Lead-free Perovskite Solar Cells

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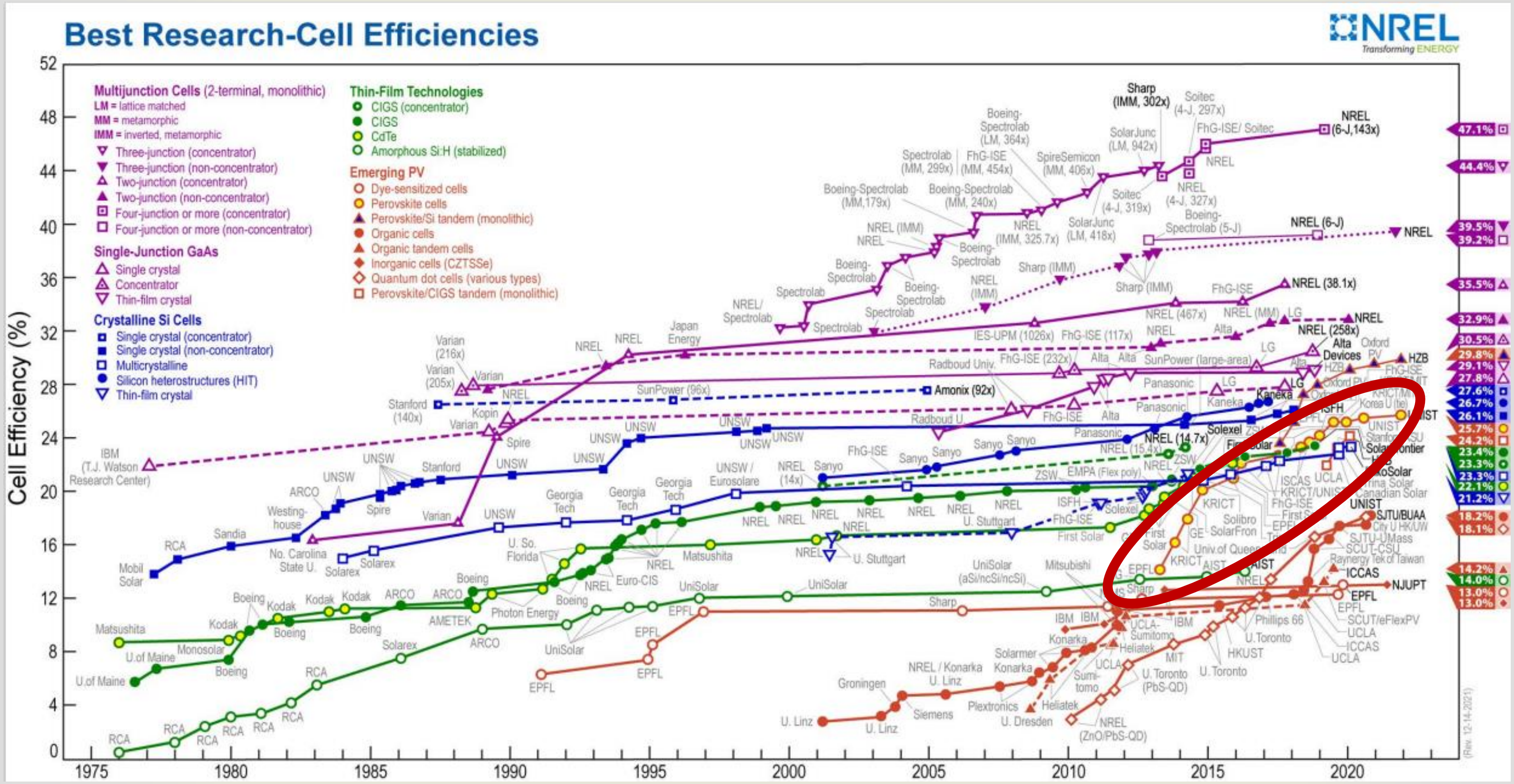
Rapid Progress of PSC on 2012-2022



World Record Efficiency for Perovskite Solar Cells

Perovskite solar cells with atomically coherent interlayers on SnO_2 electrodes

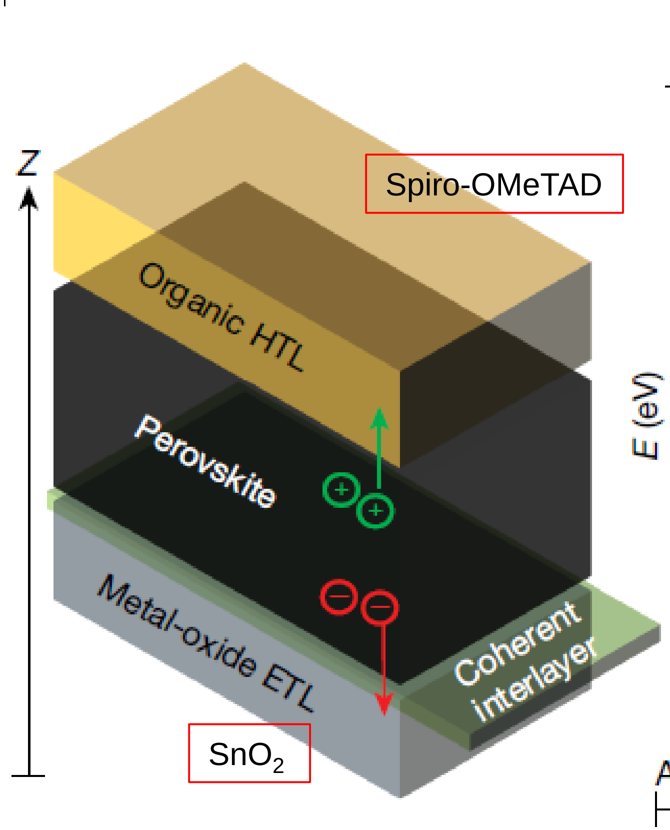
Nature **2021**, *598*, 444–450.

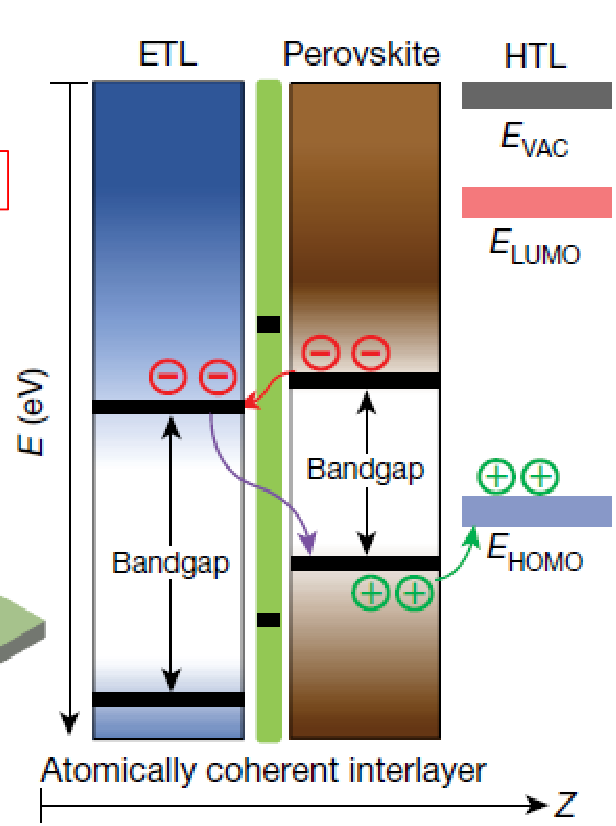
New world record of PCE 25.8% for a $FAPbI_3$ PSC

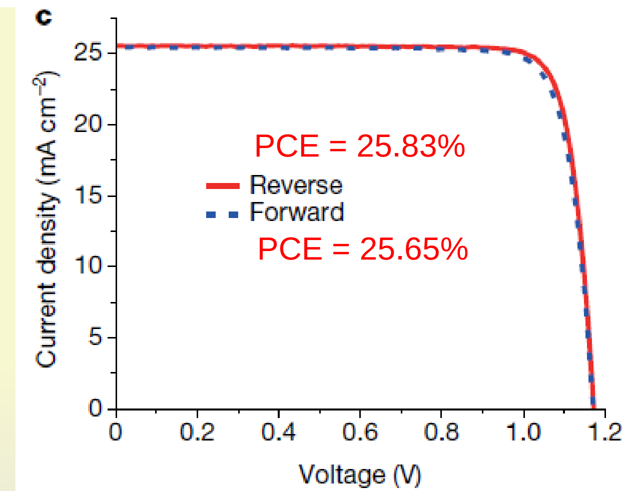
https://doi.org/10.1038/s41586-021-03964-8

Received: 30 March 2021

Hanul Min[1,5], Do Yoon Lee[1,5], Junu Kim[2], Gwisu Kim[1], Kyoung Su Lee[1], Jongbeom Kim[1], Min Jae Paik[1], Young Ki Kim[3], Kwang S. Kim[2], Min Gyu Kim[4]✉, Tae Joo Shin[3]✉ & Sang Il Seok[1]✉



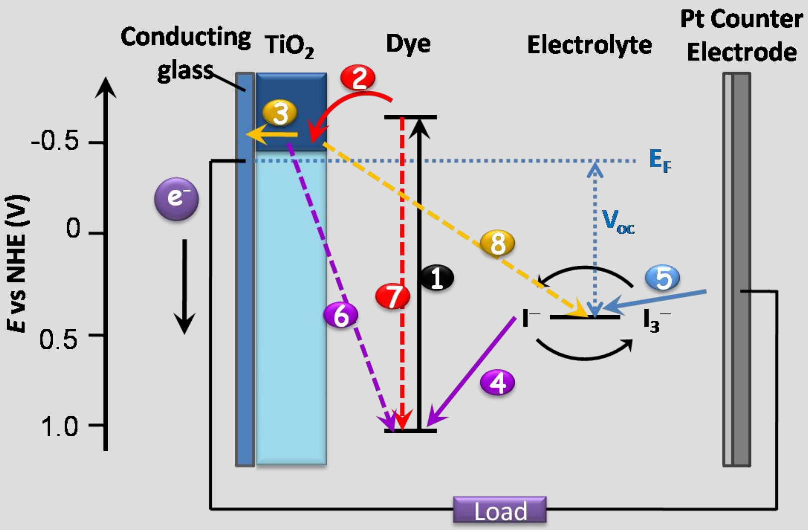


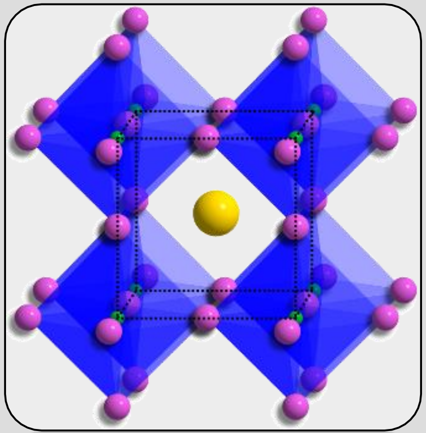


NREL certified PCE = 25.7%

Sang Il Seok
UNIST, Korea

From DSSC to PSC





Perovskite Crystal Structure

TiO_2 NT

J. Phys. Chem. C **2008**, *112*, 19151-19157
Energy Environ. Sci. **2011**, *4*, 3420-3425

TiO_2 NP

ACS Nano **2012**, *6*, 10862-10873
J. Phys. Chem. Lett. **2013**, *4*, 1570-1577

YD dyes

Chem. Eur. J. **2009**, *15*, 1403-1412
Energy Environ. Sci. **2010**, *3*, 949-955
Angew. Chem. **2010**, *49*, 6646-6649
Science **2011**, *334*, 629-633
Energy Environ. Sci. **2012**, *5*, 6460-6464
Energy Environ. Sci. **2012**, *5*, 9843-9848

LD dyes

Energy Environ. Sci. **2011**, *4*, 1788-1795
Energy Environ. Sci. **2012**, *5*, 6933-6940
Energy Environ. Sci. **2014**, *7*, 1392-1396

Gel-type DSSC

ACS AMI **2013**, 5, 10098-10104

Solid-state DSSC

ChemSusChem **2015**, *8*, 2529-2536

Relaxation Mechanism

Angew. Chem. **2014**, *53*, 9339-9342
J. Phys. Chem. Lett. **2016**, *7*, 2450-2455
J. Phys. Chem. Lett. **2020**, *11*, 5699-5704
Angew. Chem. **2020**, *59*, 19001-19005

Cabon-based Devices

ACS Energy Lett. **2016**, *1*, 1086-1093
J. Mater. Chem. A **2016**, *4*, 3872-3878
J. Mater. Chem. A **2017**, *5*, 739-747
Angew. Chem. **2017**, *56*, 13819-13823

GO-based PSC

Adv. Energy Mater. **2018**, *8*, 1701640
Adv. Funct. Mater. **2018**, *28*, 1803200
Nano Energy **2019**, *62*, 781-790

Tin-based PSC, one step

Energy Envir. Sci. **2018**, *11*, 2353-2362
ACS Energy Lett. **2018**, *3*, 2077-2085
Adv. Mater. **2019**, *31*, 1804835
ChemSusChem **2021**, *14*, 4415-4421

Tin-based PSC, two steps

ACS Energy Lett. **2020**, *5*, 2508-2511
ACS Energy Lett. **2021**, *6*, 485-492
ACS Energy Lett. **2021**, *6*, 4179-4186
JPCL **2021**, *12*, 10106-10111

Major Problems for PSC:

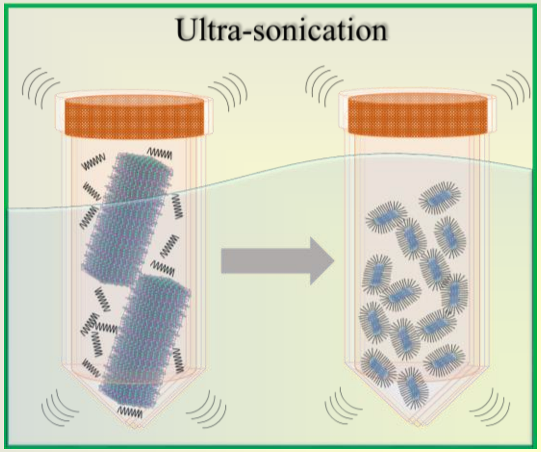
1. Lead Issue
2. Stability Issue

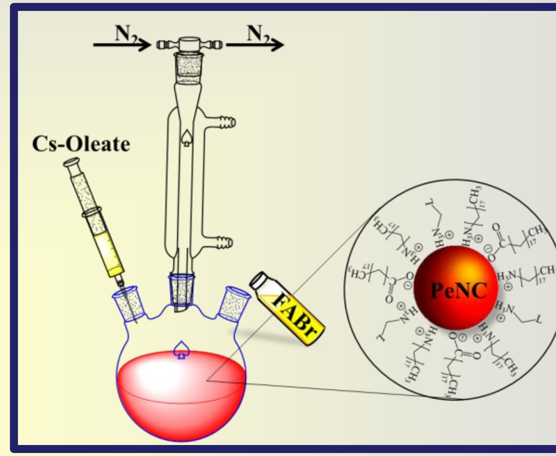
Our Recent Research

- **Tin-based Perovskite Solar Cells (PSC)**
- **Perovskite Nanocrystals for Optoelectronics**
- **Photocatalytic CO_2 Reduction**
- **Mechanistic Understanding of Principles**

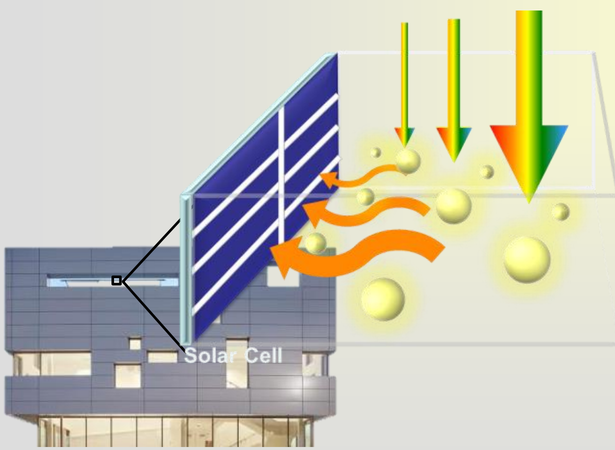
Perovskite Nanocrystals for Optoelectronics

Synthetic Methods: Ultra-sonication (Top-Down) and Hot-addition (Bottom-Up)



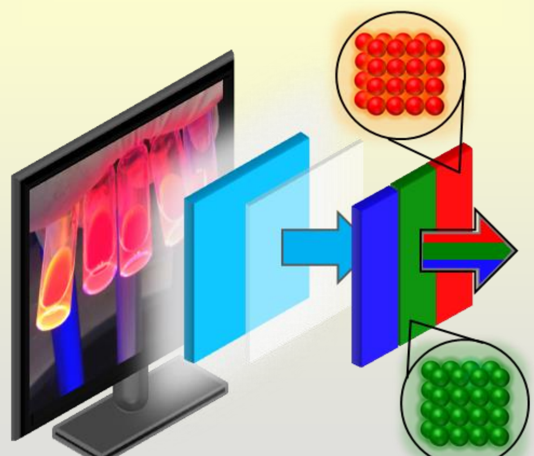


A. Solar Concentrator



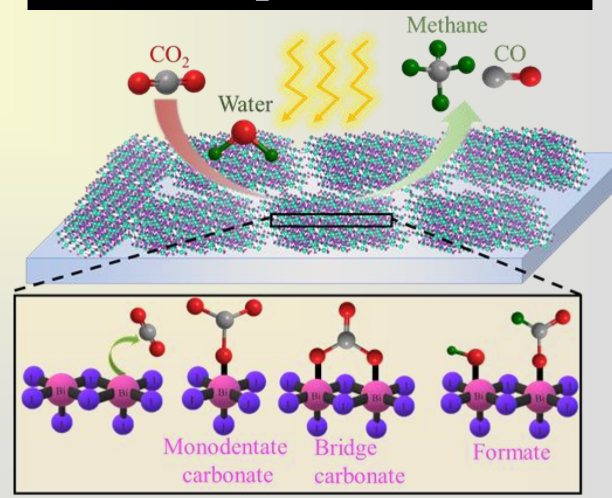
ACS AEM **2021**, *4*, 10565-10573

B. LED / Display



J. Mater. Chem. C **2021**, *9*, 17341–17348

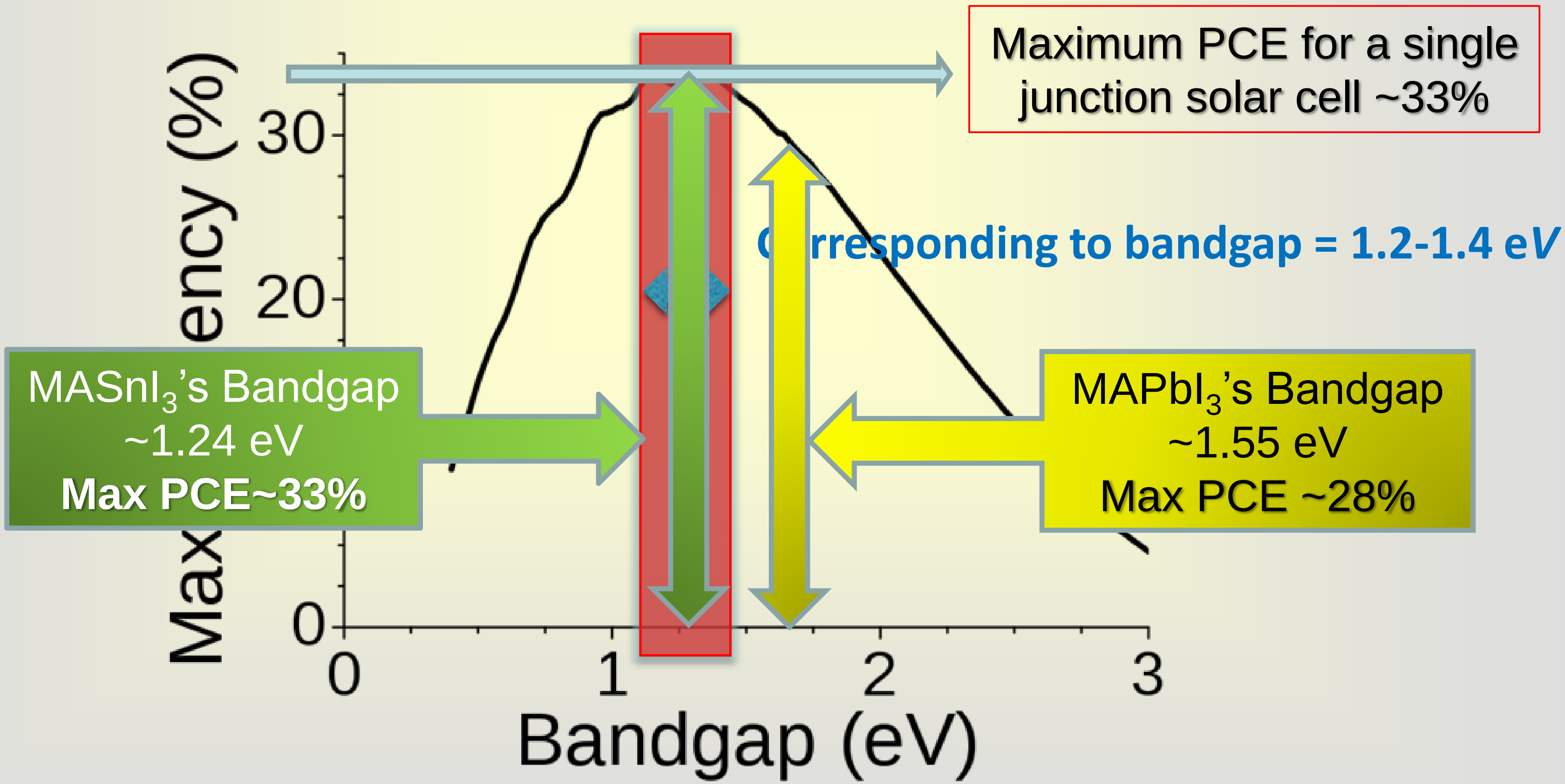
C. CO_2 Reduction



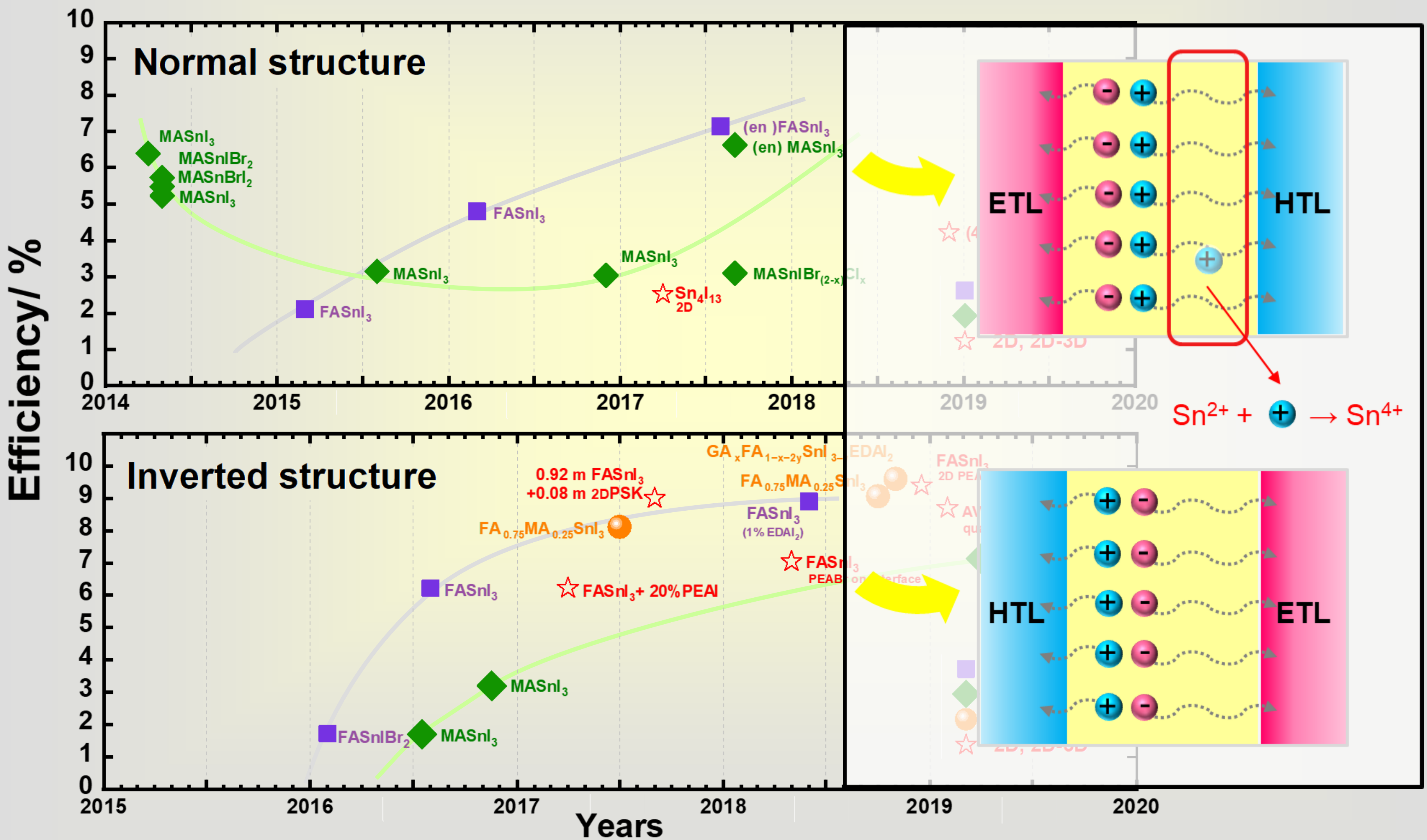
J. Am. Chem. Soc. **2019**, *141*, 20434-20442

Why Tin Perovskite Solar Cells?

