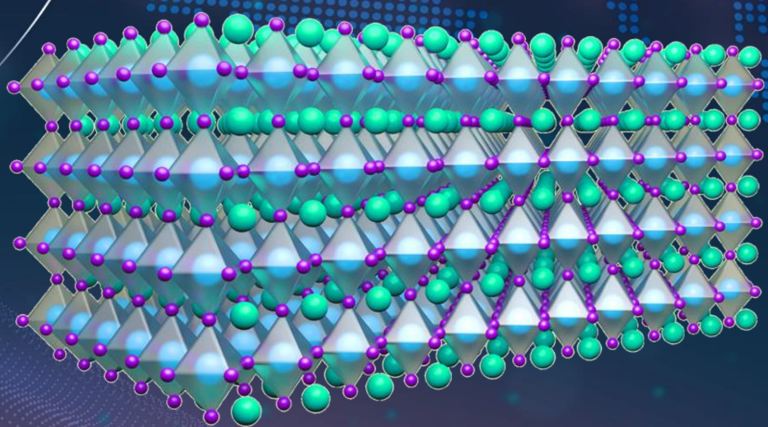
Halide Perovskite Solar Cells: Strategies for high Stability

Prof. Mónica Lira-Cantu

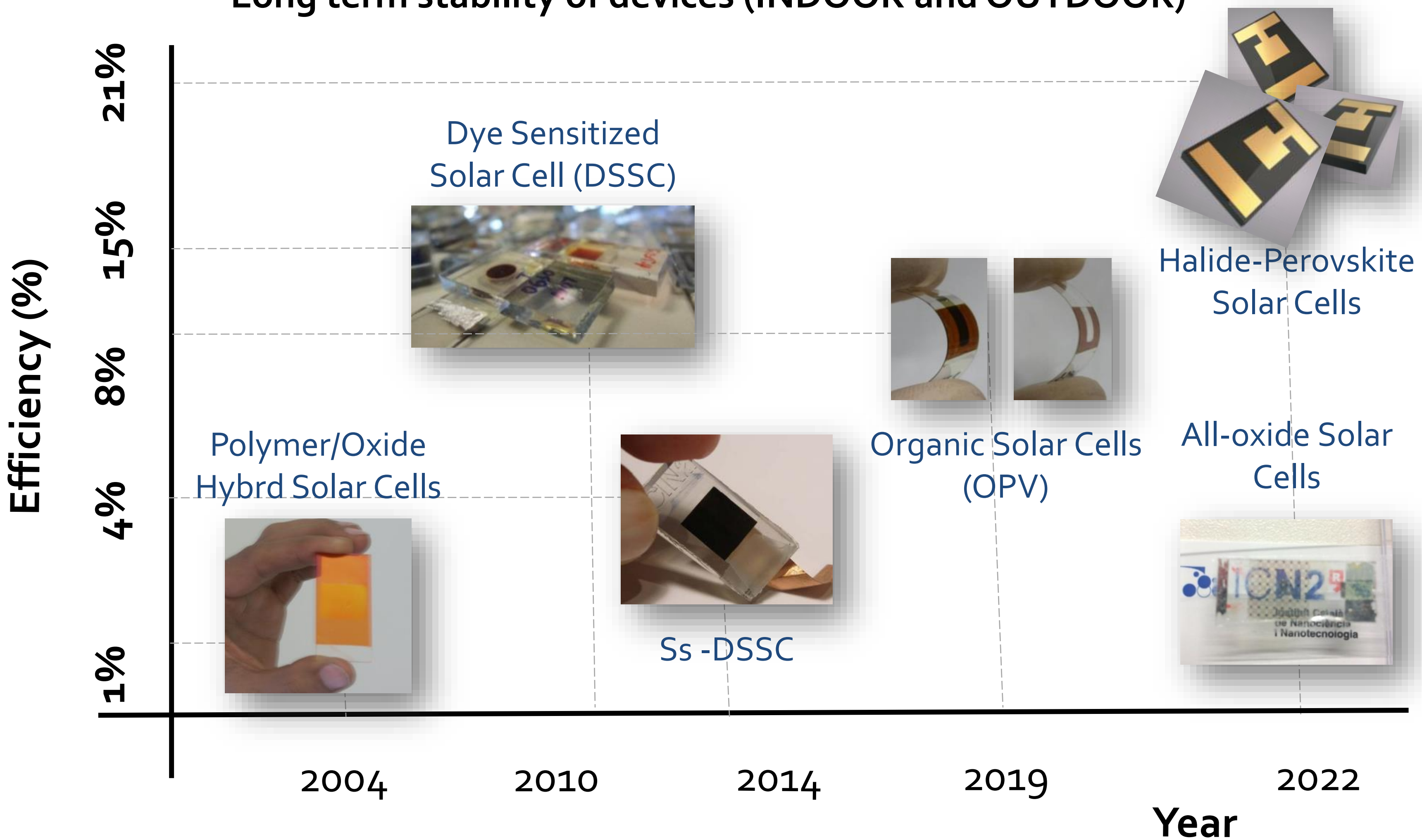
Catalan Institute of Nanoscience and Nanotechnology (ICN2)



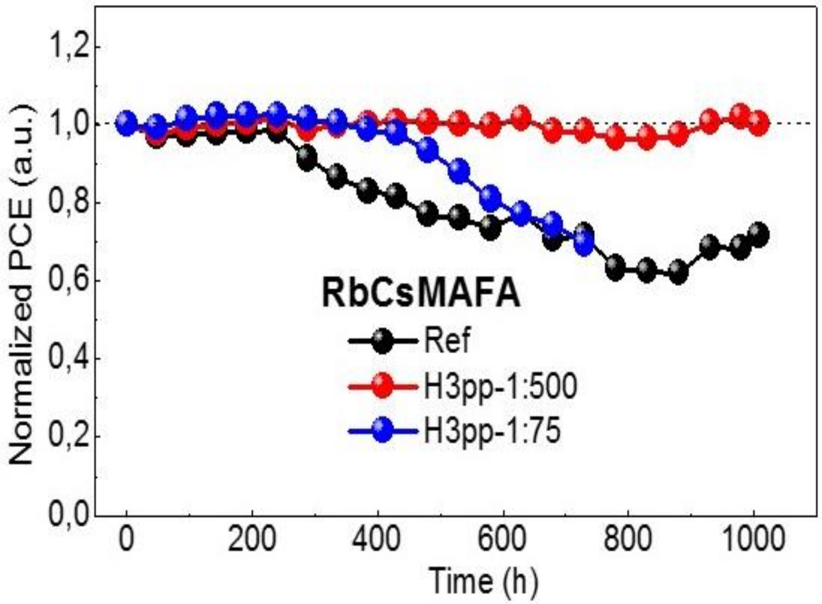
Ben-Gurion University of the Negev, September 5-7, 2022, Israel

stable Emerging Photovoltaics

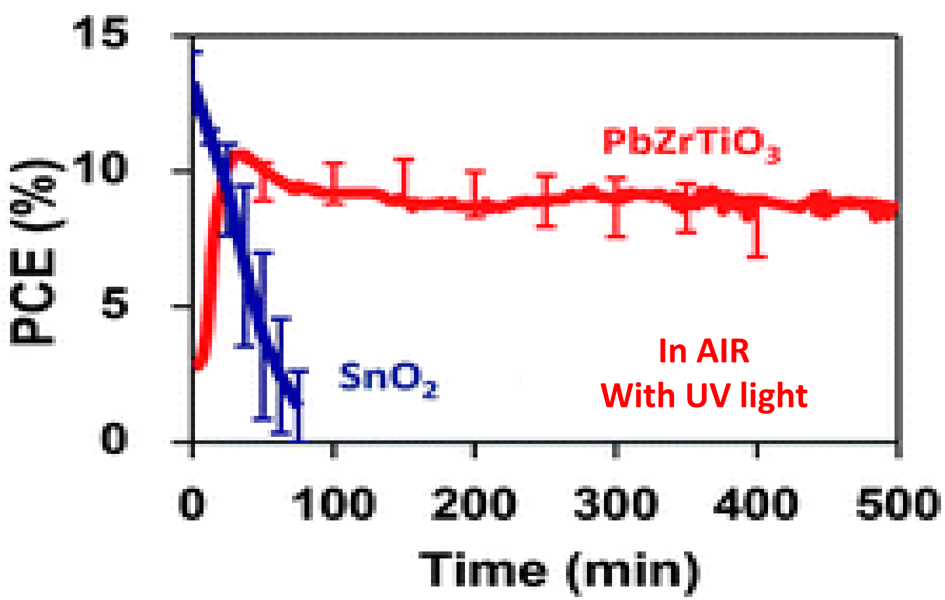
Long term stability of devices (INDOOR and OUTDOOR)



Strategies for high stability



Application of additives

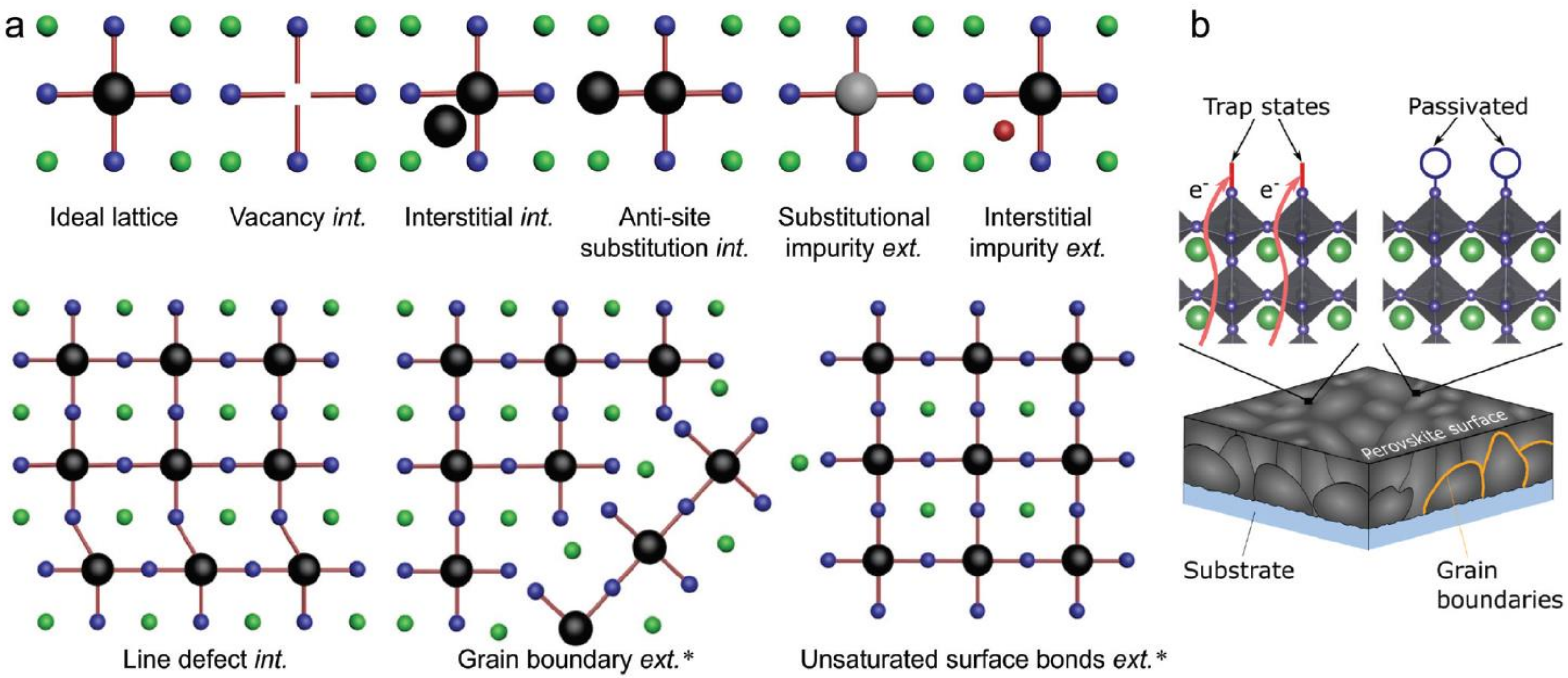


Use of Ferroelectric Oxides

Nanostructured Materials for Photovoltaic Energy

Institut Català de Nanociència i Nanotecnologia

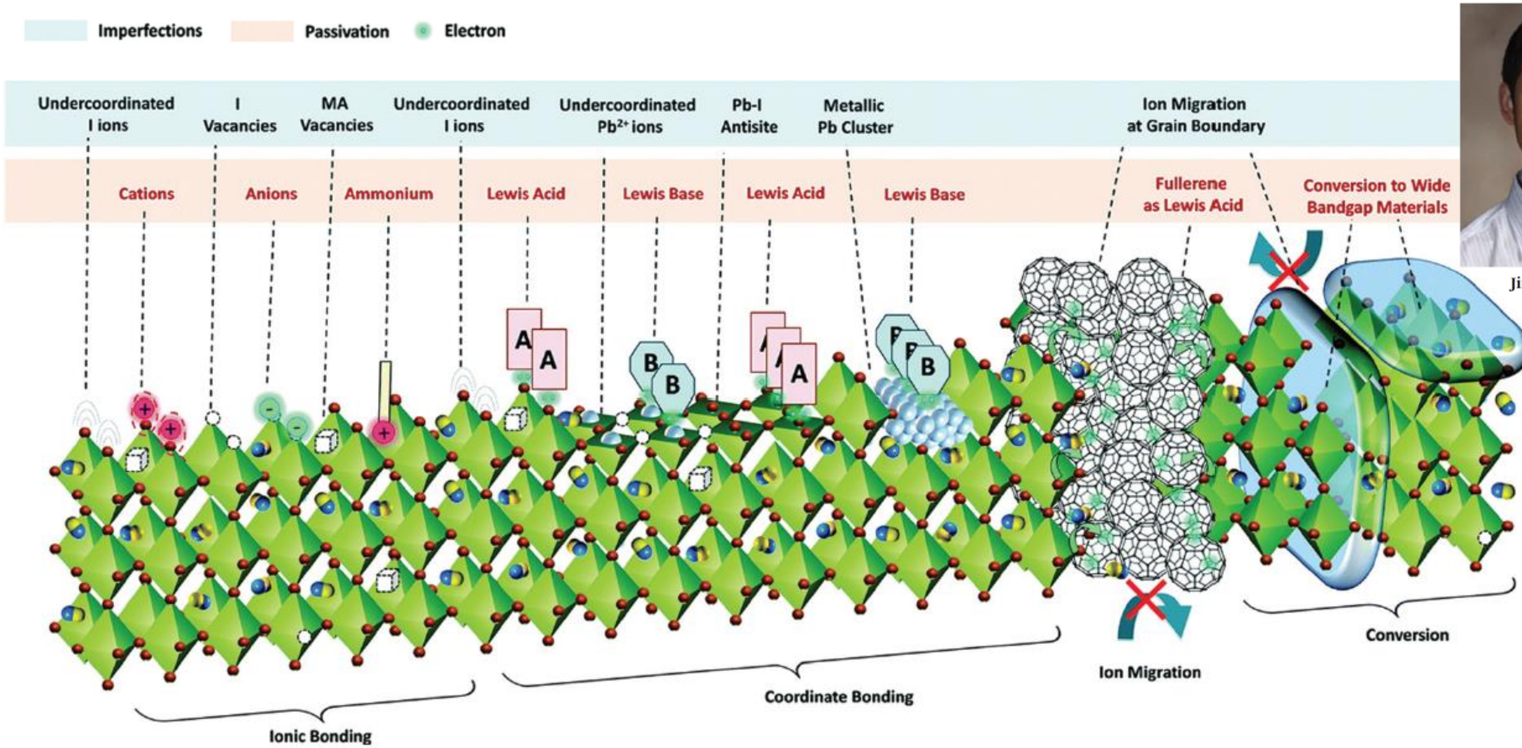
Defects in Halide Perovskites

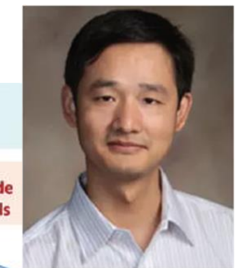


Defects are recombination centers and induce device degradation under non-equilibrium conditions.

