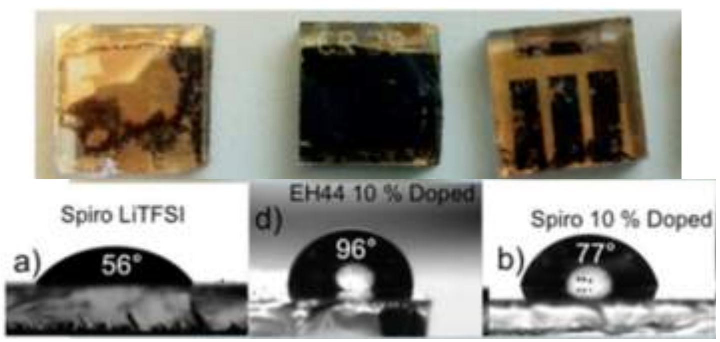
Contact Layers: doping, redox, thermal stability…

Li-Free, hydrophobic HTMs

<u>HTM Wish List</u>
- Facile synthesis/purification
- Hydrophobic (incl. Li-free)
- Suitable HOMO level
- Easily tunable
- Good hole mobility



EH44 offers improved hydrophobicity



Li-Free: Employs predoped HTM as a dopant
HTM + AgTFSI → $HTM^{+}TFSI^{-}$ + Ag(s)

$MAPbI_3$ active layer

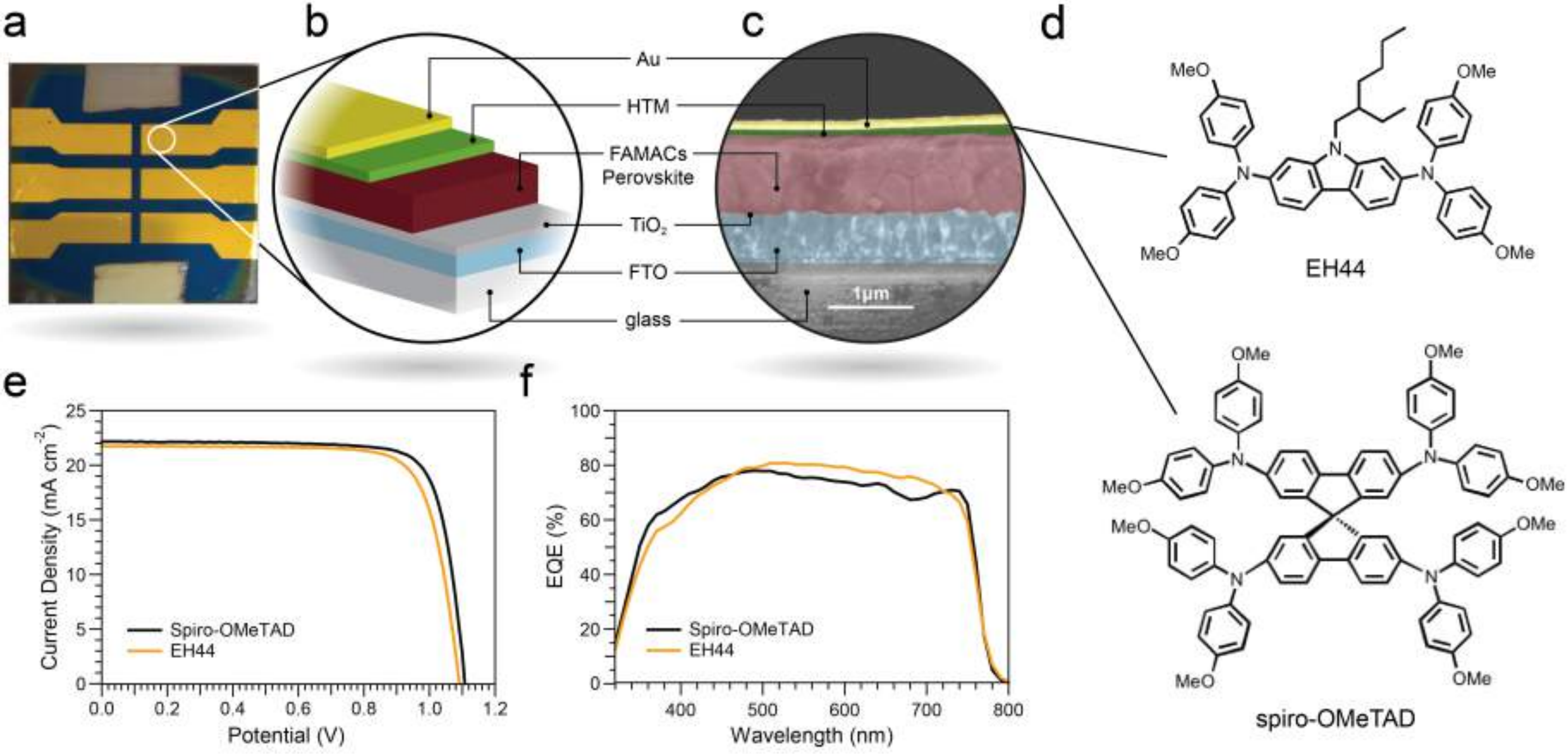
HTM	PCE (%) [max]	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	SPO (%)
spiro Li-TFSI	10.2 *[13.3]*	17.5	0.99	0.55	8.4
EH44 TFSI	10.2 *[13.2]*	18.6	0.94	0.60	7.9

T. Leijtens, T. Giovenzana, S. N. Habisreutinger, J. S. Tinkham, N. K. Noel, B. A. Kamino, G. Sadoughi, A. Sellinger and H. J. Snaith, *Appl. Mater. Interfaces*, **2016**, 8, 5981–5989.

Alan Sellinger - CSM

Optimized EH44 vs. Spiro-OMeTAD

Alan Sellinger - CSM



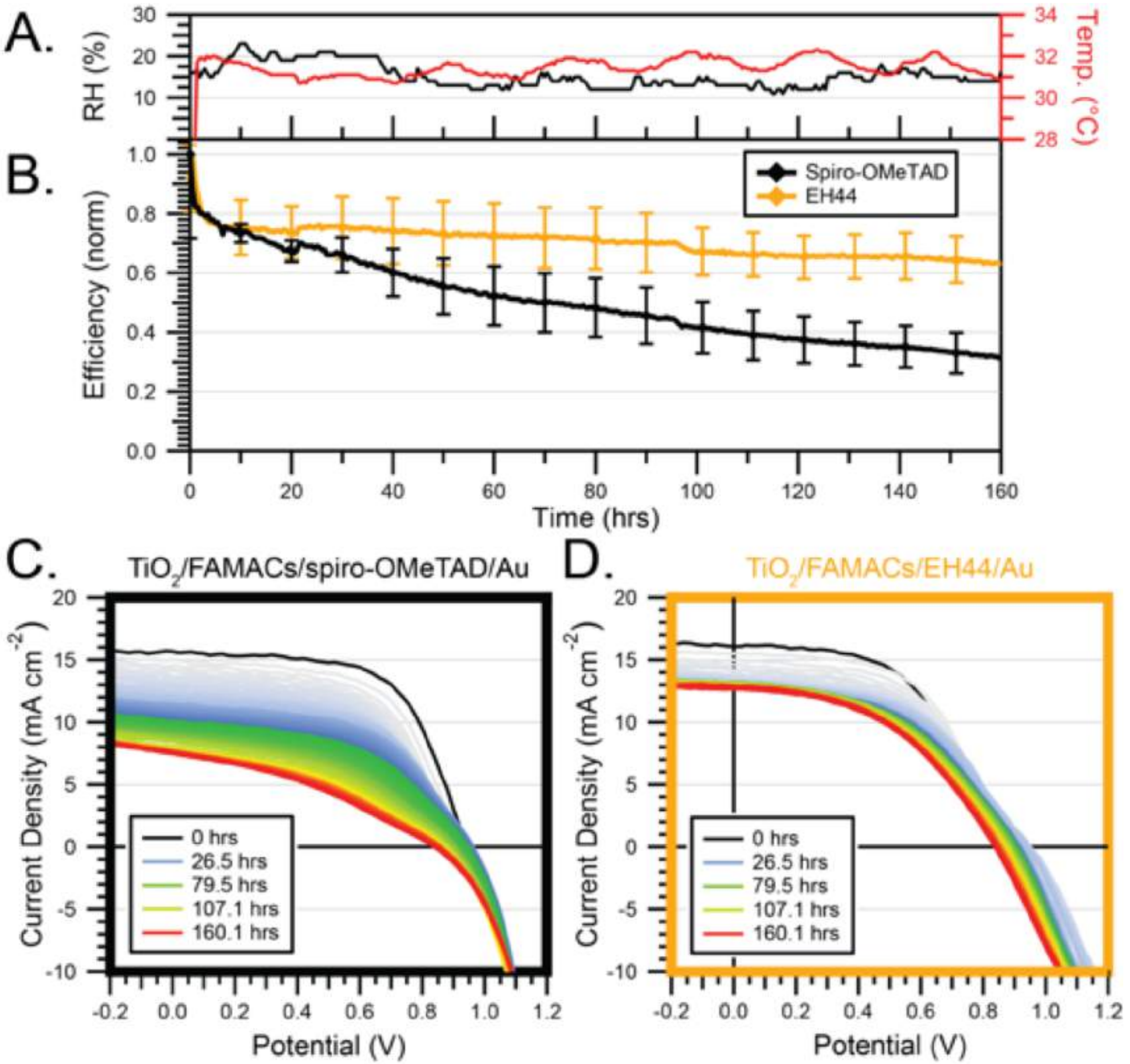
Tailored Interfaces of unencapsulated perovskite solar cells for >1000 hour operational stability. Christians, Schulz, Tinkham, Schloemer, Harvey, Tremolet de Villers, Sellinger, Berry, Luther, *Nature Energy*, 2018.

