Open Questions in Organometal Halide Perovskites: Ferroelectricity, Ion migration, and Long carrier lifetime

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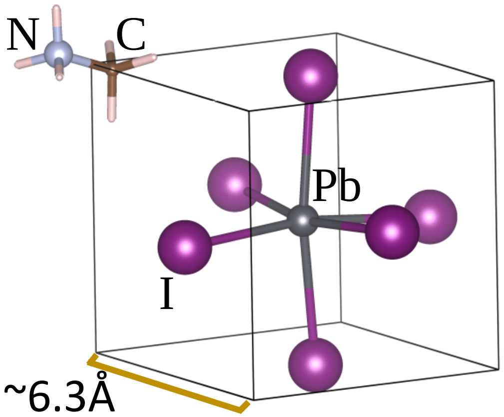
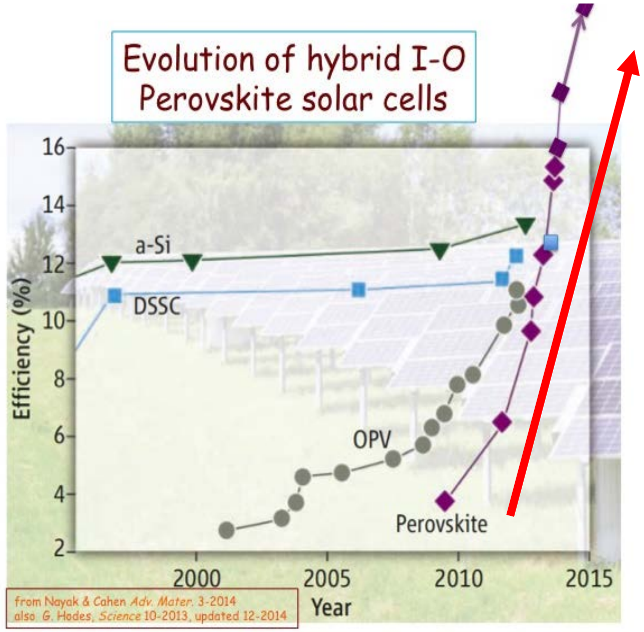
OMHPs as High Efficiency Solar Cell

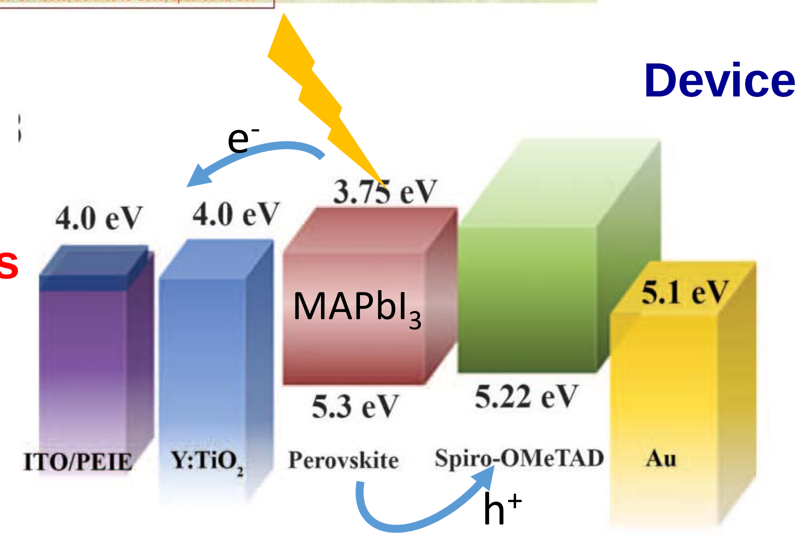
Unit cell of $CH_3NH_3PbI_3$ ($MAPbI_3$)





OMHP: Organometal Halide Perovskite

- High power conversion efficiency (PCE) reached **20%** in 2015!
  (Best silicon solar cell has PCE around 26%)
- Fast improvement
  PCE increased from 9% to 20% within **two years**
- Cheap to make
  abundant elements → Pb, I, C, N, H
  easy to make **<$1/m²**
  (Silicon > **$10/m²**)



Sci. Rep. 2, 591 (2012), *Science* 345, 542 (2014), *Nature* 501, 395 (2013)

Many Things are Unknown …

- **Polar order**
  The *A*-site organic molecule has permanent dipole moment.
  Is $MAPbI_3$ ferroelectric?

- **Current-Voltage (*J*-*V*) hysteresis**
  The origin is not fully clear.
  Ferroelectricity?
  Trap states at interface/surface?
  Ion migration?

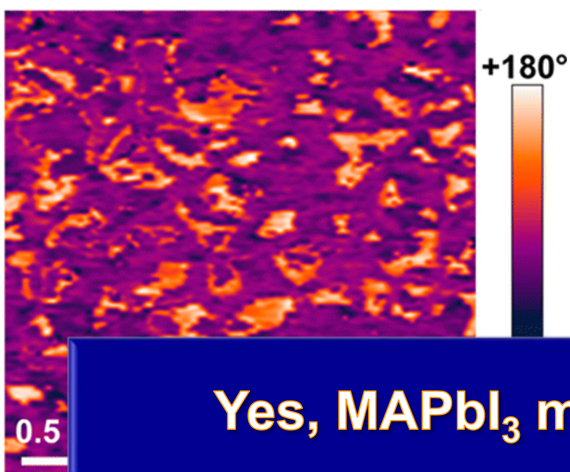
- **Carrier lifetime**
  $MAPbI_3$ has exceptionally long carrier life time.
  The intrinsic origin remains elusive.

Understanding these properties is essential to further optimize OMHP-based solar cells

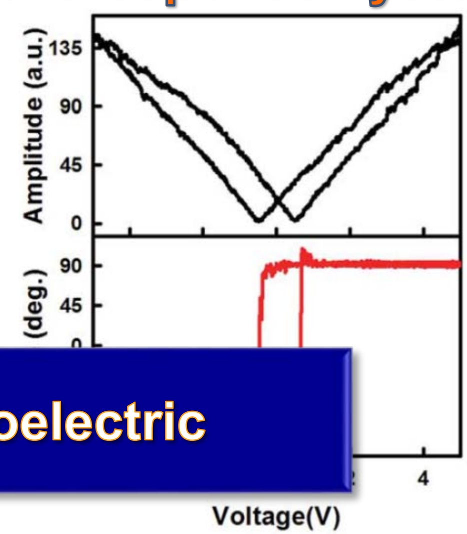
Polar order: Ferroelectricity?