Shockley-Queisser Theoretically PCE Limit

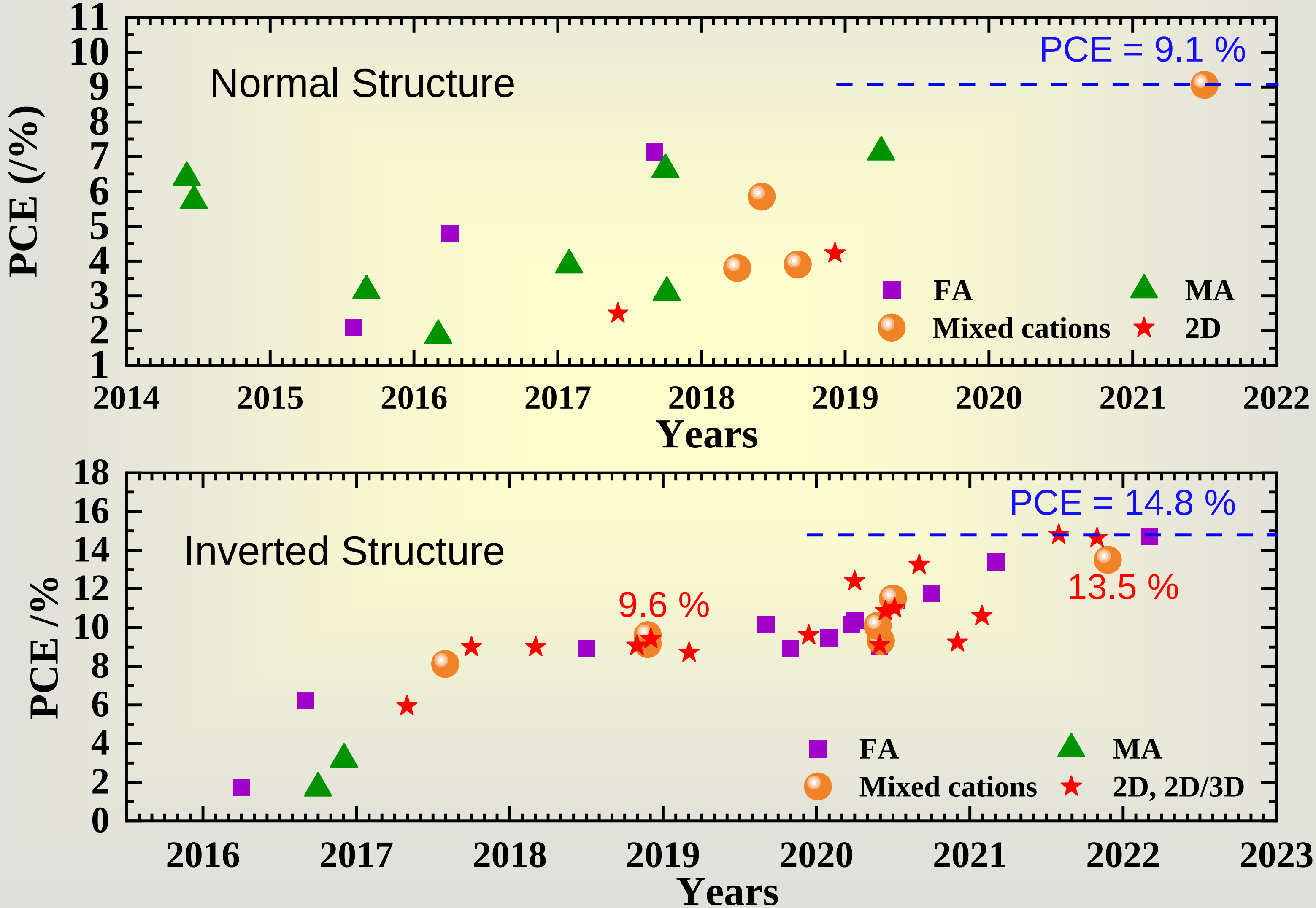


Progress of TPSC during 2014-2019



ACS Energy Lett. **2019**, *4*, 1930-1937.

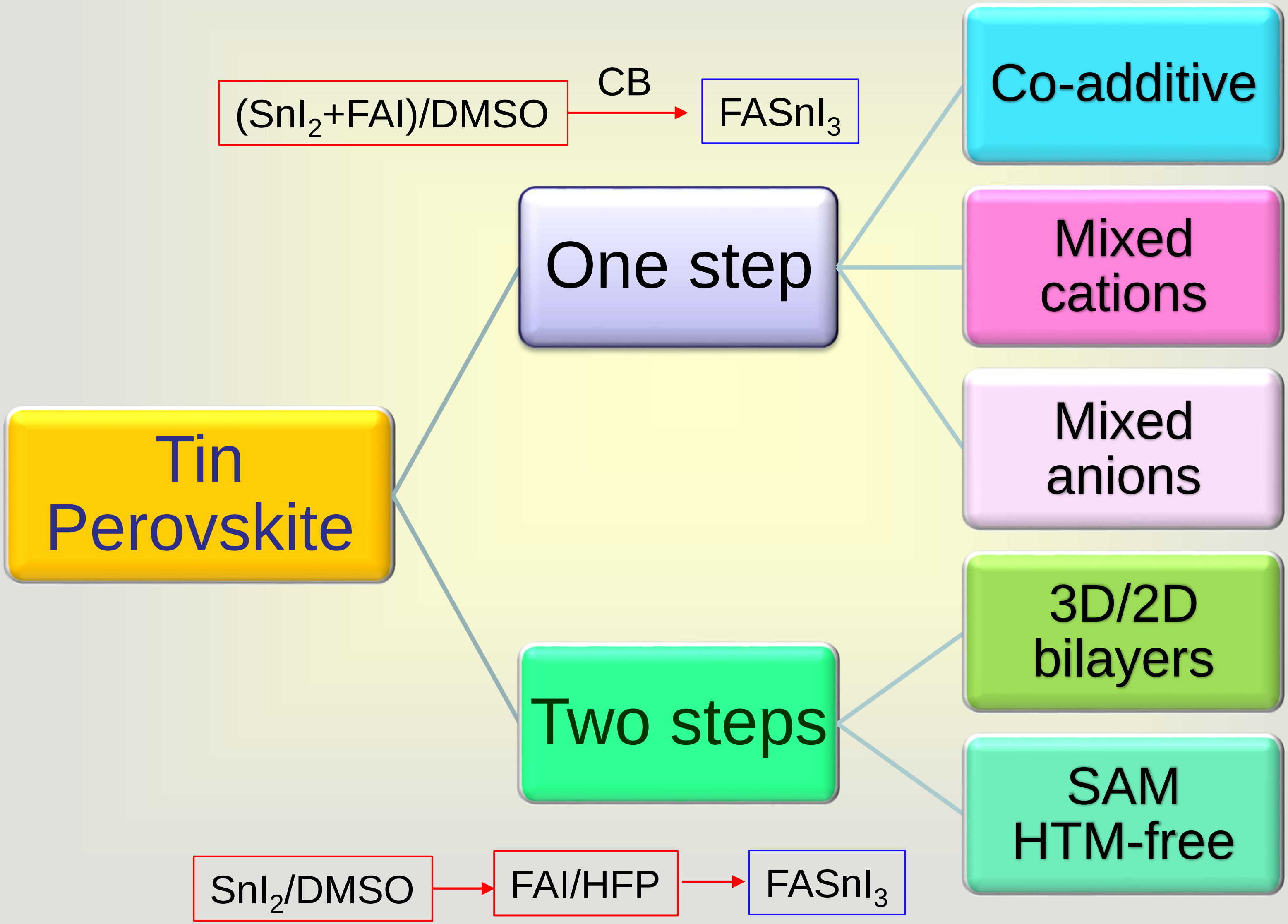
Recent Progress of TPSC



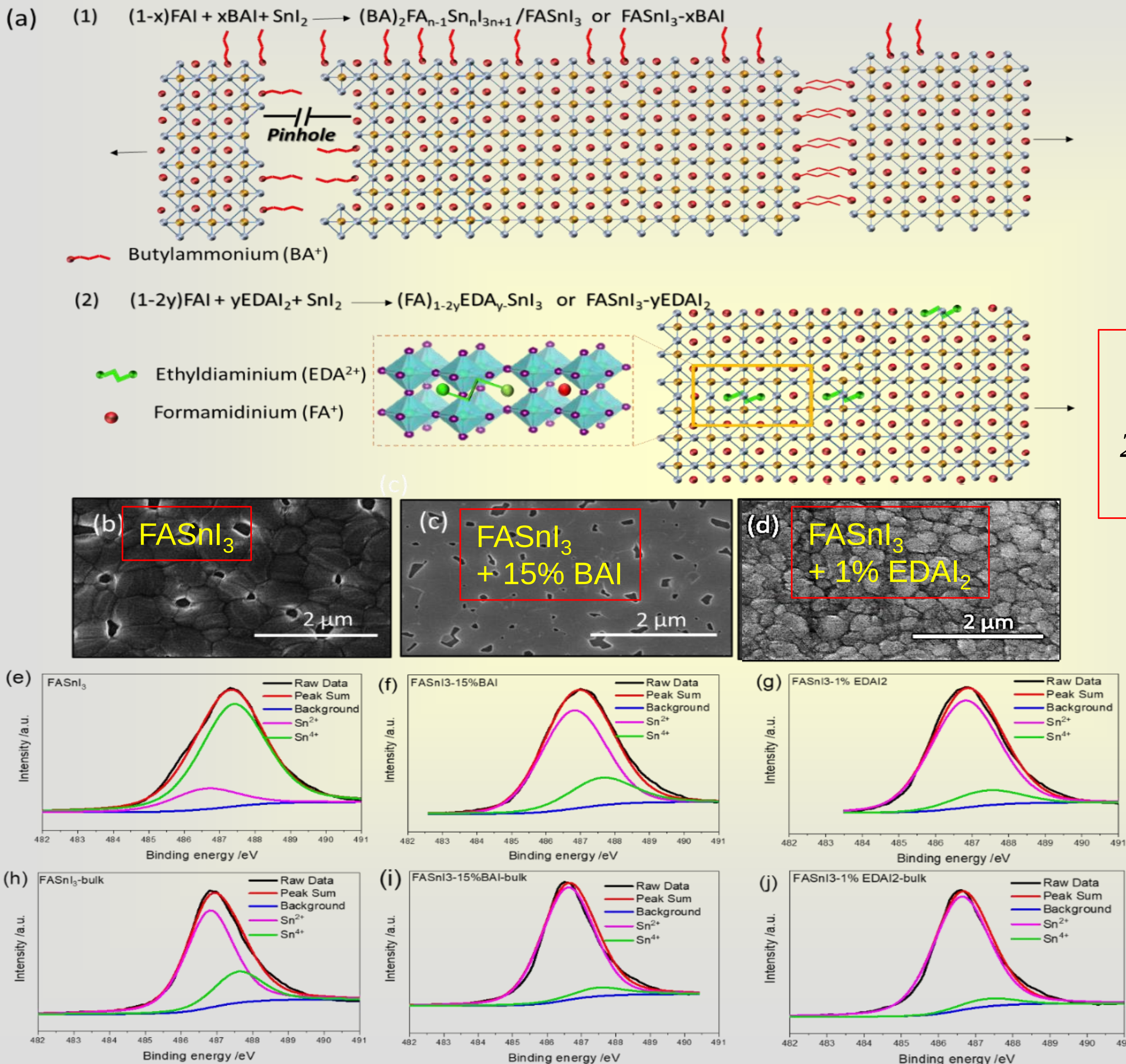
Strategies for Tin-based PSC:

1. FA-based Perovskites
2. Inverted Structure
3. SnF_2 and $EDAI_2$
4. Mixed Cations
5. Quasi-2D and 2D/3D Structure
6. Surface Passivation

Pure Tin Perovskite Solar Cells



Inverted Planar Device : Effect of $EDAI_2$



Case I: Adding Butylammonium Iodide (BAI)

xBAI + (1-x) FAI + SnI_2

$\rightarrow (BA)_x FA_{(1-x)} SnI_3$

x = 0, 10, 15 and 20 %

Formation of 2D Structures?

2 BAI + (n-1) FAI + n SnI_2

$\rightarrow (BA)_2(FA)_{n-1}Sn_nI_{3n+1}$

Case II: Adding Ethylenediammonium Diiodide ($EDAI_2$)

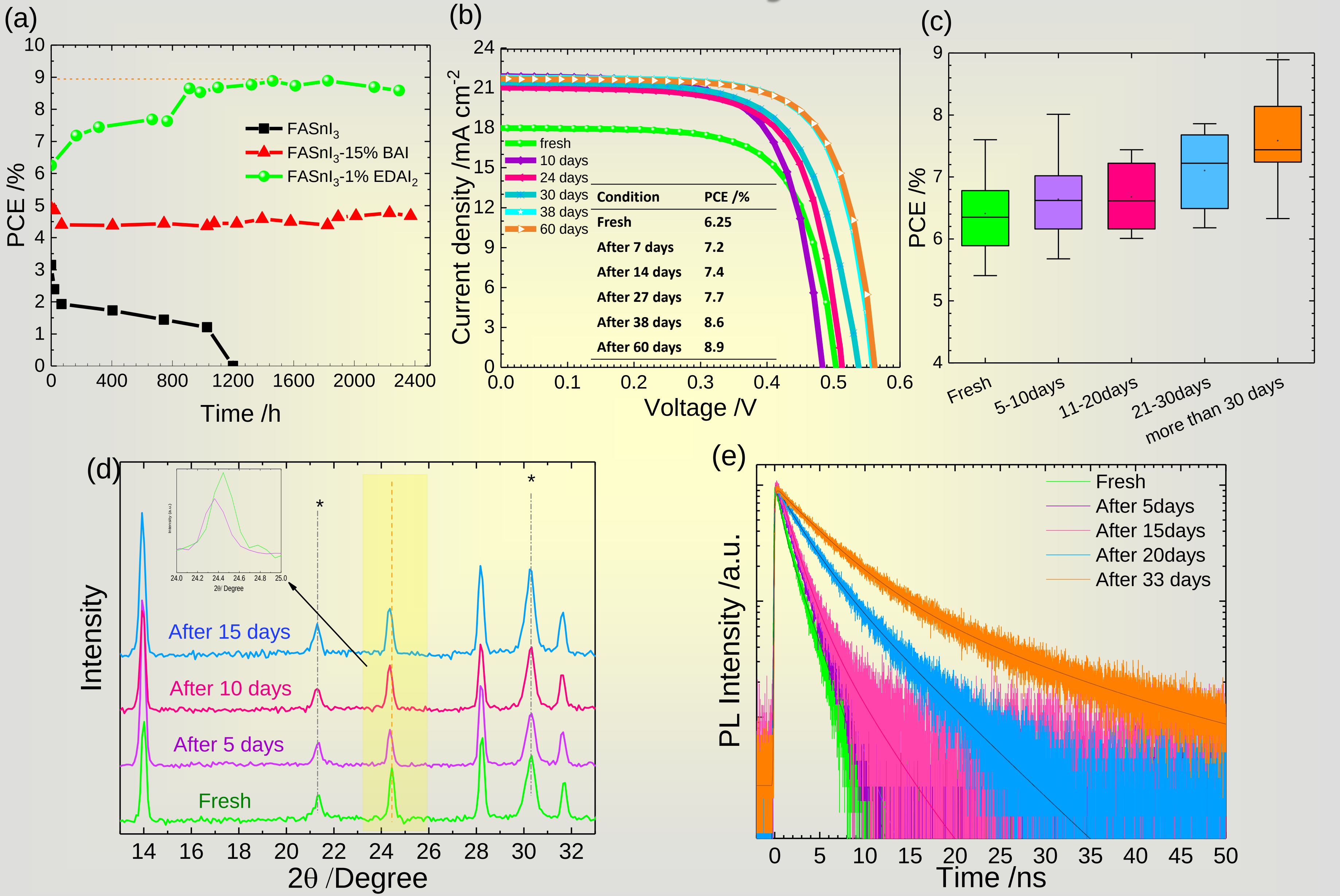
$x EDAI_2$ + (1-2x) FAI + SnI_2

$\rightarrow (EDA)_x FA_{(1-2x)} SnI_3$

x = 0, 1, 2, 3 and 5 %

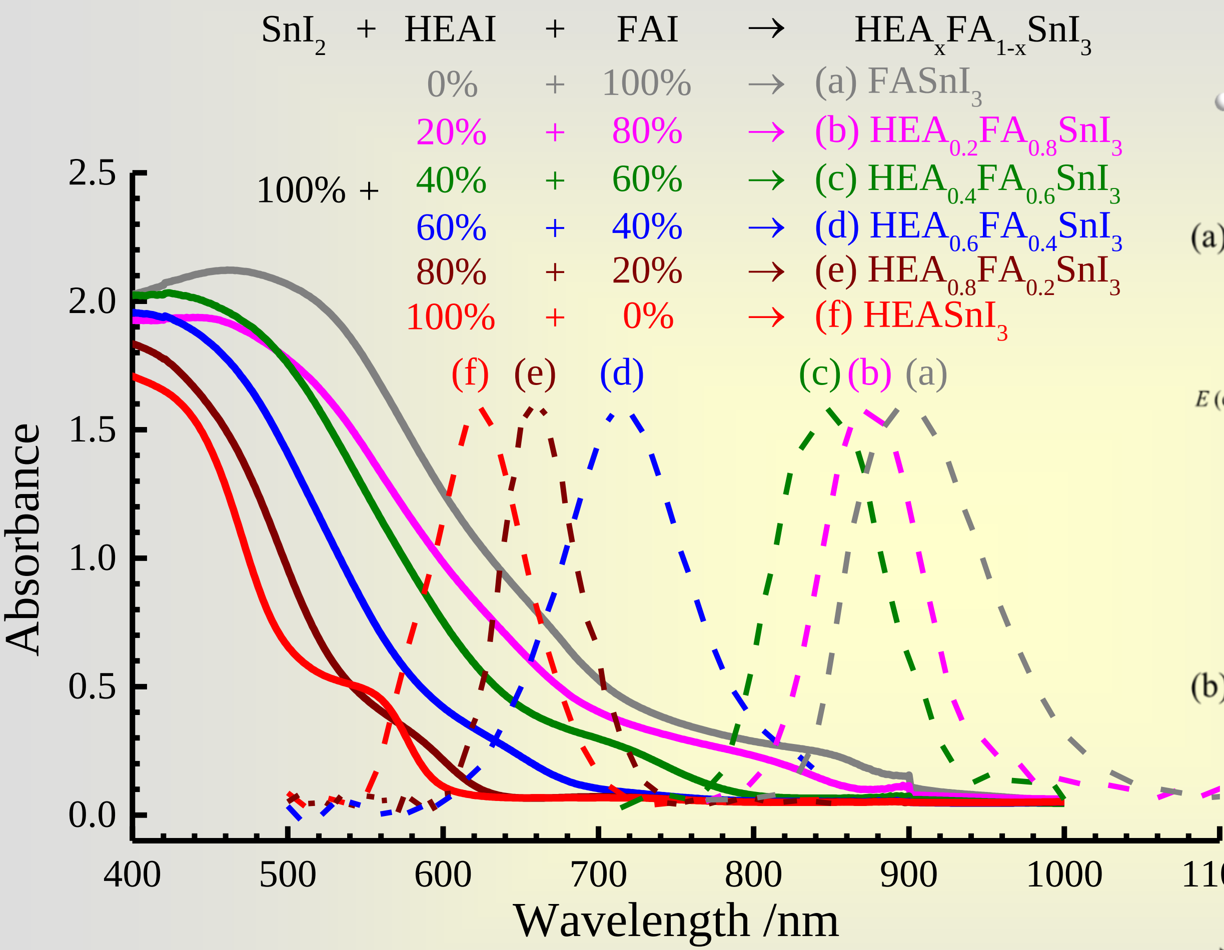
Energy Environ. Sci. 2018, 11, 2353-2362.

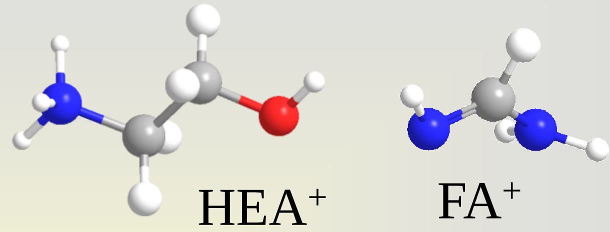
Slow Passivation and Crystal Relaxation

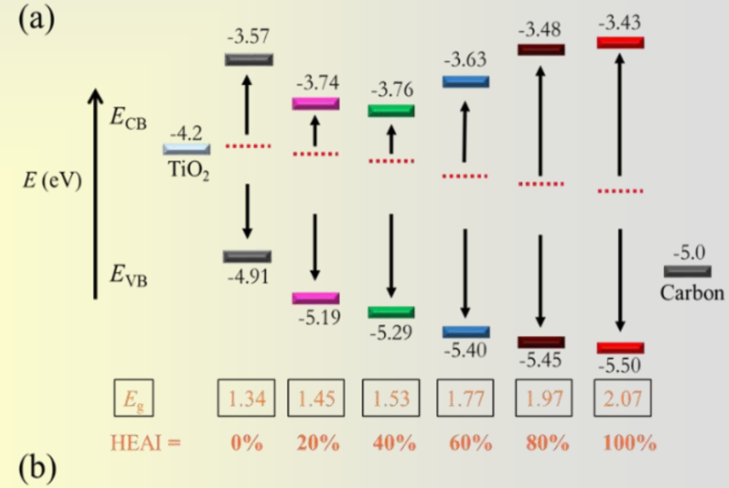


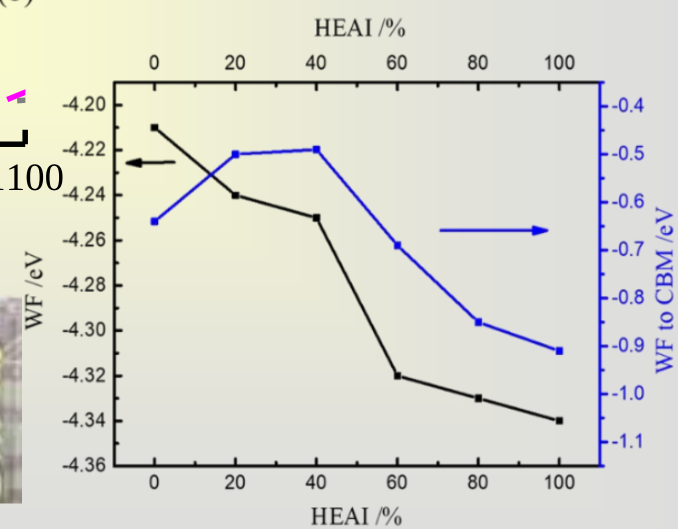
Energy Environ. Sci. 2018, 11, 2353-2362.