Mater. Horiz., 2020, 7, 397--410

Defect passivation and suppressing ion migration





Jinsong Huang

Defects

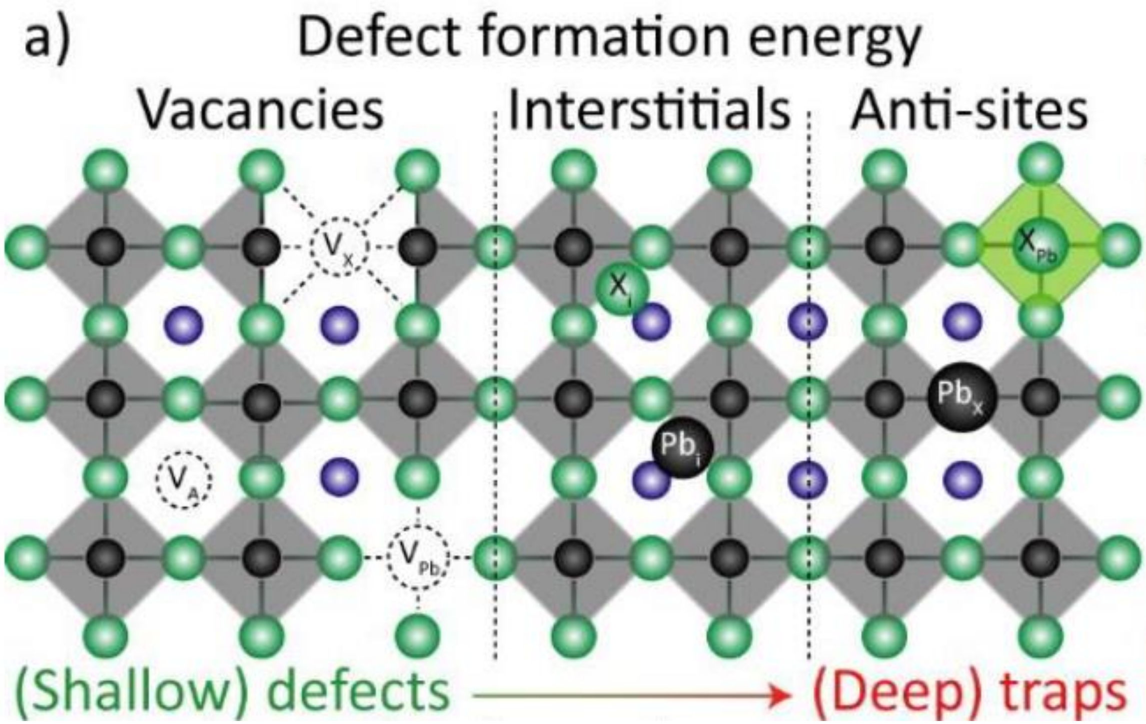
→ Deep level traps → Major non-radiative recombination centers (affect Voc and Efficiency)

→ Shallow level charge traps → Ion migration

B. Chen, et al., Chem. Soc. Rev., 2019, 48, 3842--3867

Defect Formation

ionic-electronic propoerties



non-radiative recombination

Increasing formation energy (or decreasing probability of occurrence)

Point defects

Deep level traps:

- undercoordinated halides ions
- undercoordinated Pb_{2+} ions,
- lead clusters
- Pb–I antisite defects (PbI_3) – from process fabrication

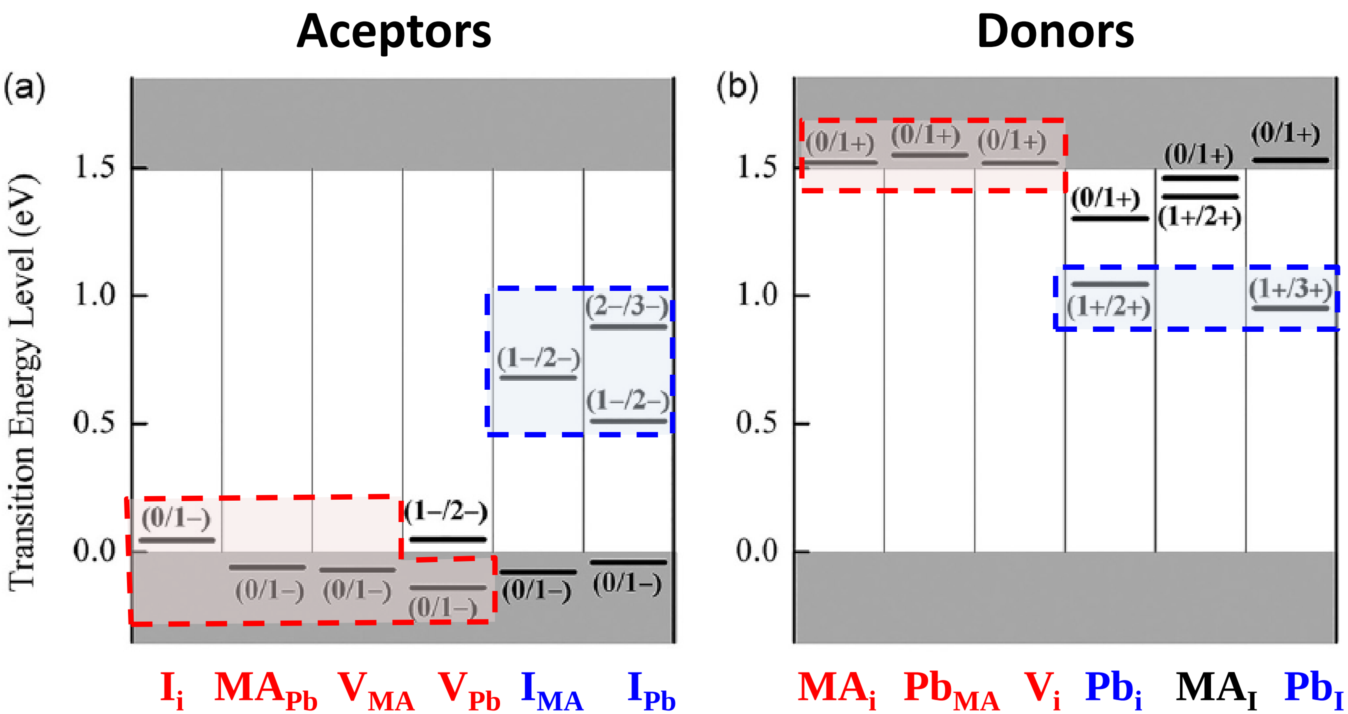
Shallow level traps:

- I or MA vacancies in the bulk of the material

Example: 12 Point defects in the methylammonium lead triiodide ($MAPbI_3$):
Three types of vacancies (V_{MA}, V_{Pb}, V_I)
Three types of interstitial sites (MA_i, Pb_i, I_i)
Two types of cation substitutions (MA_{Pb}, Pb_{MA})
Four types of antisite substitutions (MA_I, Pb_I, I_{MA}, I_{Pb})

B. Chen, et al., Chem. Soc. Rev., 2019, 48, 3842--3867

Point defects

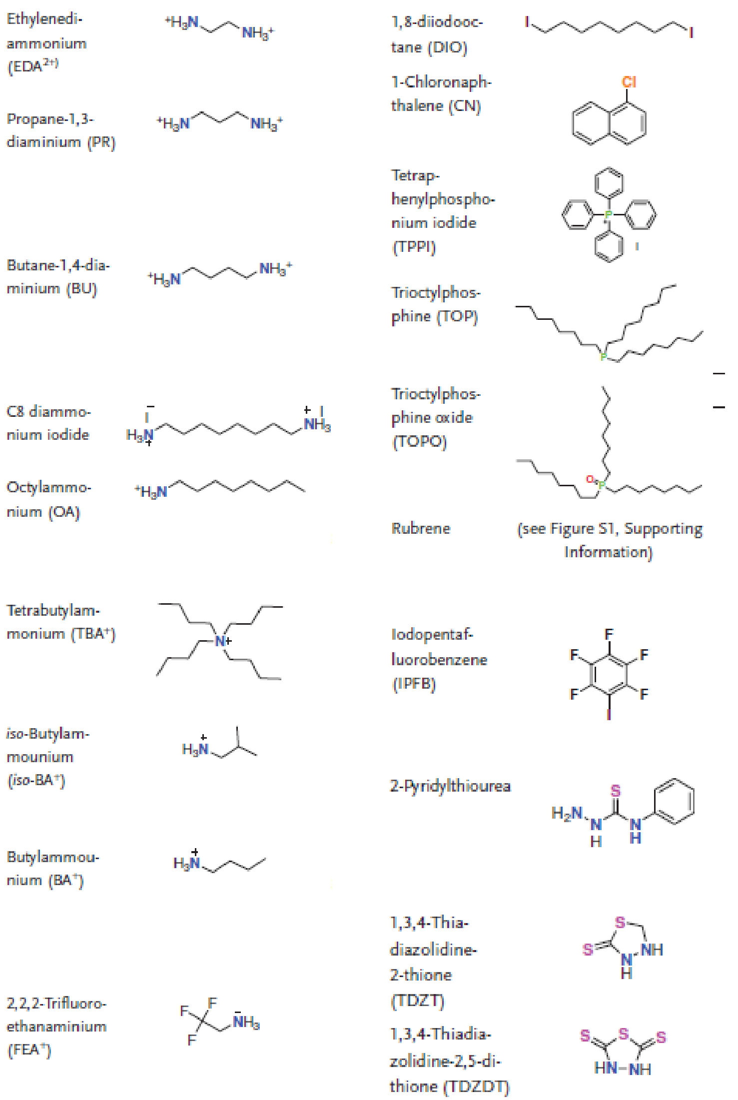


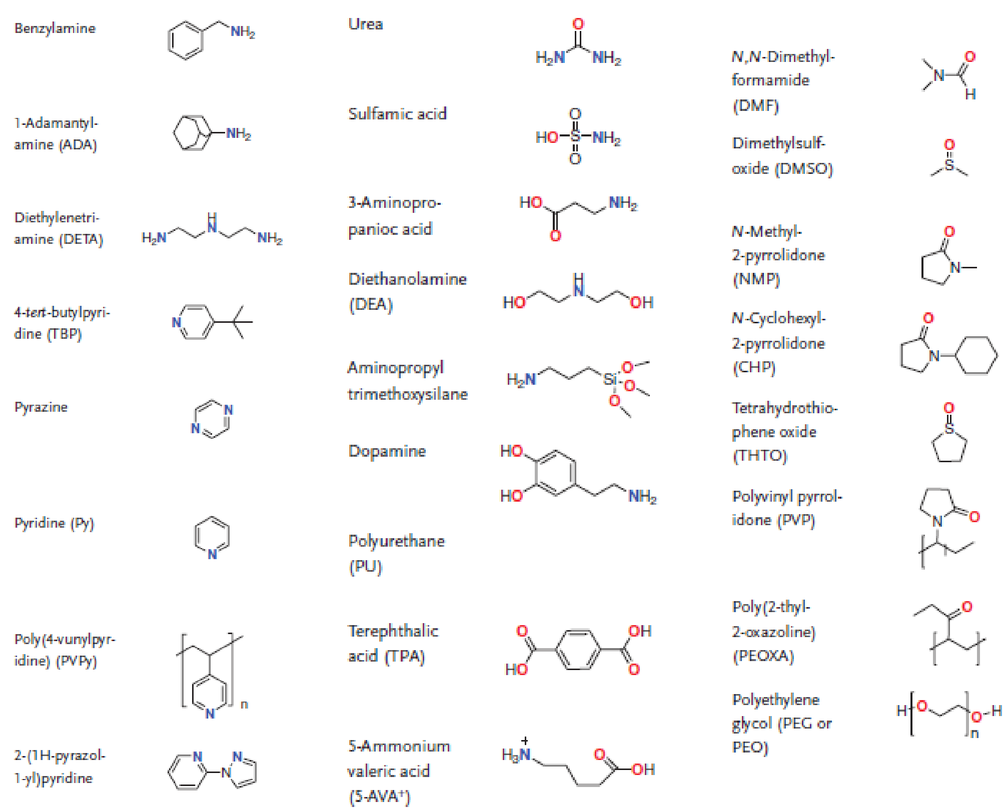
Shallow Point Defects - Low formation Energy

Deep Point Defects - High formation Energy

B. Chen, et al., Chem. Soc. Rev., 2019, 48, 3842--3867

Additive engineering to passivate defects

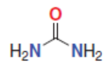




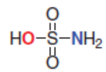
H. Zhang, et al., Perovskite photovoltaics: The significant role of Ligands in Film Formation, Passivation and Stability. Adv. Mater. ***2019****, 31, 1805702*

Additive engineering in PSC

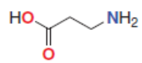
Urea



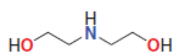
Sulfamic acid



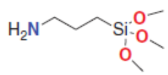
3-Aminopro-
panioc acid



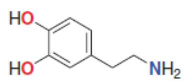
Diethanolamine
(DEA)



Aminopropyl
trimethoxysilane

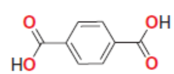


Dopamine

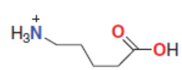


Polyurethane
(PU)

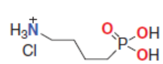
Terephthalic
acid (TPA)



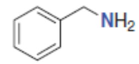
5-Ammonium
valeric acid
(5-AVA⁺)



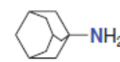
==4-phospho-
nobutan-
1-aminium==



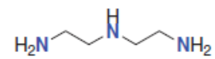
Benzylamine



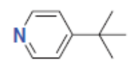
1-Adamantyl-
amine (ADA)



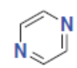
Diethylenetri-
amine (DETA)



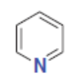
4-*tert*-butylpyri-
dine (TBP)



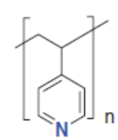
Pyrazine



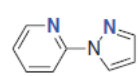
Pyridine (Py)



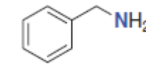
Poly(4-vunylpyr-
idine) (PVPy)



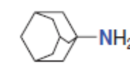
2-(1H-pyrazol-
1-yl)pyridine



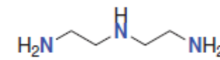
Benzylamine



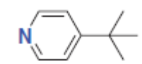
1-Adamantyl-
amine (ADA)



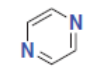
Diethylenetri-
amine (DETA)



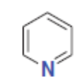
4-*tert*-butylpyri-
dine (TBP)



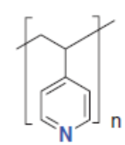
Pyrazine



Pyridine (Py)