- **XRD and Raman spectra** demonstrate no inversion symmetry
  J. Phys. Chem. Lett. 5, 3937 (2014), *Inorg. Chem.* 52, 9019 (2013)
- **Polarization–Electric field (*P*-*E*)** loop measurement
  J. Phys. Chem. Lett. 5, 3937 (2014)
- **Piezoelectric Force Microscopy (PFM)** observed switchable ferroelectric domains
  J. Phys. Chem. Lett. 5, 3335 (2014), *J. Mater. Chem.* A 3, 7699 (2015), *J. Phys. Chem. Lett.* 6, 1729 (2015)

Ferroelectric domains



Piezoresponse Hysteresis



Yes, $MAPbI_3$ may be ferroelectric

J. Phys. Chem. Lett. 5, 3335 (2014)

J. Mater. Chem. A 3, 7699 (2015)

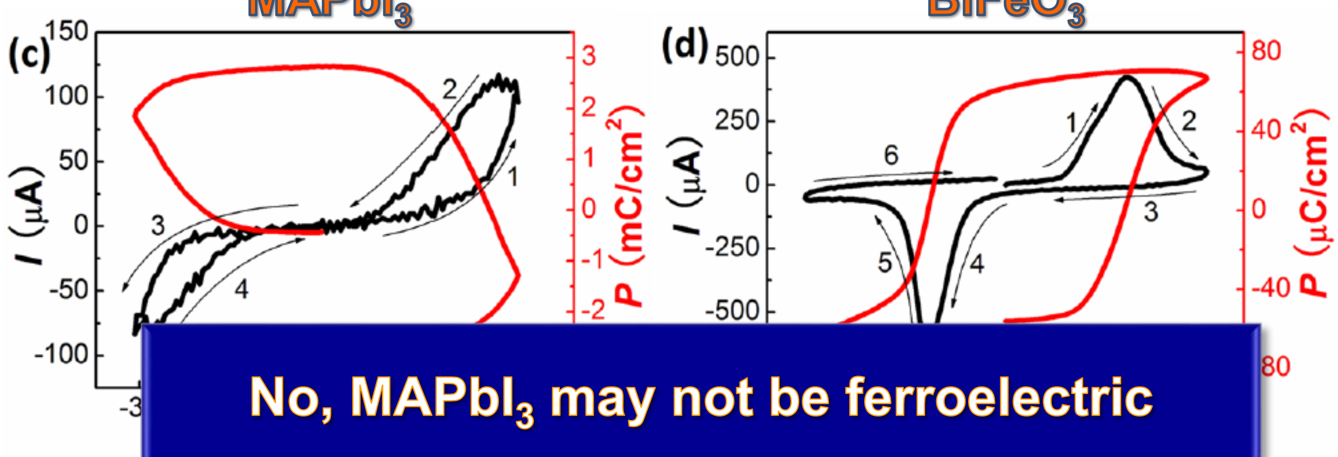
Polar order: Ferroelectricity?

Conflicting experimental observations:

- **PFM and *P-E* hysteresis** do not support ferroelectric polarization directly
  Nat. Mater. 14, 193 (2015)
- ***P-E* and *I-E* hysteresis** do not show ferroelectricity (large leakage current)
  J. Phys. Chem. Lett. 6, 1155 (2015)
- ***P-E* hysteresis**→ observe huge polarization (>1000μC/cm^2) →Non-ferroelectric process (e.g., ion migration). is dominant.
  Appl. Phys. Lett. 106, 173502 (2015)

I/*E* and *P*/*E* hysteresis measurements

$MAPbI_3$ **$BiFeO_3$**



No, $MAPbI_3$ may not be ferroelectric

Au/$MAPbI_3$/PEDOT:PSS/ITO Au/$BiFeO_3$(260 nm thick)/$SrRuO_3$

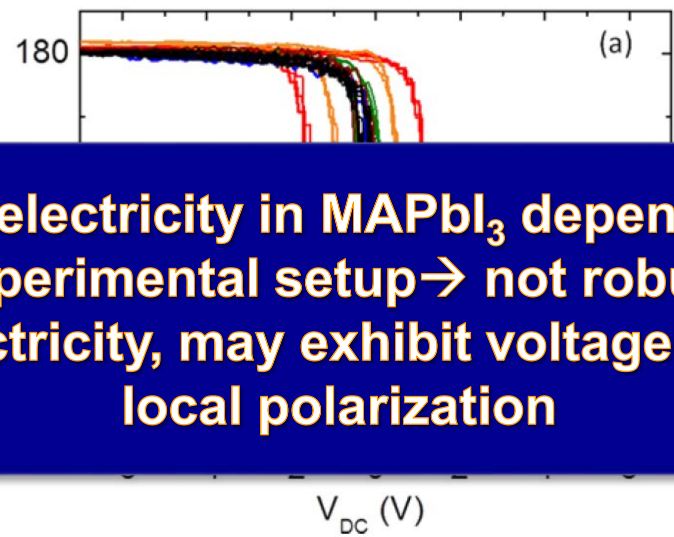
Polar order: Ferroelectricity?

More conflicting experimental observations:

- Different scan rates give different results (using **PFM**)
  Low scan rate: “No ferroelectricity”
  Fast scan rate: “Yes ferroelectricity”
  → **poor polarization retention/coercivity**. On the time scale around 1 s.
  J. Phys. Chem. Lett. 6, 1408 (2015)

- Crystal size affects polarization retention. **Large crystal shows longer retention**
  J. Phys. Chem. Lett. 6, 1729 (2015)

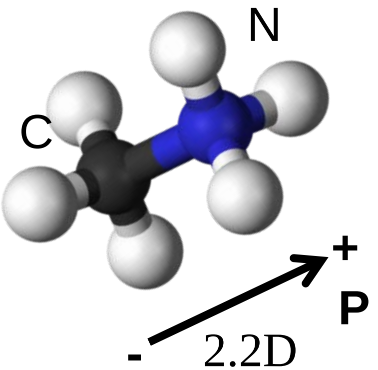
Piezo-phase hysteresis performed at different acquisition times



Ferroelectricity in $MAPbI_3$ depends on experimental setup→ not robust ferroelectricity, may exhibit voltage-induced local polarization

A Site Molecule and Ferroelectricity

- *A* site MA^+ has permanent dipole moment, which may induce different polar order
  - Randomly oriented → Paraelecric
  - Aligned → Ferroelectric
  - Anti-aligned → Anti-ferroelectric