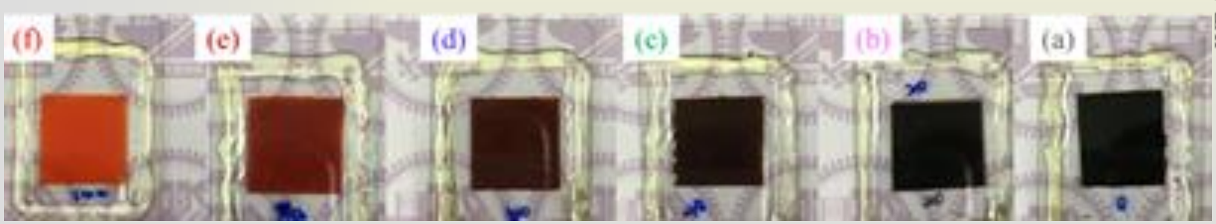
Design of Mixed Organic Cation Tin Perovskites







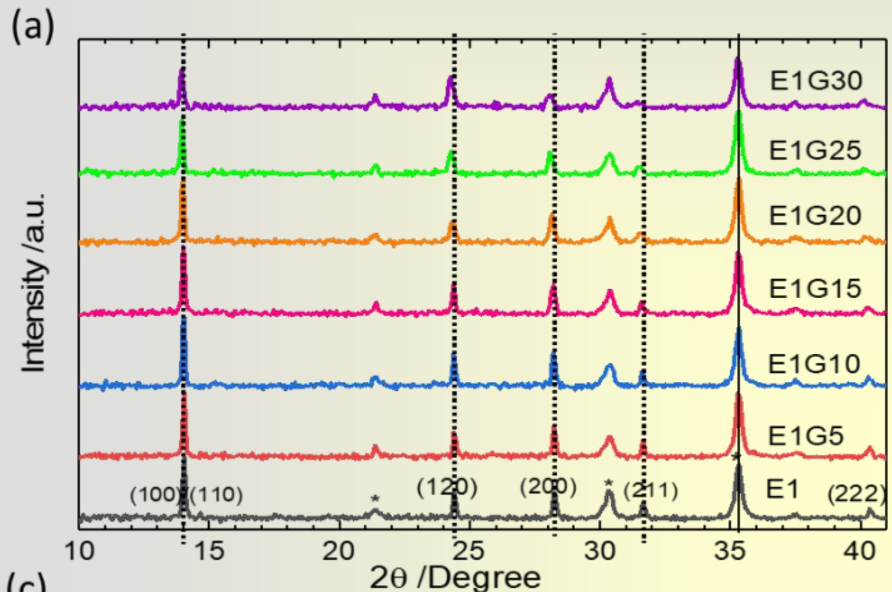


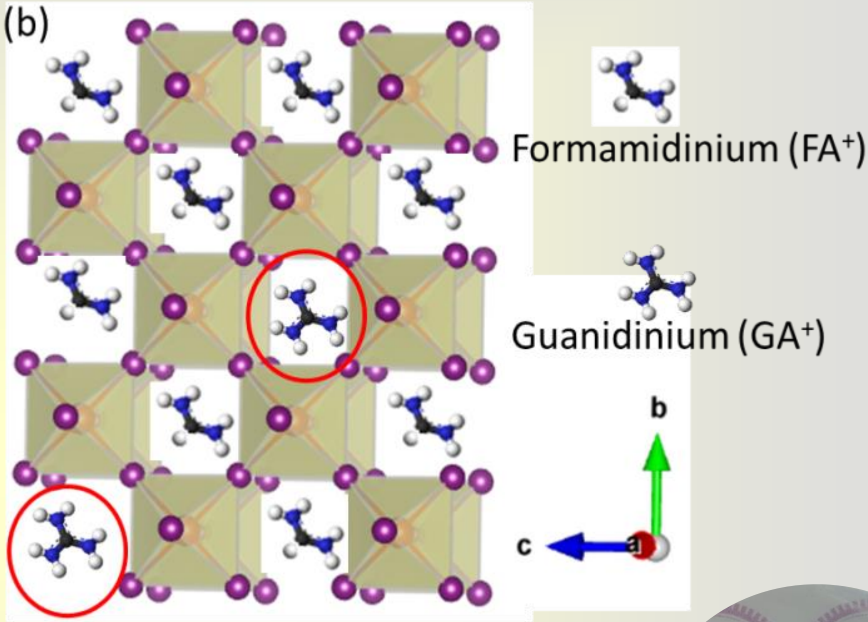


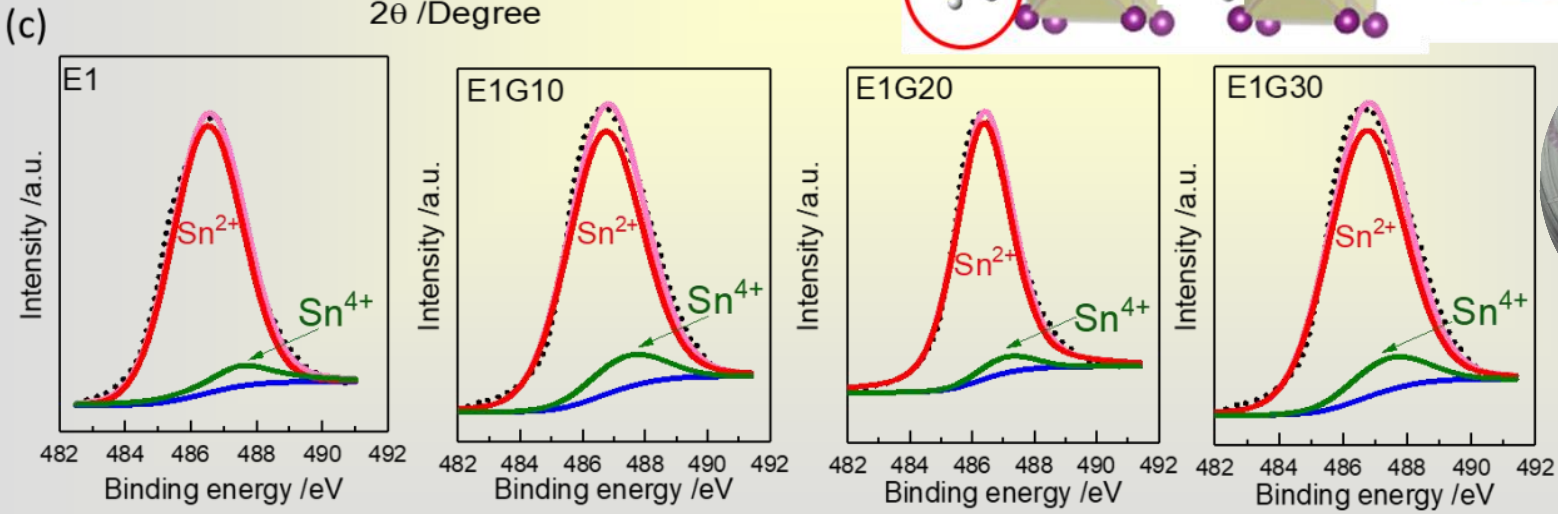
ACS Energy Lett. **2018**, *3*, 2077-2085.

Hybrid Organic Cations: The Effect of GA^+/FA^+

$$SnI_2 + (1\text{-}x\text{-}2y)\ FAI + x\ GAI + y\ EDAI_2 \longrightarrow GA_xFA_{(1-2y-x)}SnI_3\text{-}\ y\%\ EDAI_2 \quad \text{or} \quad EyGx$$

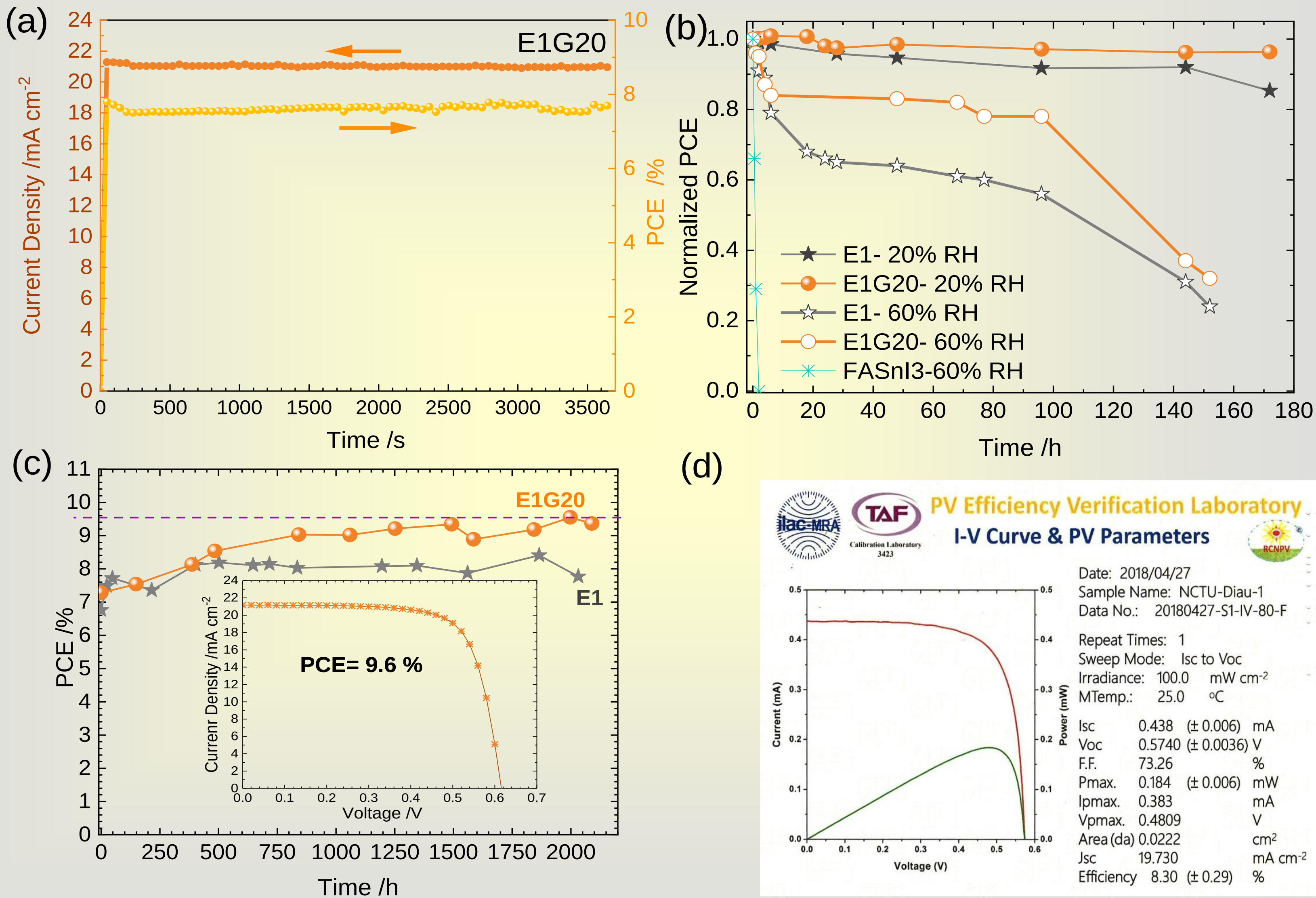






Adv. Mater. **2019**, *19*, 1804835.

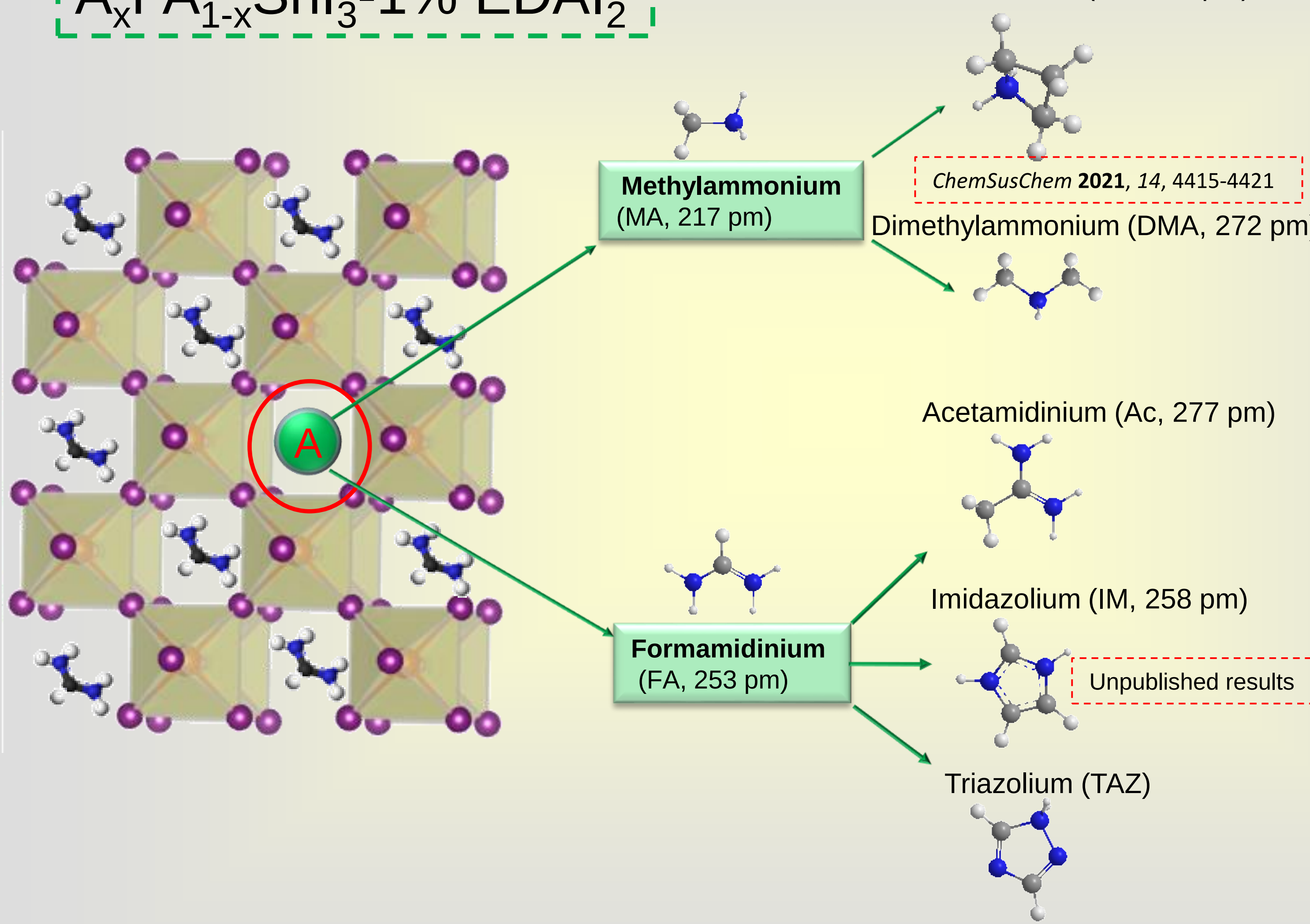
The Issue of Stability

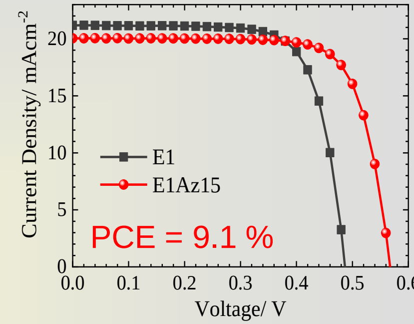


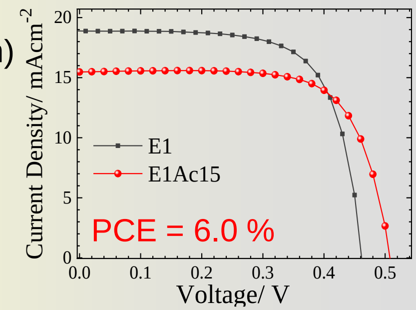
Adv. Mater. **2019**, *19*, 1804835.

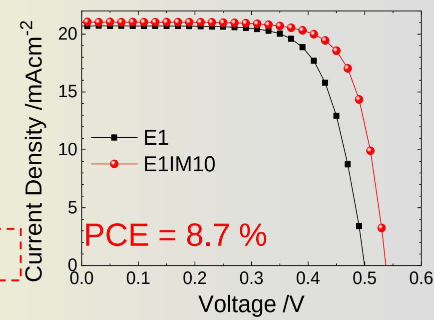
Other Potential Organic Cations/co-cations

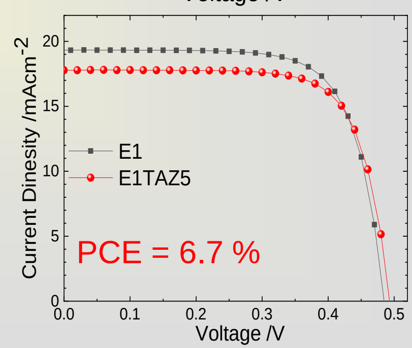
$A_xFA_{1-x}SnI_3$-1% $EDAI_2$







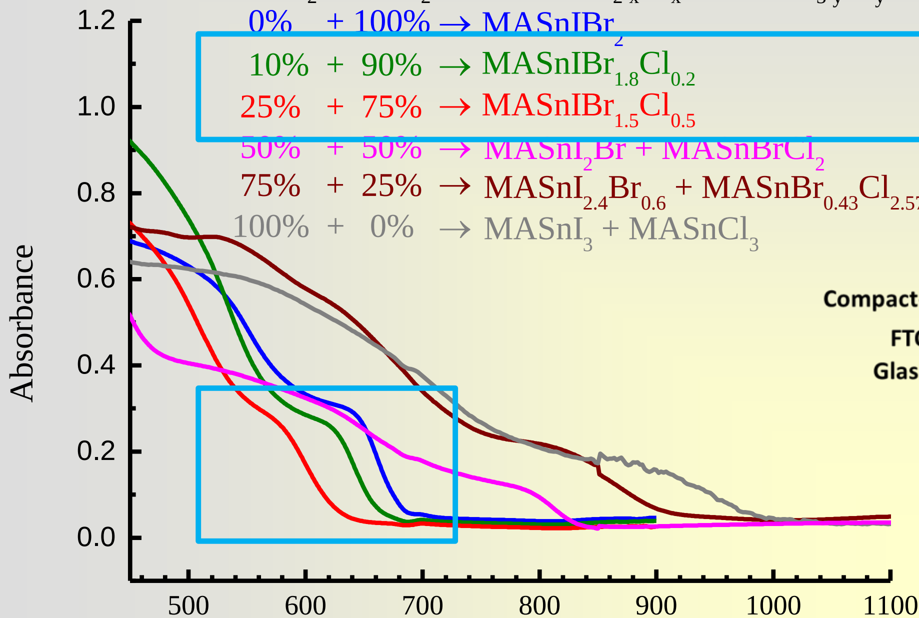




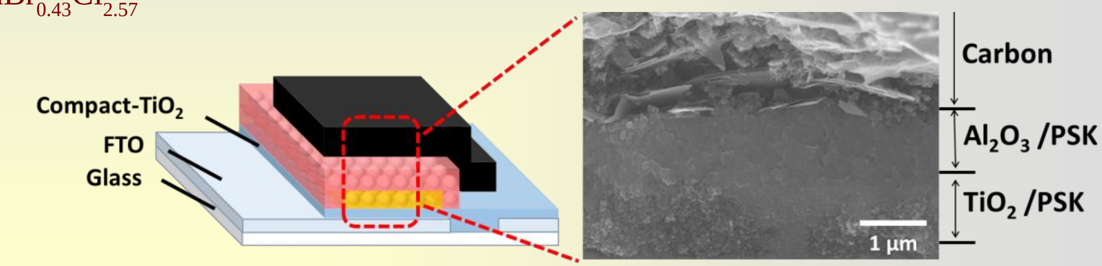
Design of Mixed Tri-halide Tin Perovskites

(a)

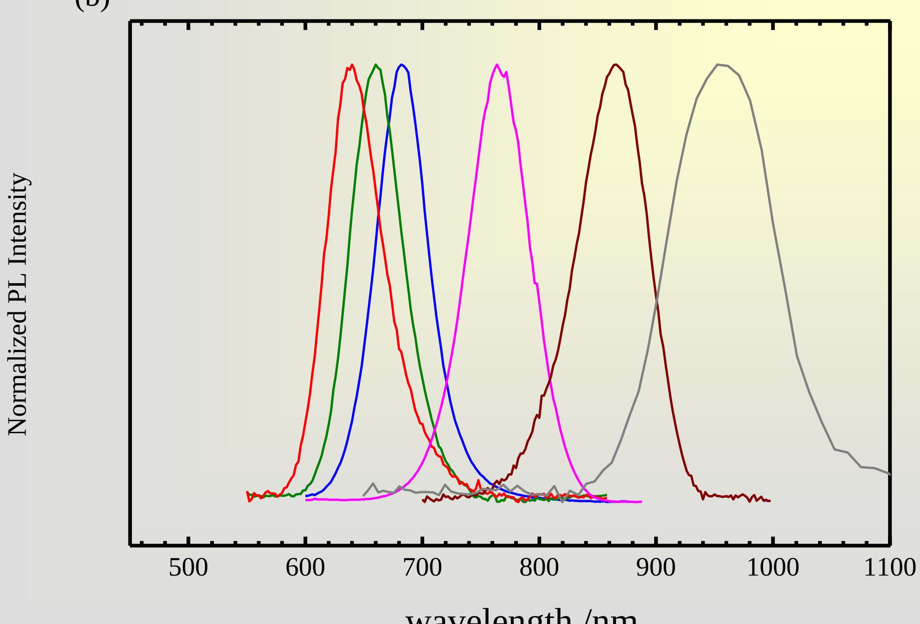
$MAI + SnCl_2 + SnBr_2 \rightarrow MASnIBr_{2-x}Cl_x$ or $MASnI_{3-y}Br_y$ / $MASnBr_zCl_{3-z}$

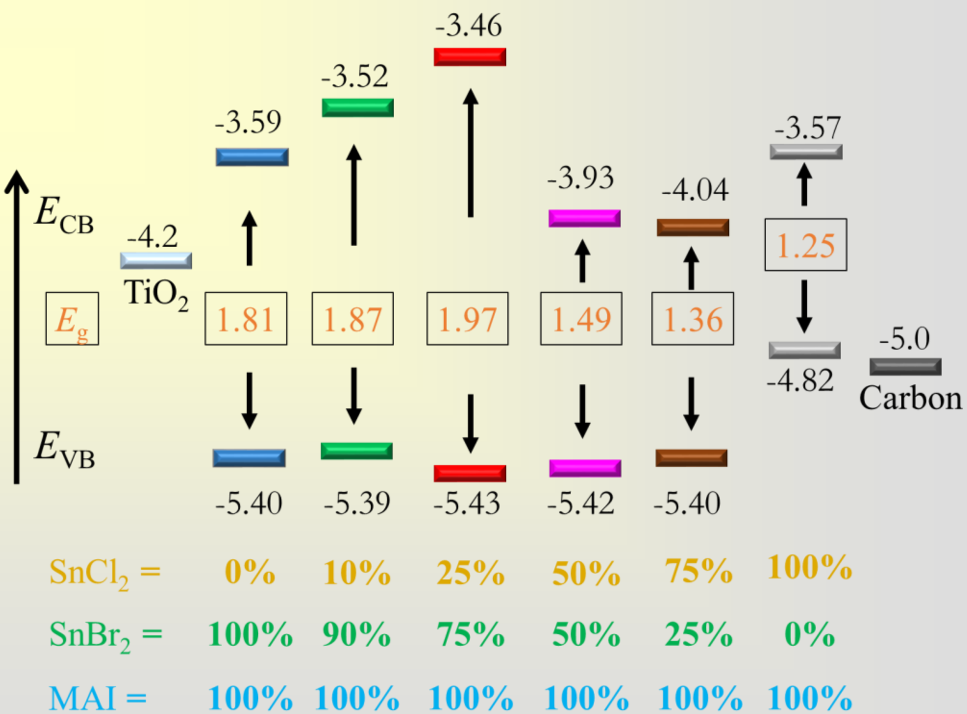


Mixed tri-halide tin perovskites



(b)





Angew. Chem. Int. Ed. **2017**, *56*, 13819-13823.