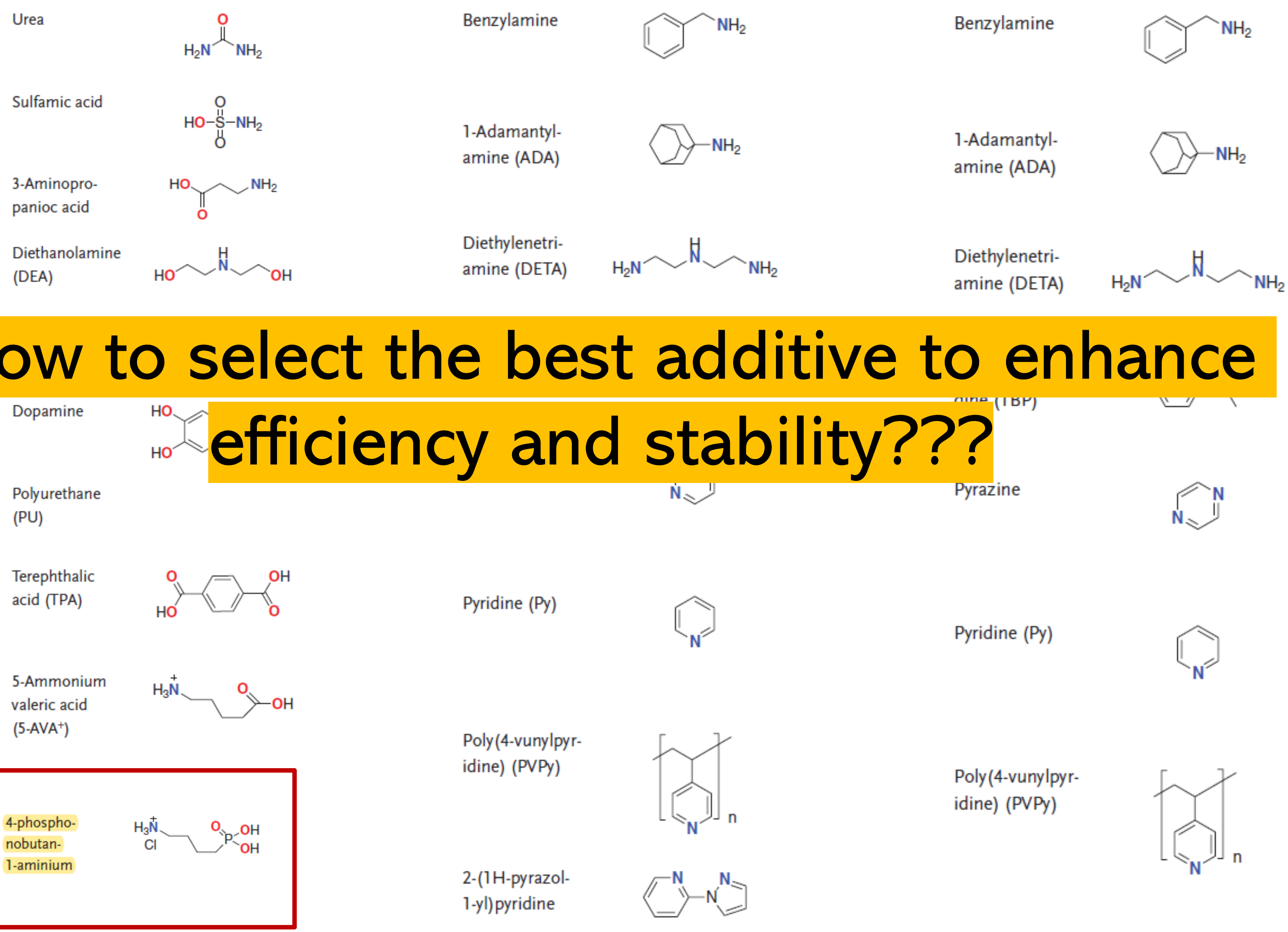


Poly(4-vunylpyr-
idine) (PVPy)



H. Zhang, et al., Adv. Mater. **2019**, *31*, 1805702

Additive engineering in PSC

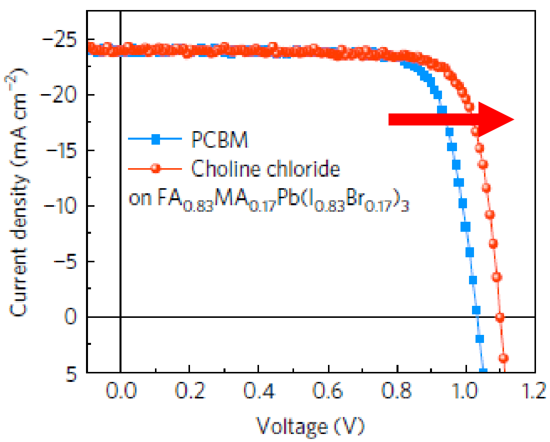


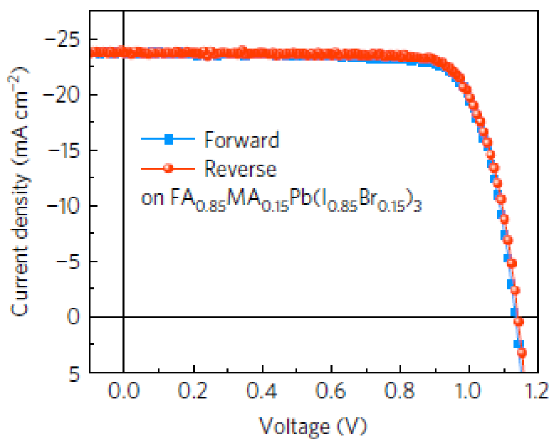
How to select the best additive to enhance efficiency and stability???

H. Zhang, *et al.*, *Adv. Mater.* **2019**, *31*, 1805702

Passivation with zwitterions

(positively and negatively charged functional groups)





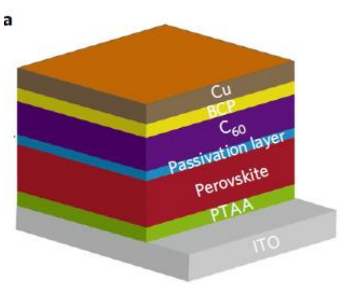
Deep defect passivation

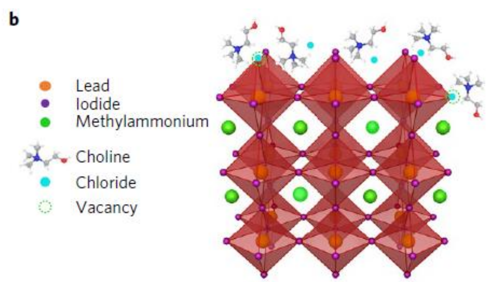
anionic Pb-I and cationic Pb clusters

Non-radiative recombination:

Voltage Increase

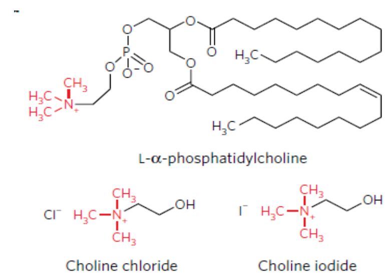
Efficiency Increase

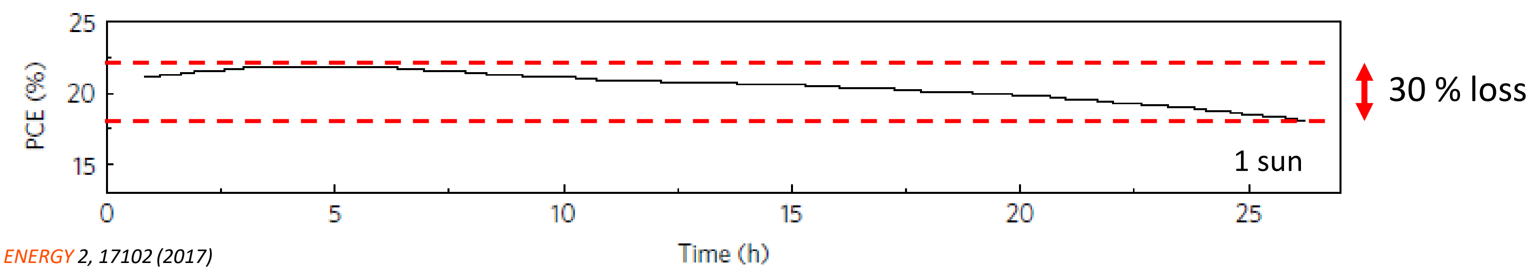




positive charged ammonium group ($-N(CH_3)_3^+$)

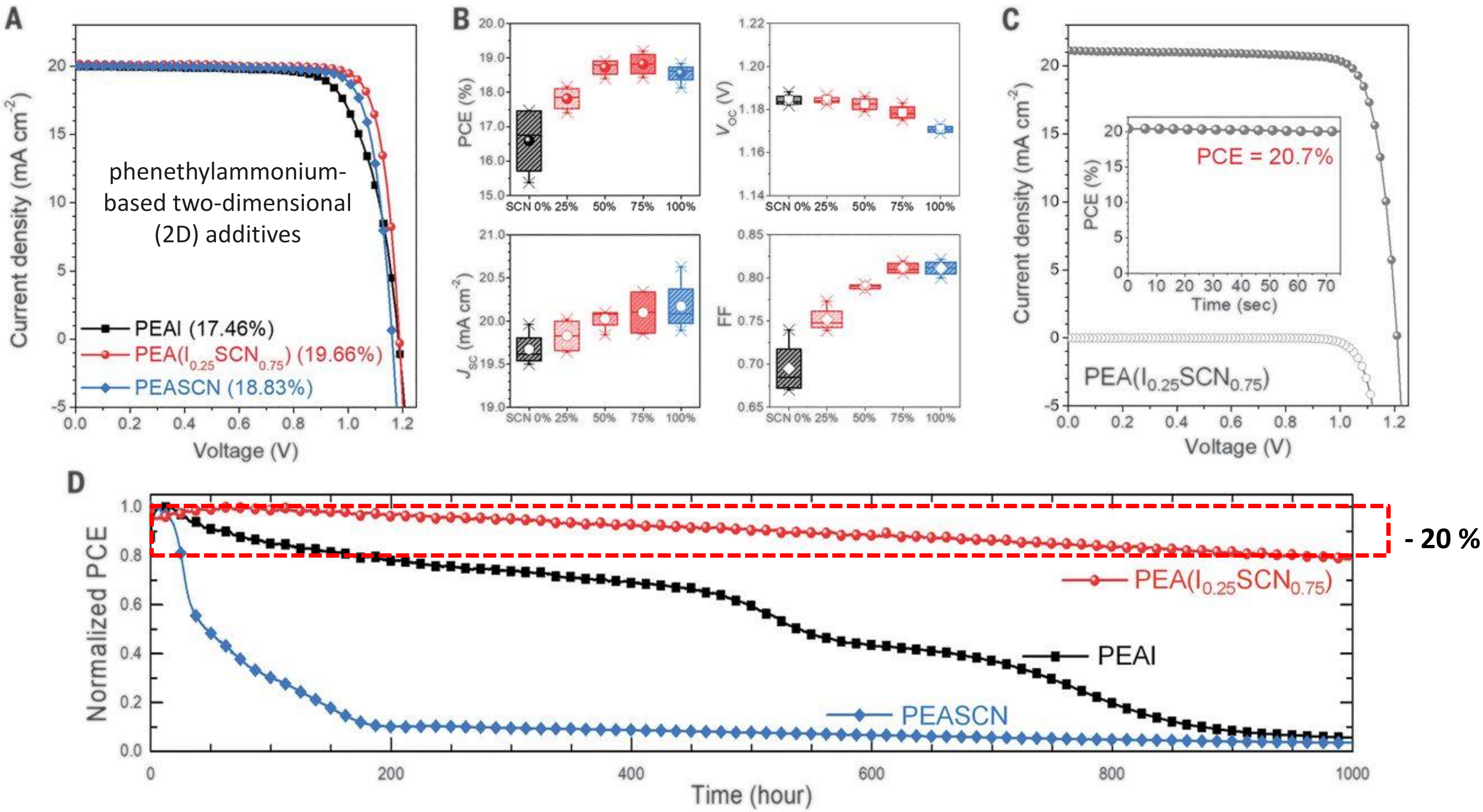
negative charged phosphate ($-PO_4^-$)





J. Huang, et al., *NATURE ENERGY* 2, 17102 (2017)

Efficient, stable silicon tandem cells enabled by anion-engineered wide-bandgap perovskites



Byungha Shin, et al., Science 10 Apr 2020: Vol. 368, Issue 6487, pp. 155-160, DOI: 10.1126/science.aba3433

NMPE Nanostructured Materials for Photovoltaic Energy

ICN2 Institut Català de Nanociència i Nanotecnologia — Excelencia Severo Ochoa

ISOS Protocols for PSCs

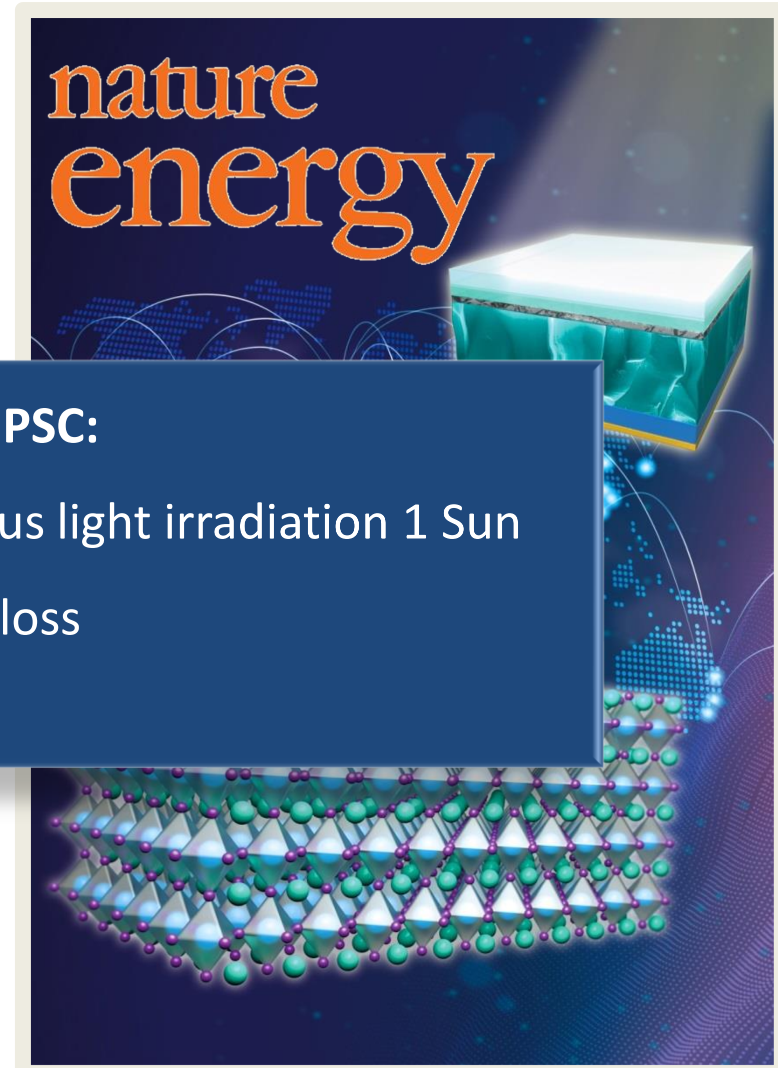
nature energy | CONSENSUS STATEMENT
https://doi.org/10.1038/s41560-019-0529-5
OPEN

Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures

Mark V. Khenkin[1,2], Eugene A. Katz…
Christoph Brabec[7,8], Francesca Brune…
Rongrong Cheacharoen[12], Yi-Bing Ch…
Konrad Domanski[16], Michał Dusza…
Yulia Galagan[22], Diego Di Girolam…
Harald Hoppe[27], Jeff Kettle[28], Hans K…
Yueh-Lin Loo[11,33], Joseph M. Luther…
Muriel Matheron[15], Michael McGe…
Ana Flavia Nogueira[38], Çağla Odab…
Francesca De Rossi[9,41], Michael Salib…
Samuel D. Stranks[46], Wolfgang Tress[25], Pavel A. Troshin[47,48], Vida Turkovic[35], Sjoerd Veenstra[22],
Iris Visoly-Fisher[1,3], Aron Walsh[49,50], Trystan Watson[41], Haibing Xie[51], Ramazan Yıldırım[39],
Shaik Mohammed Zakeeruddin[24], Kai Zhu[6] and Monica Lira-Cantu[51]*

Stable PSC:

- > 1000 h under continuous light irradiation 1 Sun
- Less than 10% Efficiency loss



Khenkin, M.V., Katz, E.A., M.Lira-Cantu, et al. Nat Energy **5,** *35–49 (2020).*