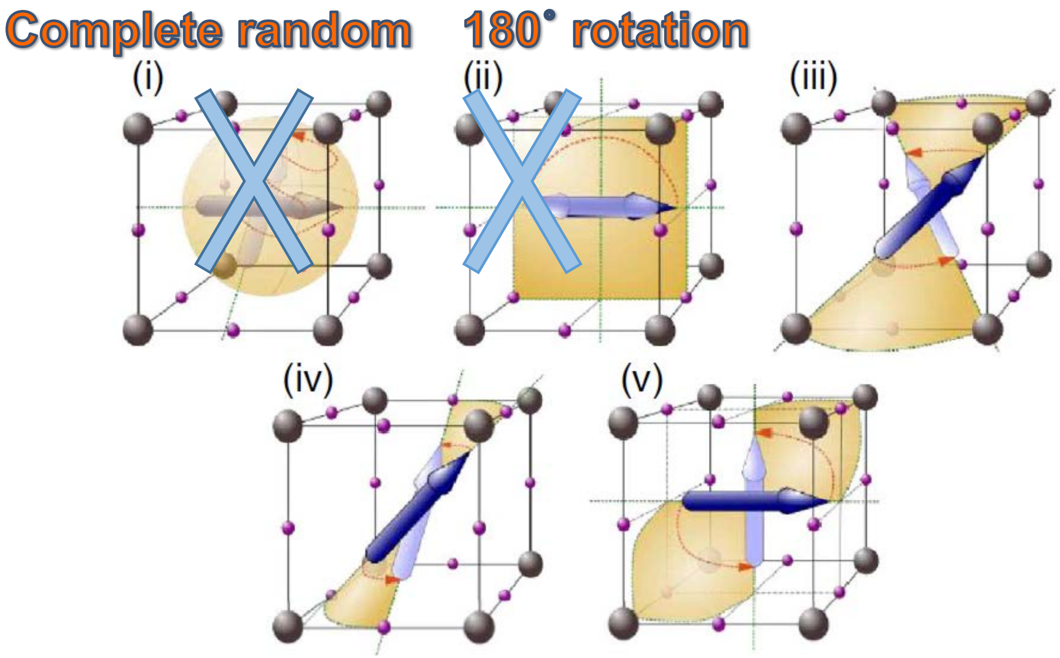
- *A* site molecules may form specific spatial distribution
  - Locally ordered nano-domains
  - Ferroelectric domains and domain walls

- A lot of effort devoted to understanding molecular behaviors
  - Time-dependent permittivity measurement *J. Appl. Phys.* 87, 6373 (1987)
  - Neutron powder diffraction *Chem. Commun.* 51, 4180 (2015)
  - Quasielastic neutron scattering *Nat. Comm.* 6, 7124 (2015)
  - *ab initio* molecular dynamics *Phys. Chem. Chem. Phys.* 16, 16137 (2014)
  - Monte-Carlo simulation *APL Mat.* 2, 081506 (2014)
  - ...

Study molecular behaviors is important for understanding Ferroelectricity

Behavior of *A* Site Molecule

- Quasielastic Neutron Scattering + Monte Carlo
  - **Residence time for MA^+ orientation is around 14±3 ps.** (consistent with previous *ab initio* MD)
  - Rotation barrier is on the level of 10 meV. (estimated from Arrhenius activity energy)
  - Suspect that MA^+ in ferroelectric domain may have larger rotation barrier (longer residence time)



(i) and (ii) are unlike to occur in the time scale 1.2~53 ps

Other rotation patterns are possible

Nat. Comm. 6, 7124 (2015)

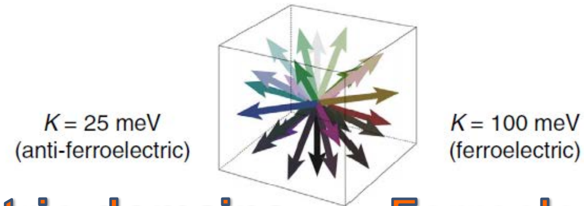
Monte-Carlo Simulation

$$\hat{H} = \sum_{\text{dipole,Efield}}^{n} (\mathbf{p}_i \cdot \mathbf{E}_0) + \sum_{\text{dipole,dipole}}^{n,m} \frac{1}{4\pi\varepsilon_0\varepsilon_r} \left(\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r^3} - \frac{3(\hat{\mathbf{n}} \cdot \mathbf{p}_i)(\hat{\mathbf{n}} \cdot \mathbf{p}_j)}{r^3} \right) - \sum_{\text{dipole,dipole}}^{n,m} K \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_j$$

Dipole-dipole interaction

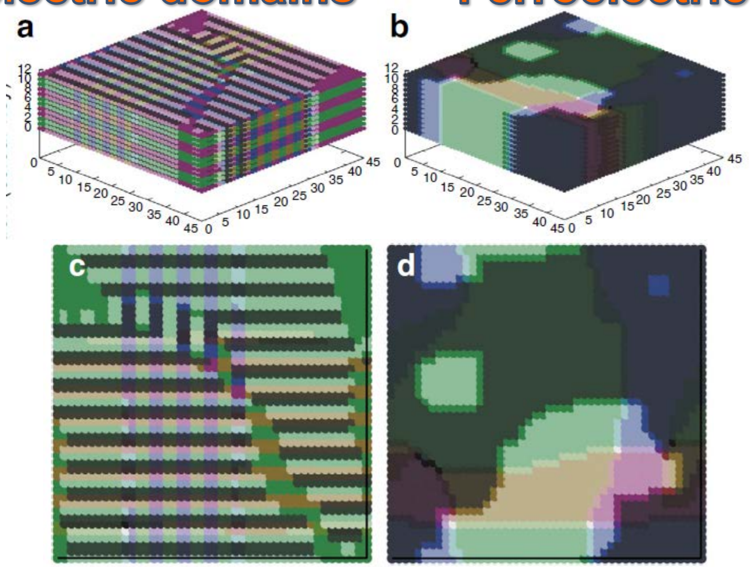
Value of *K* estimated from DFT, favors aligned dipoles

28 nm×28nm×7.5 nm



***K* = 25 meV → Antiferroelectric domains**

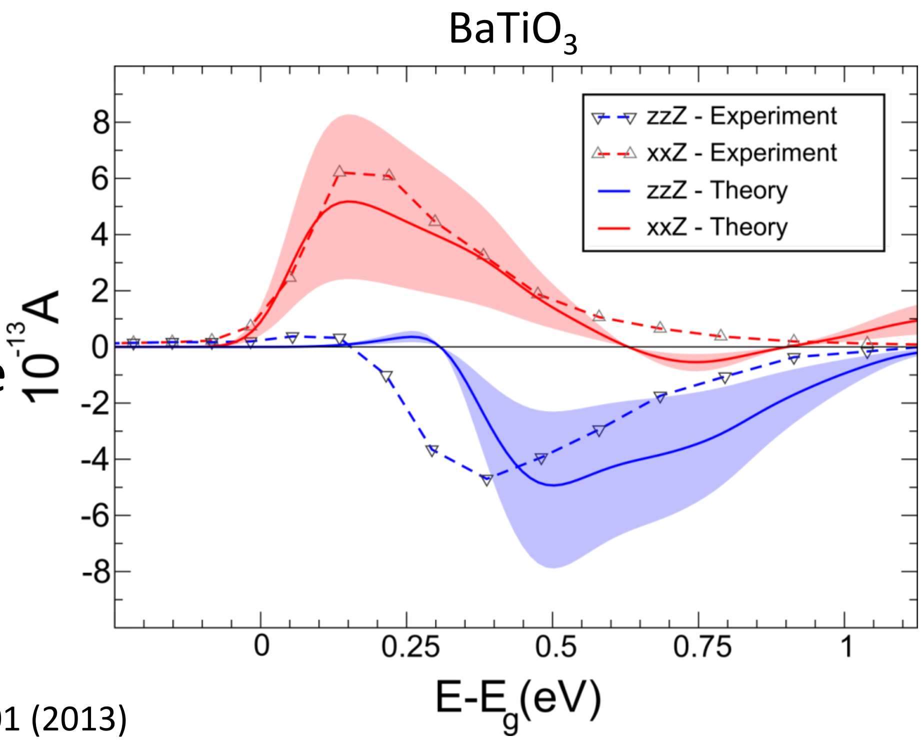
Ferroelectric domains ← *K* = 100 meV



Ferroelectric domains can form @ RT

Bulk photovoltaic effect (BPVE)