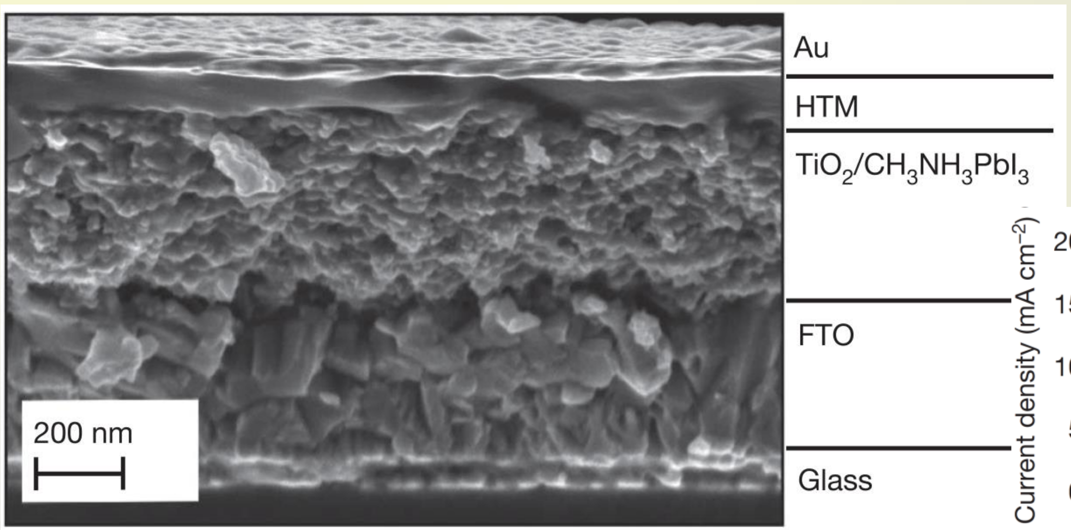
A Two-step Approach for Pb PSC

LETTER

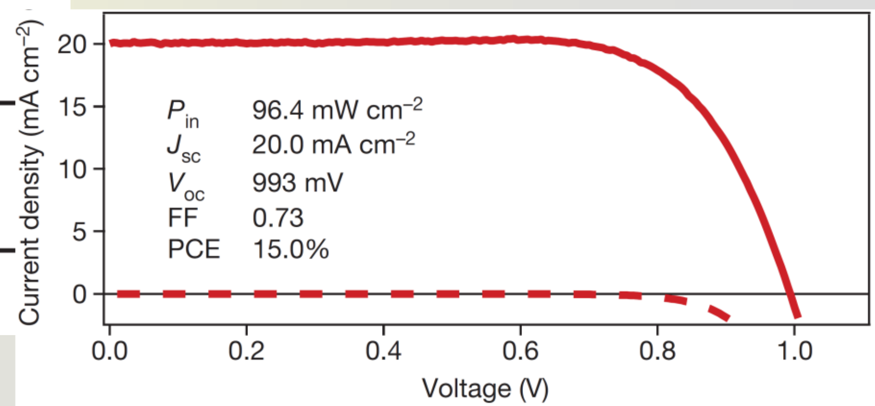
doi:10.1038/nature12340

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

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



Nature **2013**, *499*, 316-320



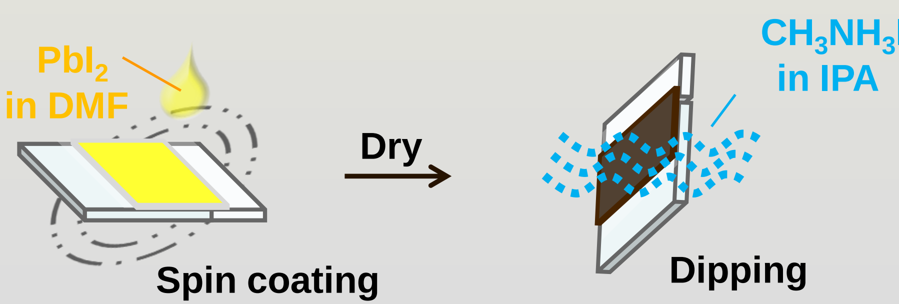
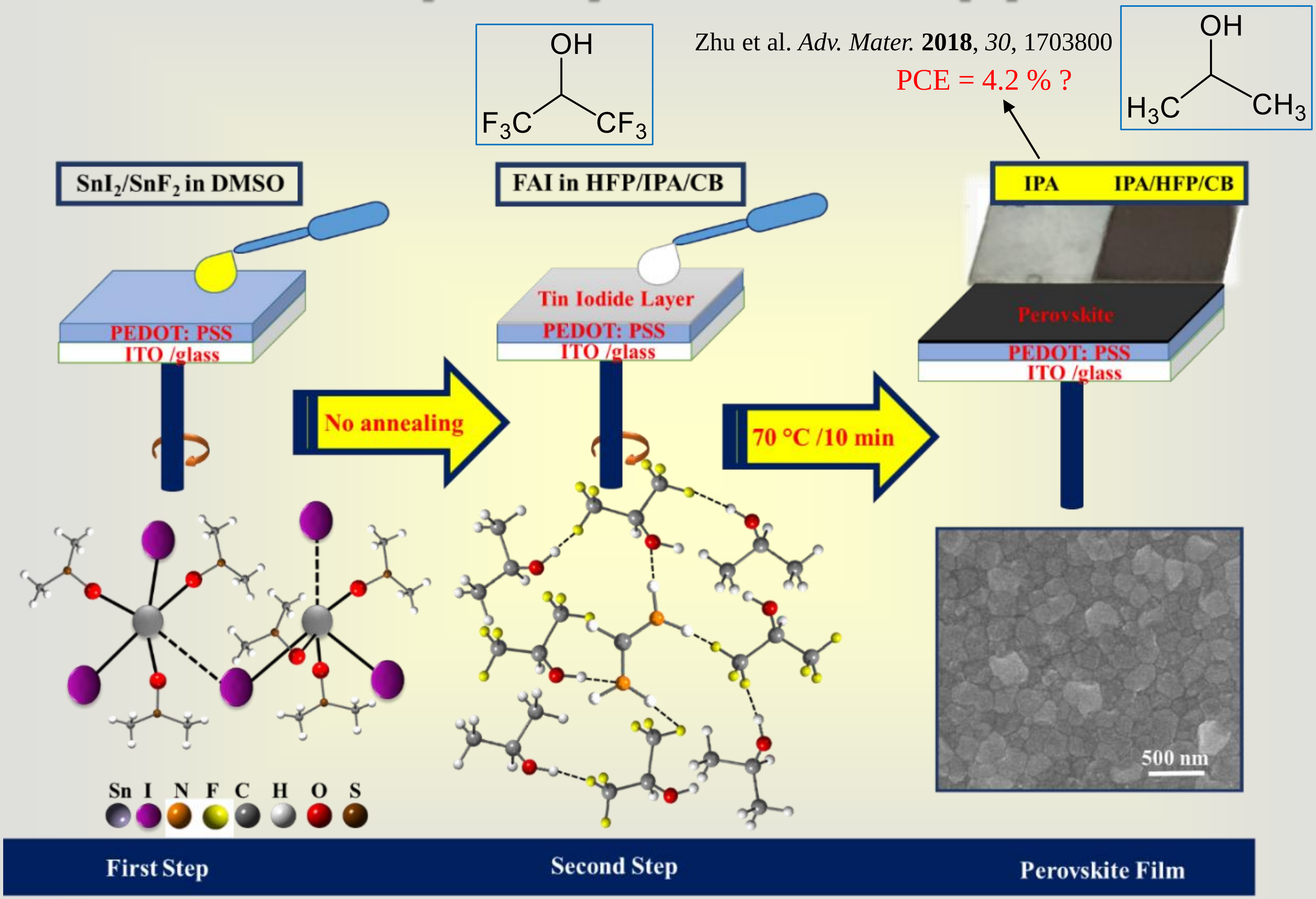


Table 1 | Photovoltaics performance at different light intensities

Intensity (mW cm^{-2})	J_{sc} (mA cm^{-2})	V_{oc} (mV)	Fill factor	PCE (%)
9.3	1.7	901	0.77	12.6
49.8	8.9	973	0.75	13.0
95.6	17.1	992	0.73	12.9

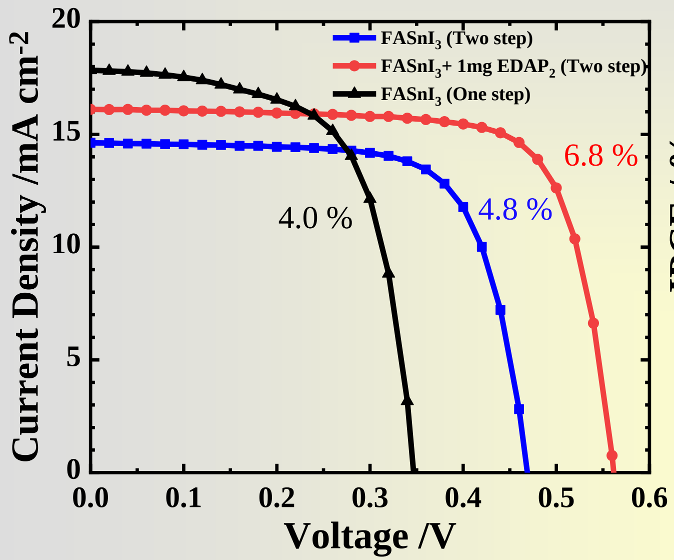
A Two-Step Deposition Approach

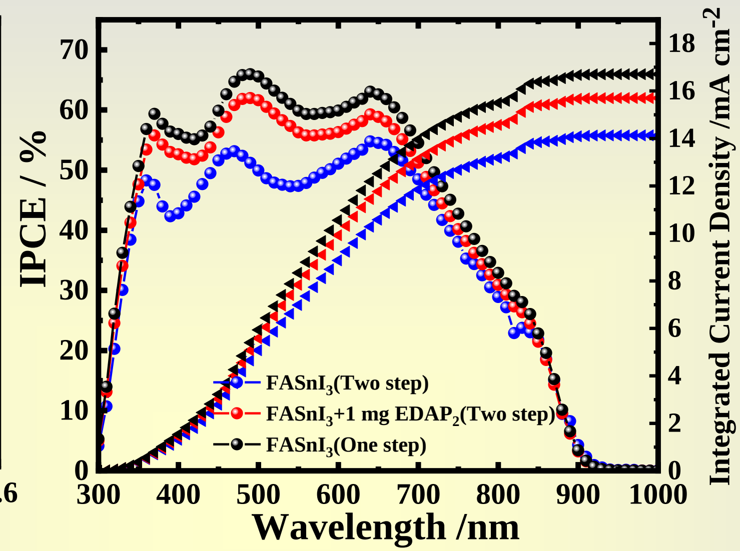


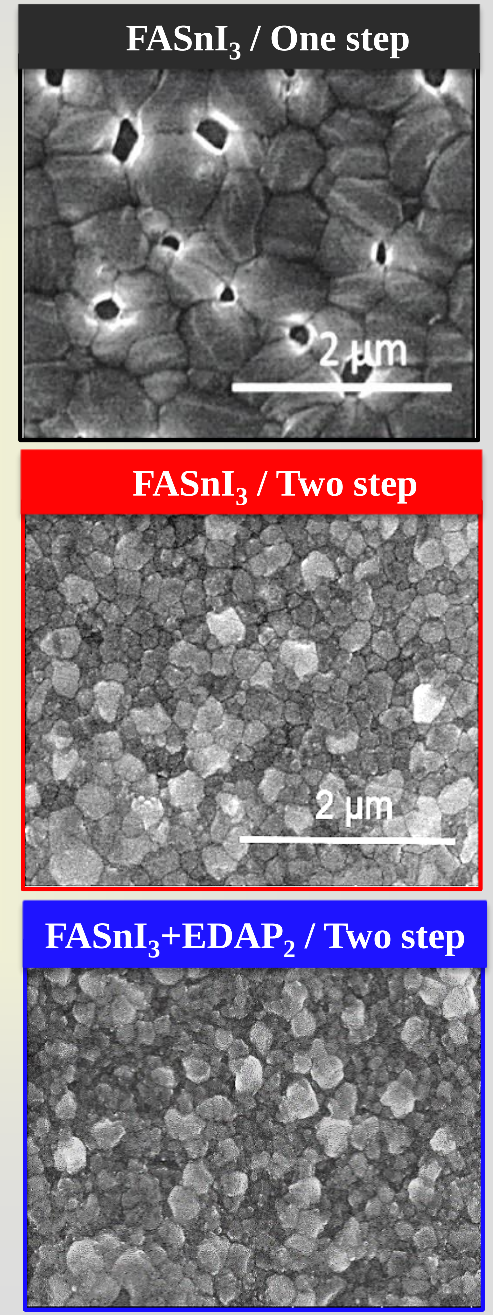
The key issue is the SOLVENT used in the second step!

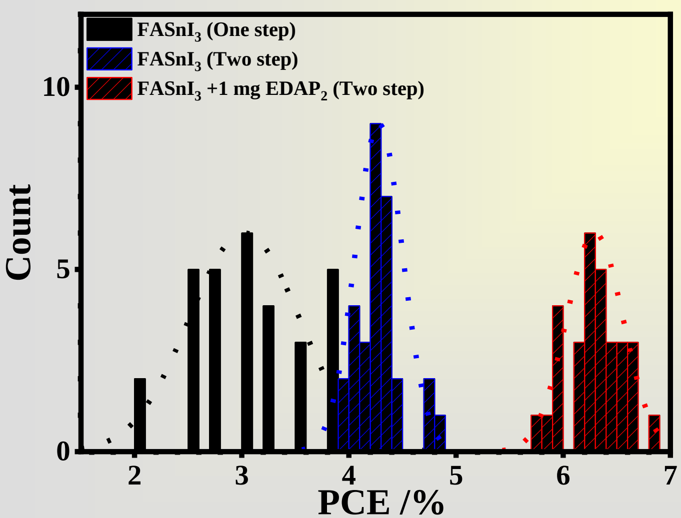
ACS Energy Lett. **2020,** *5*, 2508-2511.

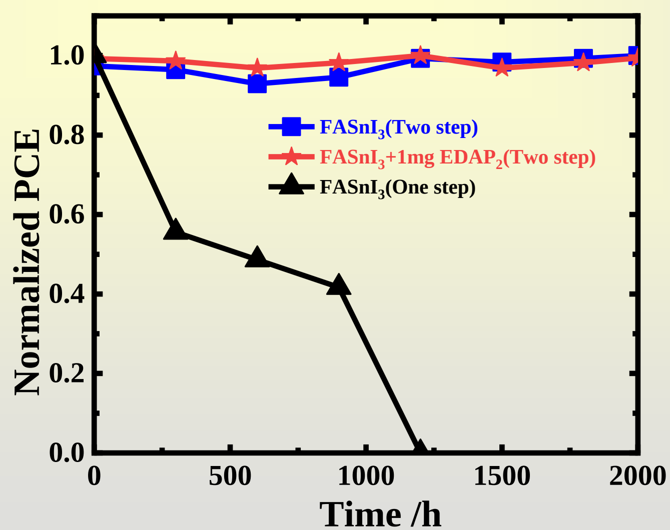
Enhanced Device Performance and Stability





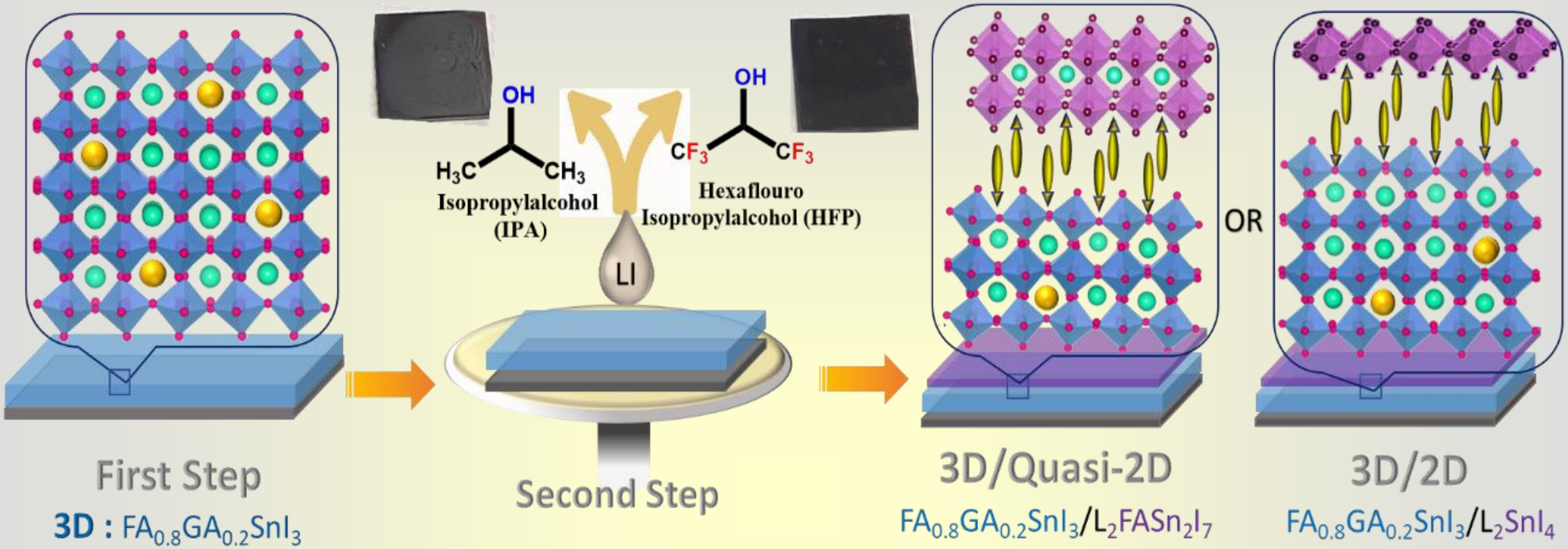


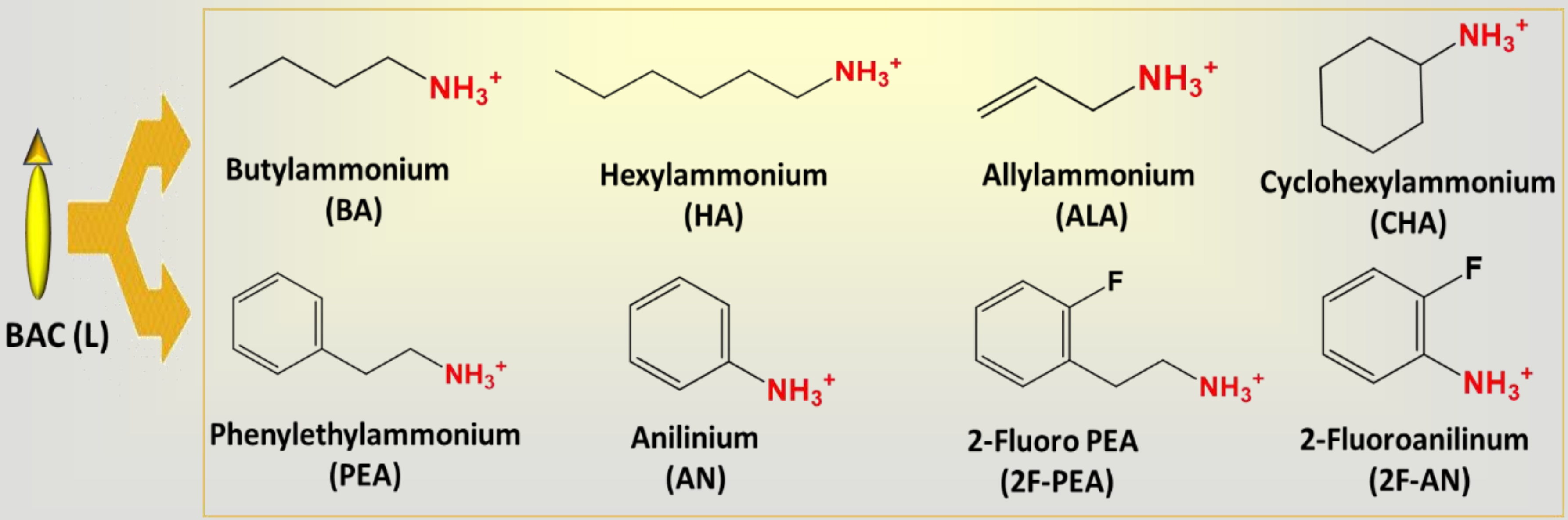




ACS Energy Lett. **2020,** *5,* 2508-2511.

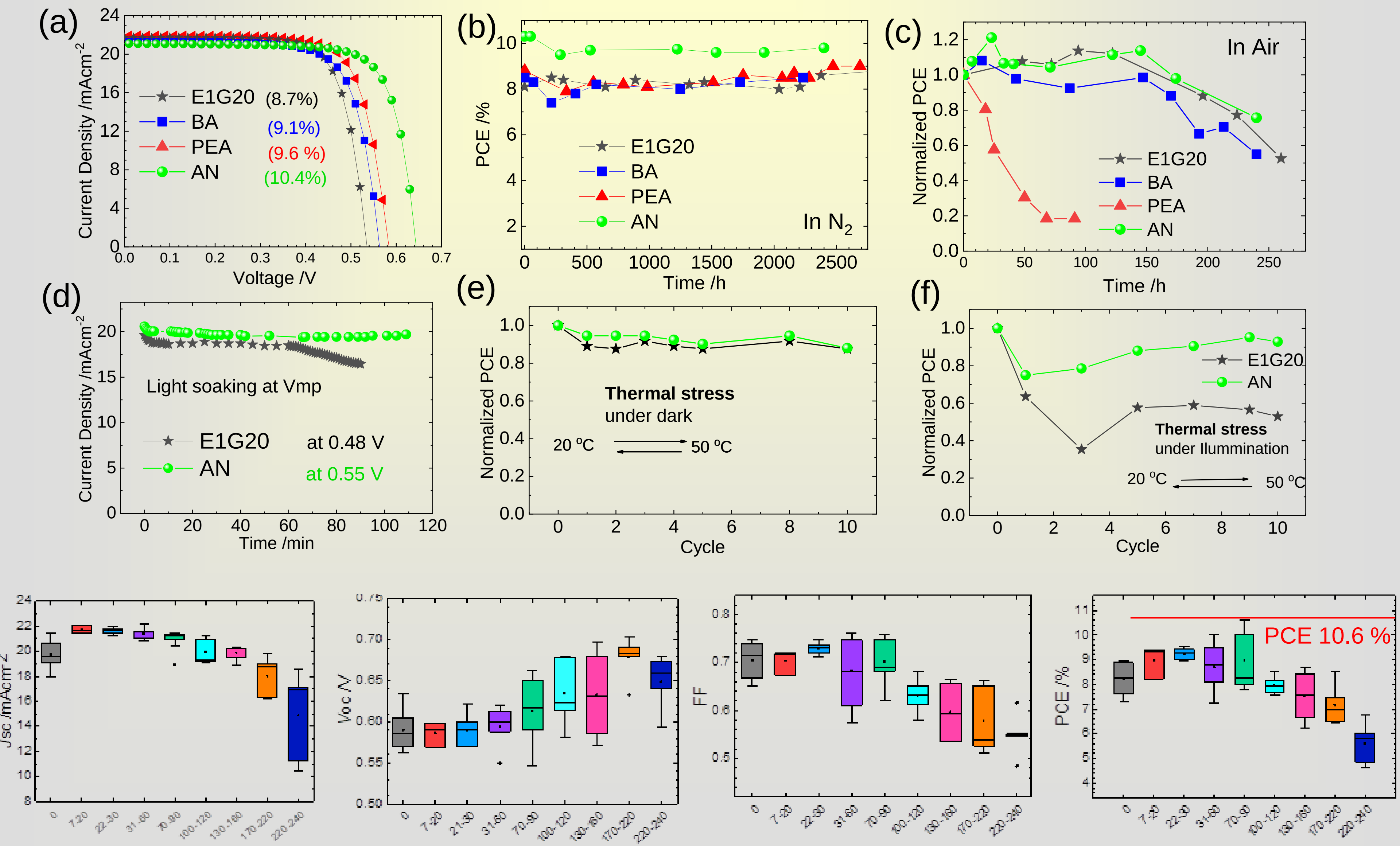
The 3D/2D Structure via Two-Step Approach





ACS Energy Lett. **2021,** *6,* 485-492.