Shallow Iodine Defects Accelerate the Degradation

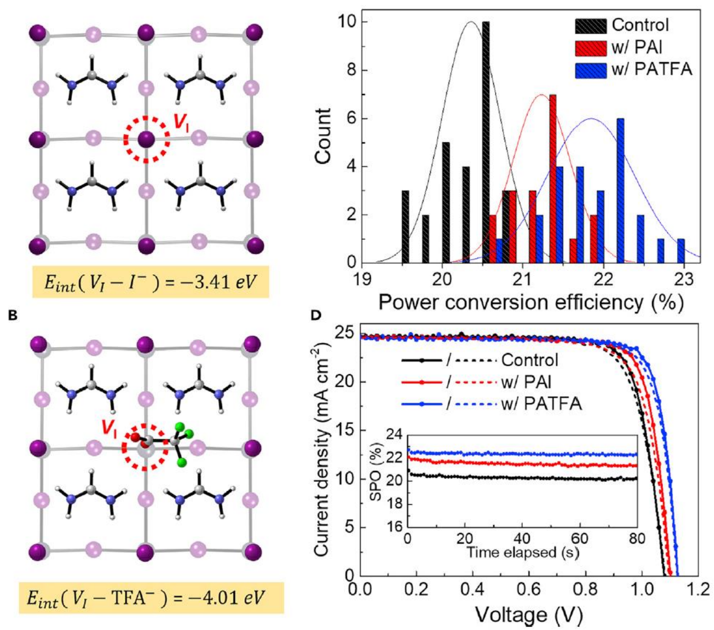
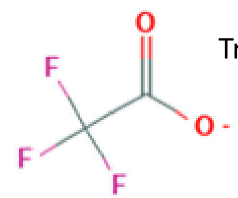


Table 1. Distribution of the Device Photovoltaic Parameters

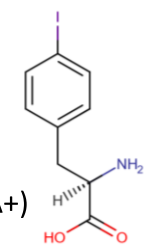
	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)	SPO (%)
Control	1.073 ± 0.012 (1.079)	24.45 ± 0.12 (24.67)	0.774 ± 0.012 (0.787)	20.32 ± 0.35 (20.95)	20.3
w/PAI	1.103 ± 0.009 (1.101)	24.49 ± 0.13 (24.62)	0.786 ± 0.014 (0.806)	21.23 ± 0.36 (21.86)	21.4
w/ PATFA	1.120 ± 0.013 (1.127)	24.51 ± 0.10 (24.61)	0.796 ± 0.019 (0.829)	21.84 ± 0.35 (22.98)	22.4

Average photovoltaic parameters of the control and treated devices. Parenthesis indicate parameters measured from champion devices for each condition. Abbreviations are V_{OC}, open-circuit voltage; J_{SC}, short-circuit current density; FF, fill factor; PCE, power conversion efficiency; SPO, stabilized power output.

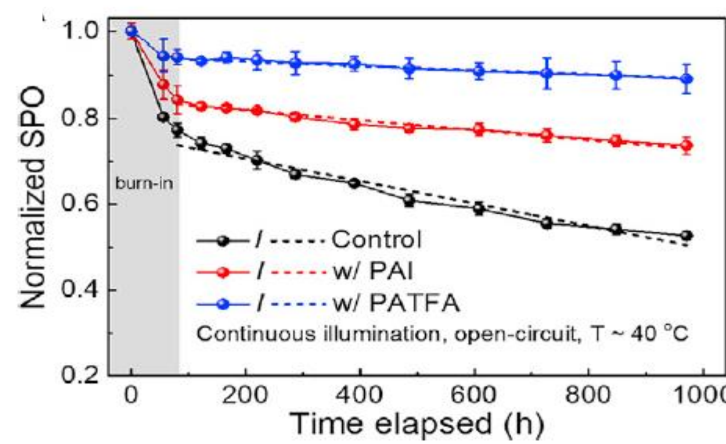
Replacement of I with an alternative anion



Trifluoroacetate (TFA-)



Phenylalanine (PA+)



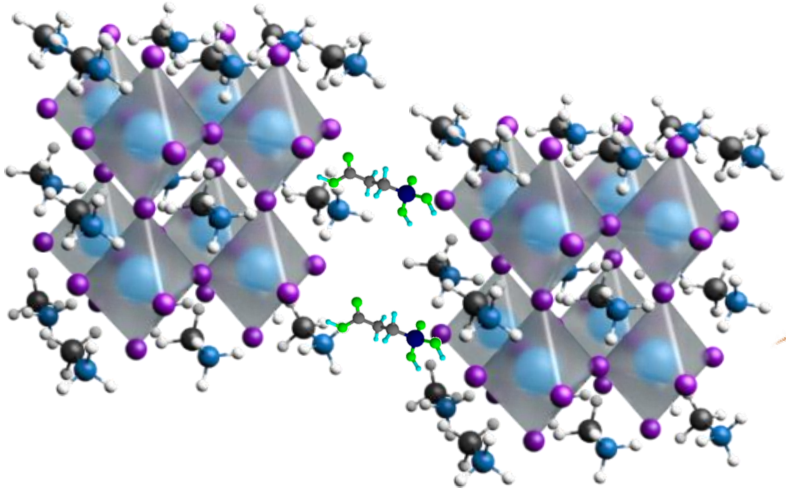
6 % loss

15 % loss

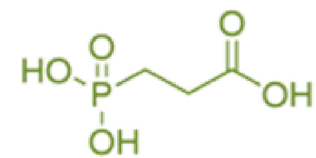
30 % loss

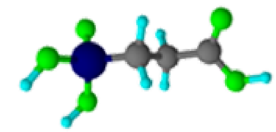
Yang Yang, et al., Joule 4, 1–17, November 18, 2020

3-Phosphonopropionic Acid

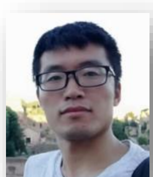


Shallow Defect Passivation

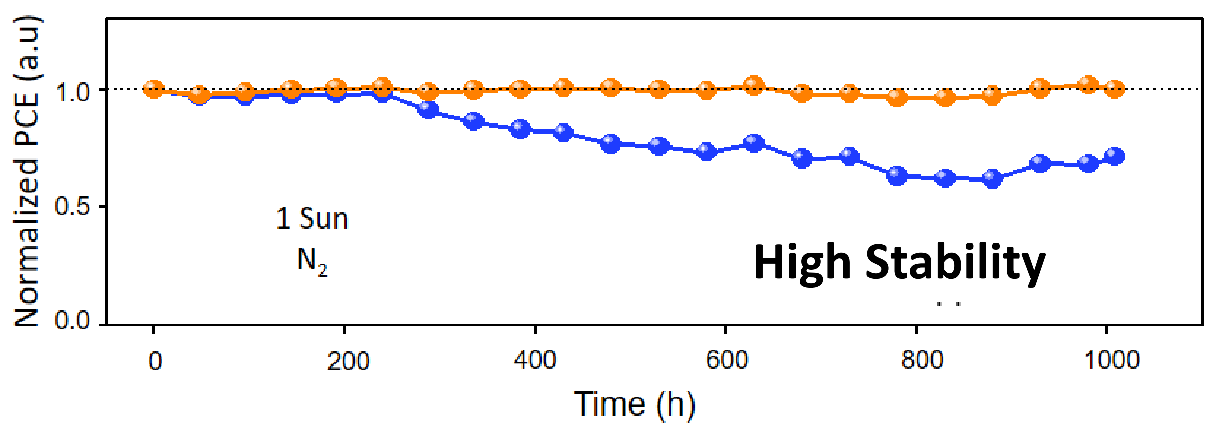




Haibing Xia



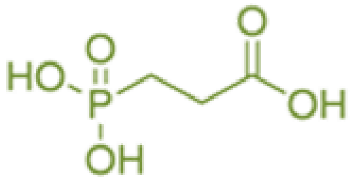
Zaiwei Wang



H. Xie, et al, Accepted Joule, 2021

M. Lira-Cantu. Nature Energy ***2****, 17115 (2017)*

Additive Selection: Why phosophonate/Carboxillate



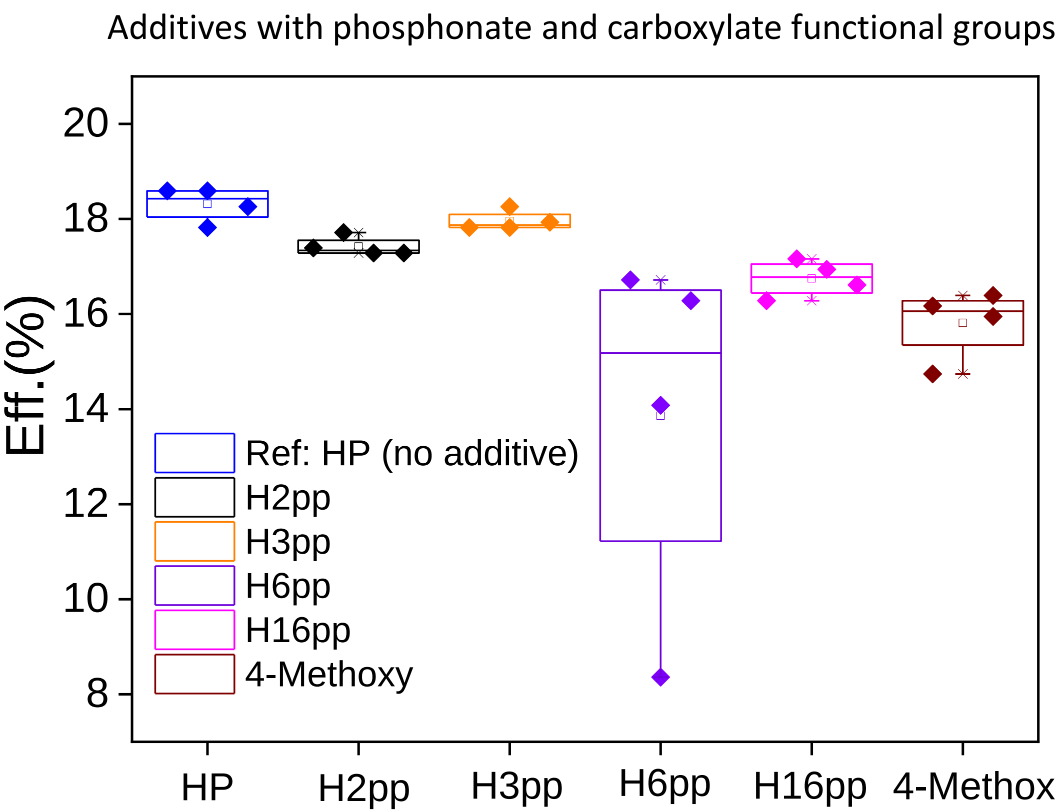
3-Phosphonopropionic Acid

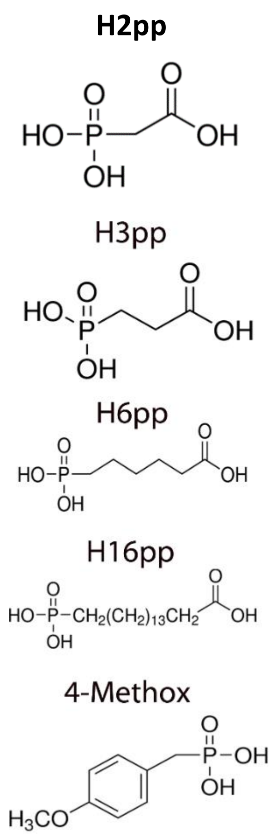
–PO(OH)$_2$ and –COOH anchoring agents in DSSCs:

– PO(OH)$_2$ was employed to increase the surface binding stability
- Carboxylic acids were employed to increase the electron injection efficiency.

Bonding through the phosphonic acid group → more stable than carboxylic or amine groups but …charge injection rates can be affected (by the tetrahedral phosphorous center and loss of conjugation)

Effect of type of molecule

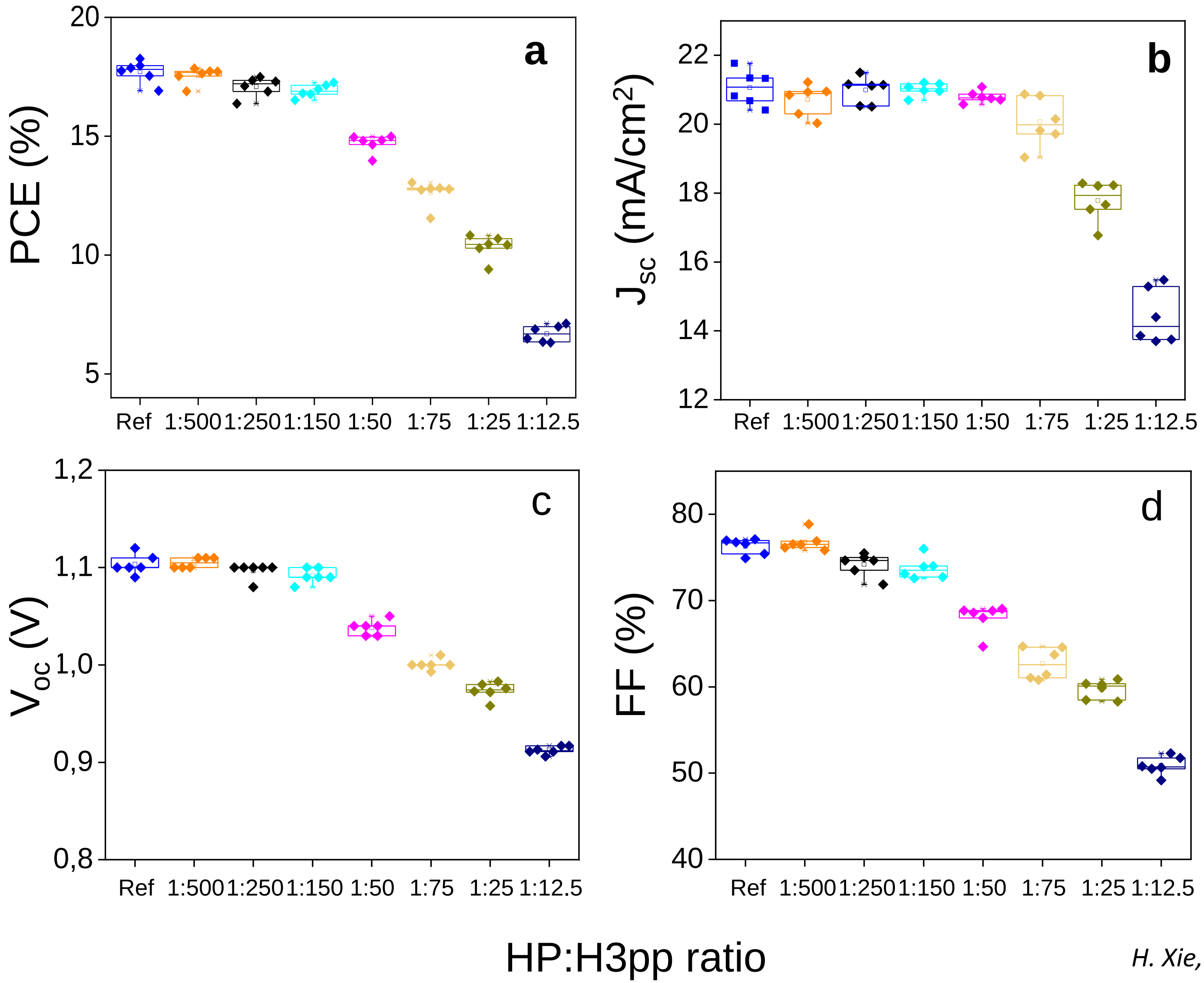




Increasing chain lenght →

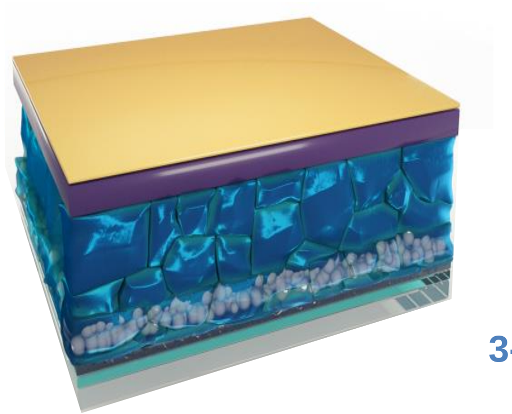
H. Xie, et al., M. Lira-Cantu, Joule, 5, 1-21, *2021*