- Intrinsically generated photocurrents and photovoltages from single phase bulk material
- Observed in experiments:
  - Inversion symmetry breaking
  - Maybe parallel, antiparallel, or even perpendicular to material polarization
  - Strong frequency dependence



Shift current is the main mechanism for BPVE

S. M. Young and A.M. Rappe, *Phys. Rev. Lett.,* **109**, 116101 (2013)
S. M. Young, F. Zheng, and A. M. Rappe, *Phys. Rev. Lett*., **109**, 236601 (2013)
V. I. Belinicher and B. I. Sturman, *Sov. Phys. Usp*. 23(3), 199 (1980)

Shift Current

$$J_q = \sigma_q^{rs} E_r E_s$$

Transition intensity

$$\sigma_q^{rs} = -\pi e \left(\frac{e}{mc\hbar}\right)^2 \sum_{n',n''} \int_{BZ} dk \left(f[n''k] - f[n'k]\right) \delta\left(\omega'' - \omega' \pm \omega\right) \langle n''k| \hat{P}^r |n'k\rangle \langle n'k| \hat{P}^s |n''k\rangle$$

$$\times \left[\langle n''k| i\frac{\partial}{\partial k_q} |n''k\rangle - \langle n'k| i\frac{\partial}{\partial k_q} |n'k\rangle - \frac{\partial}{\partial k_q}\phi(\langle n''k| \hat{\mathbf{P}} |n'k\rangle) \right]$$

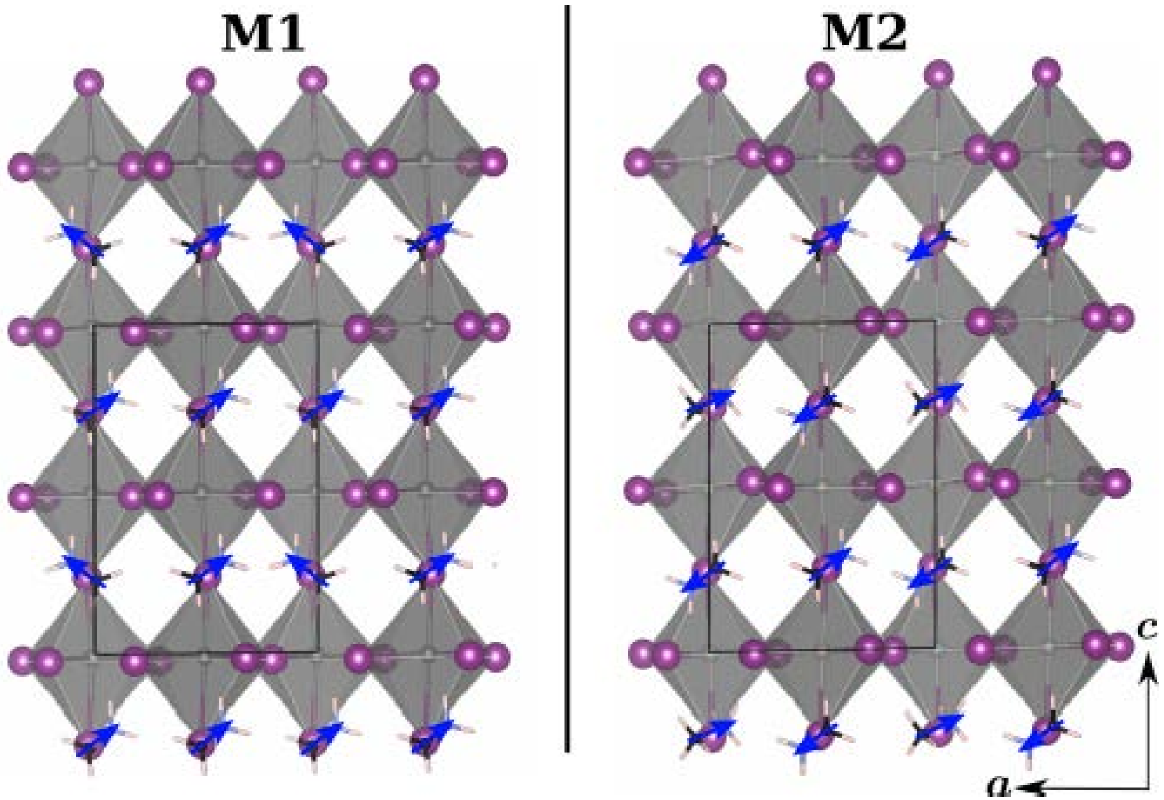
Shift vector

- Quadratic in ***E*** field, linear in light intensity! $J_q = \sigma_q^{rr} E_r E_r = \bar{\sigma}_q^{rr} I_r$
- Need to break inversion symmetry
- Rank 3 tensor

Phys. Rev. B. 23, 5590 (1981), *Phys. Rev. B.* 61, 5337 (2000)

Shift Current in $MAPbI_3$

- Bulk photovoltaic effect emerges when system loses inversion symmetry
  Shift current effect on two cases: Polar & Non-polar