Stability: Spiro vs. EH44

- **EH44 helps but doesn't solve stability**
- **Dynamic changes in all PV parameters …**
- **What about other interface?**
  - TiO_2 – most studied photocatalytic semiconductor
  - Substrate drives the crystallization

    ETL options

    - ZnO, SnO_2, fullerenes



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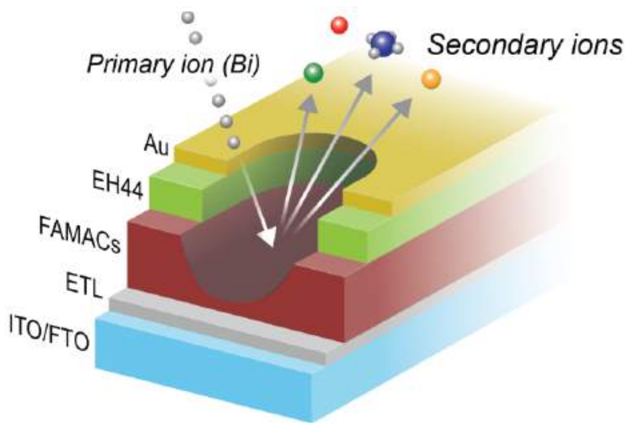
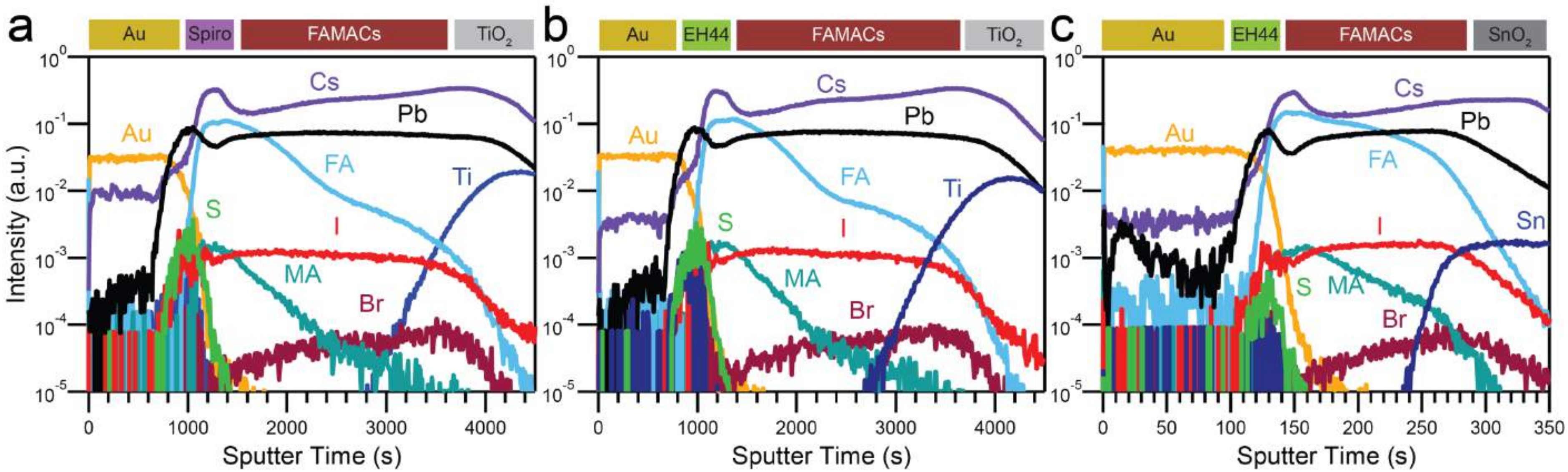
Vertical composition: HTLs and SnO_2 vs TiO_2

Steve Harvey



- ToF-SIMS profiles of fresh, full device stacks
- Changes in perovskite active layer observed between TiO_2 and SnO_2
- Crystallization influenced by substrate



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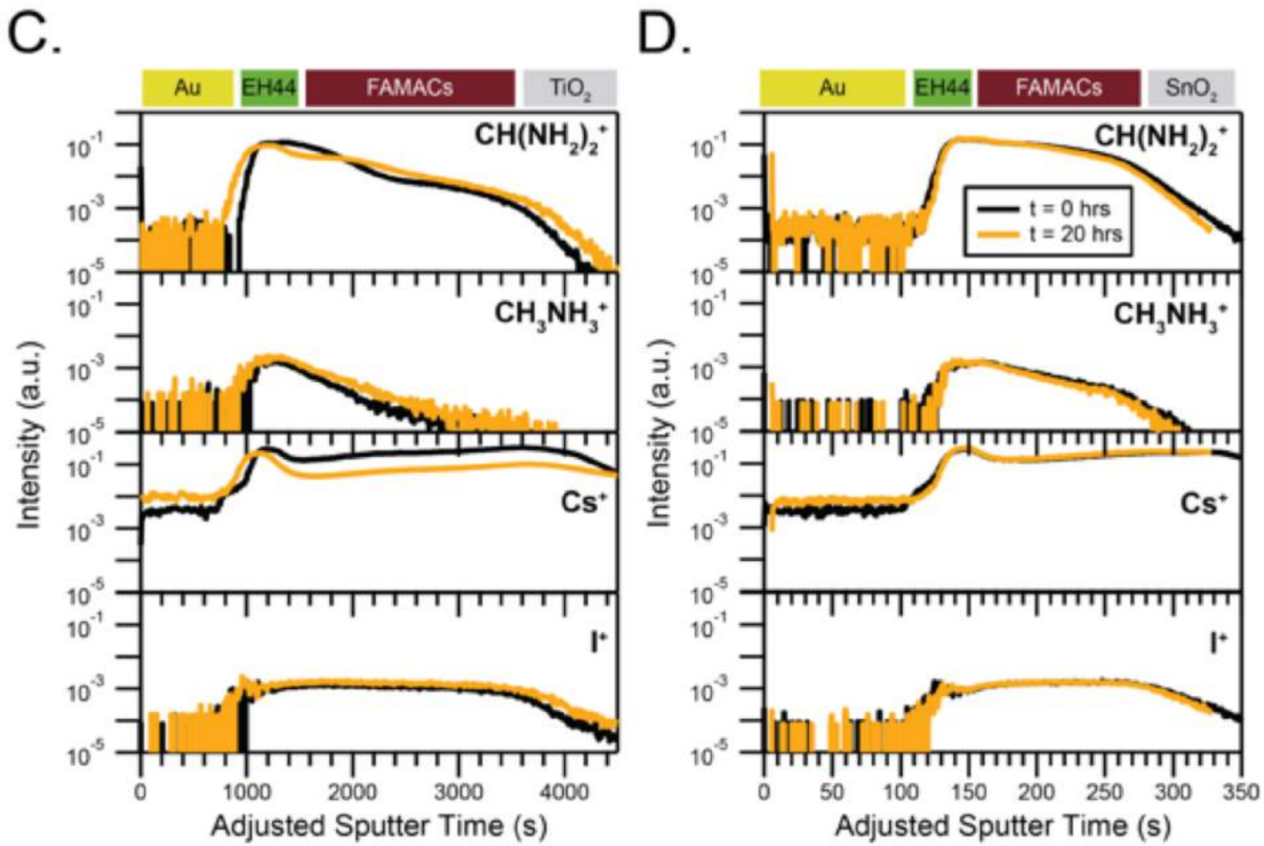
ETL interface: SnO_2 vs TiO_2