Effect of molecule H3pp concentration

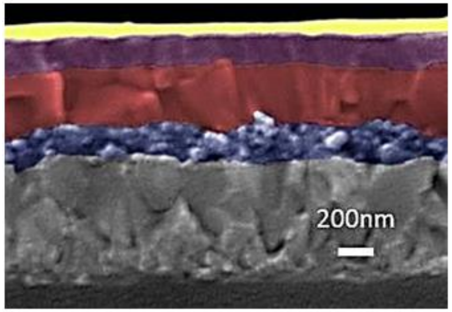


H. Xie, Joule, In revision, 2021

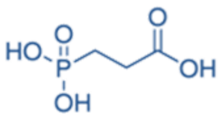
Champion Solar Cell: 21.1 % eff



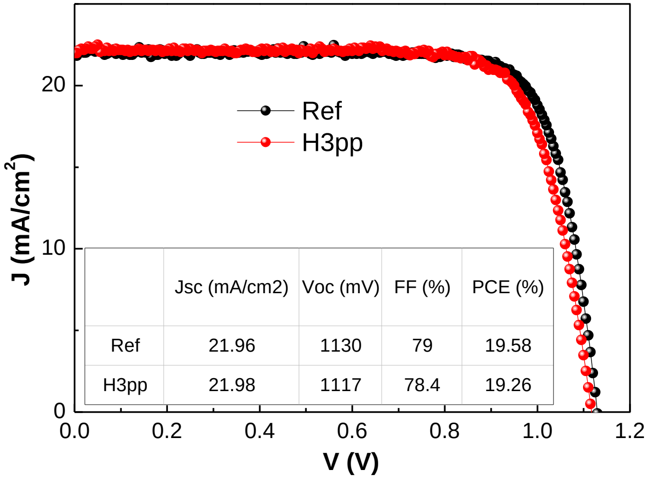
Au
Spiro-OMeTAD
Perovskite:H3pp
m-TiO_2/Perovskite
c-TiO_2/FTO



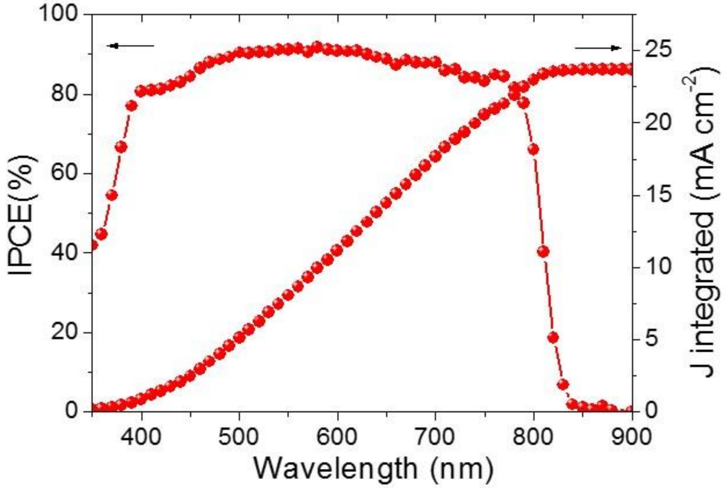
3-Phosphonopropionic Acid



$Rb_{0.05}Cs_{0.05}MA_{0.15}FA_{0.75}Pb_{1.05}(I_{0.95}Br_{0.05})_3$
(RbCsMAFA),



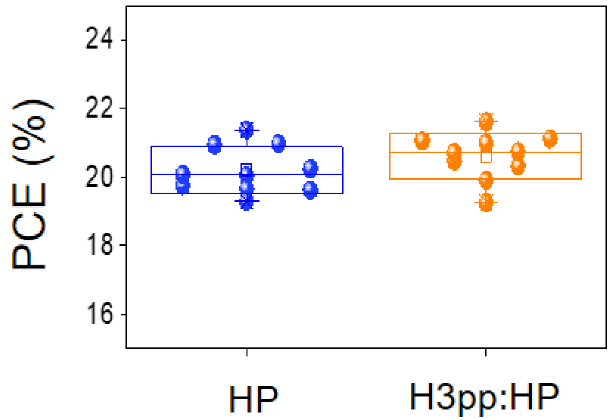
	Jsc (mA/cm2)	Voc (mV)	FF (%)	PCE (%)
Ref	21.96	1130	79	19.58
H3pp	21.98	1117	78.4	19.26

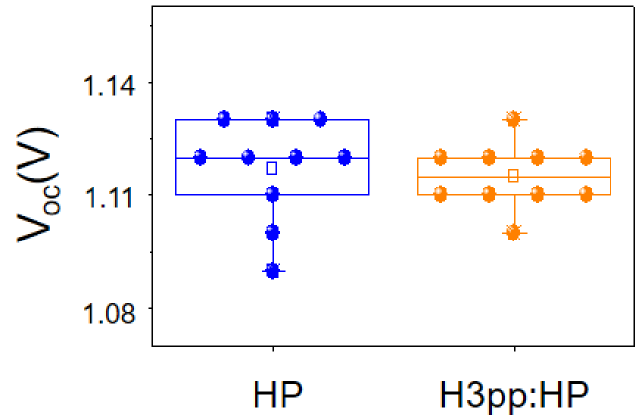


H. Xie, et al., M. Lira-Cantu, Joule, 5, 1-21, 2021

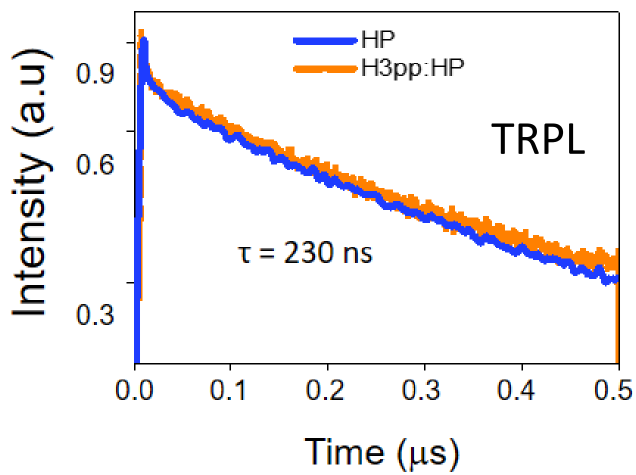
*M. Lira-Cantu. Nature Energy **2**, 17115 (2017)*

Recombination behaviour

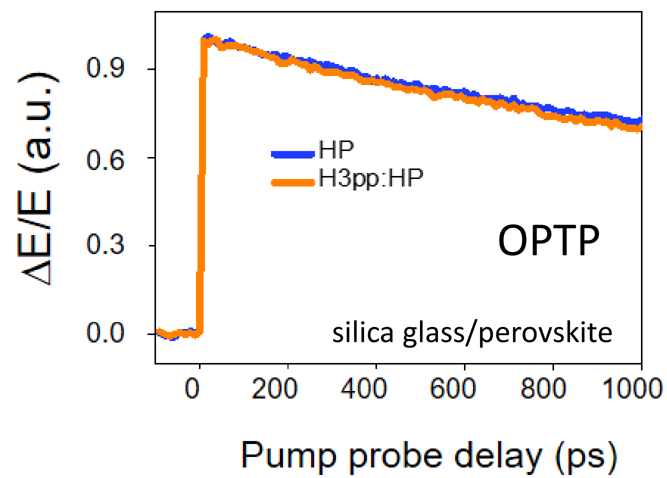




Optical-pump THz-probe (OPTP)



Charge carrier life time (non-radiative recombination)



Light-induced mobile charges

H. Xie, et al, Accepted Joule, 2021

*M. Lira-Cantu. Nature Energy **2**, 17115 (2017)*

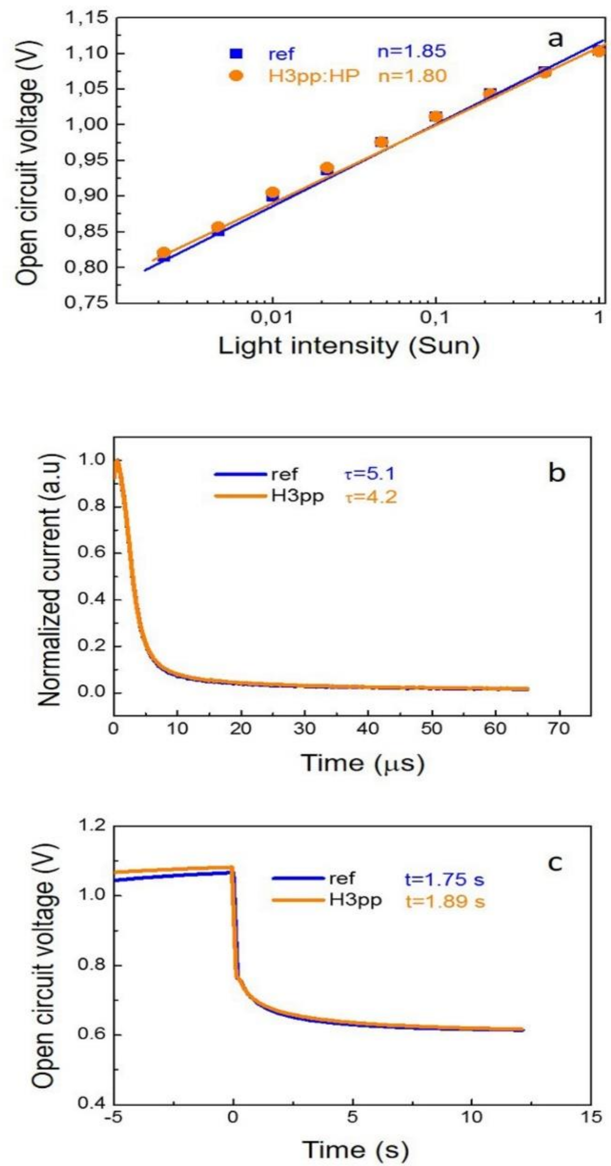
FTO/c-TiO_2/m-TiO_2/HP/spiro-OMeTAD/Au

Effect of additive

(a) Light intensity dependent V_{oc}

(b) Transient photocurrent

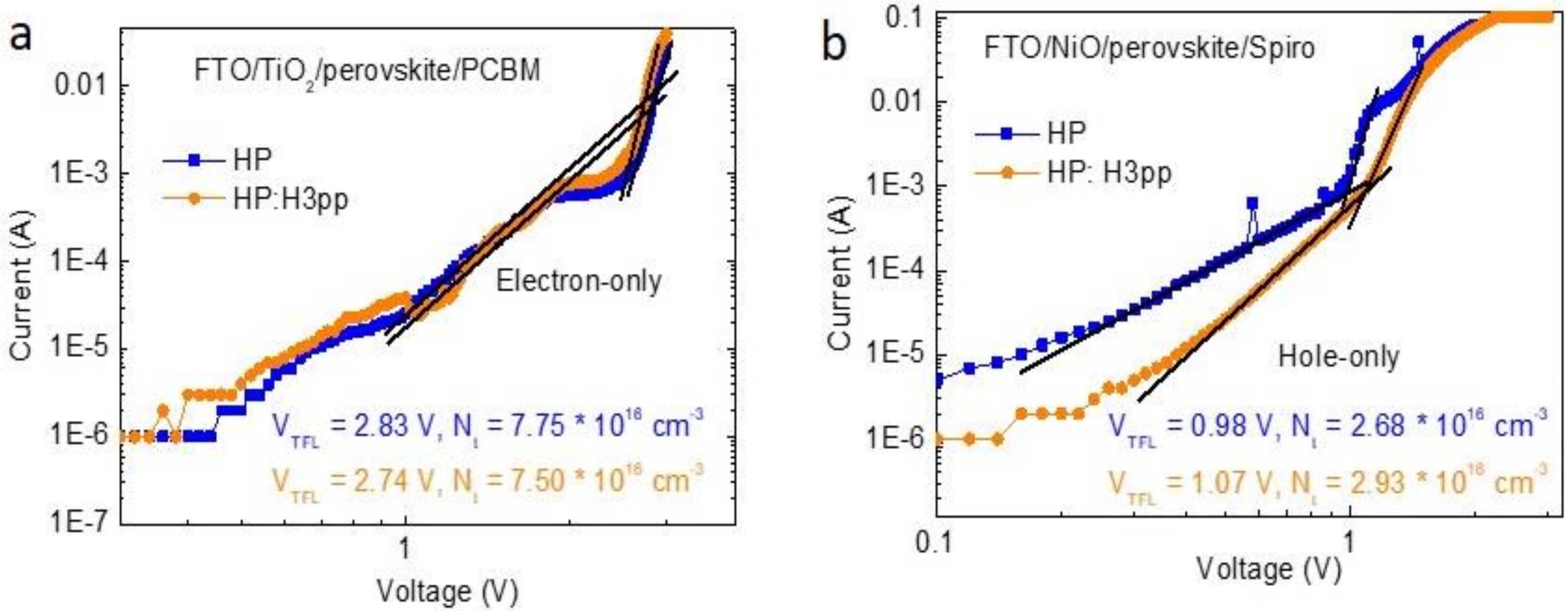
(c) Open circuit voltage decay.



- Ideality factors with n_{id} = 1.80 and 1.85
- Very similar p-n junction quality and trap-assisted recombination
- Similar carrier transport and recombination properties

Haibing, X. et al., Joule, 2021

Effect of additive: Trap density

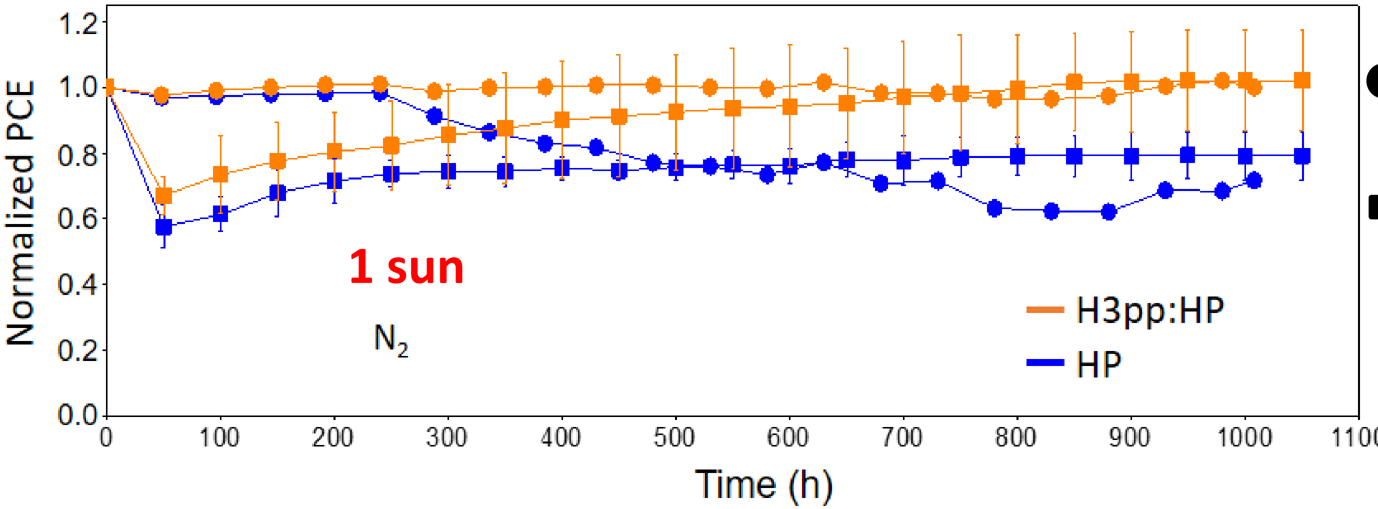


Space-charge-limited current (SCLC) for electron-only (a) and hole-only (b) devices with and without the addition of the H3pp additive.