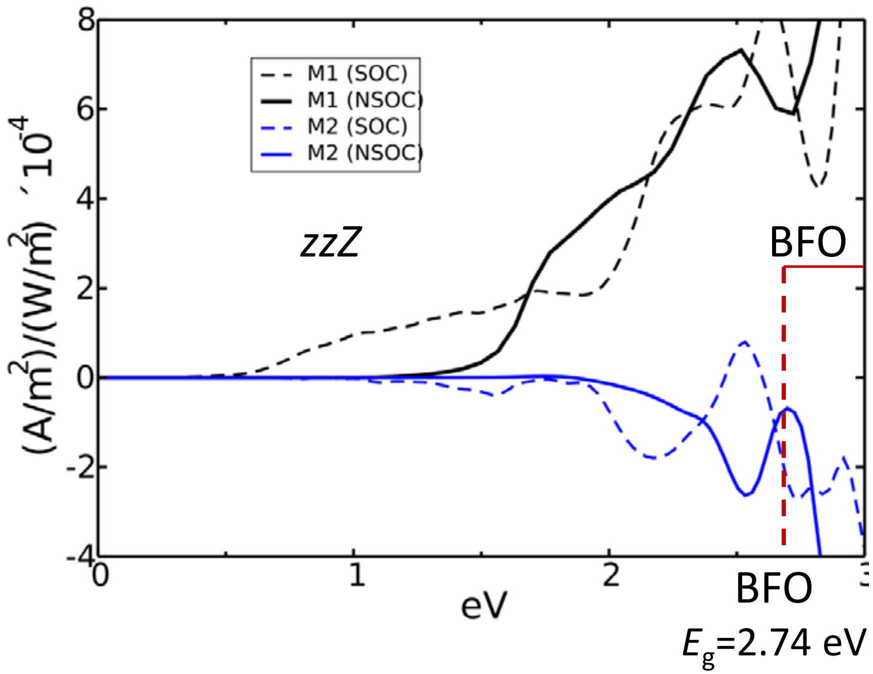


5 $\mu C/cm^2$ Polarization Along *c*	Near Net Zero Polarization
Large $Pb\text{-}I_3$ displacement	Small $Pb\text{-}I_3$ displacement
Polar	**Non-polar**

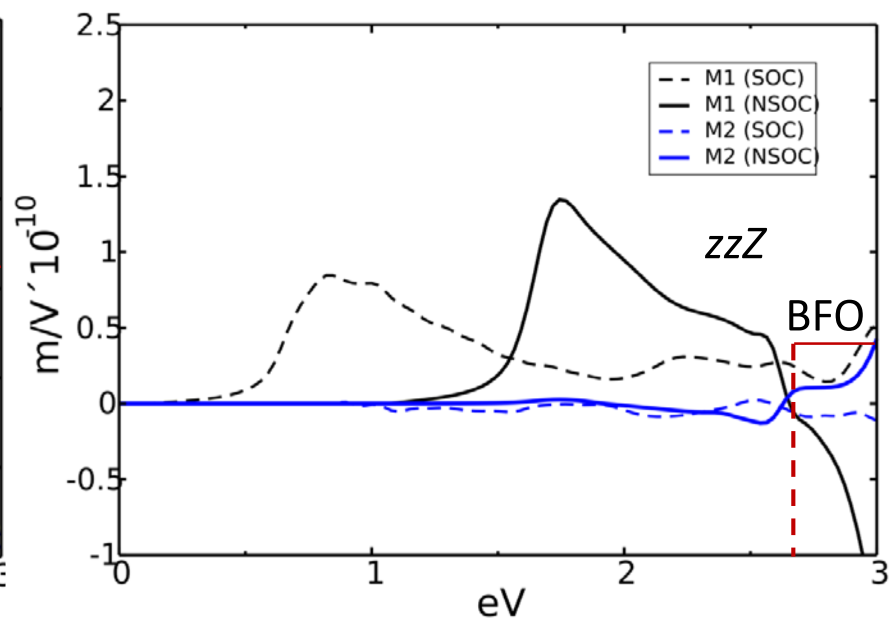
Shift Current in $MAPbI_3$

- Higher response than $BiFeO_3$ (BFO)

Shift current (thin limit)



Glass coefficient (thick limit)



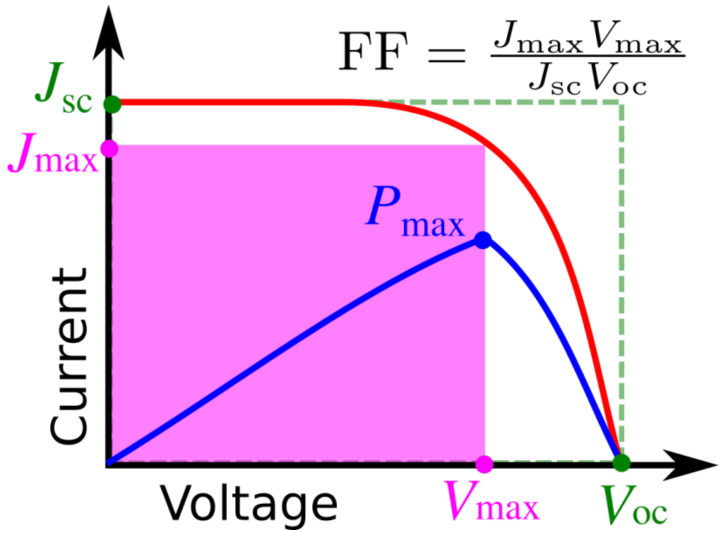
Polar (M1) gives larger response than Non-polar (M2)

Higher response than BFO may explain large V_{oc}

J. Phys. Chem. Lett. 6, 31 (2015)

Current-Voltage Hysteresis

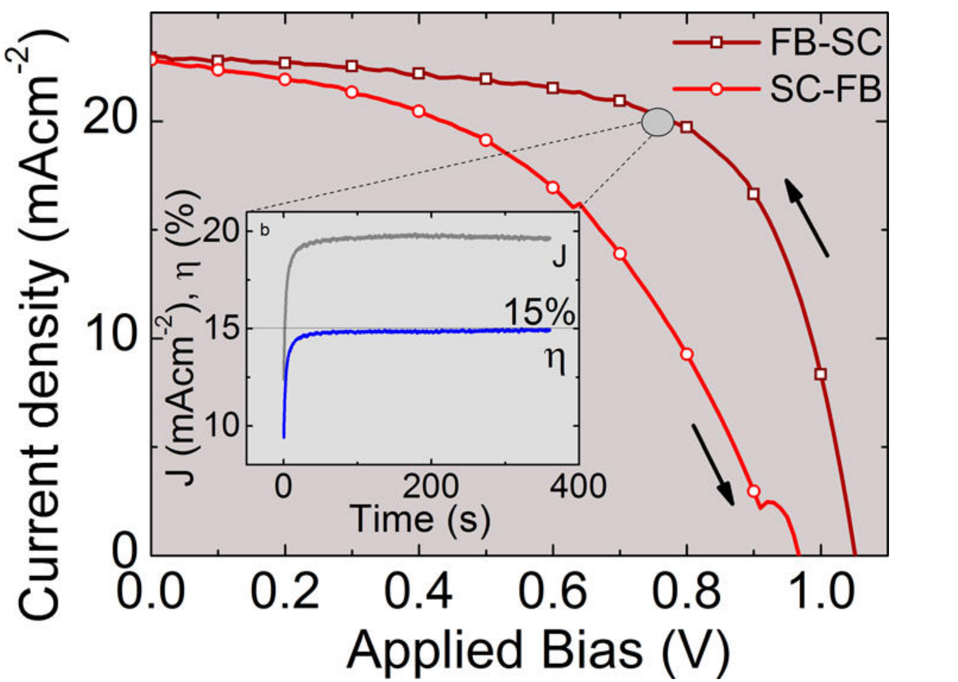
J-V curve



Power conversion efficiency:

$$\eta = J_{sc}V_{oc}\mathrm{FF}/\mathrm{P_{in}}$$

Anomalous hysteresis in $MAPbI_xCl_{1-x}$



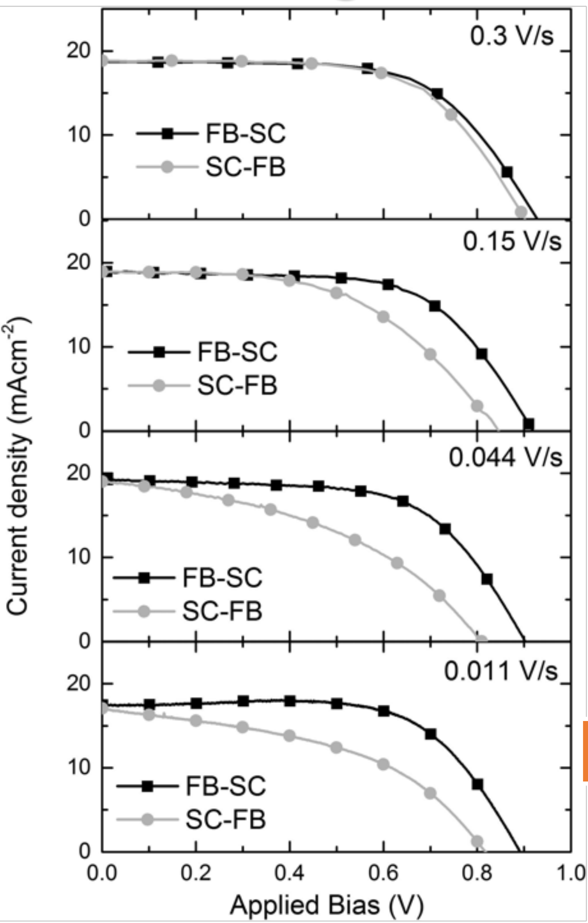
FB: Forward Bias; SC: Short Circuit

J. Phys. Chem. Lett 5, 1511 (2014)

- The rise time to reach stabilized power output is slow
- Determination of PEC is ambiguous
- *J-V* curve is sensitive to experimental conditions

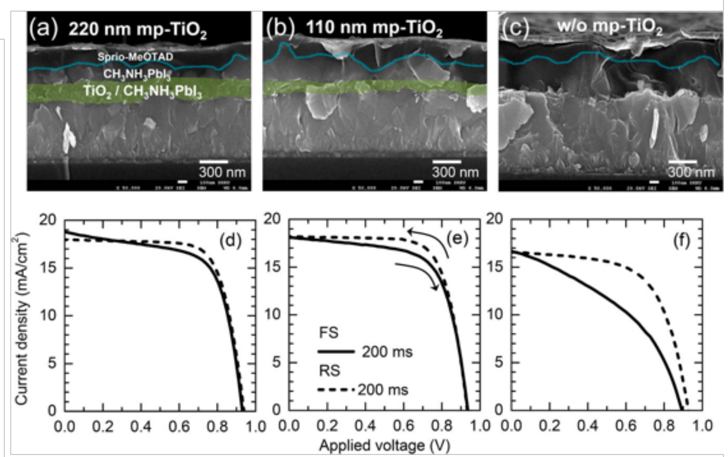
Parameters affecting *J-V* Hysteresis

Scanning rate

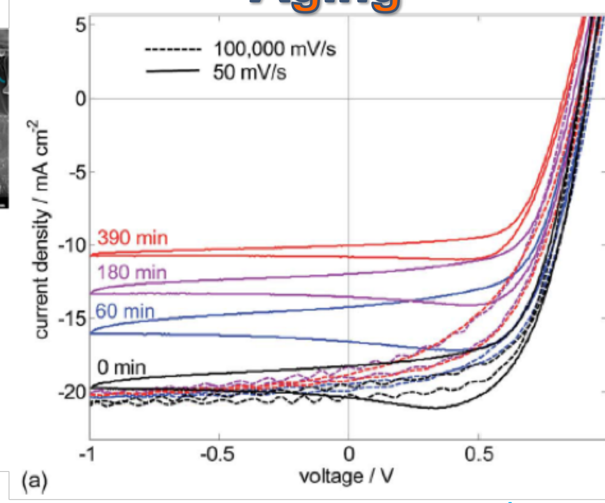


J. Phys. Chem. Lett 5, 1511 (2014)

Interface

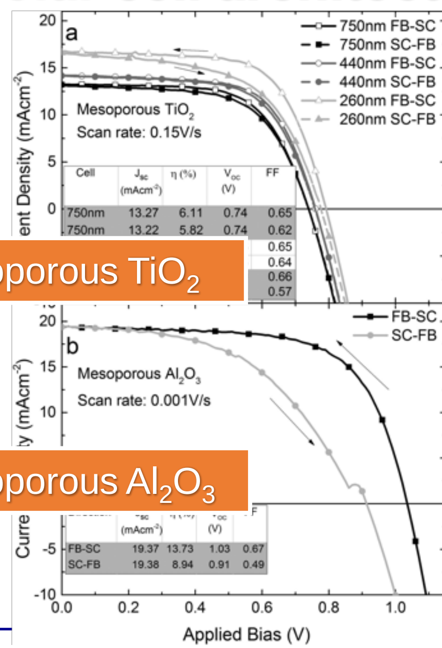


Aging



Energy Environ. Sci., 8, 995 (2015)