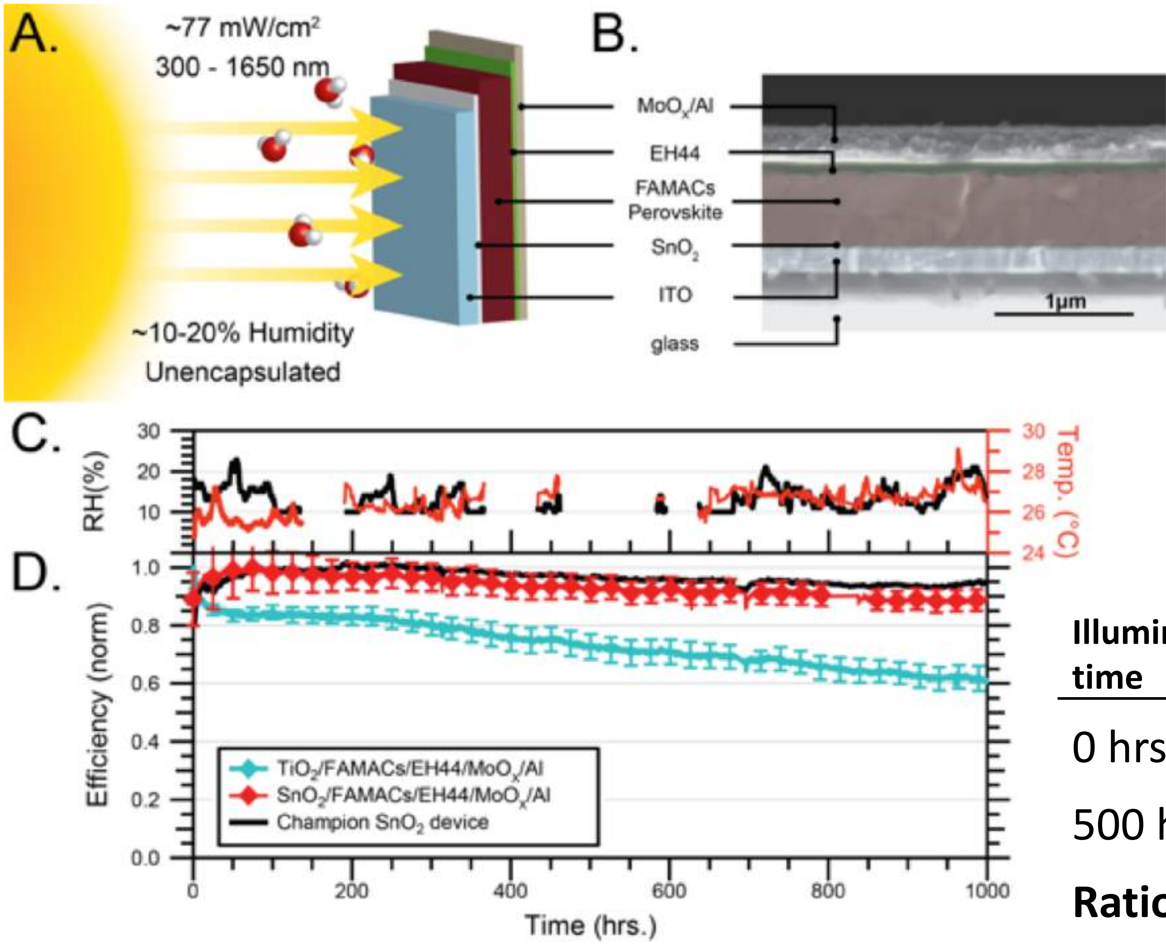
Steve Harvey

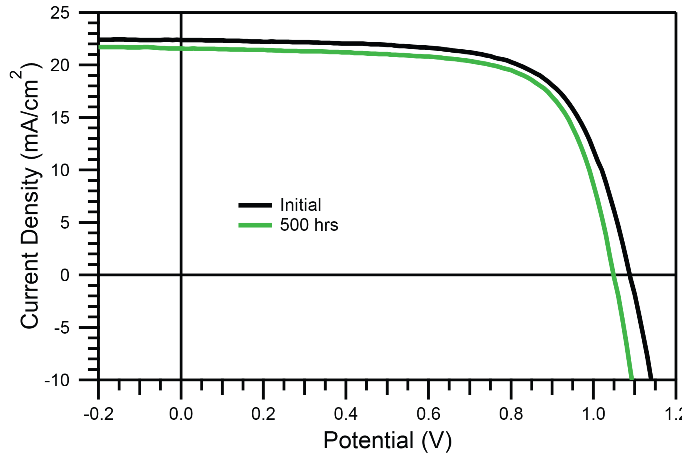
- TOF-SIMS
- **Changes in TiO2:**
  - A-site distribution (FA, MA, *Cs*)
  - Implications for: Band structure, photo-carrier dynamics
- **Changes in SnO2:**
  - More uniform profiles
  - Less vertical changes after operation



Tailored Interfaces of unencapsulated perovskite solar cells for >1000 hour operational stability. Christians, Schulz, Tinkham, Schloemer, Harvey, Tremolet de Villers, Sellinger, Berry, Luther, *Nature Energy*, 2018.

Stable unencapsulated device

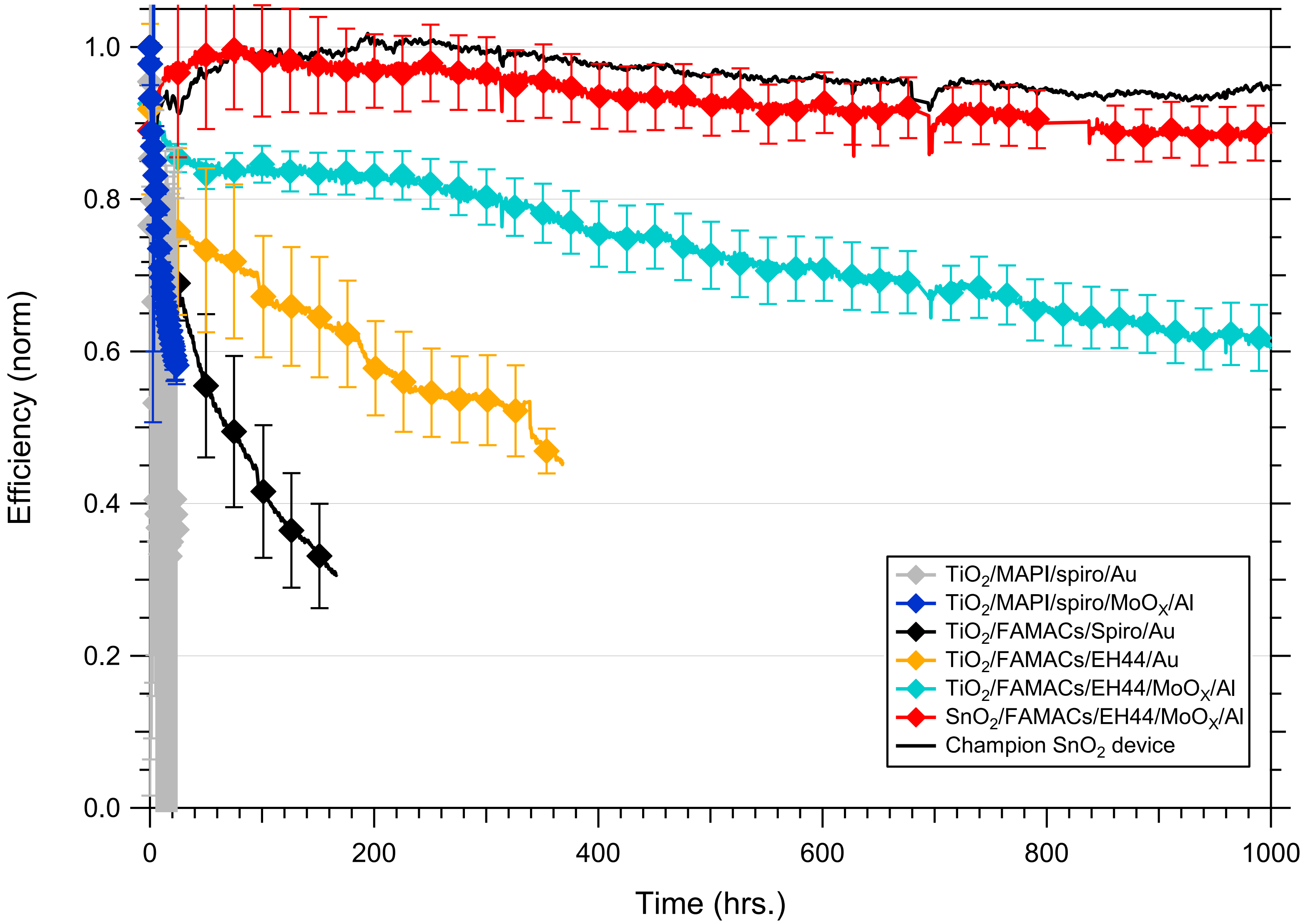




Illumination time	**J_{SC} (mA/cm²)**	**V_{OC} (V)**	**FF**	**PCE (%)**
0 hrs	22.35	1.088	0.679	16.52
500 hrs	21.55	1.049	0.698	15.78
Ratio	**0.964**	**0.964**	**1.028**	**0.955**

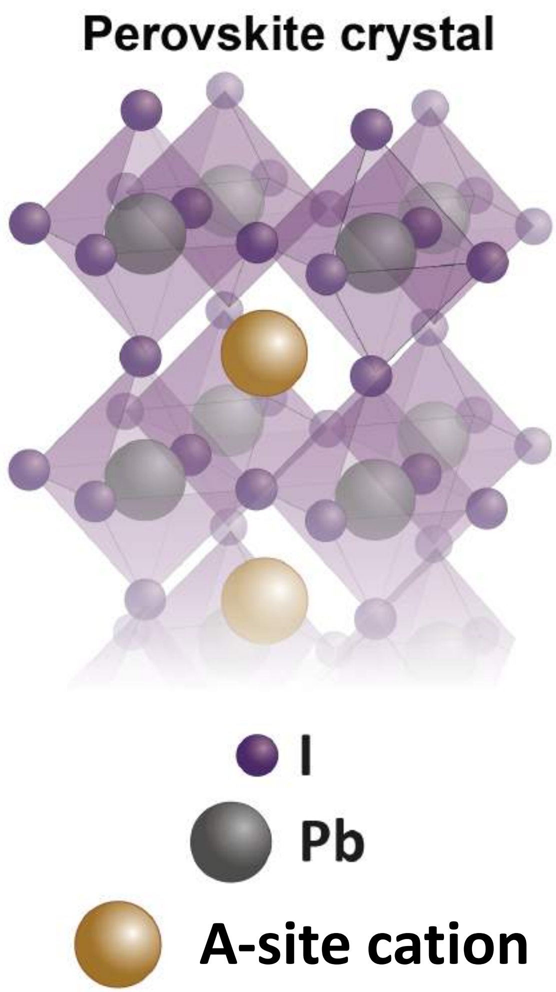
Tailored Interfaces of unencapsulated perovskite solar cells for >1000 hour operational stability. Christians, Schulz, Tinkham, Schloemer, Harvey, Tremolet de Villers, Sellinger, Berry, Luther, *Nature Energy*, 2018.