→ Passivation of deep defects is negligible.

Haibing, X. et al., Joule, 2021

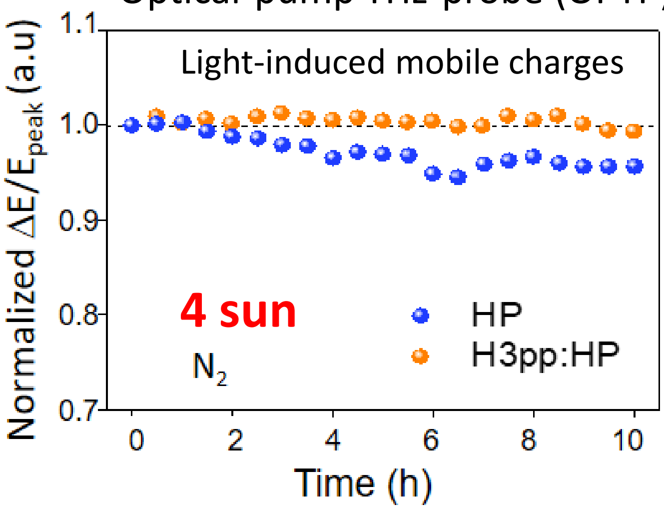
Operational stability



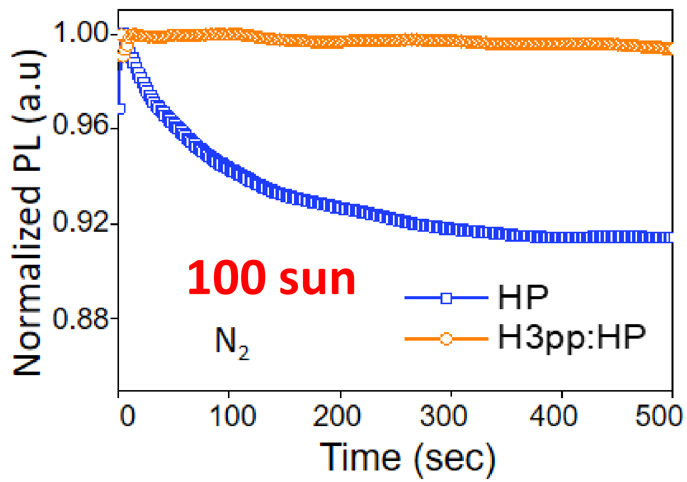
● $Rb_{0.05}Cs_{0.05}MA_{0.15}FA_{0.75}Pb_{1.05}(I_{0.95}Br_{0.05})_3$ (RbCsMAFA),

■ $Cs_{0.05}MA_{0.15}FA_{0.80}Pb_{1.05}(I_{0.85}Br_{0.15})_3$ (CsMAFA)

Optical-pump THz-probe (OPTP)

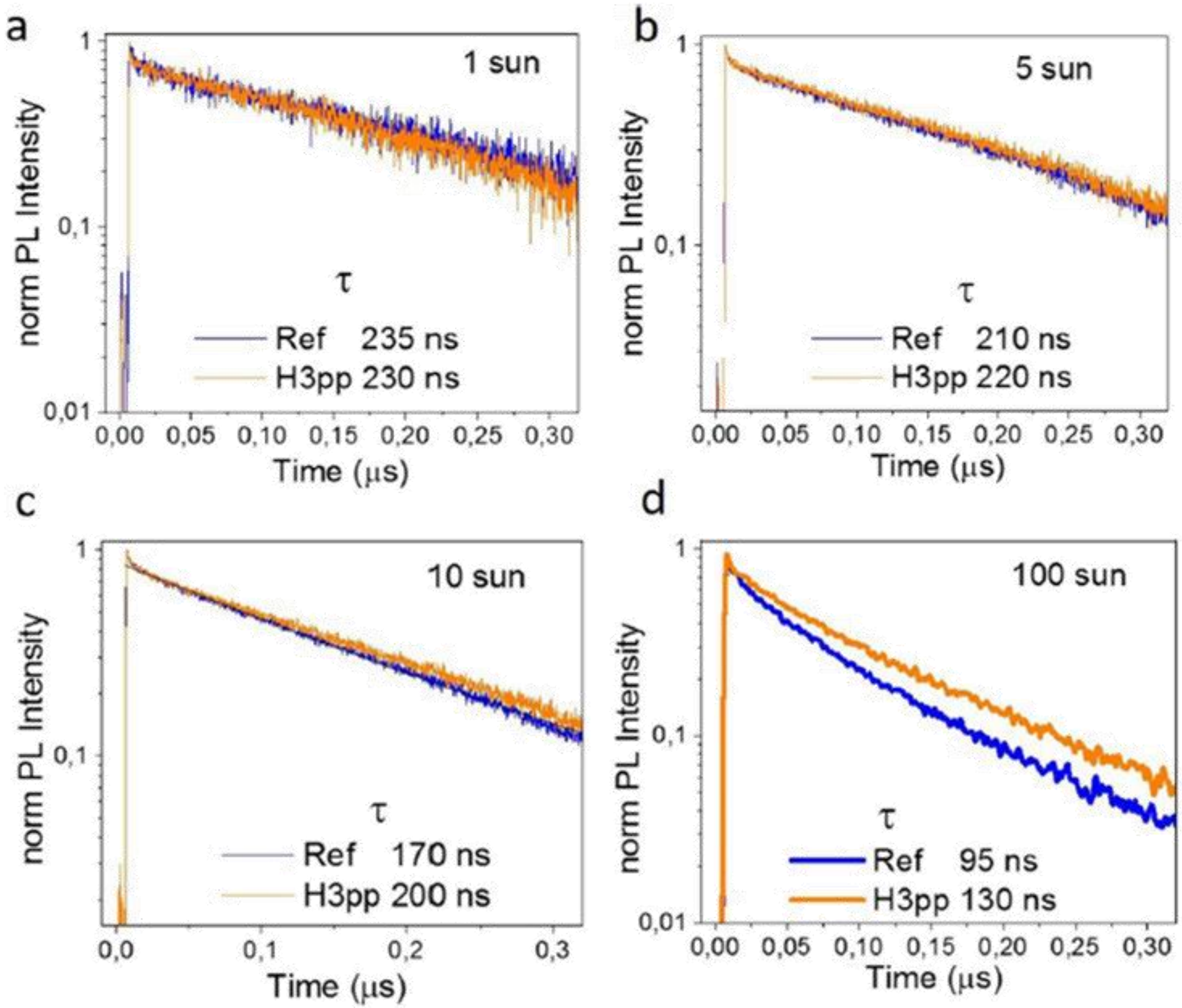


PL



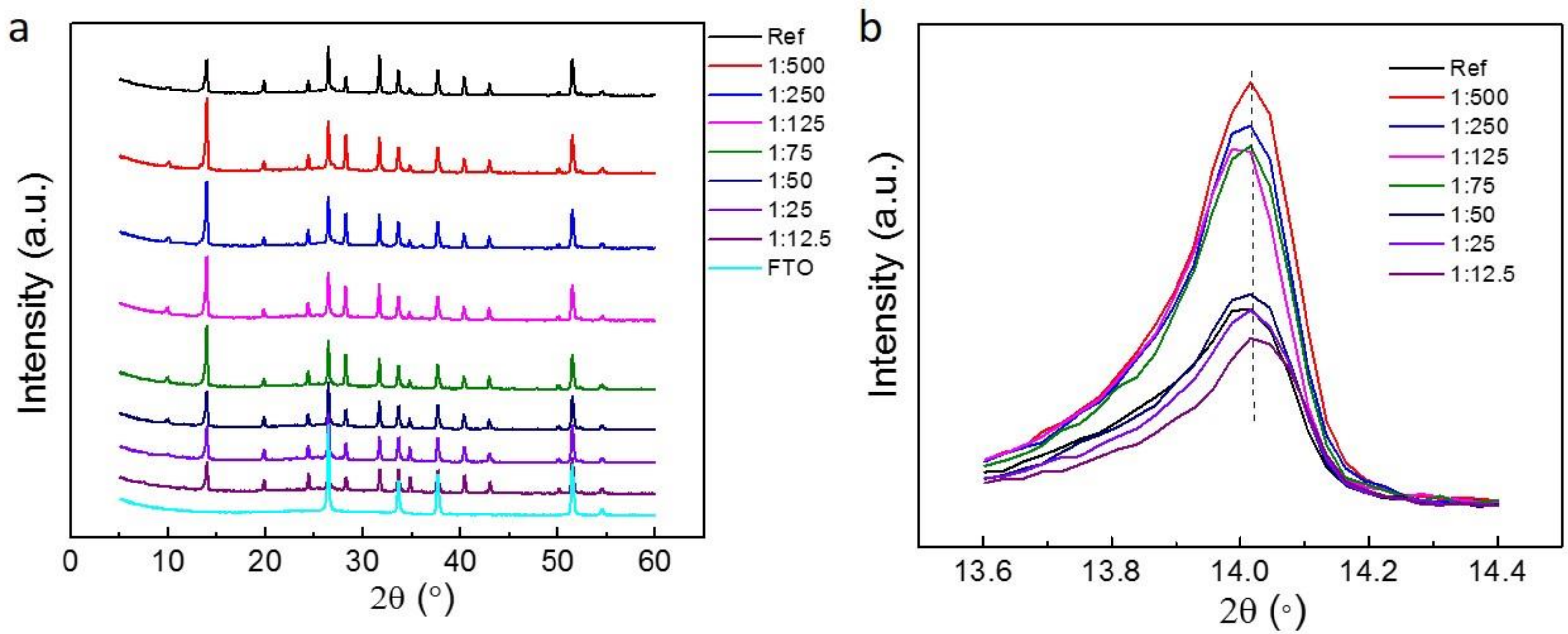
Haibing, X. et al., Joule, 2021

TRPL at different light intensity (fluences)



Haibing, X. et al., Joule, 2021

No incorporation of the additive into the structure



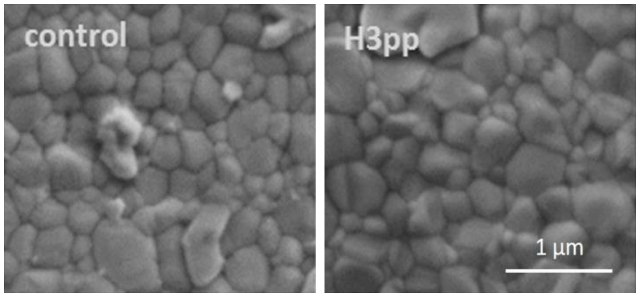
RbCsMAFA

The full width at half maximum (FWHM) of the main perovskite peak (-111) , 2θ = 14°, is 0.147 for both of the reference and H3pp-doped (1:500) samples, reflecting that **the average grain size is not affected by H3pp.**

No new peaks and peak shifts are observed, implying that **the H3pp not likely incorporates into the perovskite crystal lattice,** in agreement with the solid-state NMR results.

Haibing, X. et al., Joule, 2021

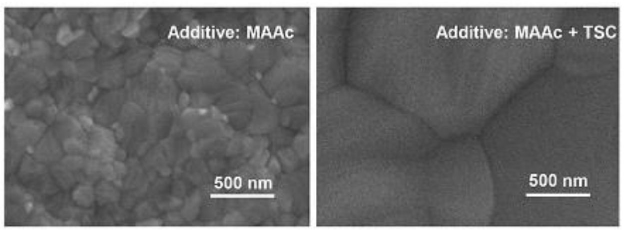
Grain Size

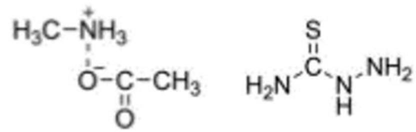


H3PP

This Work

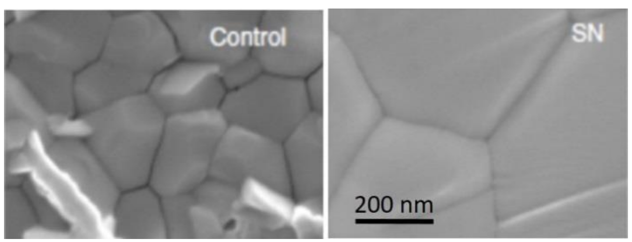
Haibing, X. Submitted

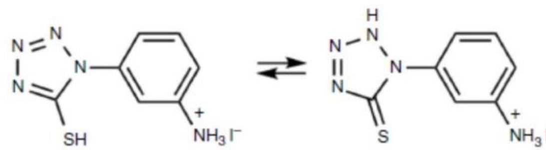




MAAc TSC

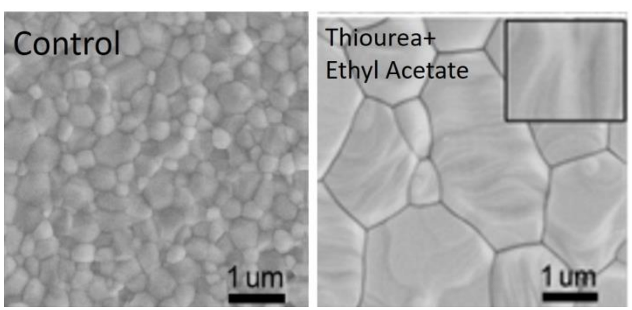
Grancini, et al. Nat. Commun. 8, 15684 (2017).

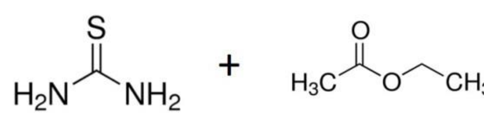




SN

Bi, D. et al. Nat. Commun. 9, 4482 (2018).





Fei, C. et al. Adv. Energy Mater. 7, 1602017 (2017).