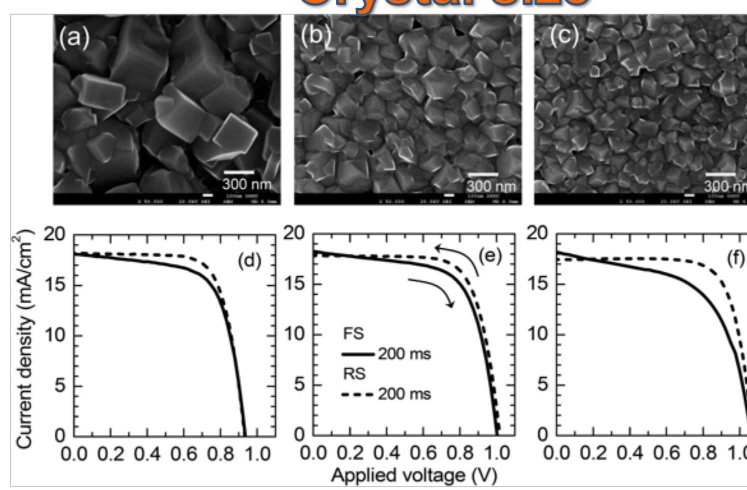
Solar cell architecture



Mesoporous TiO$_2$

Mesoporous Al$_2$O$_3$

Crystal size

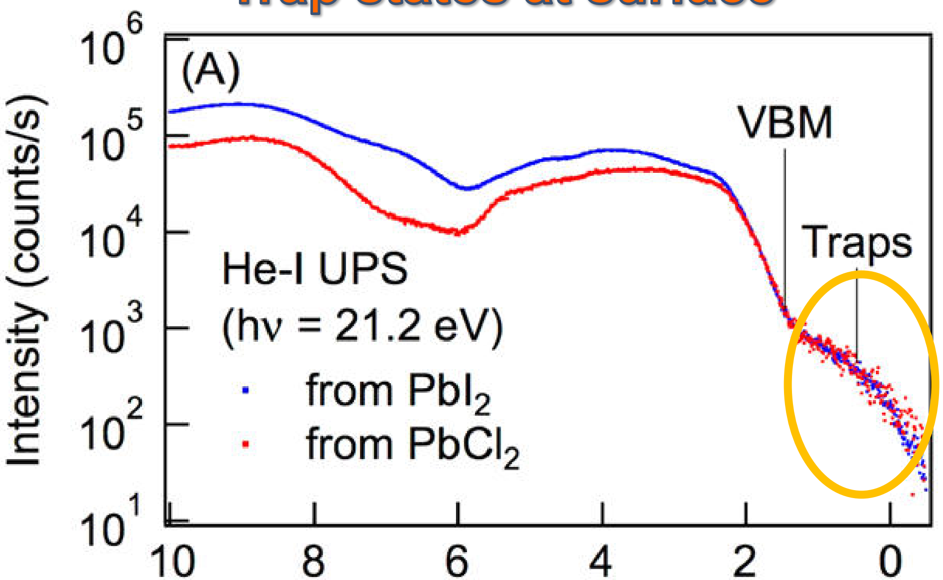


J. Phys. Chem. Lett 5, 2927 (2014)

Possible Origins of J-V Hysteresis

- Trap states at interface/surface
- Ferroelectricity: remnant polarization
- Bulk photovoltaic: large V_{oc}
- Ion migration
- Light-induced structural transformation

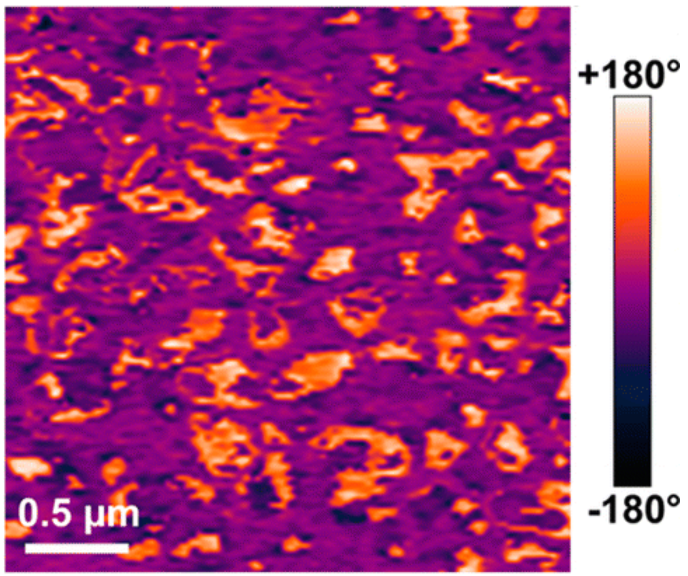
Trap states at surface



Ultraviolet photoemission spectra for $CH_3NH_3PbI_3$ thin films vapor deposited on native oxide terminated silicon from PbI_2 (blue) and $PbCl_2$ (red) precursors.

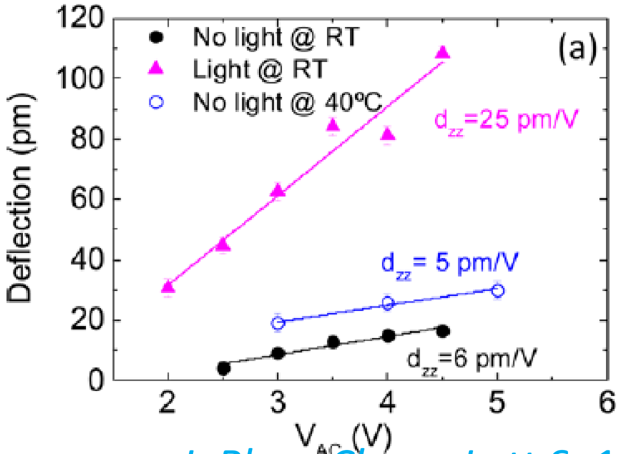
J. Am. Chem. Soc. 137, 2089 (2015)