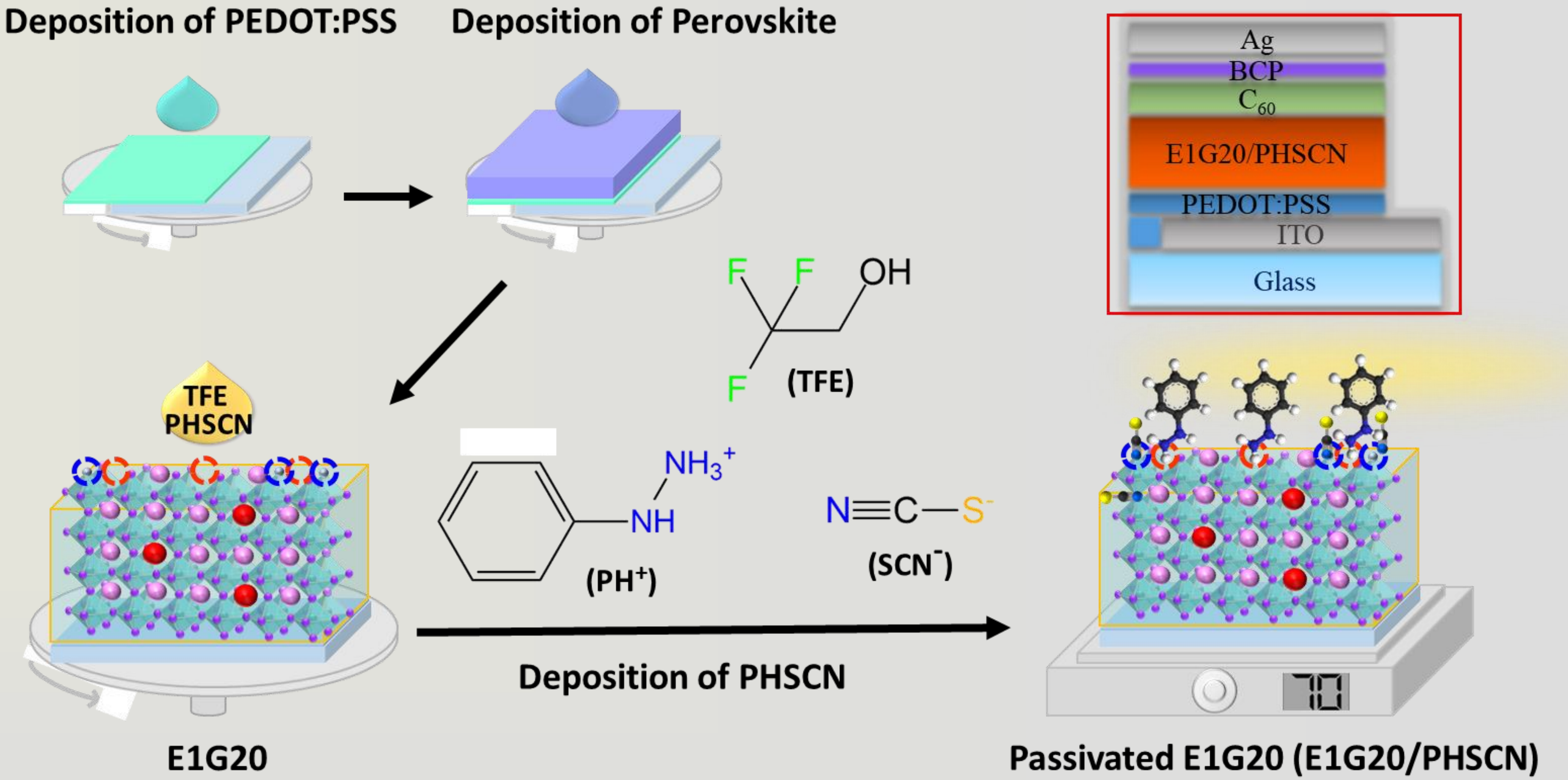
Photovoltaic Properties and Stability



ACS Energy Lett. **2021,** *6,* 485-492.

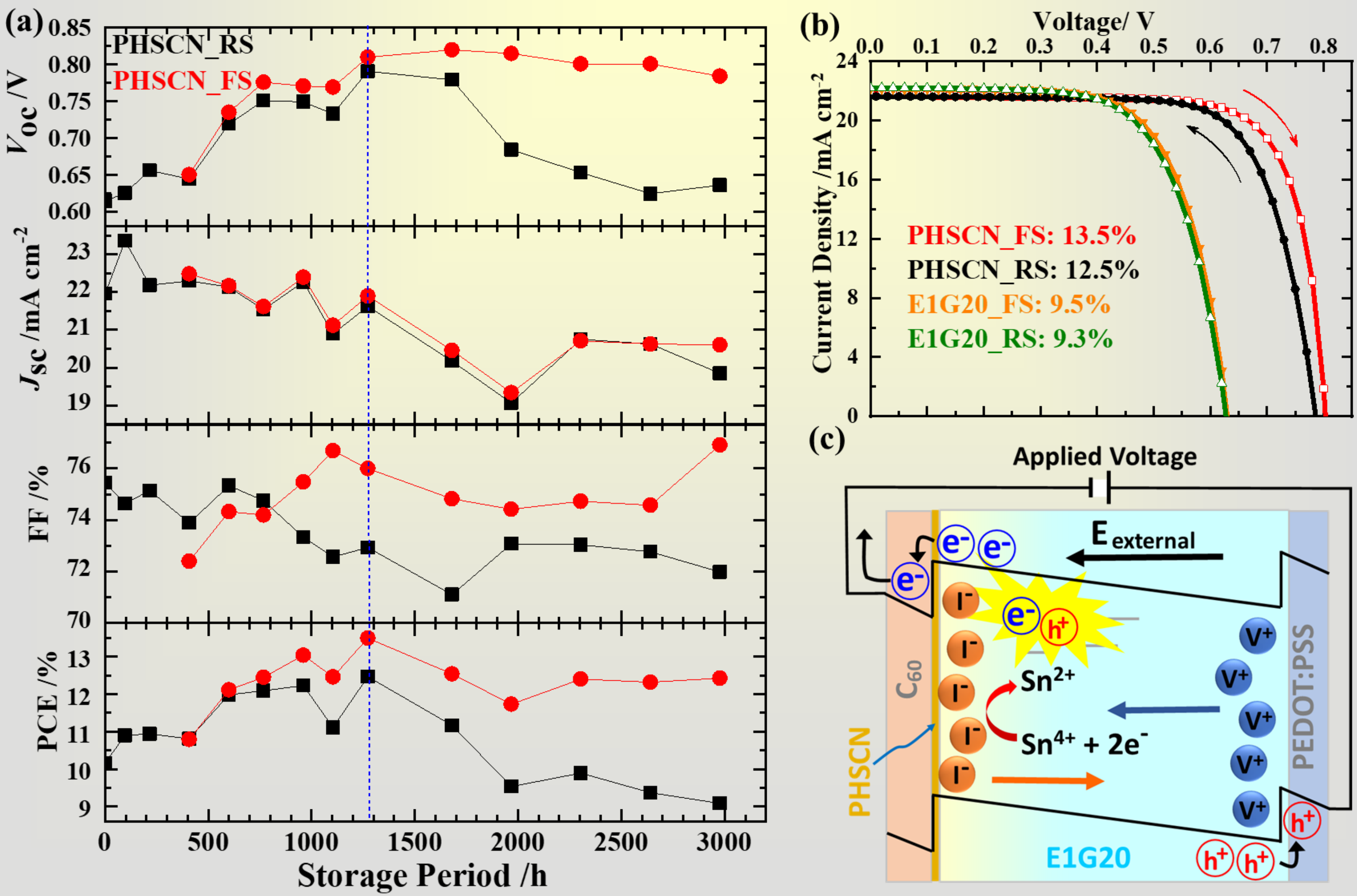
Storage in air without encapsulation (Time /h)

Surface Passivation via Phenylhydrazinium Thiocyanide (PHSCN)



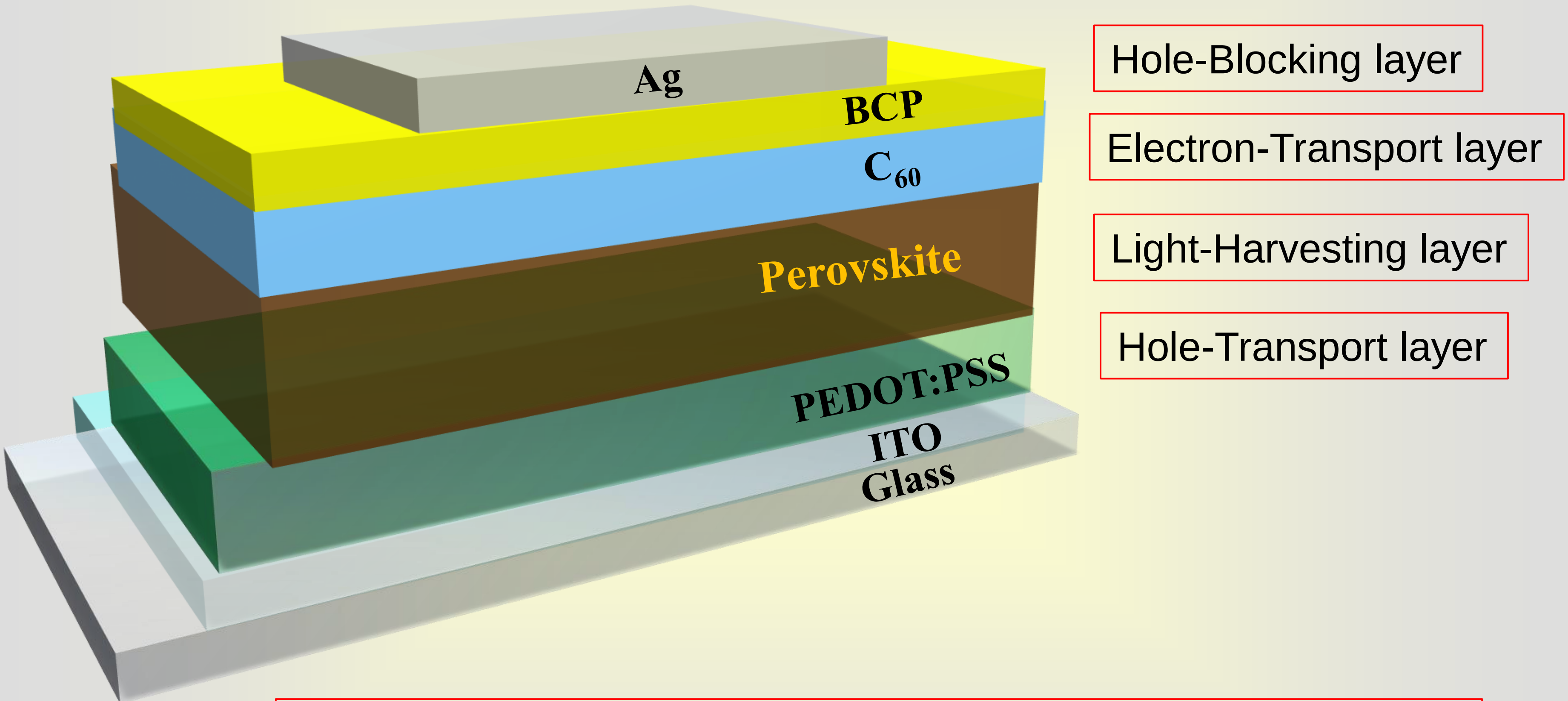
J. Phys. Chem. Lett. **2021**, *12*, 10106-10111.

Inverted Hysteresis and Device Performance



J. Phys. Chem. Lett. **2021**, *12*, 10106-10111.

The Device Structure of Tin Perovskite Solar Cells



1. Almost all high-performance TPSC use PEDOT:PSS as HTL.
2. Only one-step fabrication method was applied.
3. Only Inverted device configuration was considered.

Why only PEDOT:PSS was used as HTL for TPSC?

1. The reaction between SnI_2 and FAI is very rapid.
2. DMSO was used as the solvent to form adducts with SnI_2 to retard the crystal growth rate.
3. PEDOT:PSS was selected as HTL due to its hydrophilic nature.
4. The polar precursor/DMSO solution can be evenly spread on the surface of PEDOT:PSS to enhance the rate of nucleation.

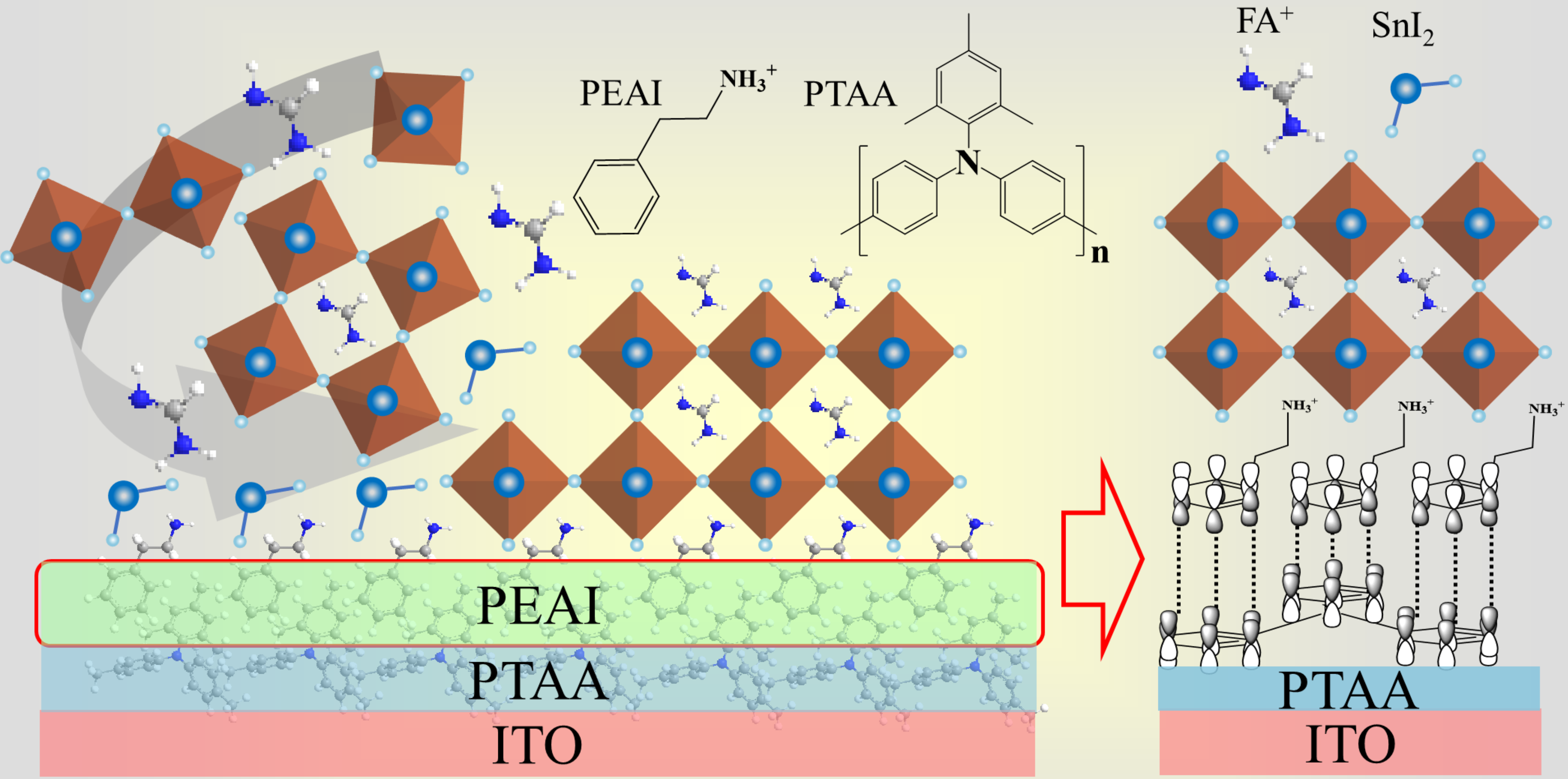
Stability Issue

PEDOT:PSS is hygroscopic so it is easy to adsorb water from the environment to degrade the device stability of a TPSC.

Solution

1. Looking for other hydrophobic HTL like PTAA as a substitute.
2. A two-step fabrication method should be applied to solve the problem.

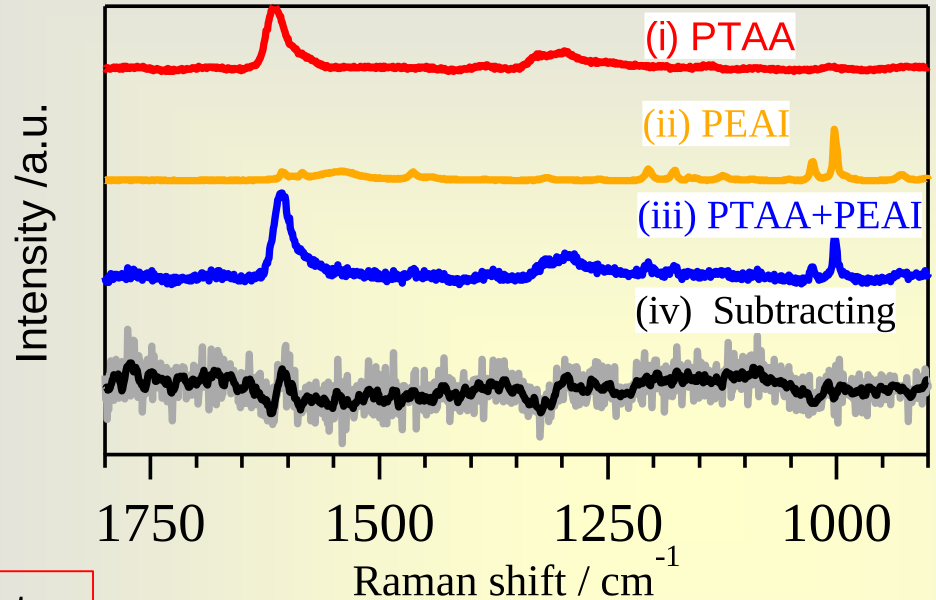
Using PTAA for Tin Perovskite Solar Cells



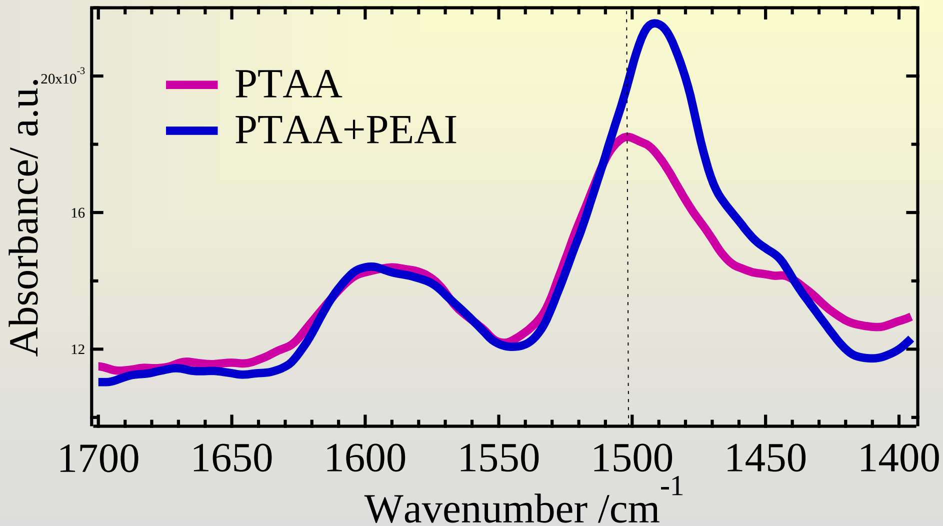
1. PTAA is a hydrophobic polymer so that a uniform TPSK film cannot be formed.
2. The PTAA surface should be modified with a suitable ligand like PEAI.
3. The π–π interaction between PTAA and PEAI plays an important role.

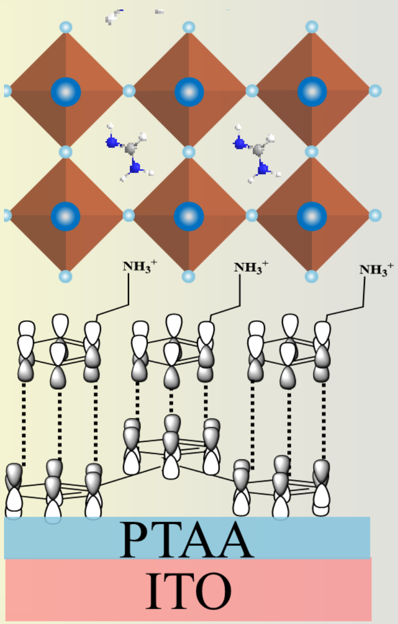
The Evidence of π–π Interaction – Raman Spectra