Stability improvements to date…

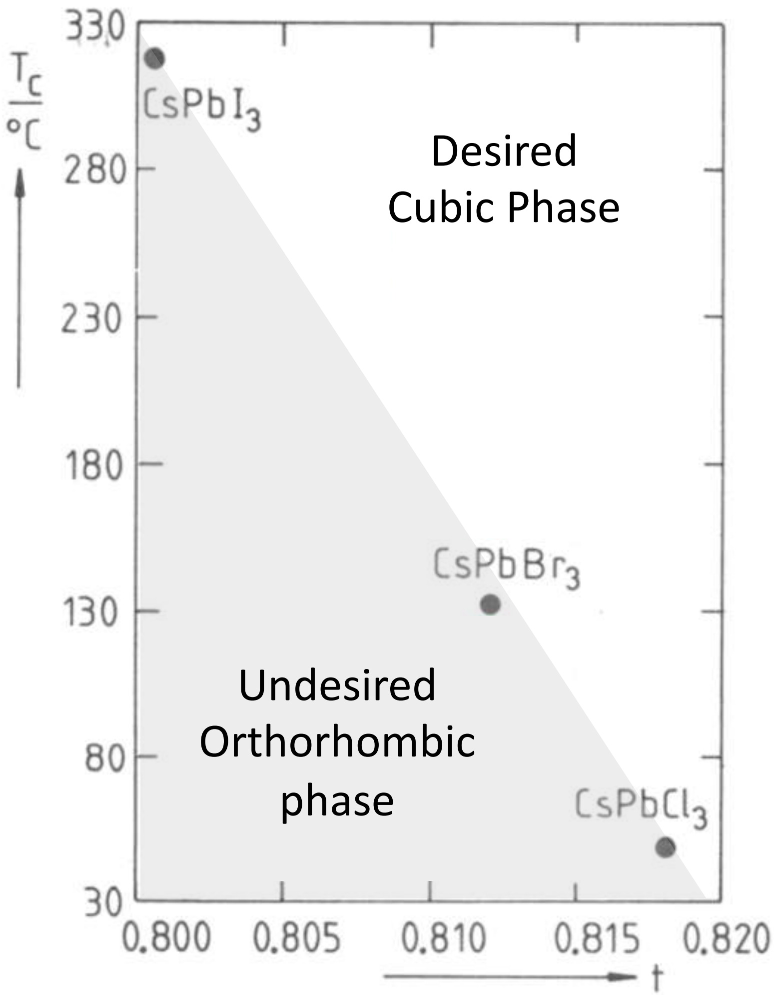


Question:

So how has this semiconductor escaped us for so long???

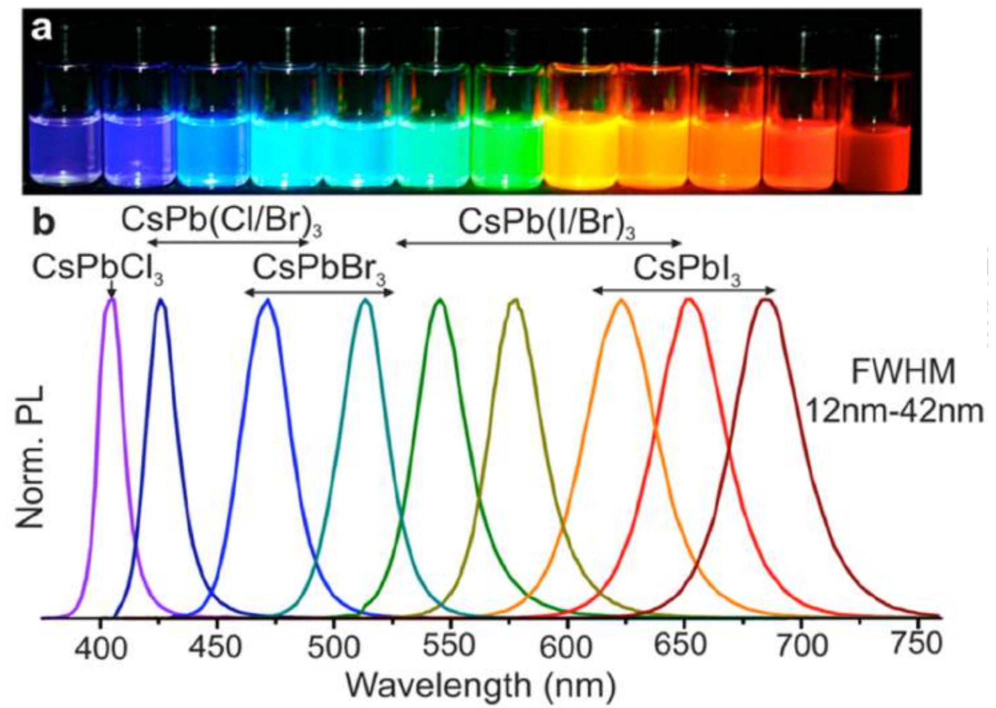


Overcoming Phase Challenge in $CsPbX_3$ Perovskites



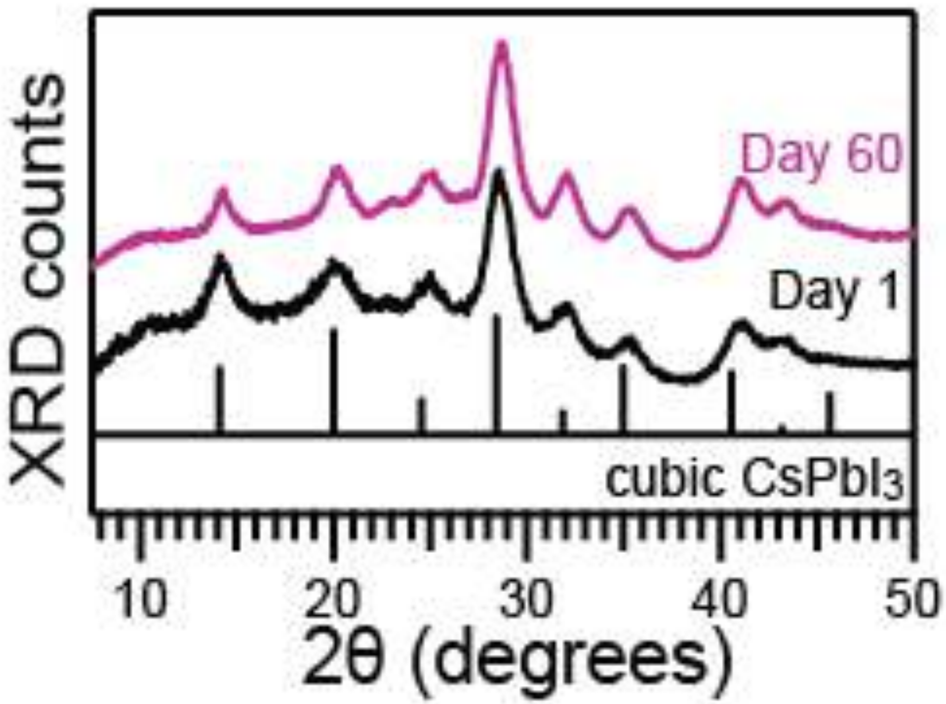
S. Sharma et al. zpch 175, (1992).

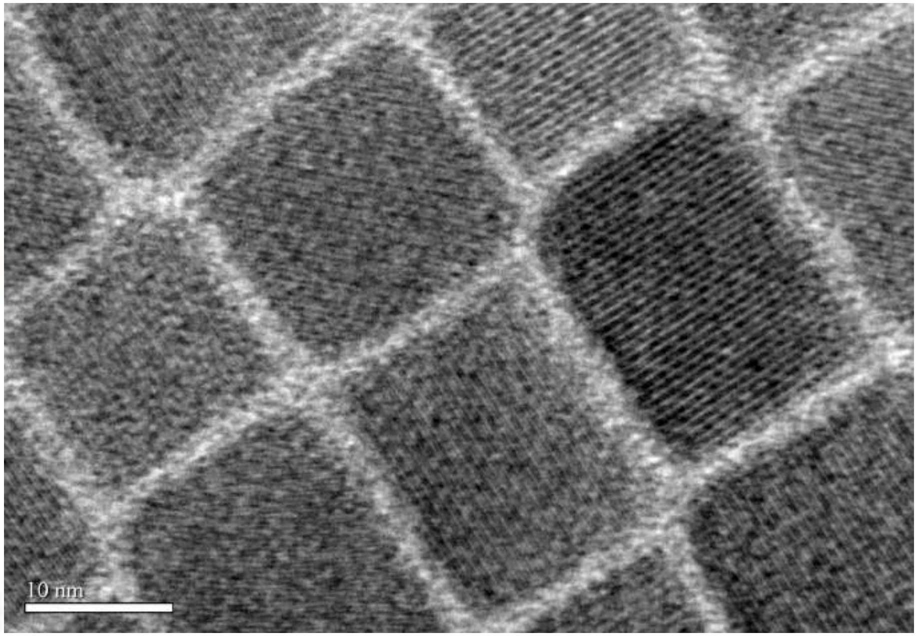
Nanocrystals with bright light emission



Protesescu, L. et al. Nano Lett. 15, 3692–3696 (2015).

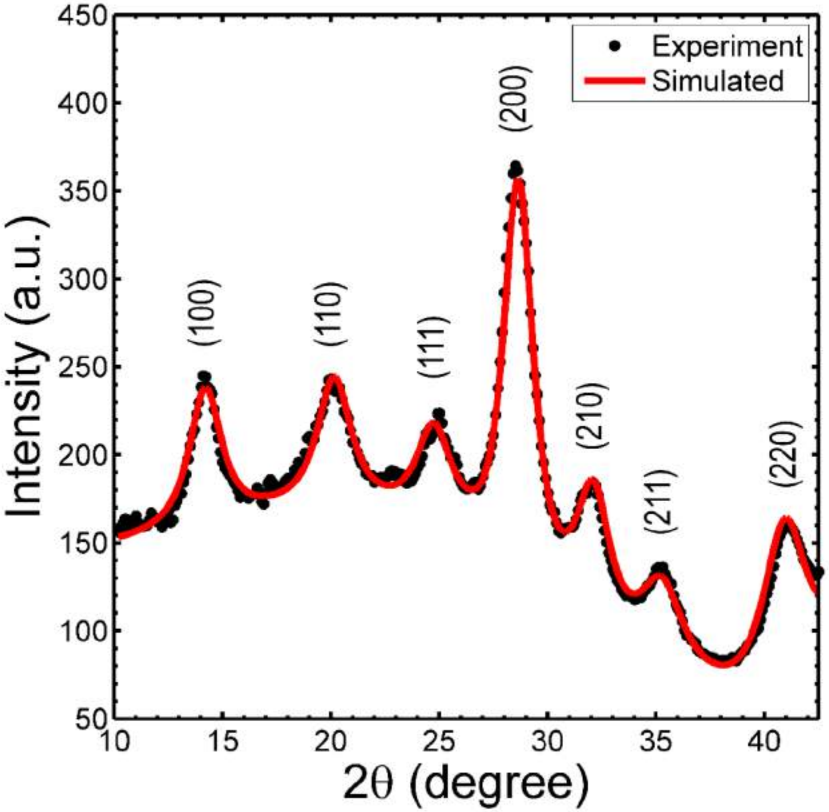
Quantum dots $CsPbI_3$ stable in the cubic phase at RT