Haibing, X. et al., Joule, 2021

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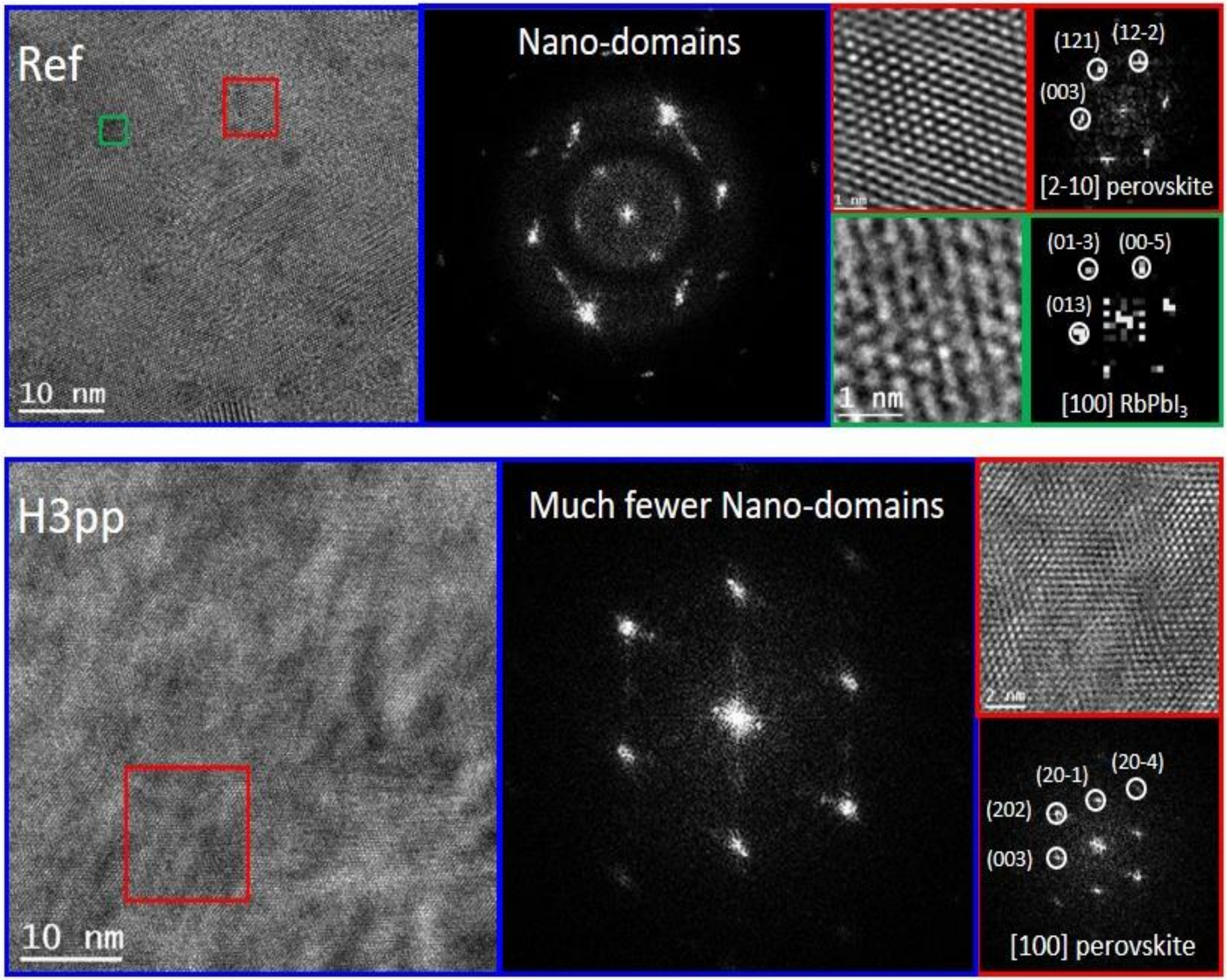
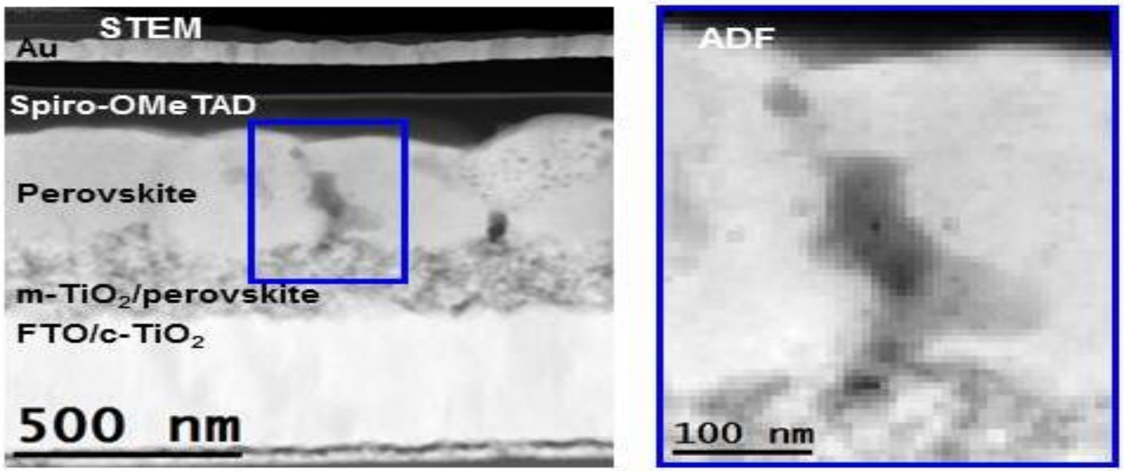
TEM

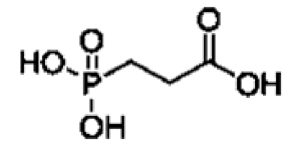
Highly homogeneous films

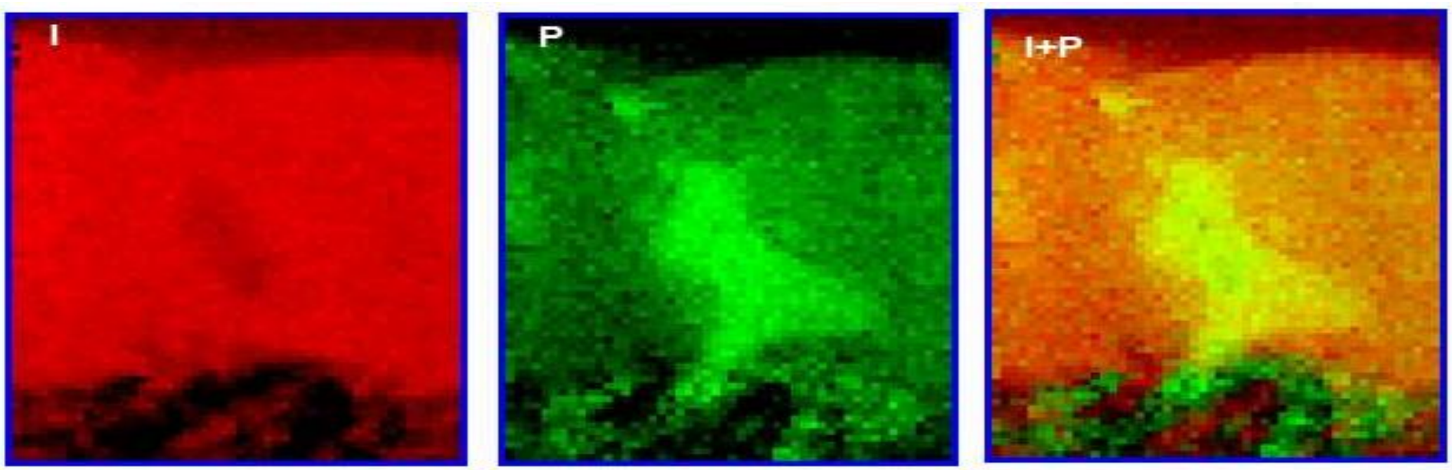


Haibing, X. et al., Joule, 2021

Electron energy loss spectroscopy (EELS) chemical composition maps







Homogeneous distribution

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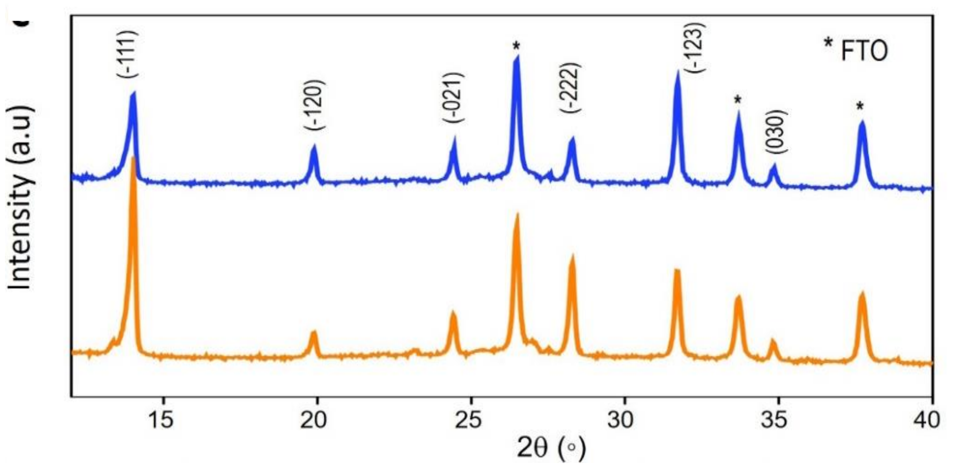
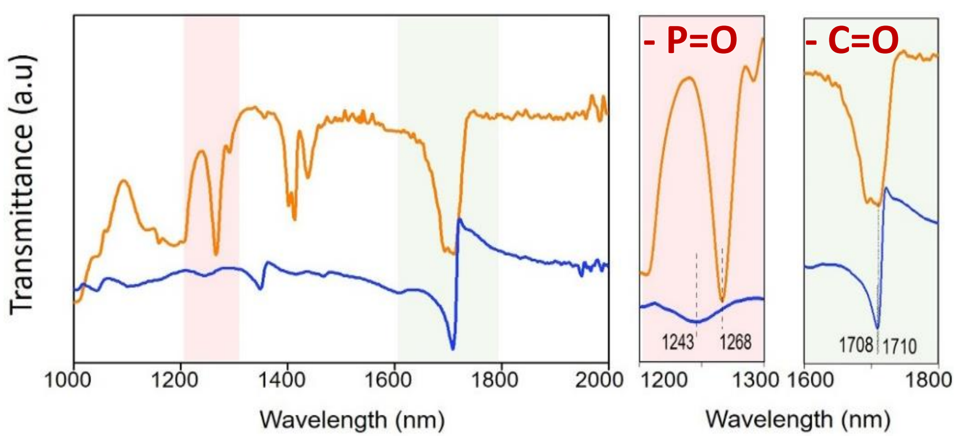


Interaction additive/HP



P=O stretching: 1,220 - 1,300 nm
C=O stretching: 1,600 - 1,800 nm.

- P=O at 1268 cm^{-1} → to 1243 cm^{-1}
- C=O unchanged

Haibing, X. et al., Joule, 2021

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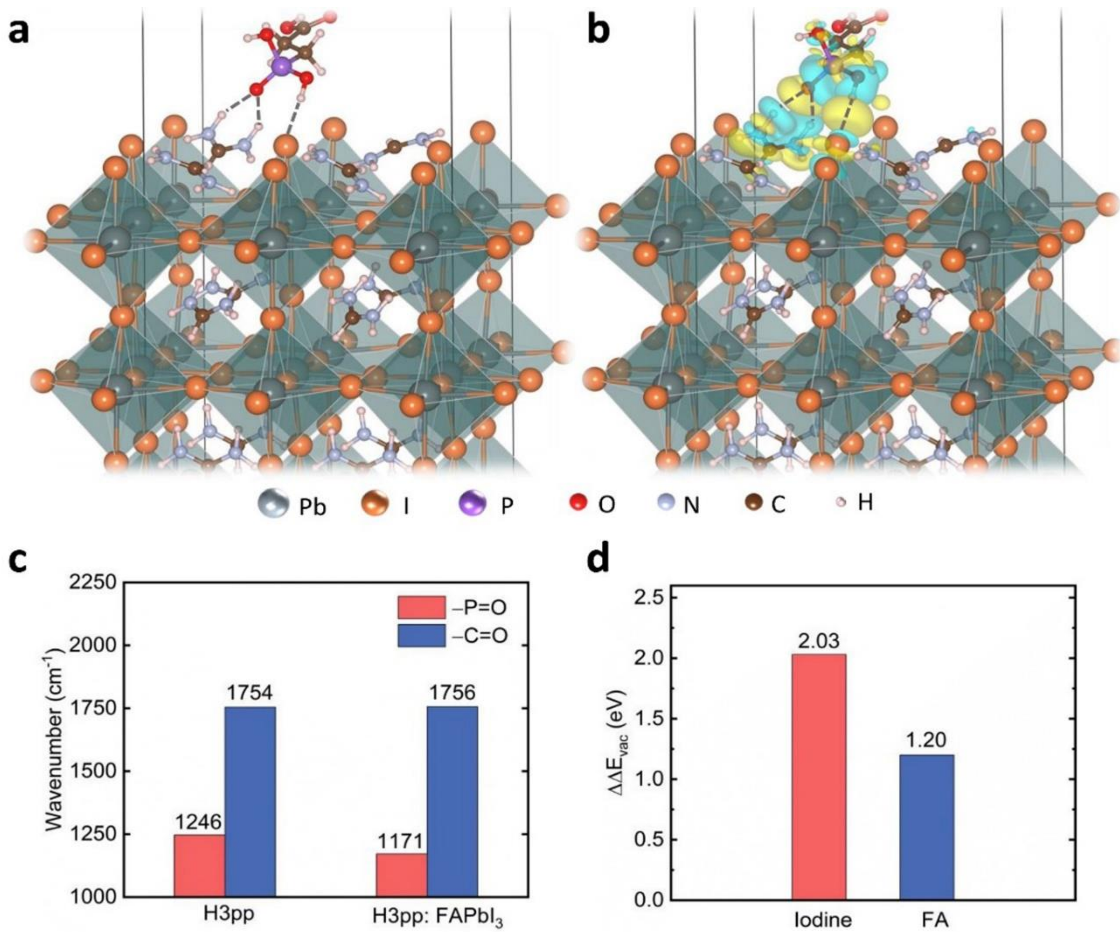
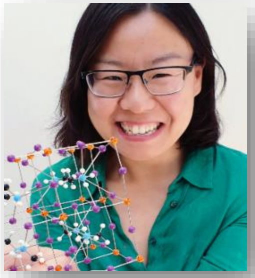
EXCELENCIA SEVERO OCHOA

DFT Calculations





Shuxia Tao

The H3pp additive strongly bonds to the perovskite through the –PO(OH)$_2$ functional group via two types of hydrogen bonds (H···I and O···H), passivating shallow point defects (e.g., FA and I vacancies).

Good correlation with the FTIR data

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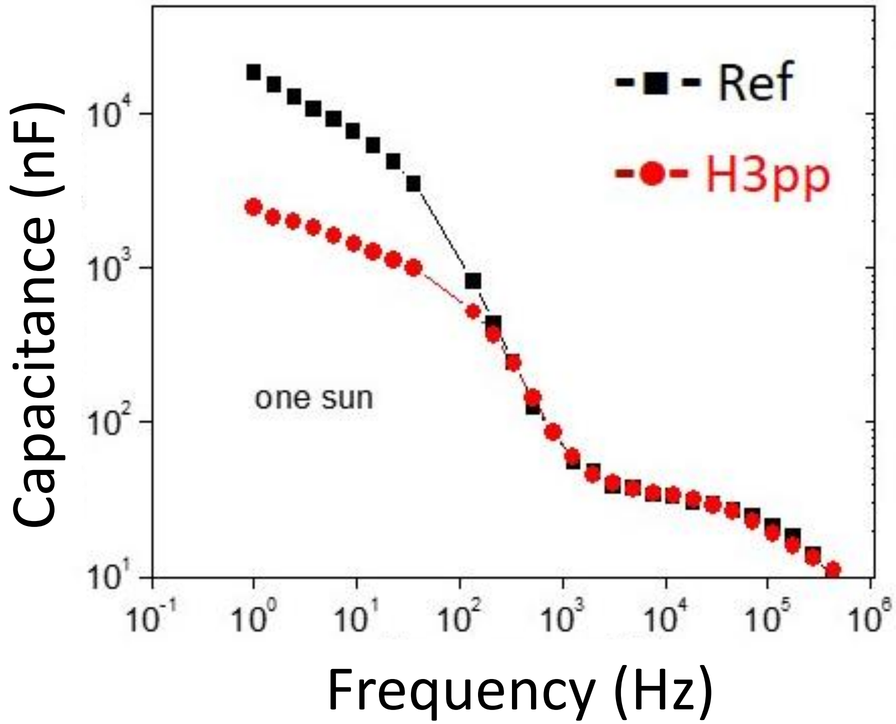
Ion Migration: Impedance Spectroscopy

Frequency (f) dependent capacitance (C)



From Nyquist Plot of impedance spectra (IS)

$C = 1/(2\pi f Z'')$

f is frequency in Hz

Z'' is the imaginary part

The capacitance in the low frequency range (1-100 Hz) is one order of magnitude lower in the H3pp doped device, indicating an **effective reduction in ion migration and charge accumulation** at the interfaces.