Raman spectra



FTIR spectra

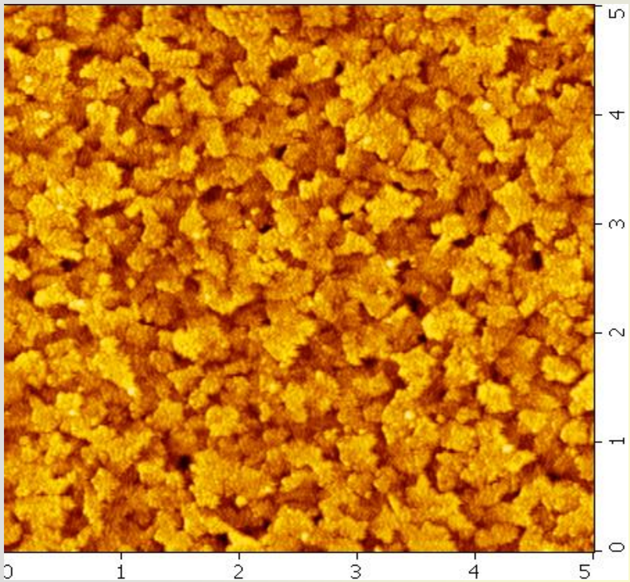




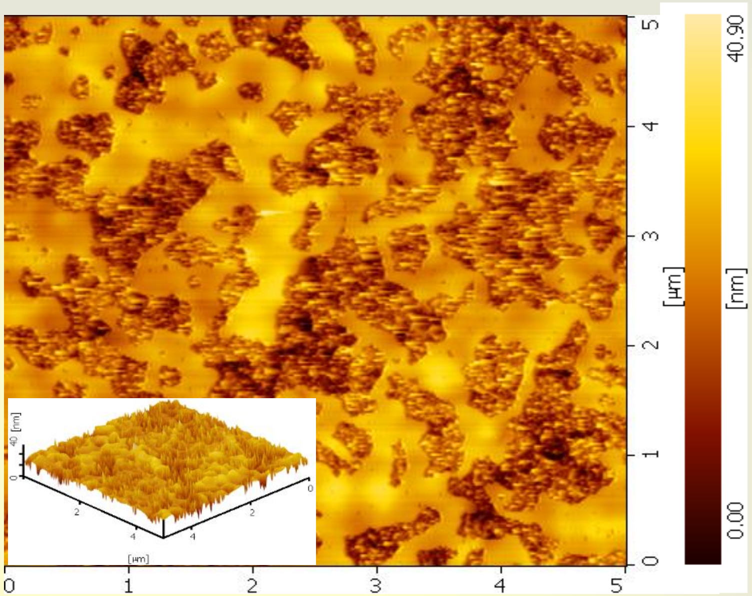
Unpublished Results

Surface Modification of PTAA with PEAI

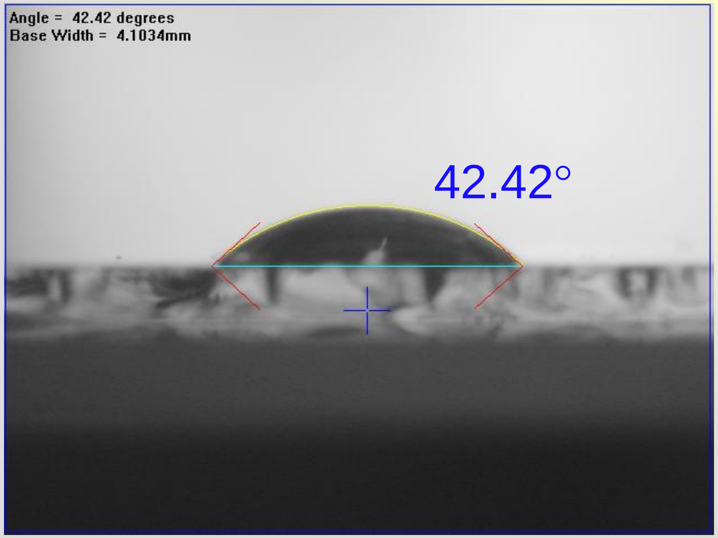
Without PEAI

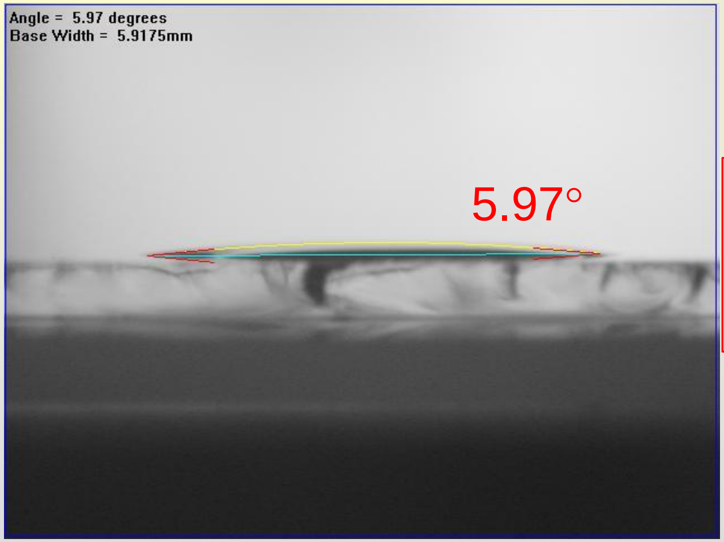


With PEAI



AFM images of PTAA film





Contact angles of precursor Solution on PTAA

Unpublished Results

Surface Morphology of TPSK Made on PTAA

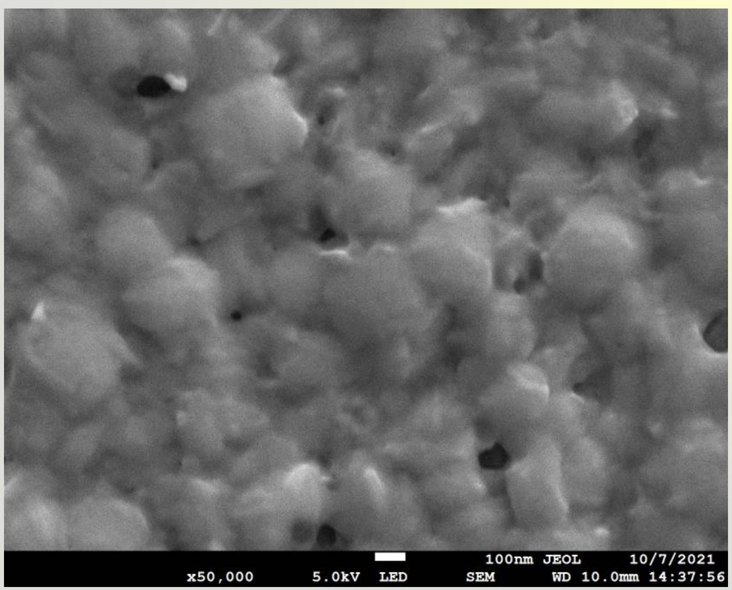
Without PEAI

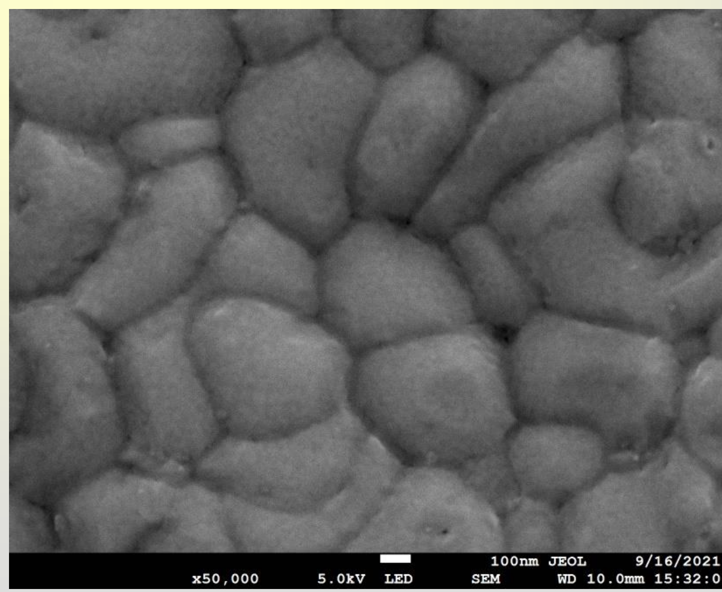
With PEAI

One-step fabrication

Photo images of TPSK

Two-step fabrication



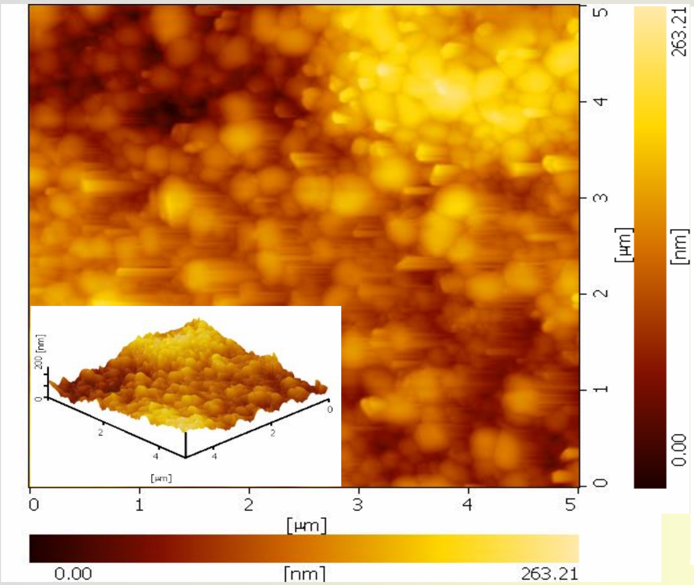


SEM images of TPSK made on PTAA via a two-step approach

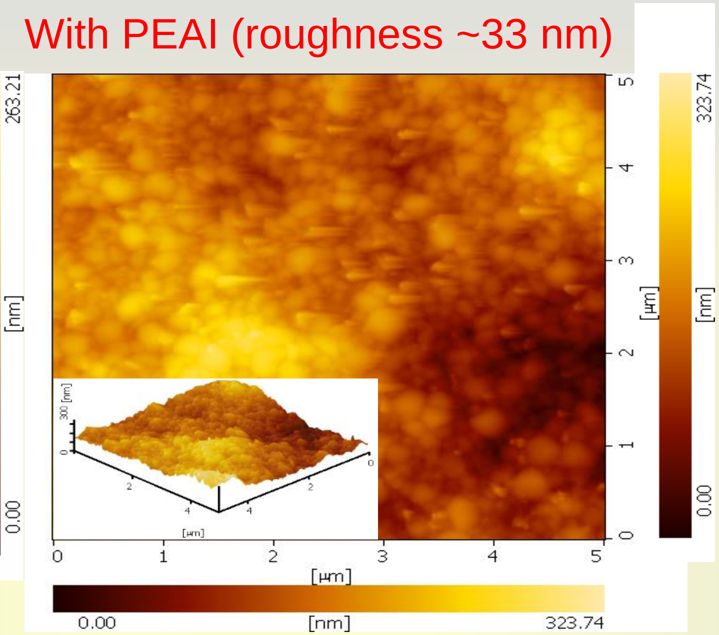
Unpublished Results

Surface Morphology of TPSK Made on PTAA

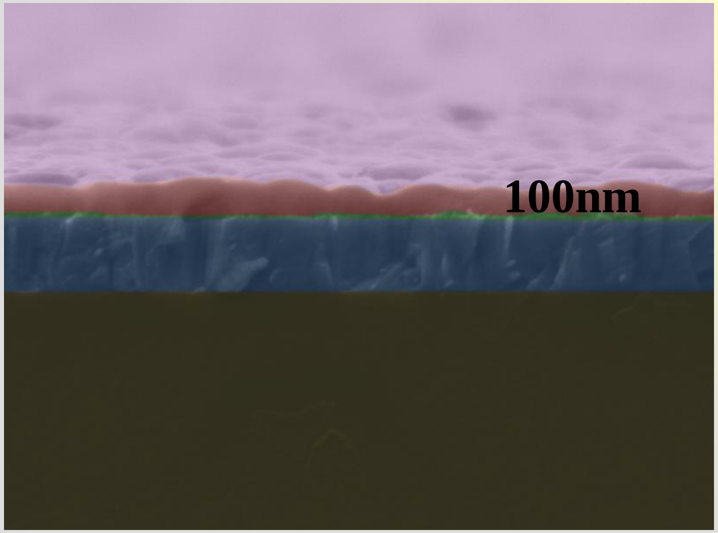
Without PEAI (roughness ~45 nm)

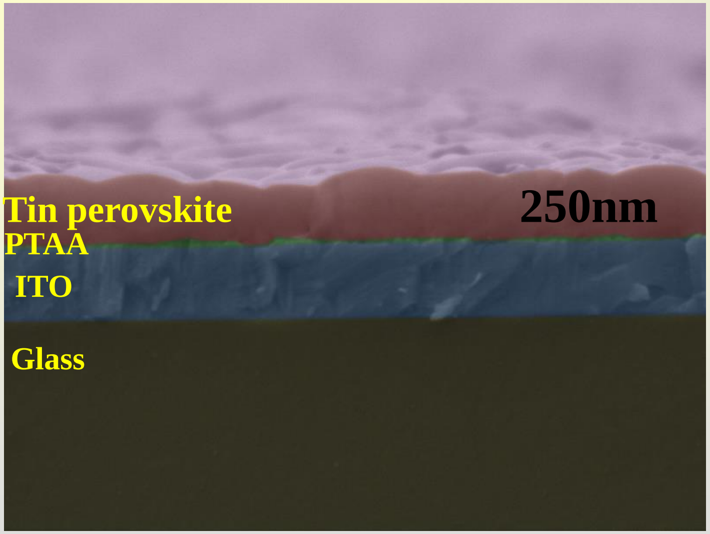


With PEAI (roughness ~33 nm)



AFM images of TPSK made on PTAA via a two-step approach

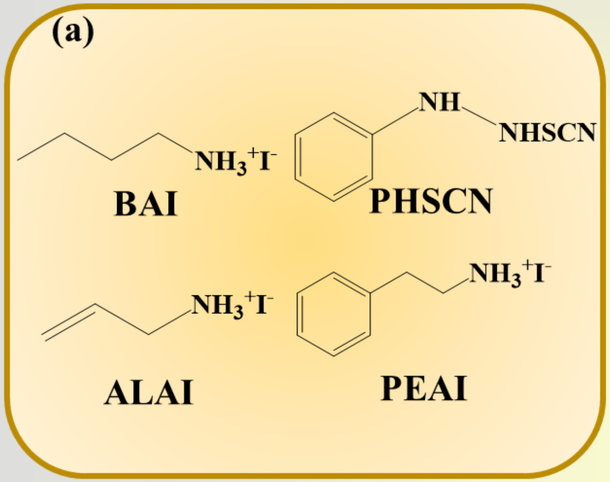


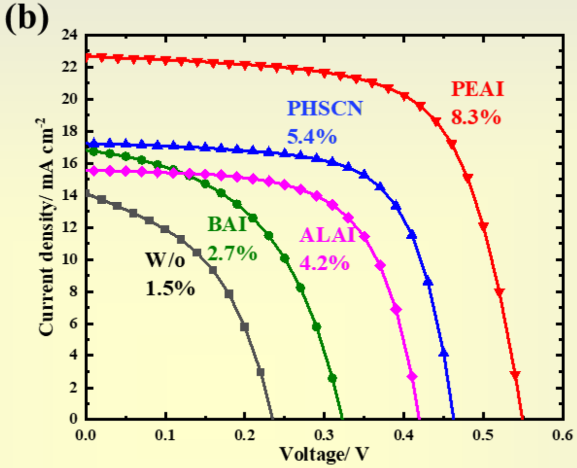


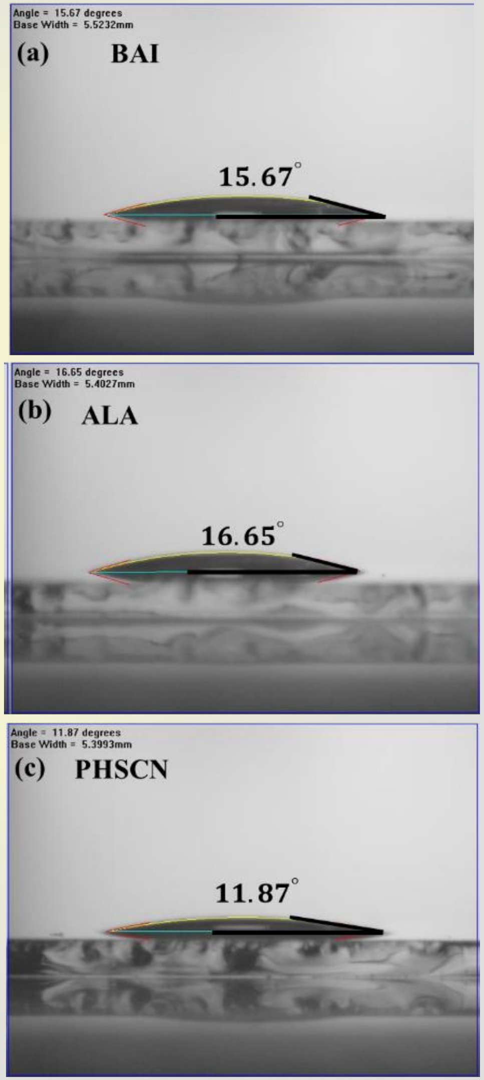
SEM side-view images of TPSK made on PTAA via a two-step approach

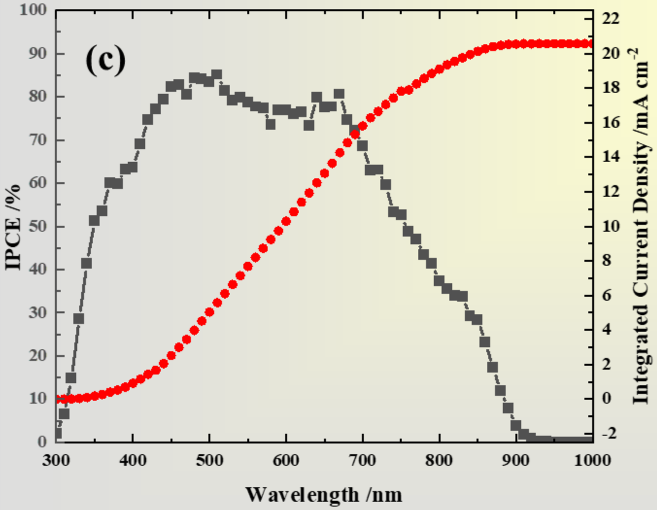
Unpublished Results

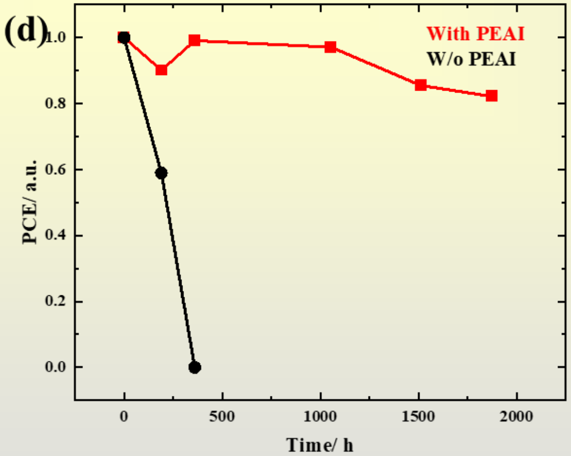
Using PTAA for Tin Perovskite Solar Cells





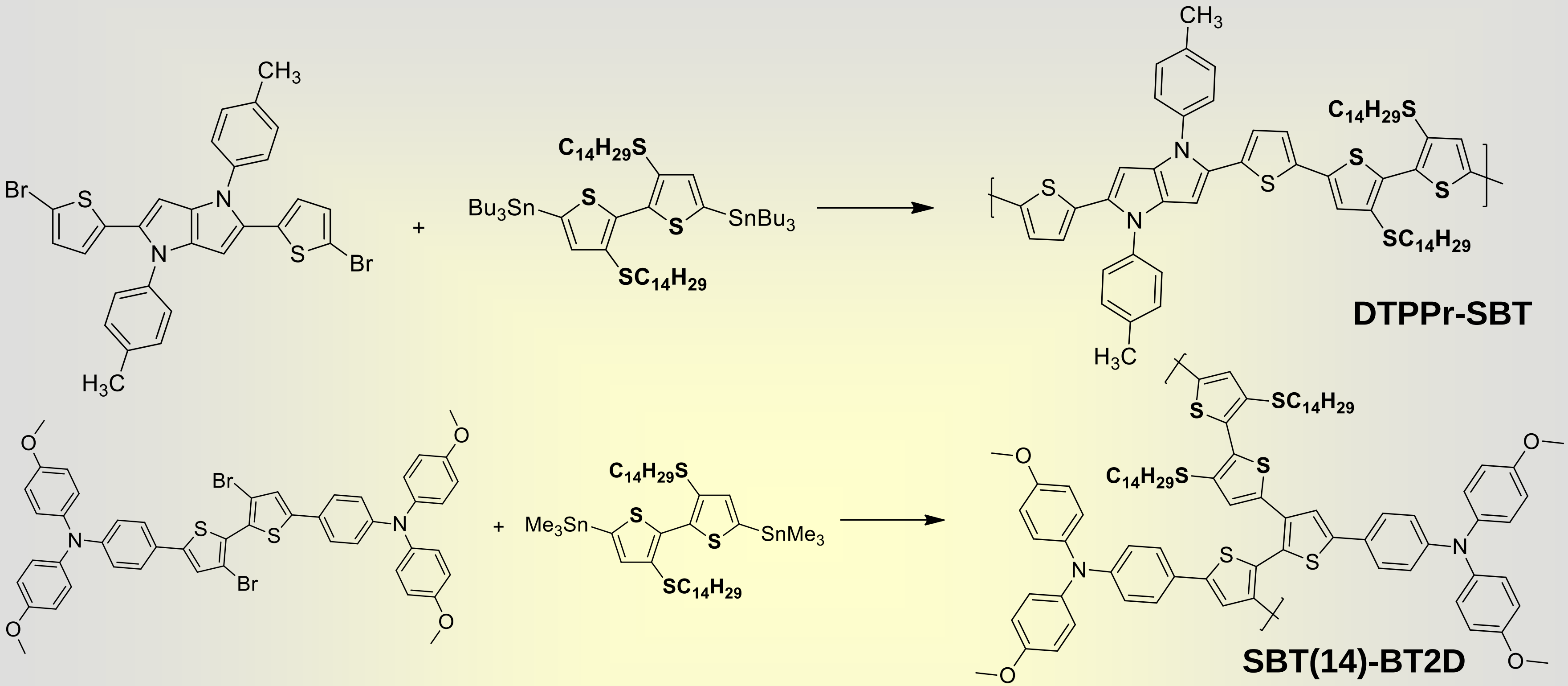


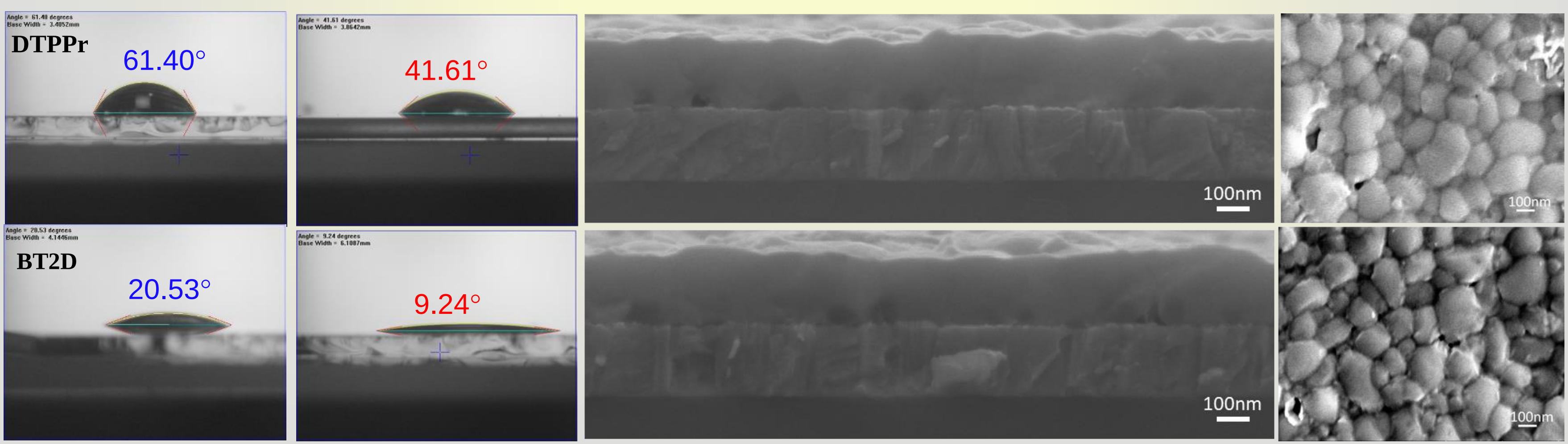




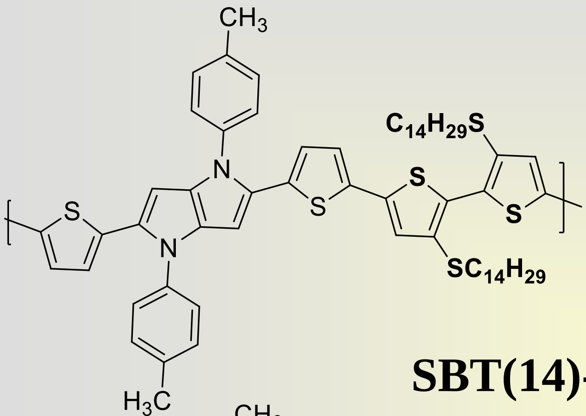
Unpublished Results

New Thiophene-based Polymers as HTM for Tin PSC

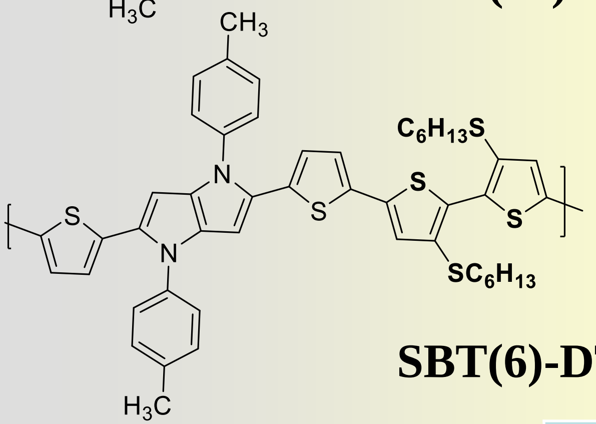




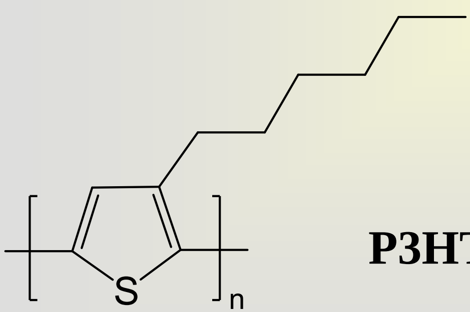
New Thiophene-based Polymers as HTM for Tin PSC



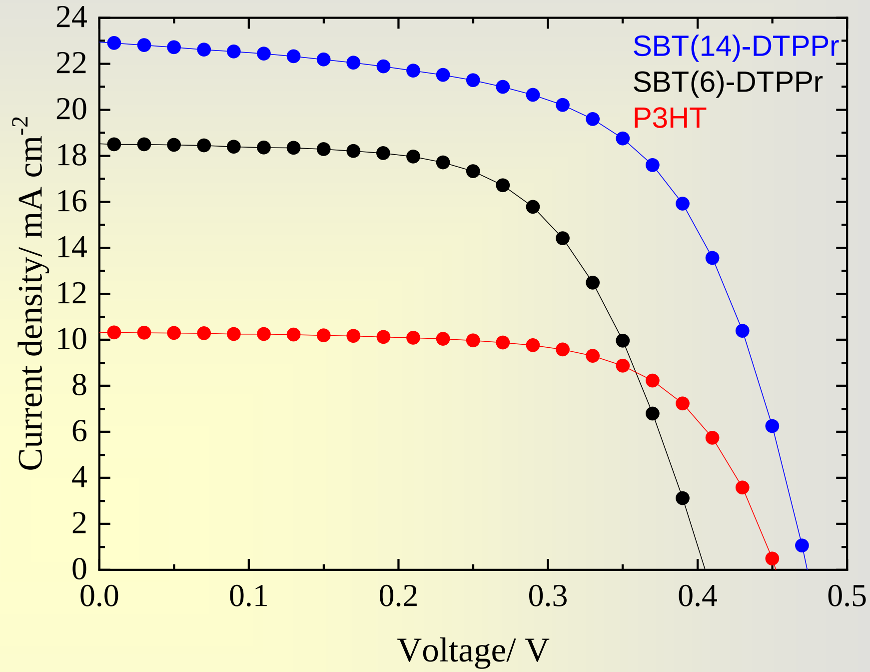
SBT(14)-DTPPr



SBT(6)-DTPPr



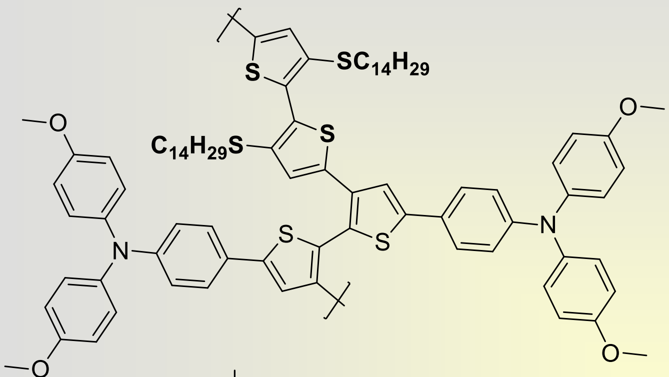
P3HT



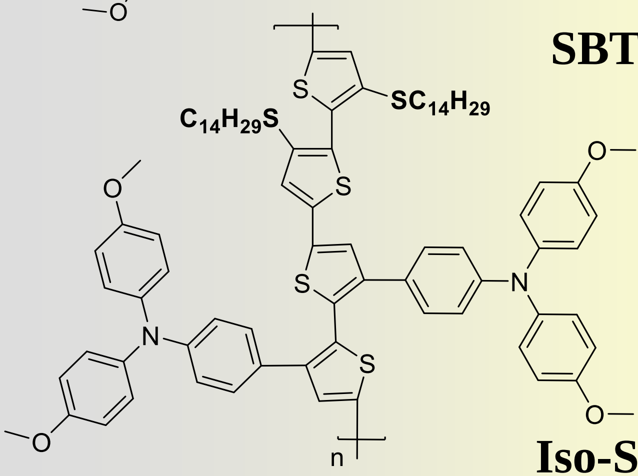
	*J*sc /mA cm^{-2}	*V*oc /V	FF /%	PCE /%
P3HT	10.32	0.45	66.5	3.1
SBT(14)-DTPPr	22.95	0.47	60.4	6.6
SBT(6)-DTPPr	18.51	0.41	60.7	4.6