Quantum dot–induced phase stabilization of α-$CsPbI_3$ perovskite for high-efficiency photovoltaics. Swarnkar, Marshall, Sanehira, Chernomordik, Moore, Christians, Chakrabarti, and Luther. *Science*, **2016**

Rietveld refinement fitting of XRD

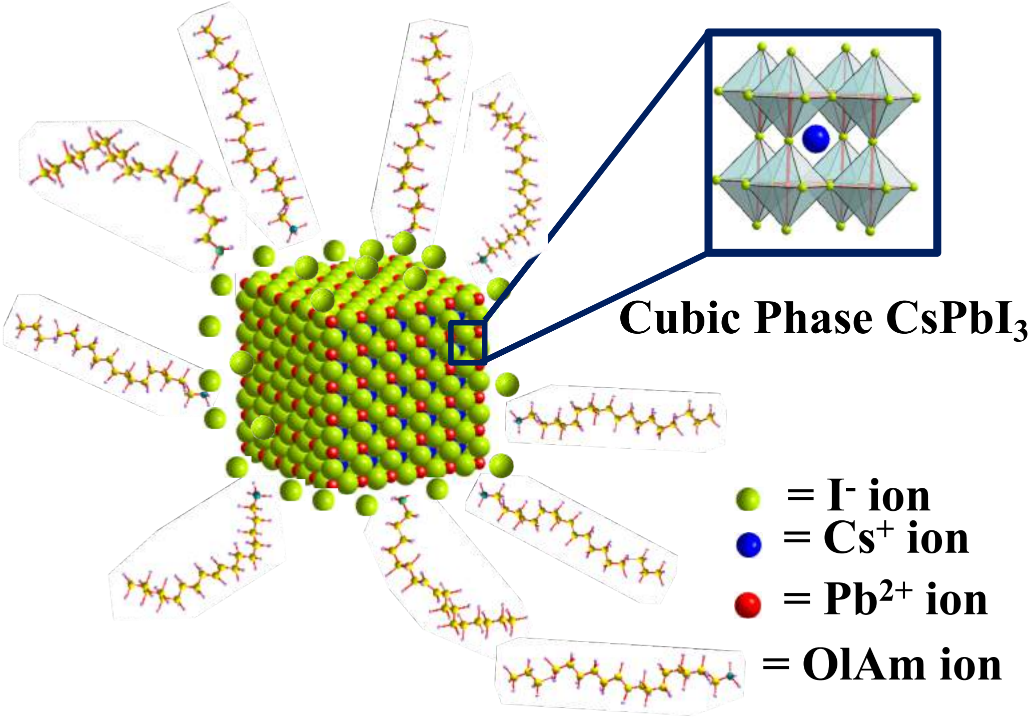


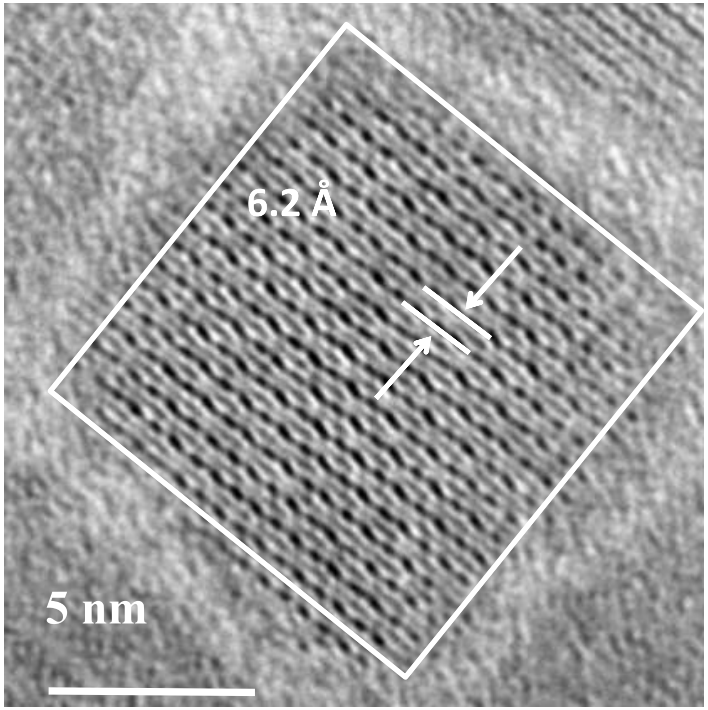
- Bulk lattice parameter is 6.2894 A at 360 °C (Temp dependent)
- $CsPbI_3$ NCs show decreasing lattice constant vs size.
- Trait also seen in other materials, like $BaTiO_3$, anatase-TiO_2, CdSe, $NaYF_4$, …

QD size (TEM)	QD size (Rietveld)	a (Å)
8 nm	9 ± 1 nm	6.231 ± 0.002
9 nm	10 ± 1 nm	6.220 ± 0.002
15.5 nm	17 ± 2 nm	6.189 ± 0.002

Quantum dot–induced phase stabilization of α-$CsPbI_3$ perovskite for high-efficiency photovoltaics. Swarnkar, Marshall, Sanehira, Chernomordik, Moore, Christians, Chakrabarti, and Luther. *Science*, **2016**

Oleylammonium ion ligand shell





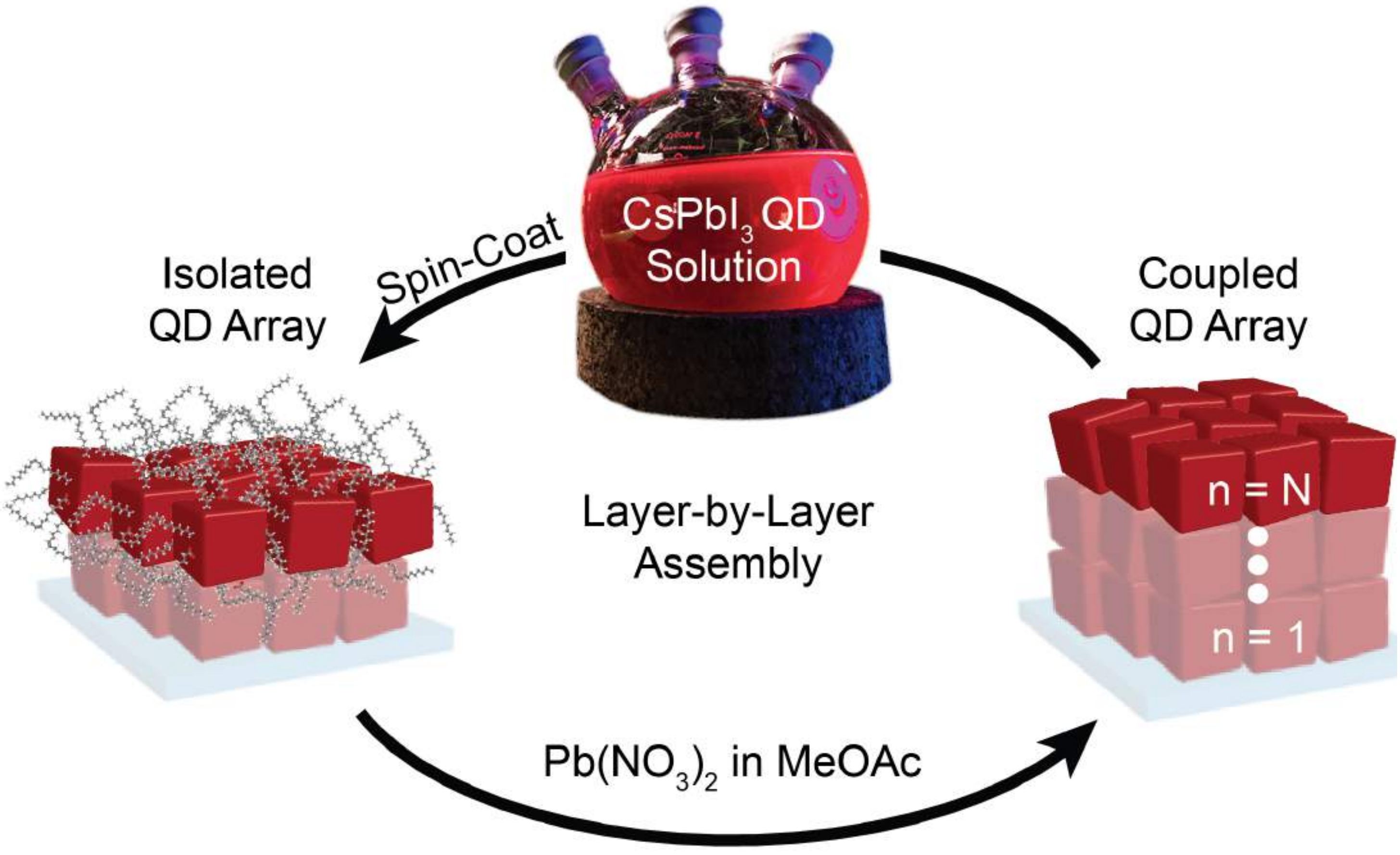
Ligands required for high temperature, colloidal synthesis

However, these ligands are bulky and insulating

Replacement of ligands:

- Enables layer-by-layer deposition
- Improves charge transport
- Complete removal of ligands leads agglomeration

Method to fabricate conductive $CsPbI_3$ QD films



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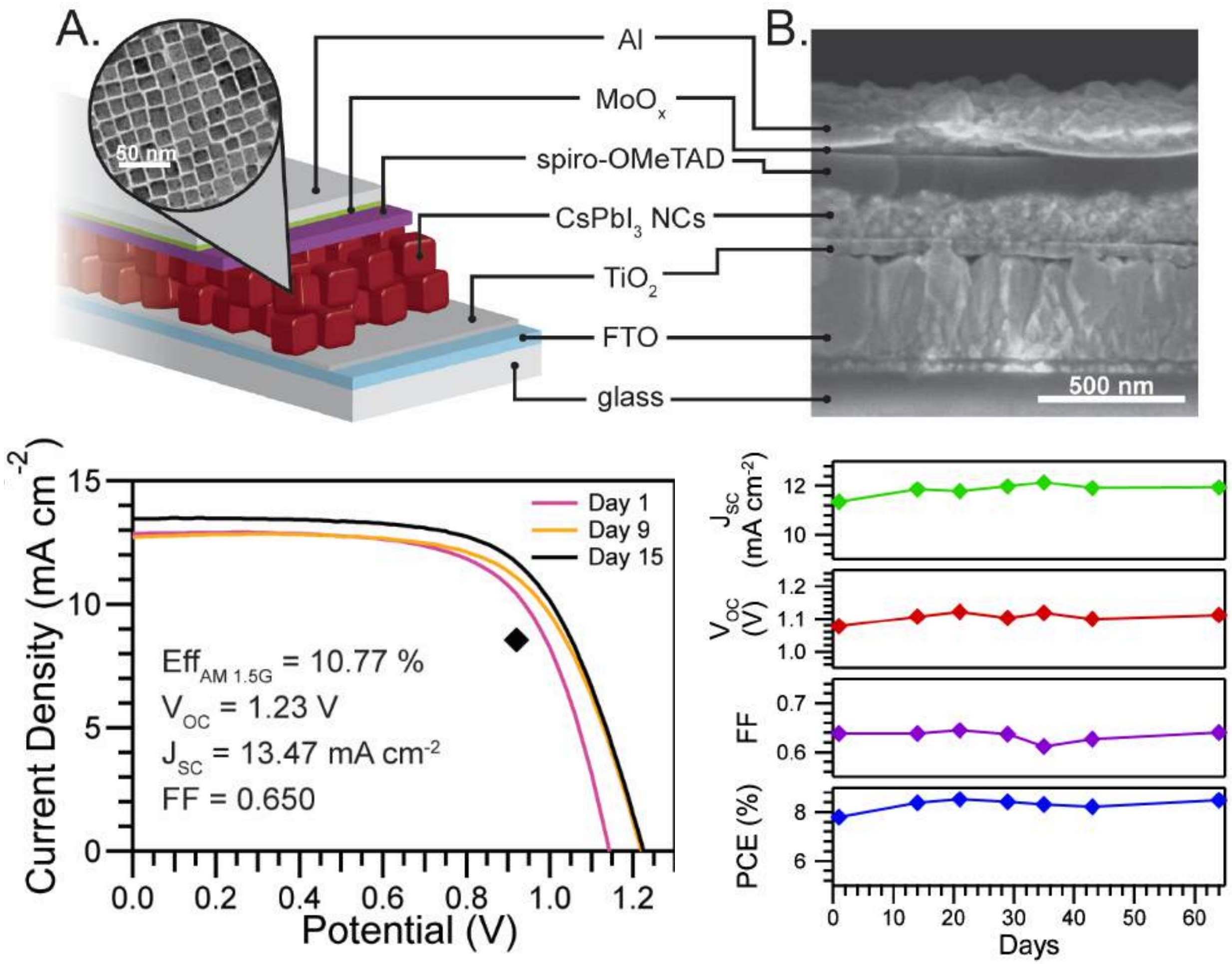
PV devices from all-Inorganic Perovskite QDs

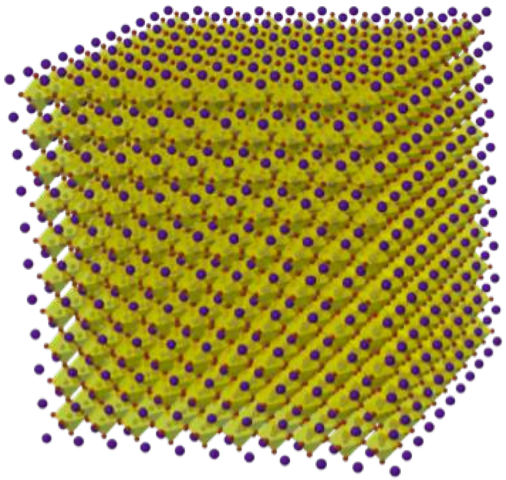


- First colloidal perovskite nanocrystal solar cell
- Layer by layer spincoating of QDs with $Pb(NO_3)_2$ treatment in MeOAc
- Highest PCE & stabilized power output of any $CsPbX_3$ solar cell
- Unprecedented *Voc*

Quantum dot–induced phase stabilization of α-$CsPbI_3$perovskite for high-efficiency photovoltaics. Swarnkar, Marshall, Sanehira, Chernomordik, Moore, Christians, Chakrabarti, and Luther. *Science*, **2016**

Perovskite NC ionic playground

AMX_3

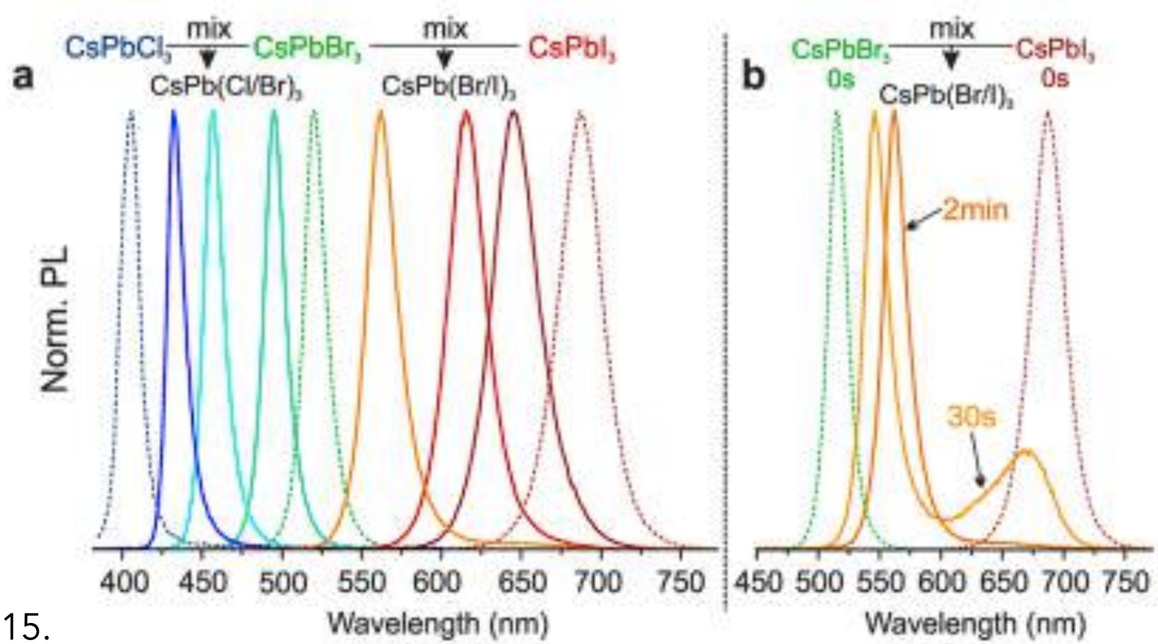


Pb^{2+}, Sn^{2+}, etc.

I^-, Br^-, Cl^-

Cs^+, MA^+, FA^+

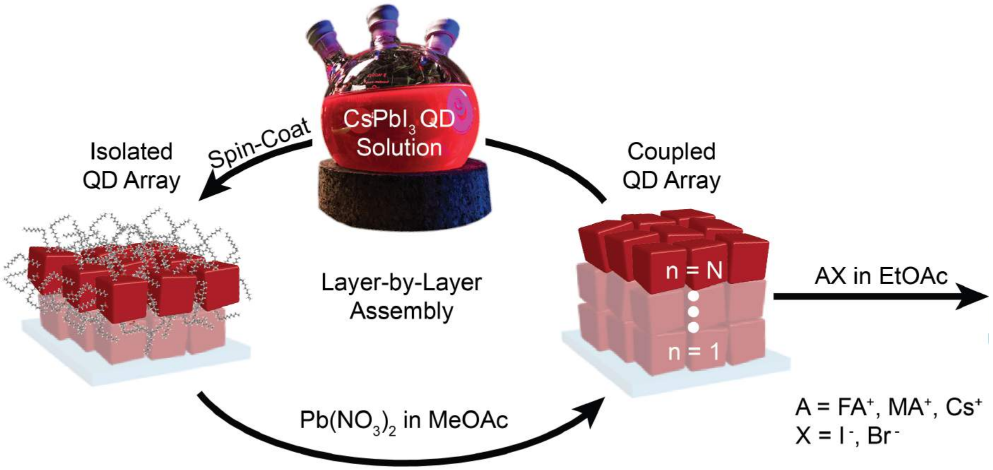
xRCOO$^-$ yNH$_3$R$^+$

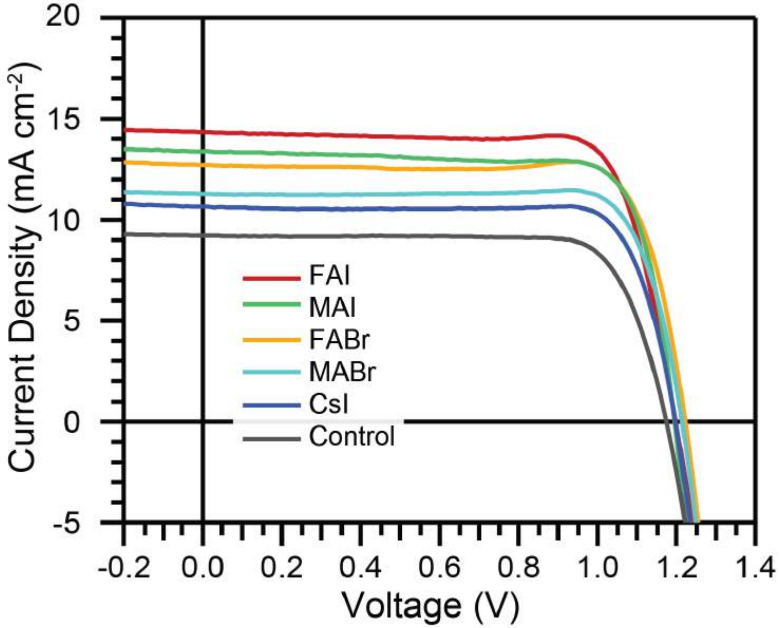


Anion exchange simply by mixing 2 types of NCs!