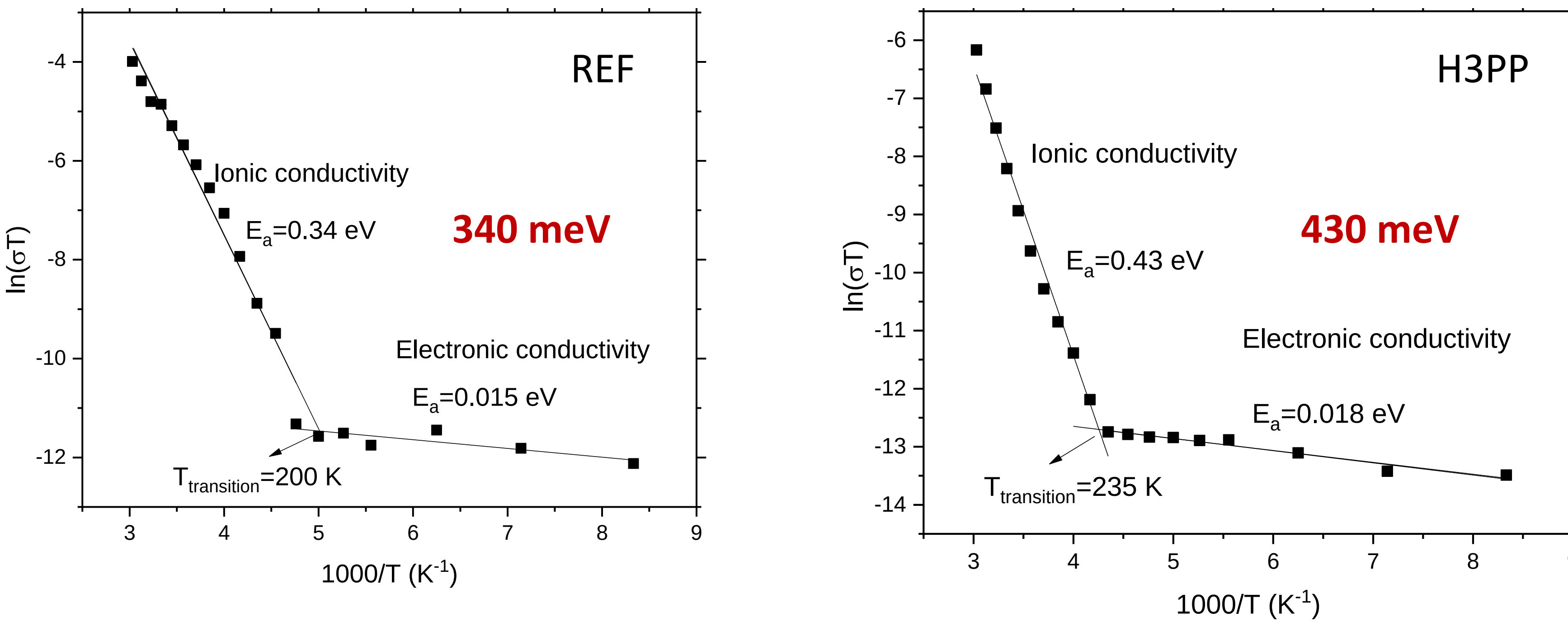
Zhao et al., Sci. Adv. 2017;3: eaao5616

J. Xing et al., Phys. Chem. Chem. Phys. 18, 30484–30490(2016).

Haibing, X. et al., Joule, 2021

Ion Migration: Activation Energy

Temperature dependent conductivity (Dark)



higher activation energy than Ref sample → indicating the ion migration is mitigated.

Zhao et al., Sci. Adv. 2017;3: eaao5616 J. Xing et al., Phys. Chem. Chem. Phys. 18, 30484–30490(2016).

Haibing, X. et al., Joule, 2021

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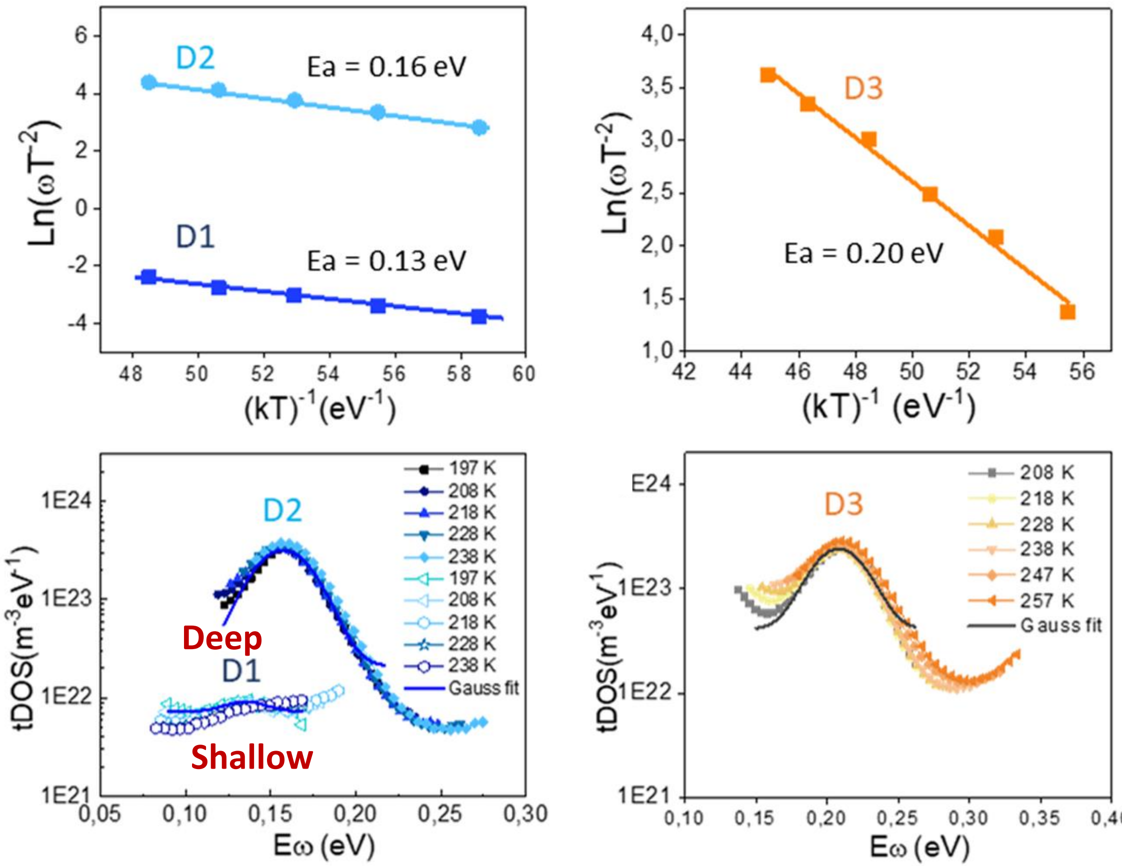
Deep Defect Vs Shallow Defect passivation

Thermal admittance spectroscopy

Feng Gao
(Linköping University)

No Additive

Additive



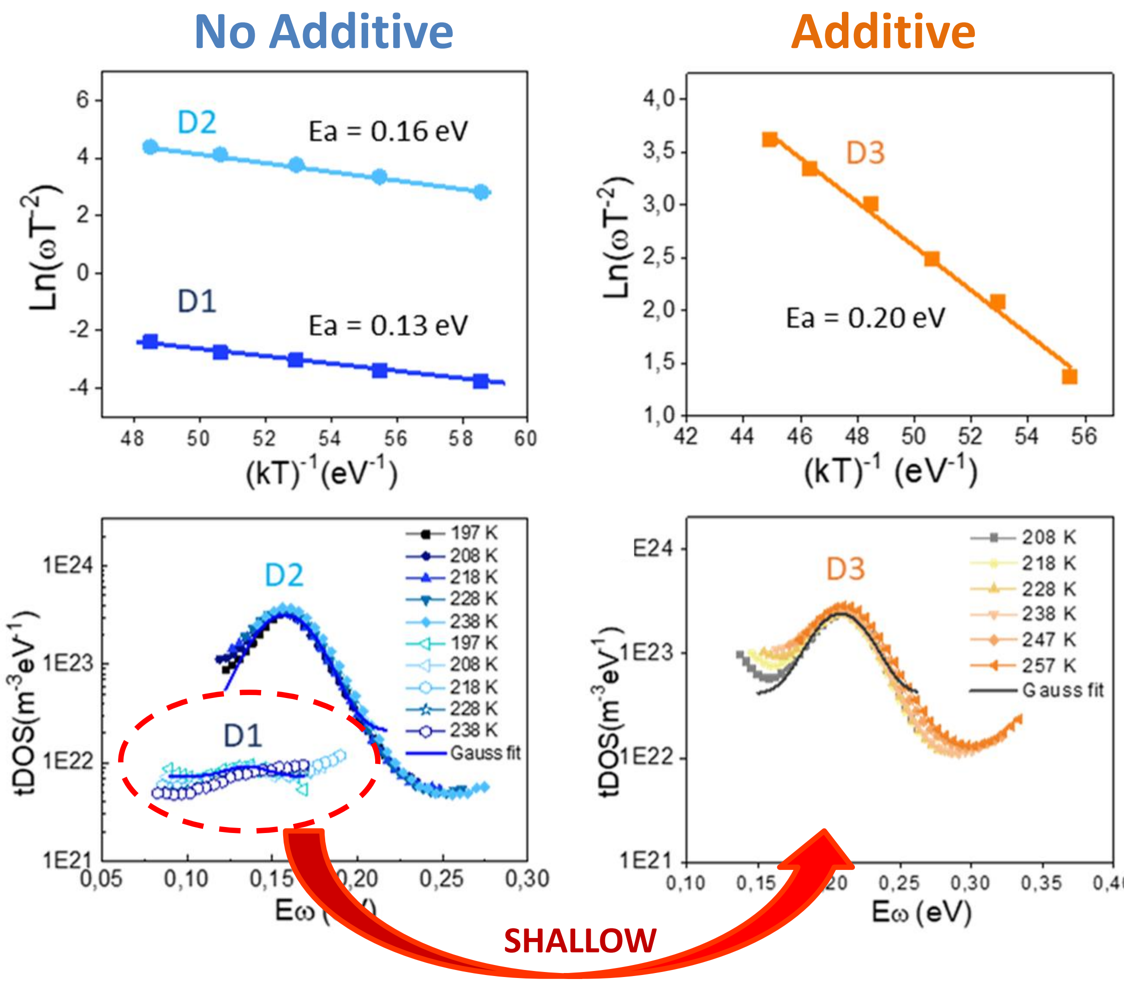
Energy levels of defects

H. Xie, et al., M. Lira-Cantu, Joule, 5, 1-21, 2021

Deep Defect Vs Shallow Defect passivation

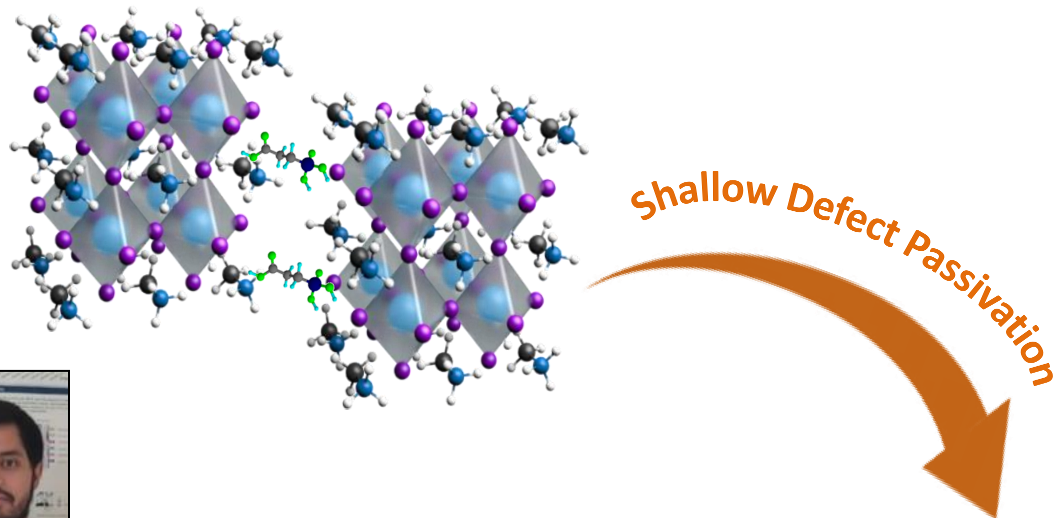
Thermal admittance spectroscopy

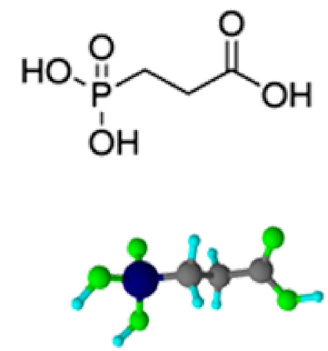
Feng Gao
(Linköping University)



Haibing, X. et al., Joule, 2021

Deep defect passivation → Efficiency
Shallow defect passivation → Stability

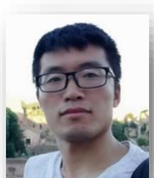




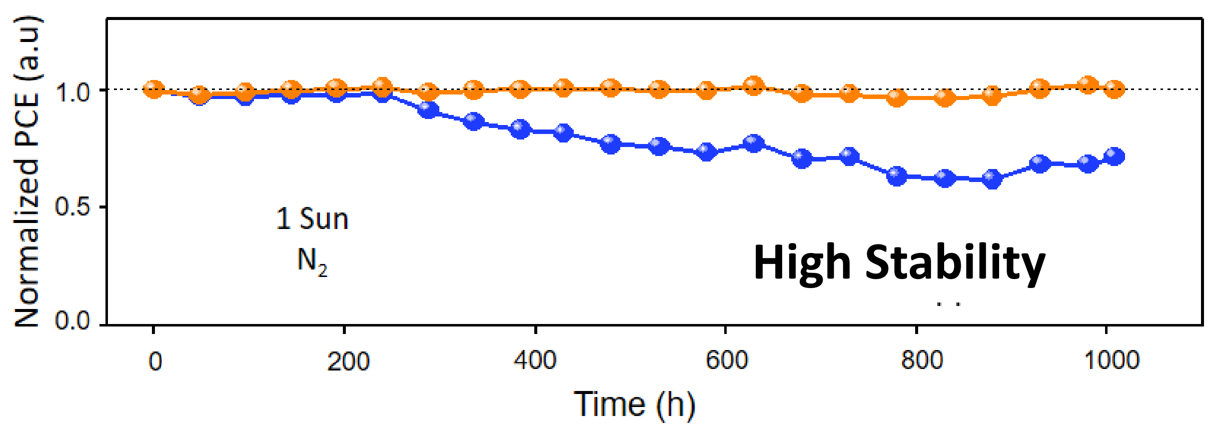
3-Phosphonopropionic Acid

Carlos Pereyra

Haibing Xia



Zaiwei Wang



H. Xie, et al., M. Lira-Cantu, Joule, 5, 1-21, 2021

M. Lira-Cantu. Nature Energy ***2****, 17115 (2017)*

Conclusions

Passivation of both shallow and deep defects is needed!

The current understanding of point defects in PSCs indicates that passivation of deep defects (e.g., Pb-I antisite defects) reduces the nonradiative losses and has a direct impact on the device performance (V_{oc} and efficiency).

In our work, the PLQE and OPTP results at low fluences (~1 sun) rule out any variation in the non-radiative defect concentration. However, analyses at increasing fluences (above 10 suns) indicate a small decrease in the deep trap density, which has an enormous impact on the device stability but not on the device performance.

The H3pp additive strongly bonds to the perovskite through the $–PO(OH)_2$ functional group via two types of hydrogen bonds (H···I and O···H), passivating shallow point defects (e.g., FA and I vacancies).

Other intrinsic factors could be influencing stability: concentration, size and structure of the additive.

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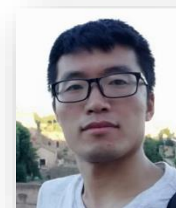
Chunxiong Bao
Xiaoxiao Sun

Anders Hagfedt

Carlos Pereyra

Haibing Xia



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To the Nanostructured Materials for Photovoltaic Energy Group

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Institució CERCA Centres de Recerca de Catalunya

UAB Universitat Autònoma de Barcelona

Thank you for your attention!

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monica.lira@icn2.cat