Unpublished Results

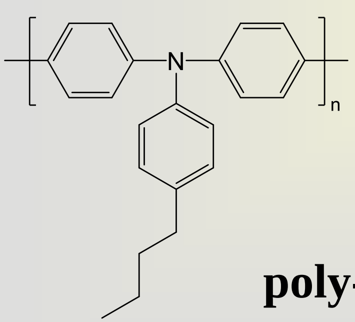
New Thiophene-based Polymers as HTM for Tin PSC



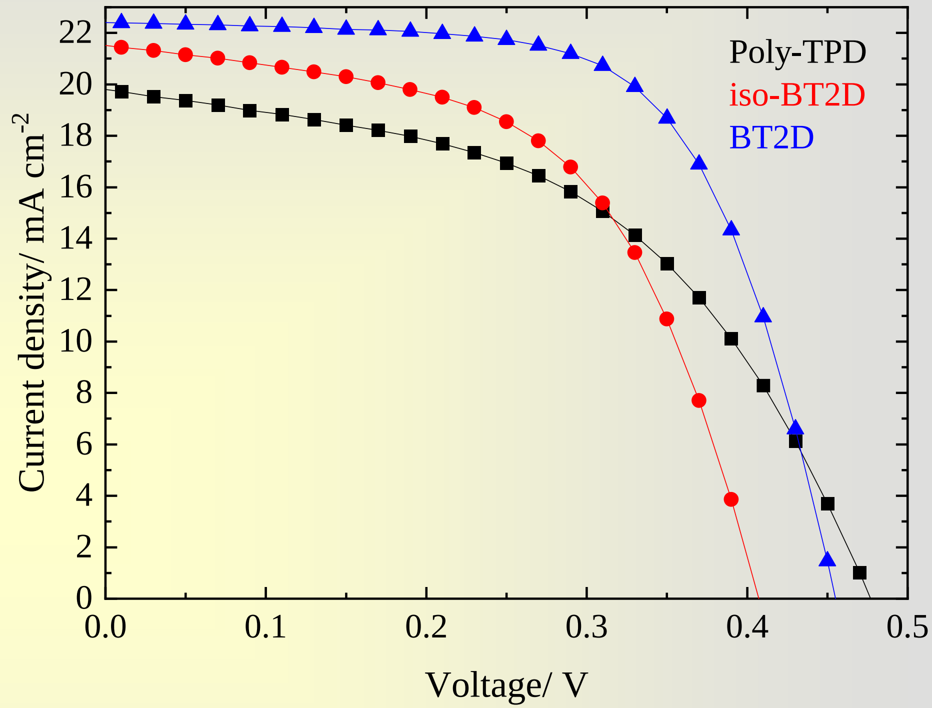
SBT(14)-BT2D



Iso-SBT(14)-BT2D



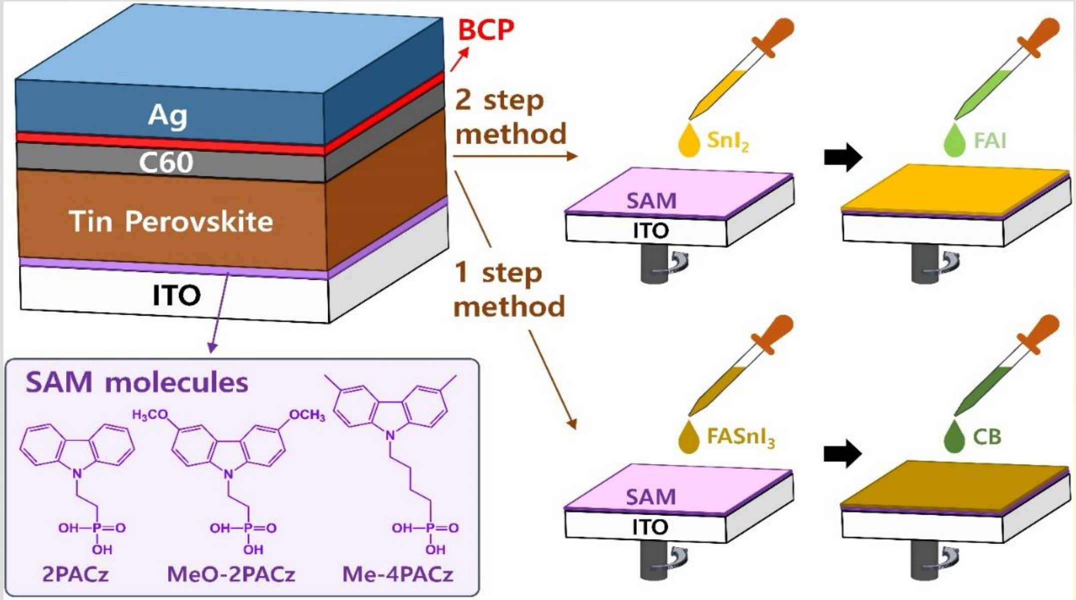
poly-TBD

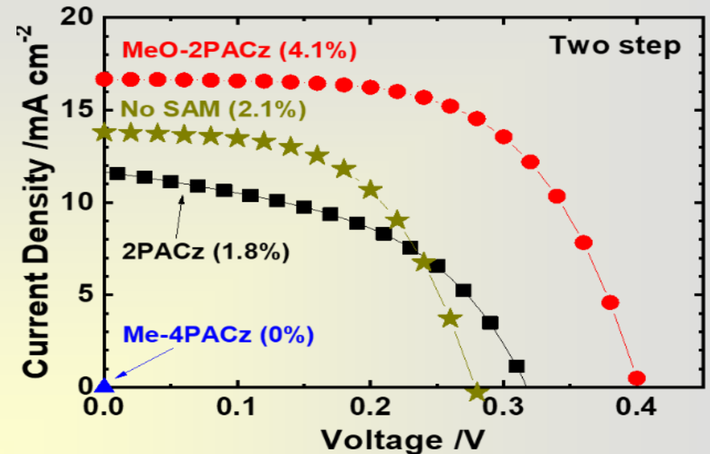


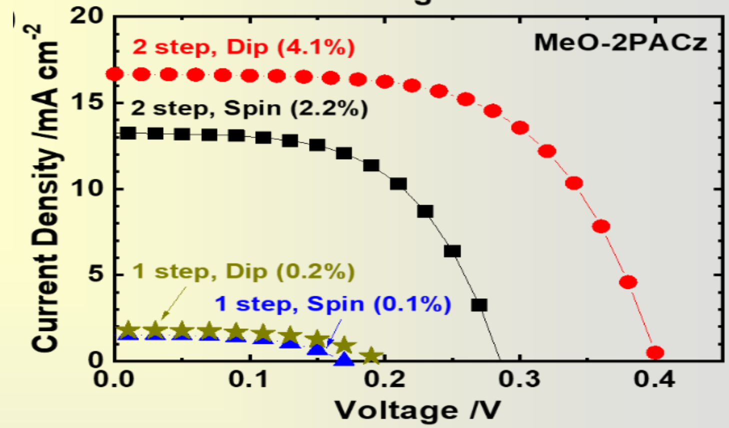
	Jsc /mA cm^{-2}	*Voc* /V	FF /%	PCE /%
BT2D	**22.67**	**0.46**	**64.5**	**6.7**
iso-BT2D	**21.50**	**0.41**	**55.2**	**4.9**
poly-TBD	**19.79**	**0.48**	**49.5**	**4.7**

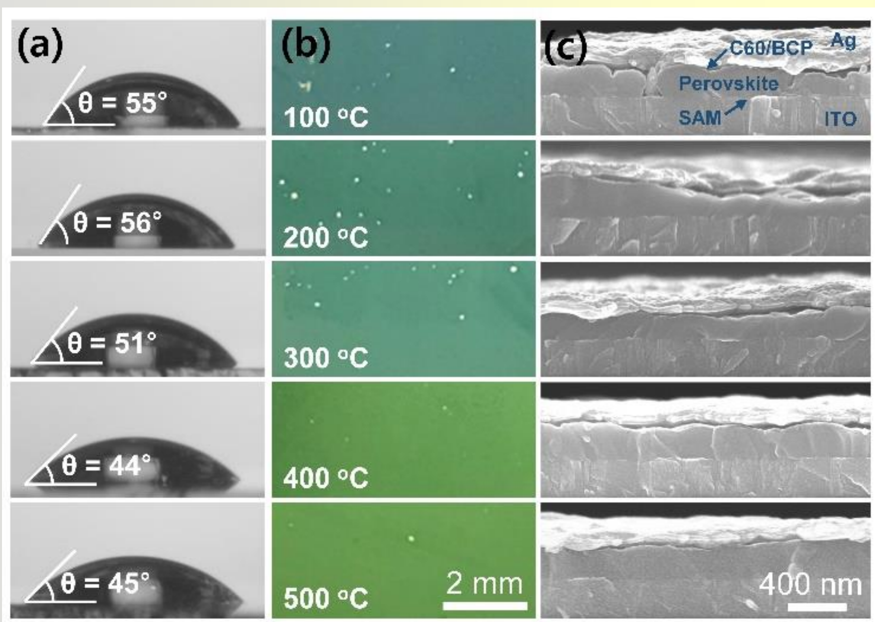
Unpublished Results

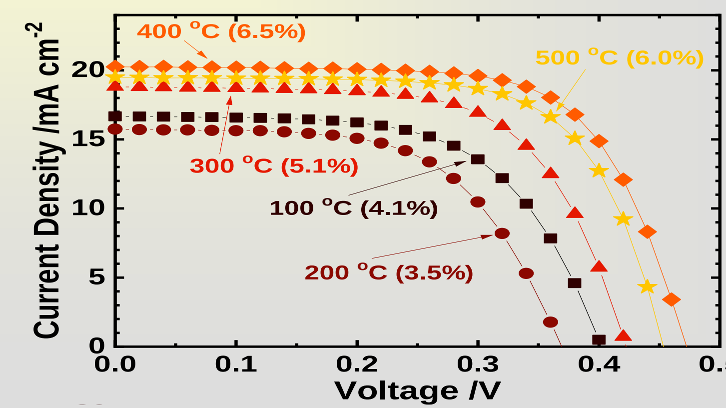
Application of SAM for Tin Perovskite Solar Cells





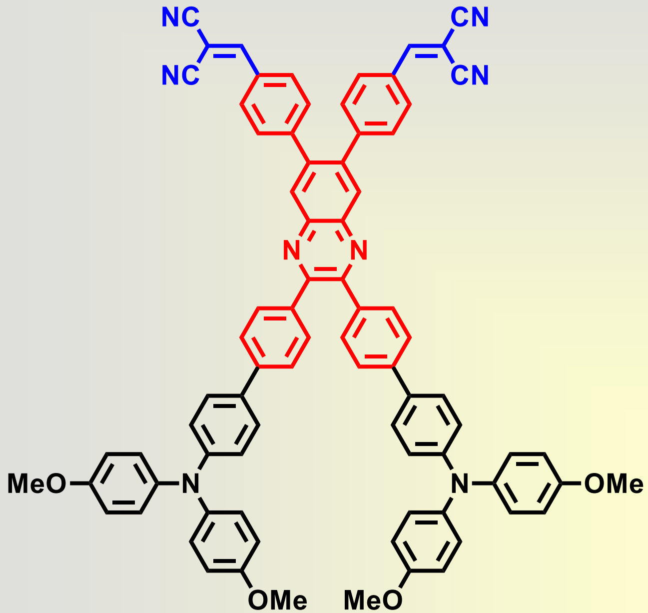




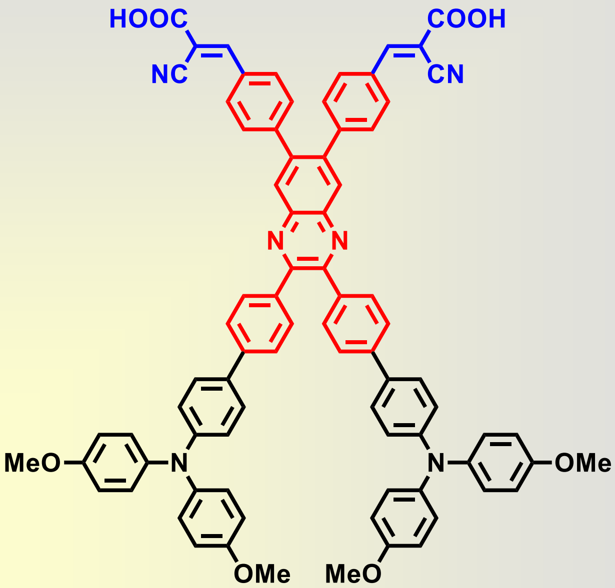


ACS Energy Lett. **2021,** *6,* 4179-4186.

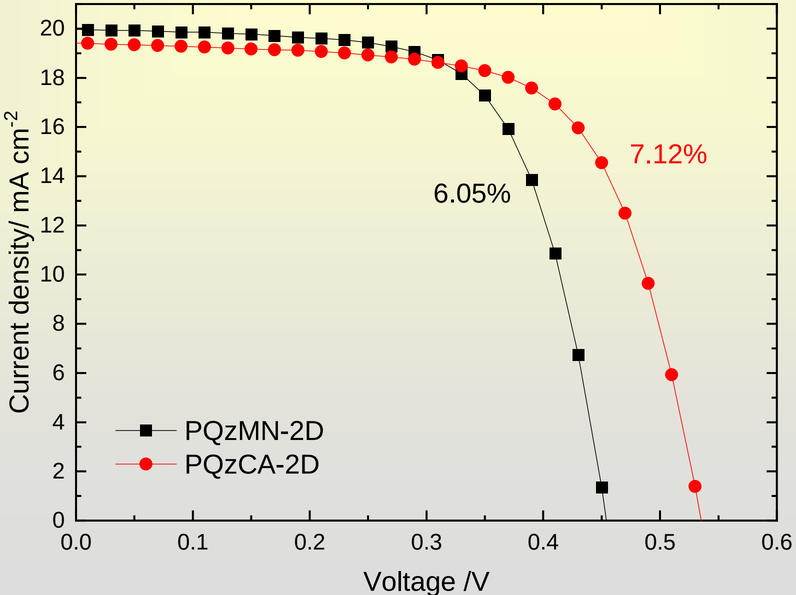
New Examples of SAM for Tin PSC



PQzMN-2D

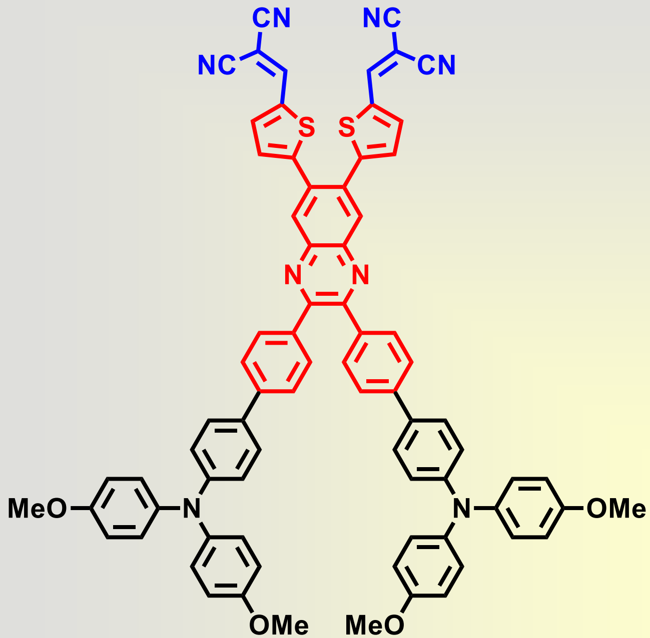


PQzCA-2D

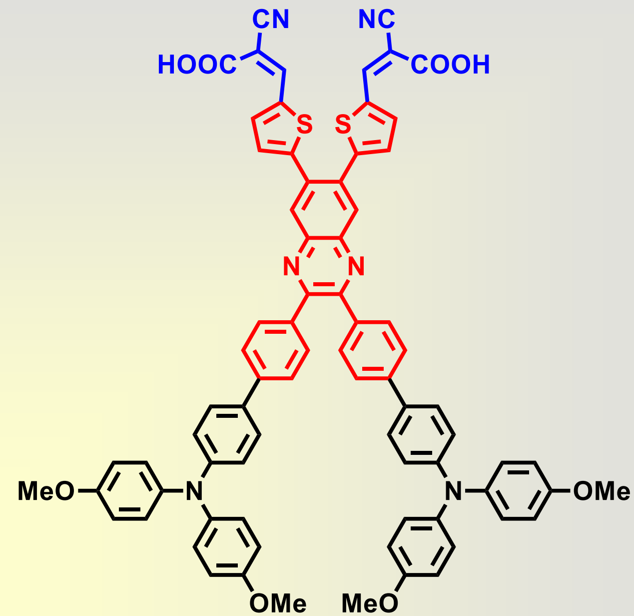


Unpublished Results

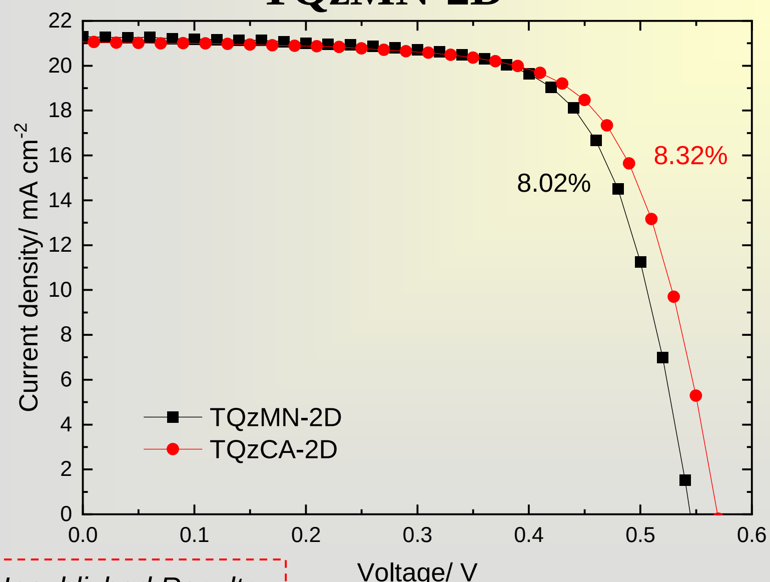
New Examples of SAM for Tin PSC

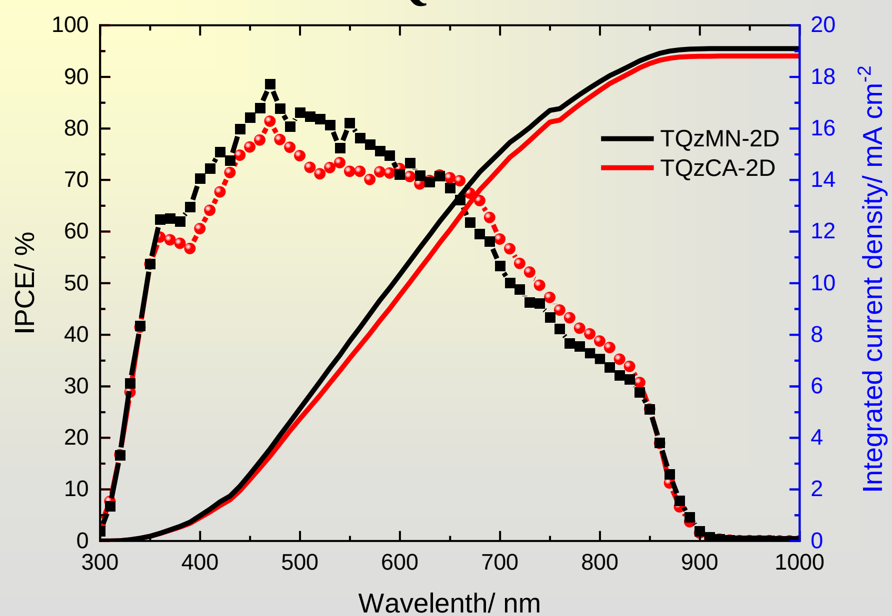


TQzMN-2D



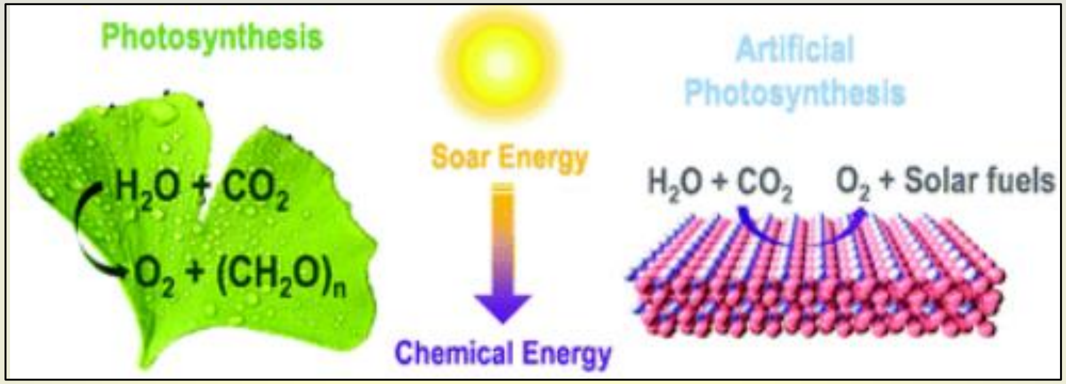
TQzCA-2D

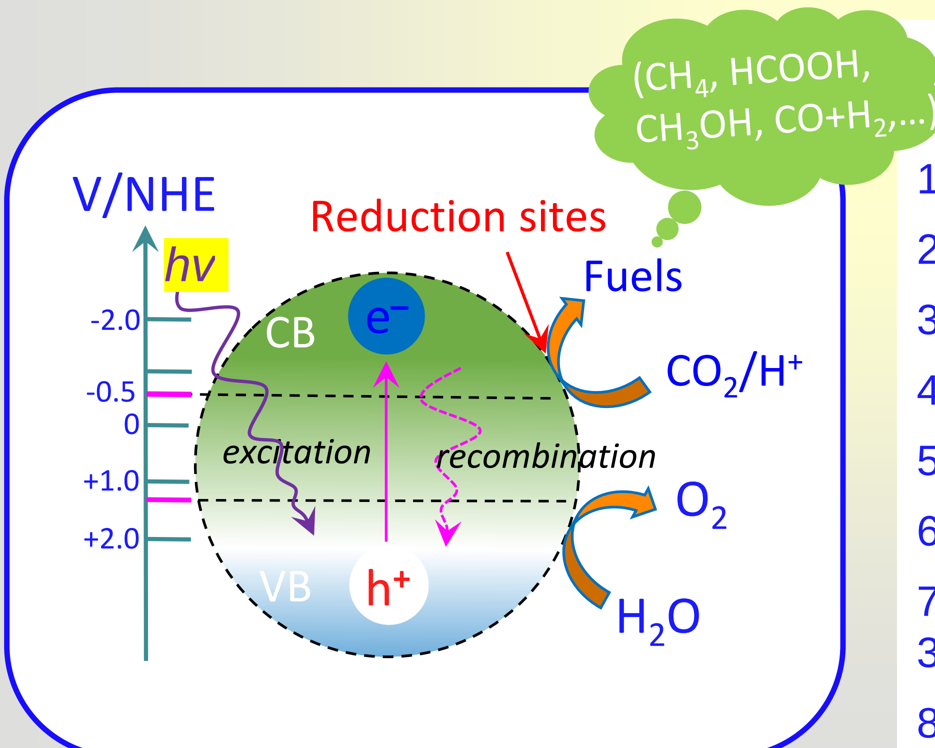




Unpublished Results

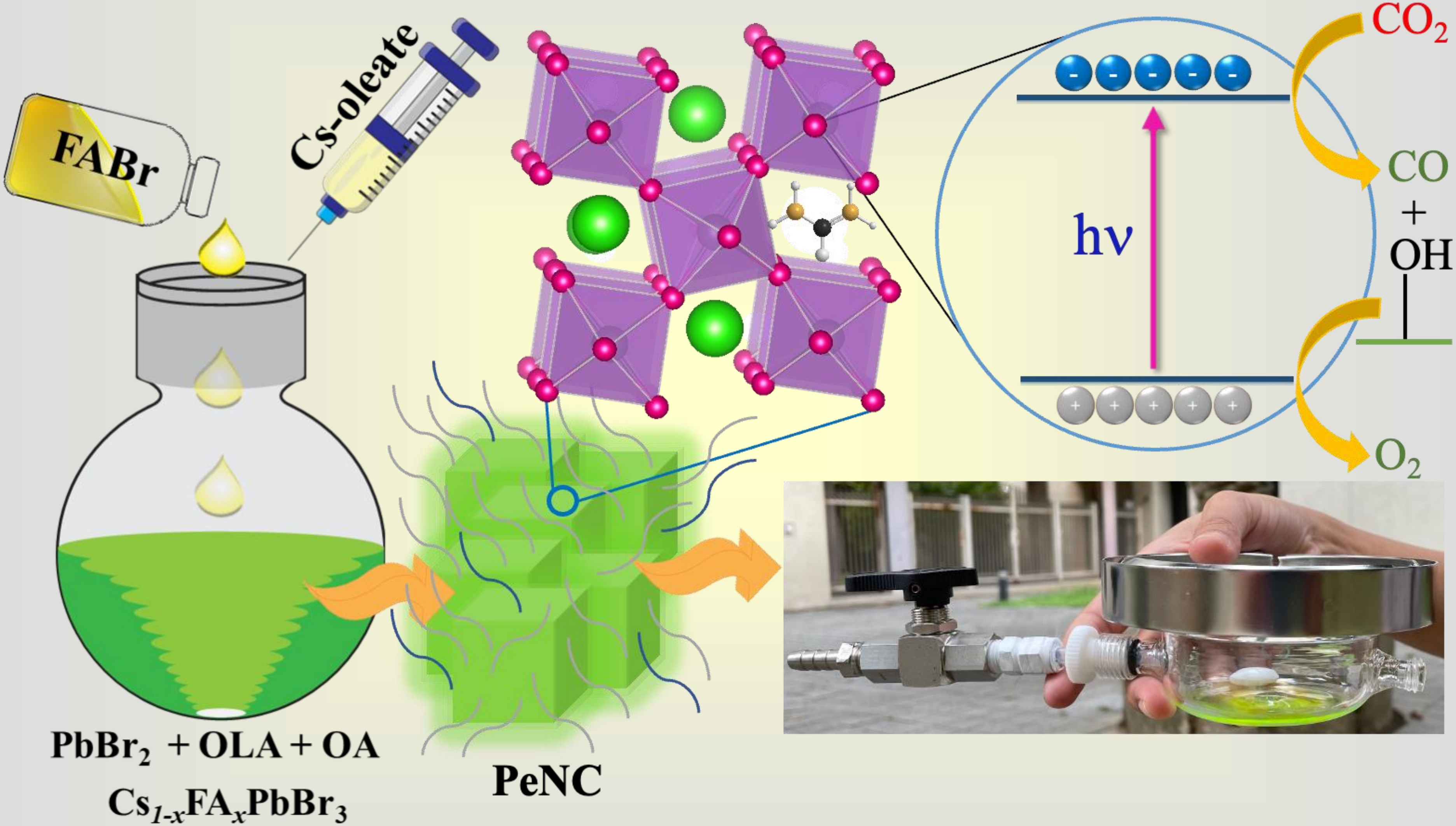
Photocatalytic CO_2 Reduction





Reactions	V/NHE at pH 7
1. $CO_2 + e^- \rightarrow CO_2^-$	-1.90
2. $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
3. $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
4. $CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48
5. $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
6. $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24
7. $CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	-0.33
8. $2H^+ + 2e^- \rightarrow H_2$	-0.41