Nedelcu, Kovalenko et al. Nano Lett 2015.

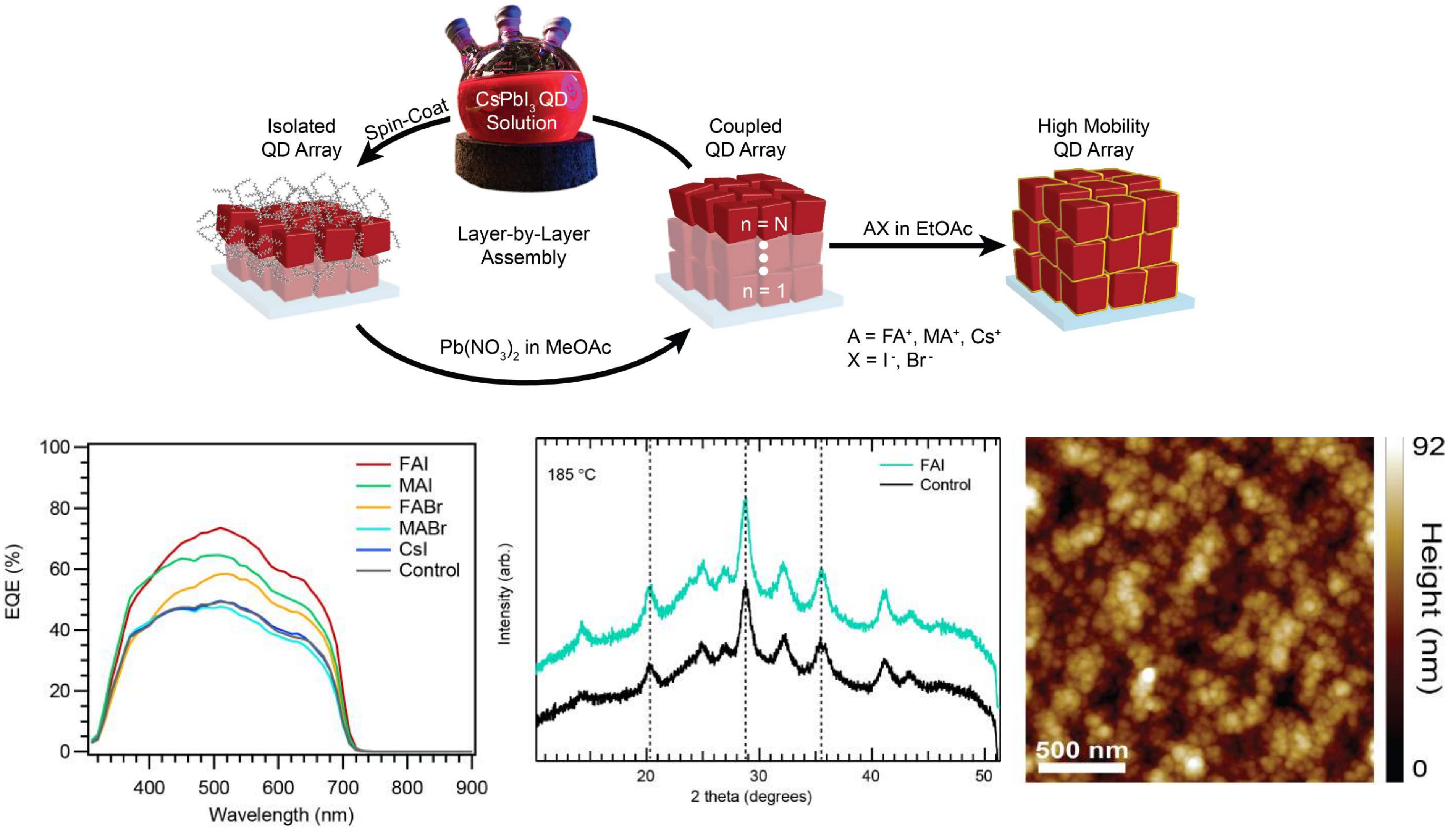
AX salt treatment on $CsPbI_3$ QD films





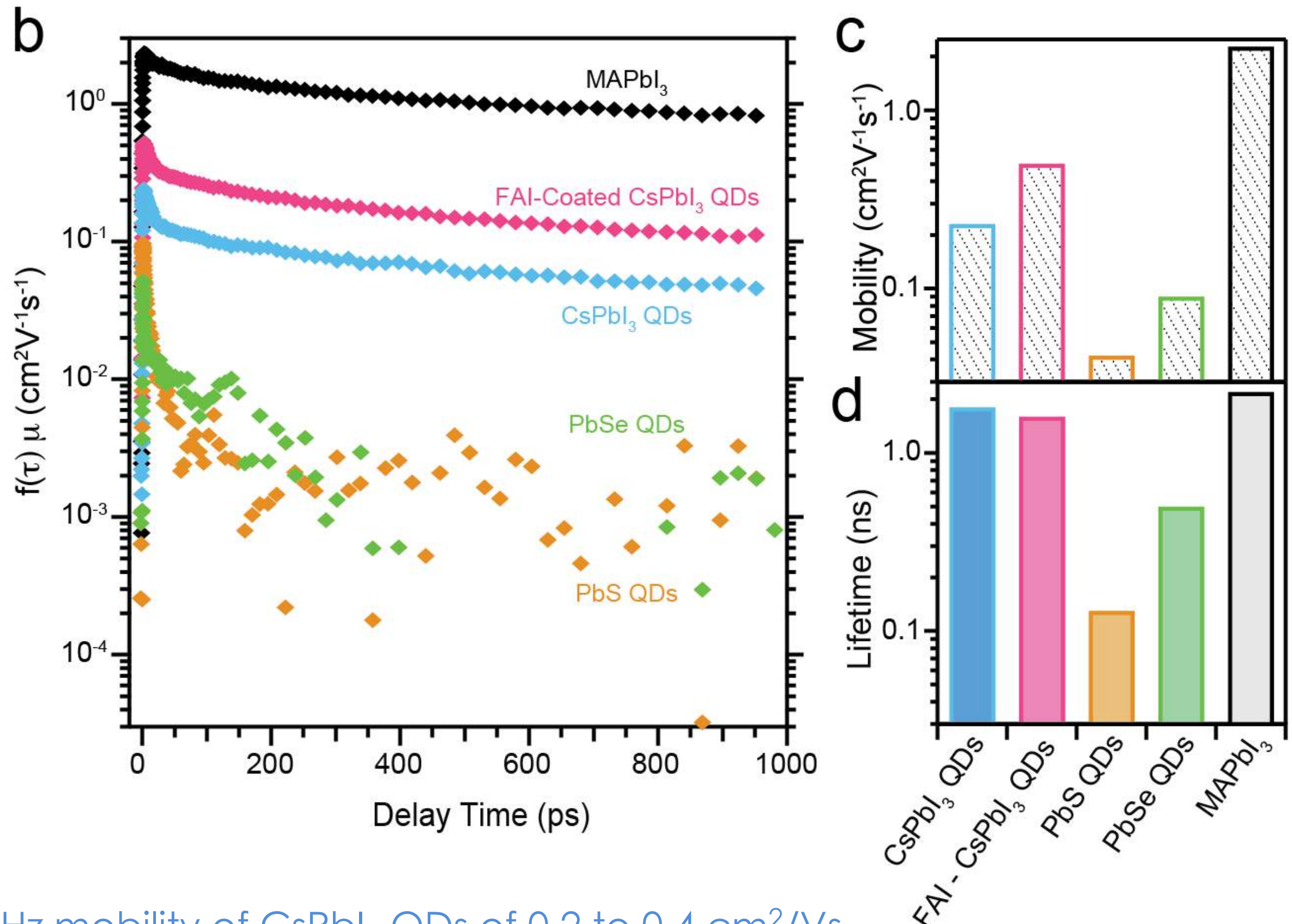
Enhanced mobility $CsPbI_3$ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells. Sanehira, Marshall, Christians, Harvey, Ciesielski, Wheeler, Schulz, Lin, Beard, and Luther. *Science Advances,* **2017**

CsPbI$_3$ QD films with tailored surface properties



Enhanced mobility CsPbI$_3$ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells. Sanehira, Marshall, Christians, Harvey, Ciesielski, Wheeler, Schulz, Lin, Beard, and Luther. *Science Advances*, **2017**

FAI treatment enhances mobility

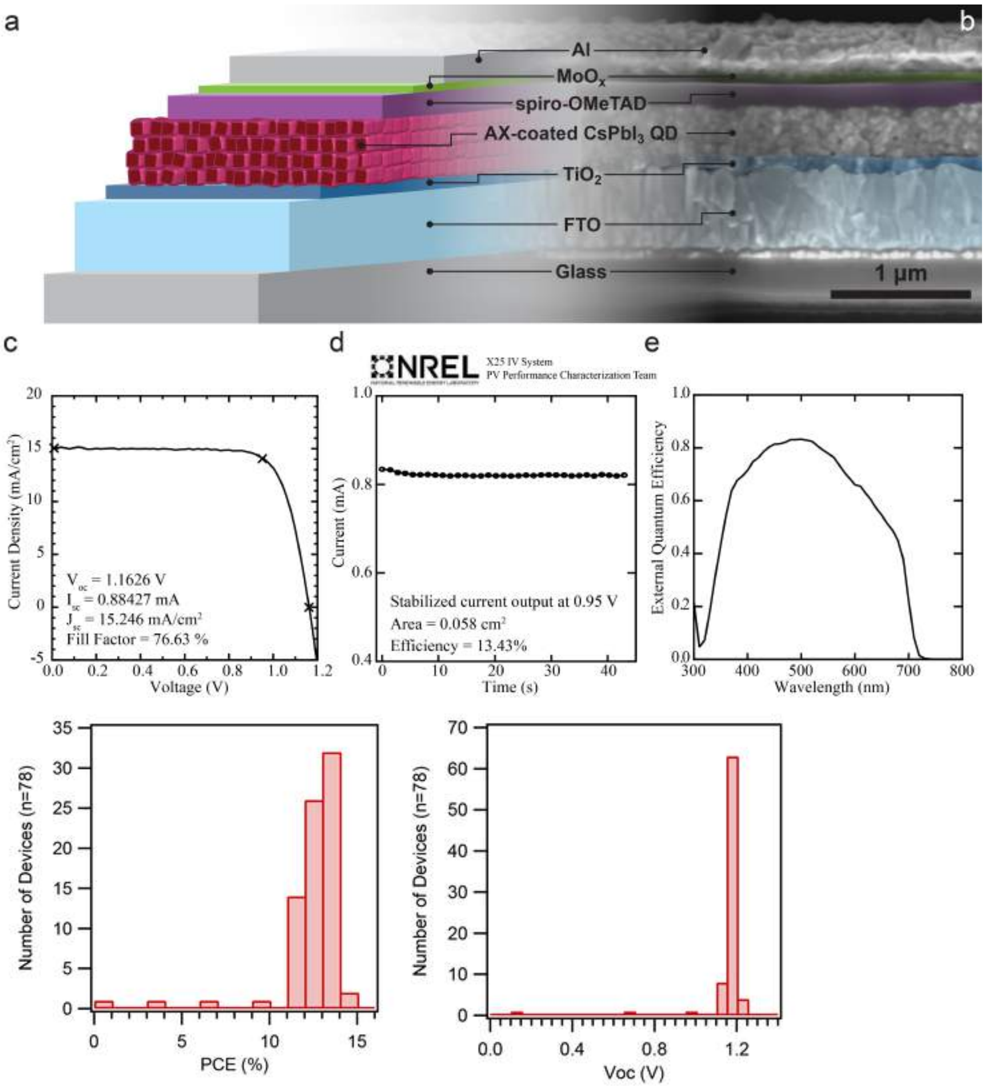


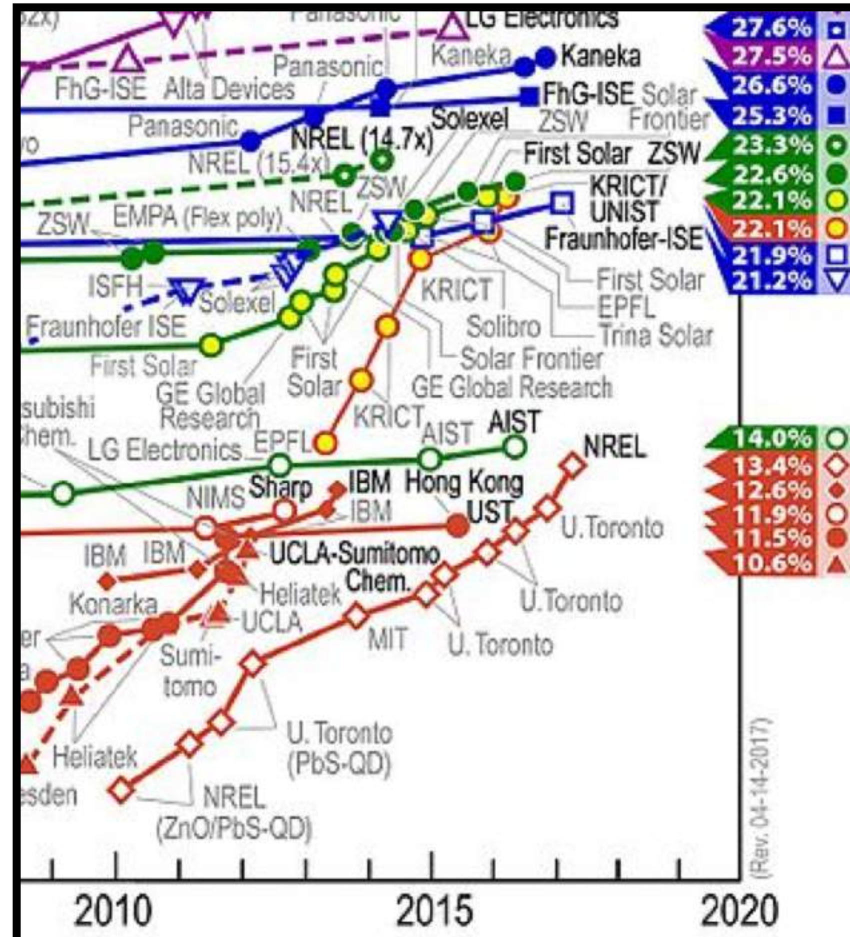
TR-THz mobility of $CsPbI_3$ QDs of 0.2 to 0.4 cm^2/Vs
2 orders of magnitude higher than SOA PbS and PbSe

Matt Beard, NREL

Enhanced mobility $CsPbI_3$ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells. Sanehira, Marshall, Christians, Harvey, Ciesielski, Wheeler, Schulz, Lin, Beard, and Luther. *Science Advances*, **2017**

FAI treatment leads to record QD solar cell





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Reasons to be interested in QD perovskites

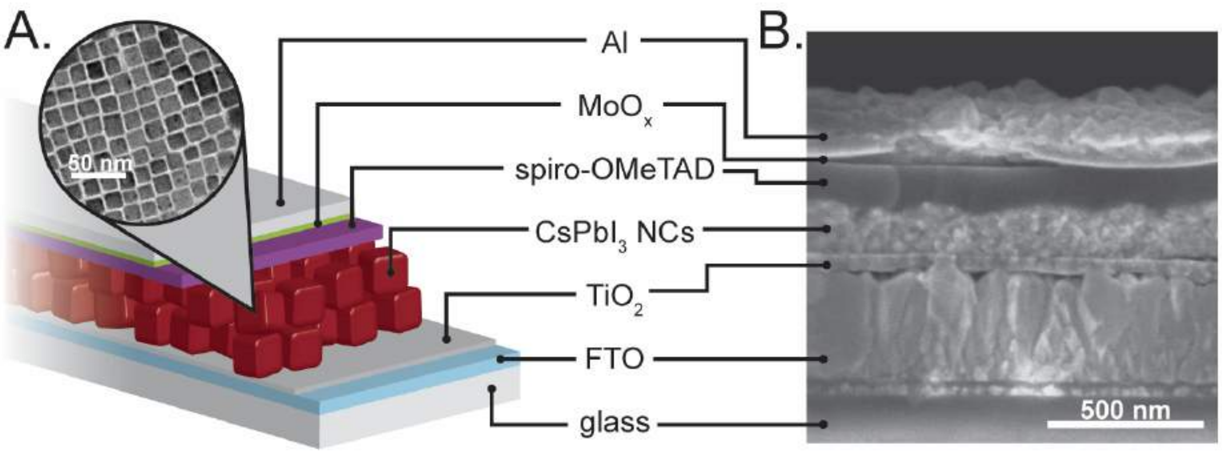
- More familiar traditional organic solvents (hexane, octane, toluene, chloroform…)
  - Ability to blend with PCBM (reduced hysteresis), other additives, polymers, etc.

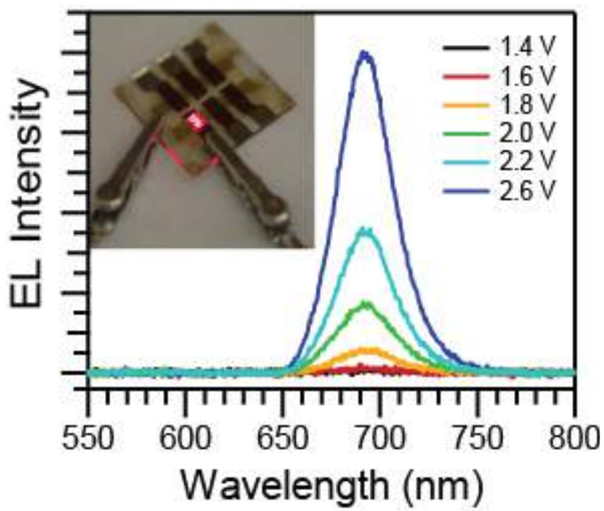
- Moves away from the complications that: large grains = better performance
  - Would be hard to implement that in fast printing module production

- No retained solvent, no need to worry about the crystallization dynamics

- Better PLQY, excellent LED potential – enhanced photon recycling

- Ideal solution processed candidate for top cell in multijunction devices





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