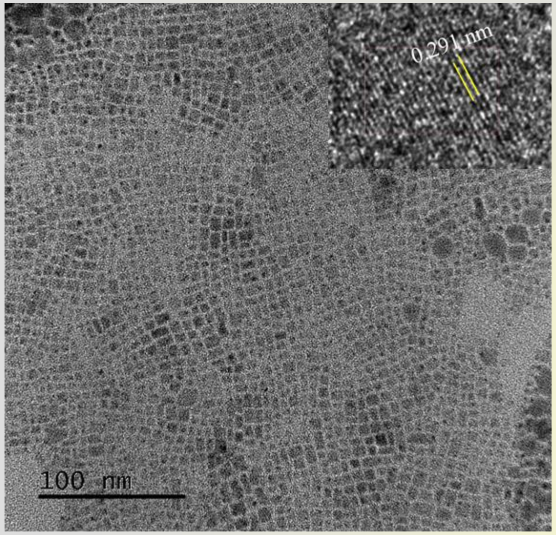
Water-Free Self-Photocatalytic CO_2 Splitting

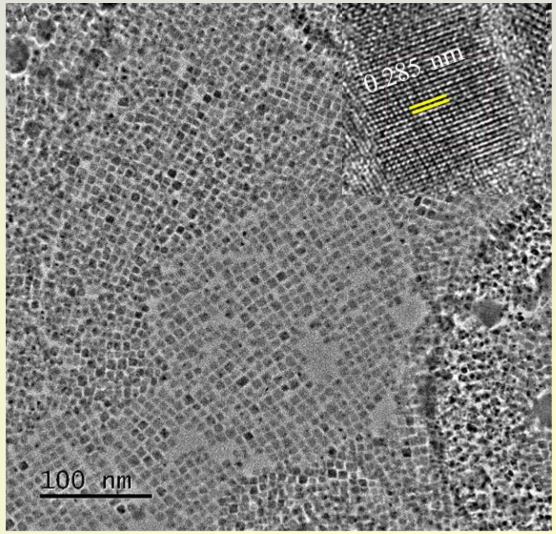


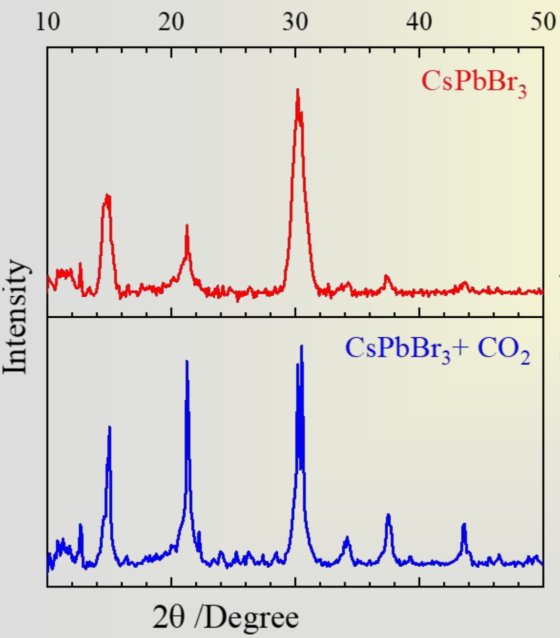
Reaction at gas-solid interface

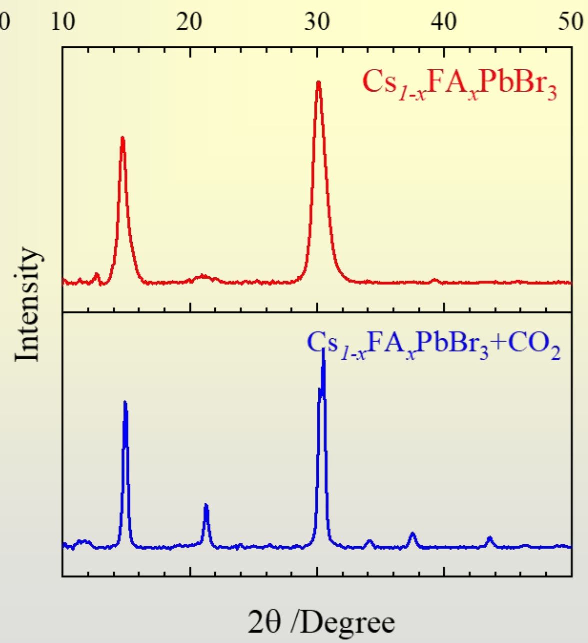
Unpublished Results

Morphology and Crystallinity

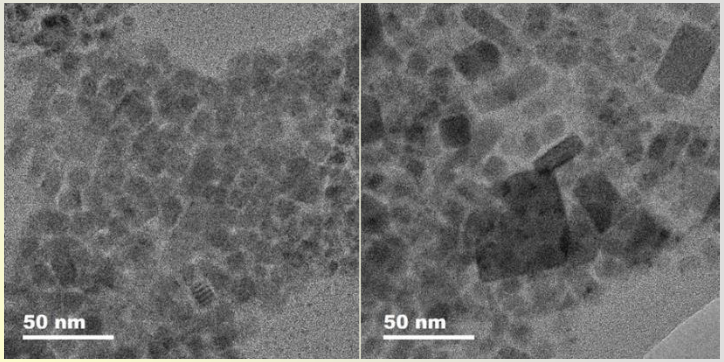








PeNC+CO_2 after irradiation for 12 h



Particle size: 8 nm → >15 nm

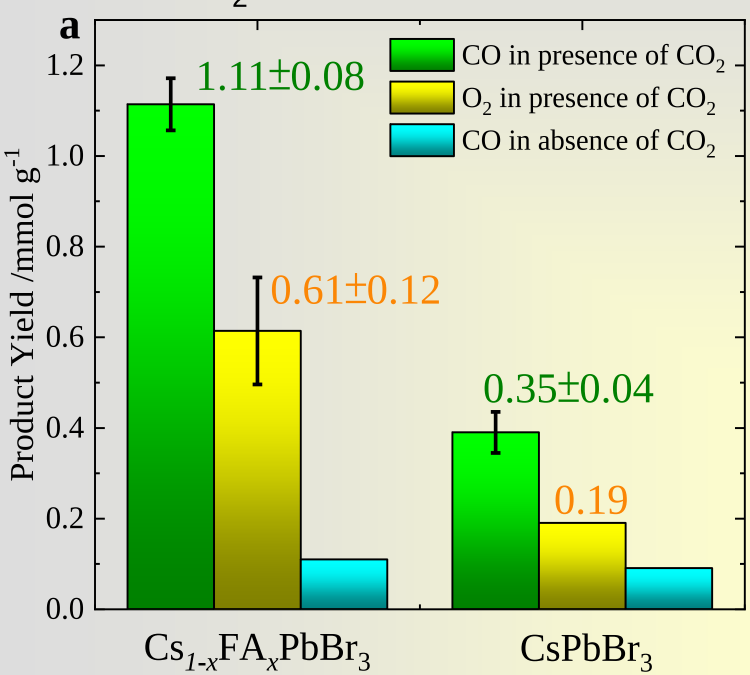
Original PeNC without irradiation
CS: Orthorhombic phase 62%
Cubic phase 38%
CF: Orthorhombic phase 93%
Cubic phase 7%

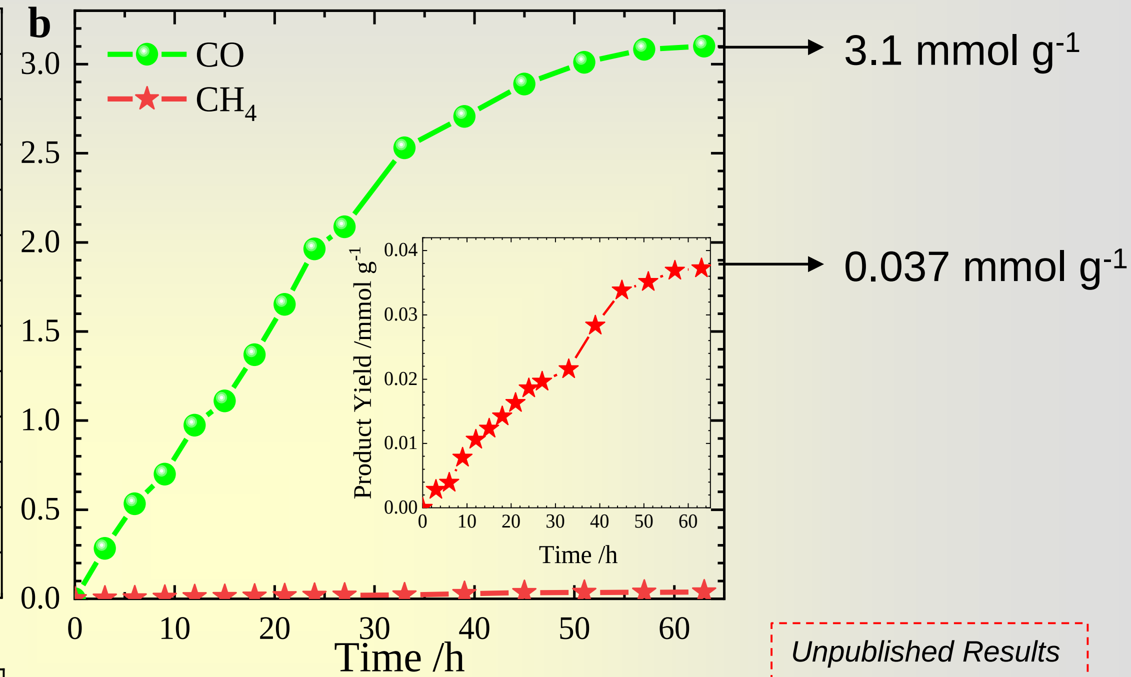
PeNC+CO_2 after irradiation for 12 h
CS: Orthorhombic phase 27%
Cubic phase 73%
CF: Orthorhombic phase 53%
Cubic phase 47%

Unpublished Results

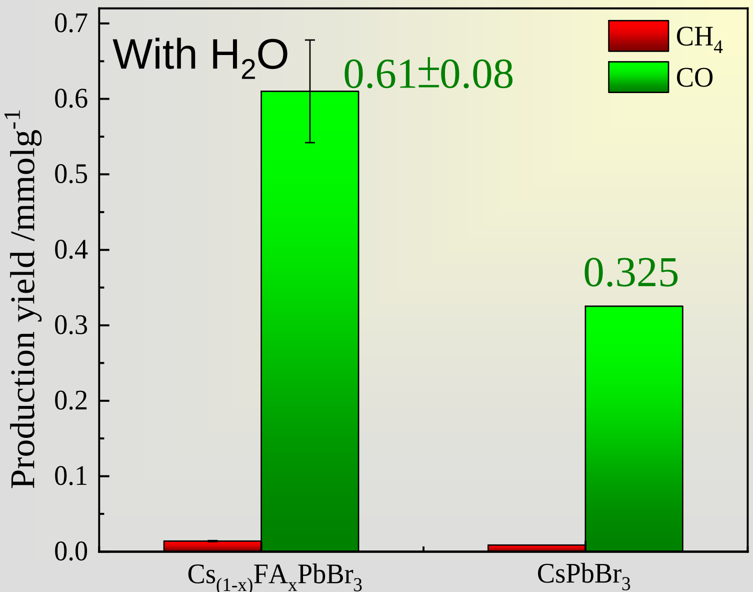
World-Record CO Production Yield (Rate)

Without H_2O





Unpublished Results



CF: 12 h irradiation without water
CO = 1.26 mmol g^{-1} → 105 μmol g^{-1} h^{-1}

CF: 12 h irradiation with water
CO = 0.70 mmol g^{-1} → 58 μmol g^{-1} h^{-1}

CS: 12 h irradiation without water
CO = 0.37 mmol g^{-1} → 31 μmol g^{-1} h^{-1}

CS: 12 h irradiation with water
CO = 0.325 mmol g^{-1} → 27 μmol g^{-1} h^{-1}

Redox Potentials for CO_2 Reduction

Overall Reaction

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \qquad \Delta G^0 = 257.2\ kJ\ mol^{-1}$$

$$E^0 = -1.335\ V$$

Half Reactions in the presence of water

$$Reduction:\ CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^0_{red} = -0.106\ V$$

$$Oxidation:\ H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad E^0_{ox} = -1.229\ V$$

Half Reactions in the absence of water

$$Reduction:\ CO_2 + H^+ + 2e^- \rightarrow CO + OH^- \qquad E^0_{red} = ???$$

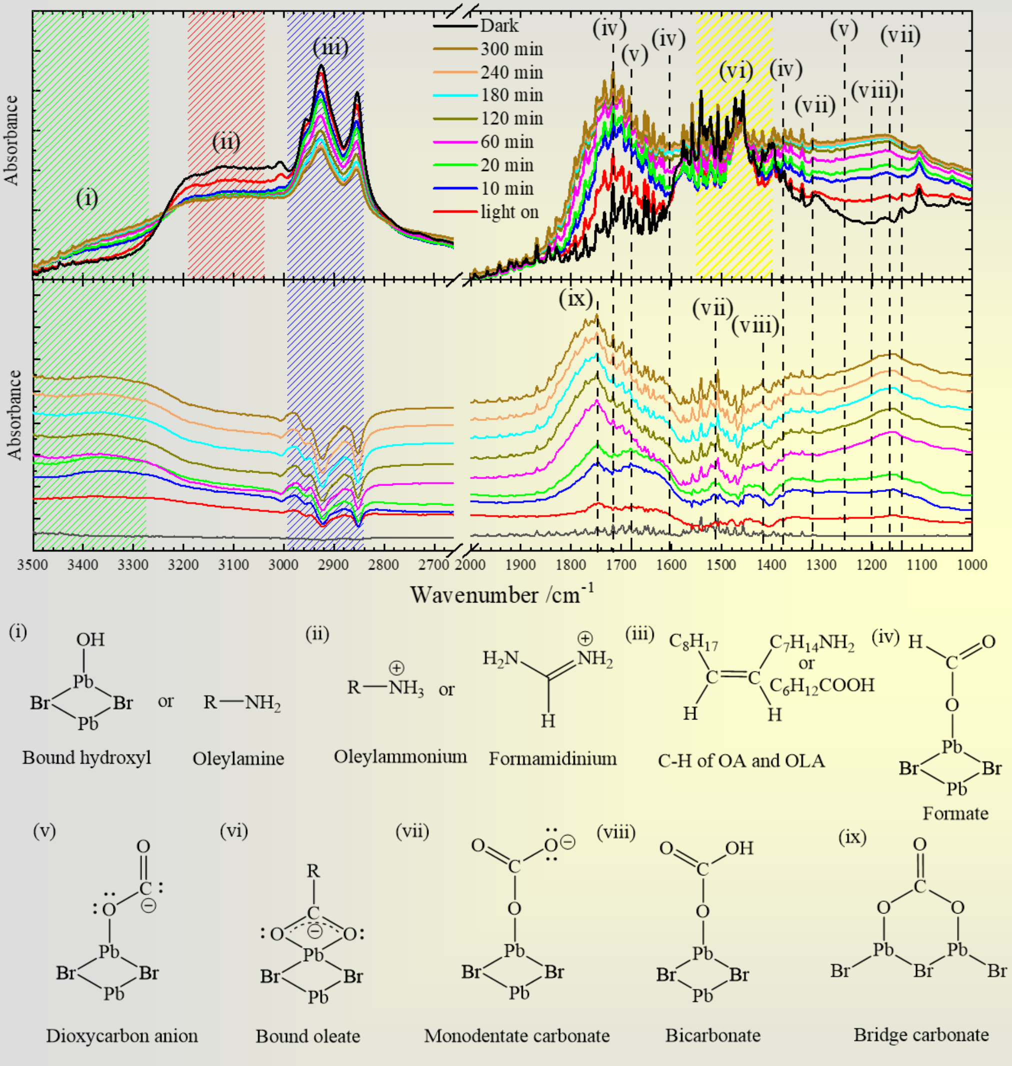
$$Oxidation:\ OH^- \rightarrow \frac{1}{2}O_2 + H^+ + 2e^- \qquad E^0_{ox} = ???$$

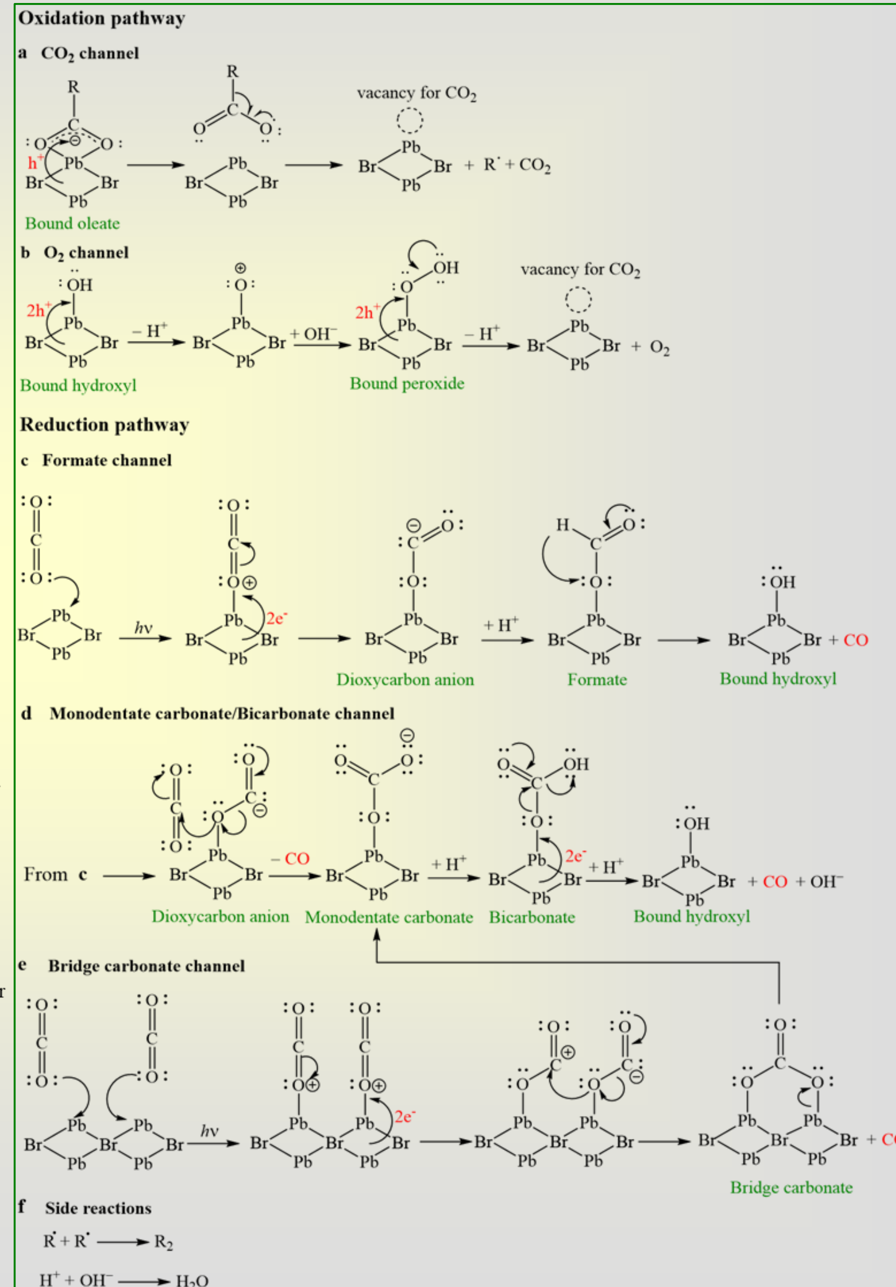
$$H_2O \rightarrow H^+ + OH^- \qquad H^+ + OH^- \rightarrow H_2O$$

$$Reduction:\ CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \qquad E^0_{red} = -0.934\ V$$

$$Oxidation:\ 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad E^0_{ox} = -0.401\ V$$

DRIFT Spectra and Reaction Mechanism





$$Reduction:\ CO_2 + H^+ + 2e^- \rightarrow CO + OH^-$$

$$Oxidation:\ 2OH^- \rightarrow O_2 + 2H^+ + 4e^-$$

Our Breakthrough Results

1. The first example of using hydrophobic PTAA for TPSC.
2. The first example of using SAM for TPSC.
3. Our two-step approach can be broadly applied for other SAM and HTM systems.
4. The first example of self-photocatalysis for CO_2 reduction.
5. The first CO_2 splitting using PeNC in the absence of water.
6. World record on CO production yield at gas-solid interface.

Acknowledgements

Lab members:

- Sumit Bhosale (Postdoctoral Fellow)
- Chun-Hsiao Kuan 管淳孝 (PhD student)
- Sudhakar Narra (Postdoctoral Fellow)
- Jian-Sing Lin 林建興 (MS student)
- Shih-Min Hsu 許詩敏 (MS Student)
- Donghoon Song 宋東勳 (Former Postdoctoral Fellow)

Collaborators:

- Prof. Ming-Chou Chen 陳銘洲 (NCU)
- Prof. Sue-min Chang 張淑閔 (NYCU)
- Prof. Chen-Hsiung Hung 洪政雄 (AS)

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