Ferroelectric domains



J. Phys. Chem. Lett 5, 3335 (2014)

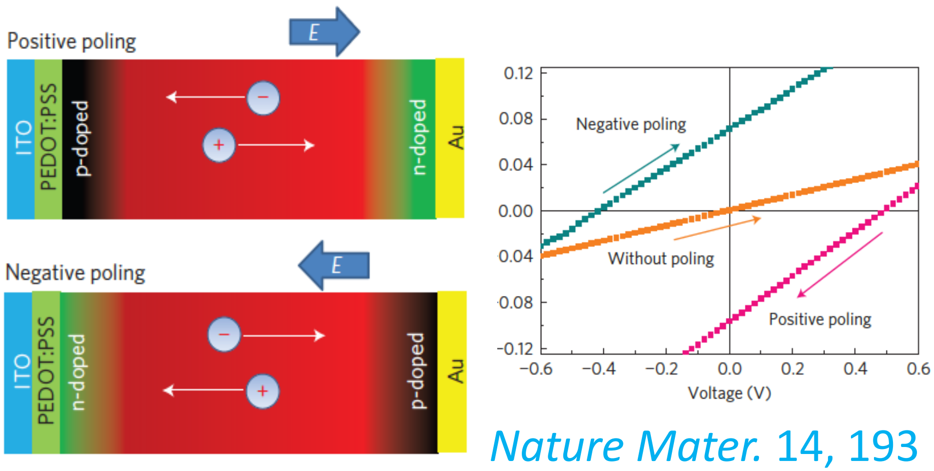
Light-enhanced piezoelectricity



J. Phys. Chem. Lett 6, 1408 (2015)

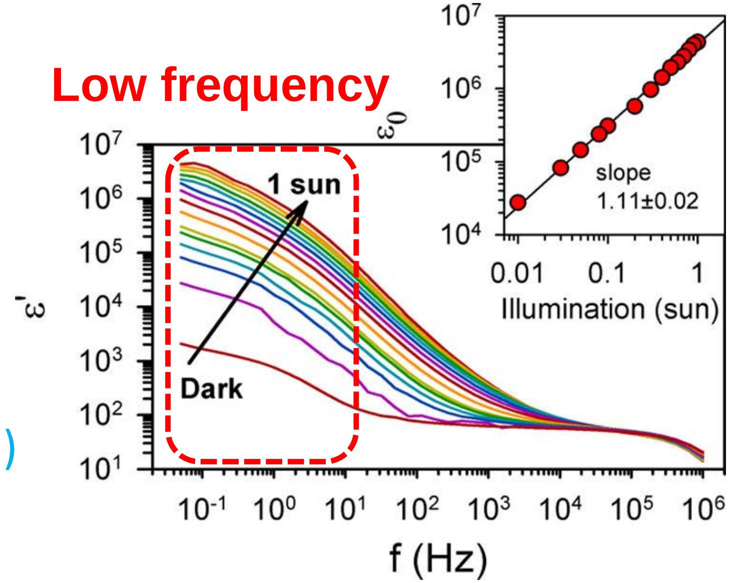
Ion Migration in OMHP

Giant switchable photovoltaic effect



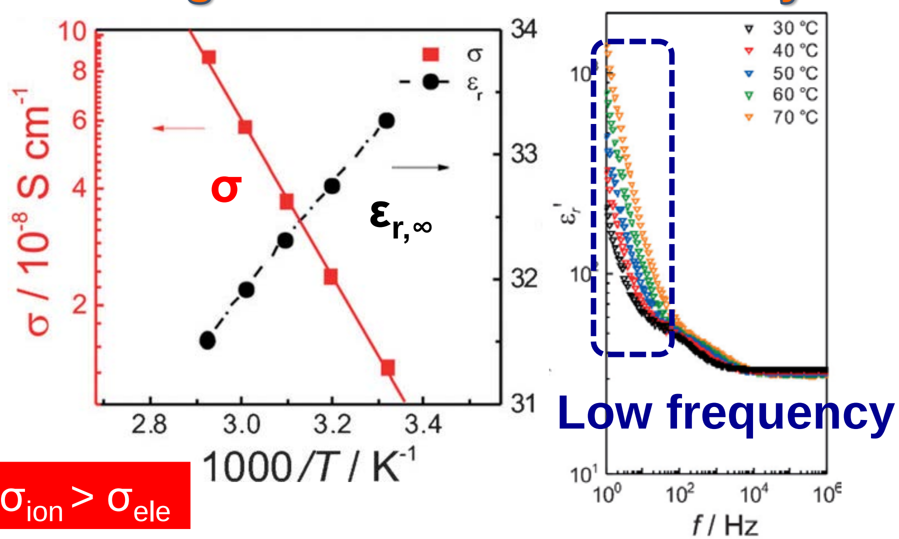
Nature Mater. 14, 193 (2015)

Photoinduced giant dielectric constant



J. Phys. Chem. Lett 5, 2390 (2014)

Significant ionic conductivity



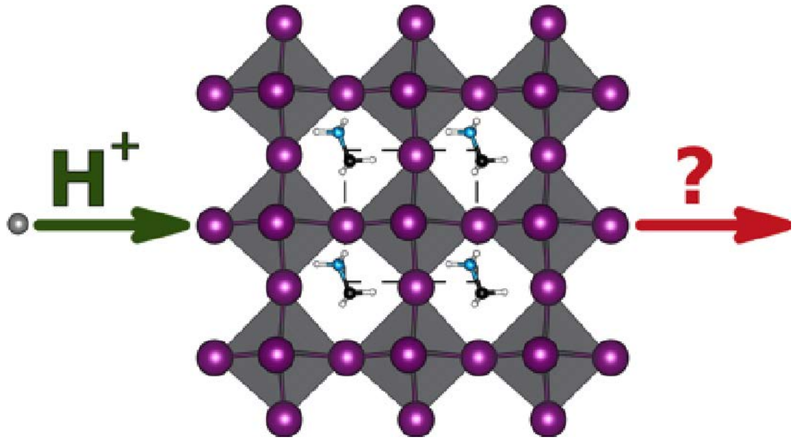
$\sigma_{ion} > \sigma_{ele}$

σ: conductivity; ε: dielectric constant

- The ionic diffusion is highly relevant for *J-V* hysteresis, ionic conductivity, low-frequency dielectric response, and material stability.

Angew. Chem. Int. Ed. 54, 1 (2015)

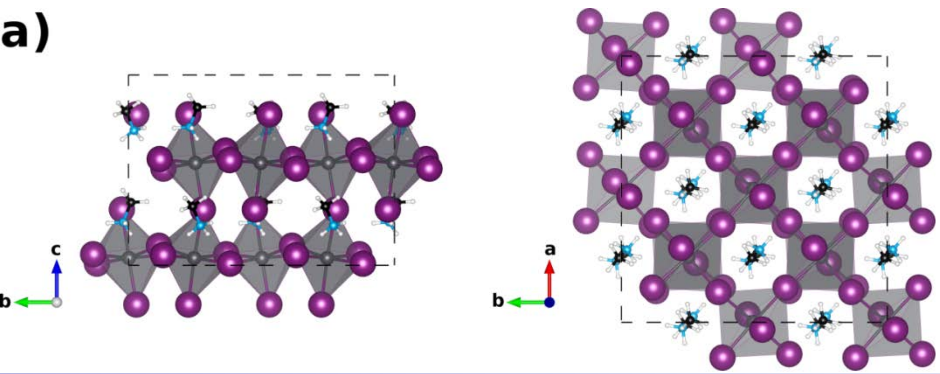
Hydrogen in $MAPbI_3$: Structural Model

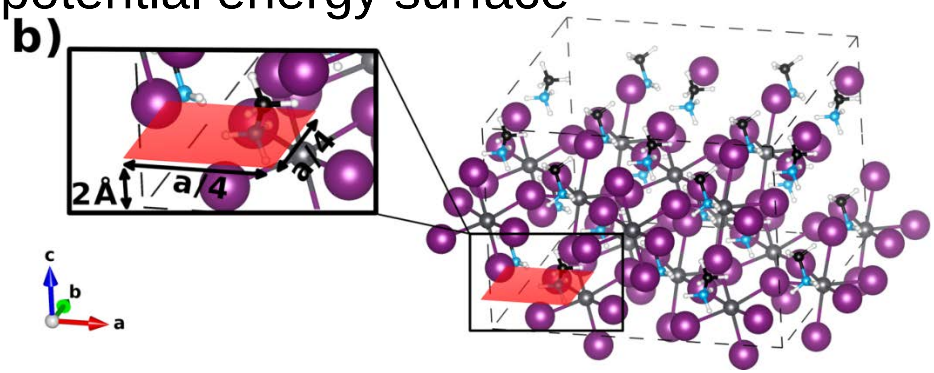


- 2×2×1 super-cell of $MAPbI_3$, 16 formula units
- PBE-DFT + dispersive corrections in VASP
- nudged elastic band (NEB) using VTST

- different charge states of hydrogen:

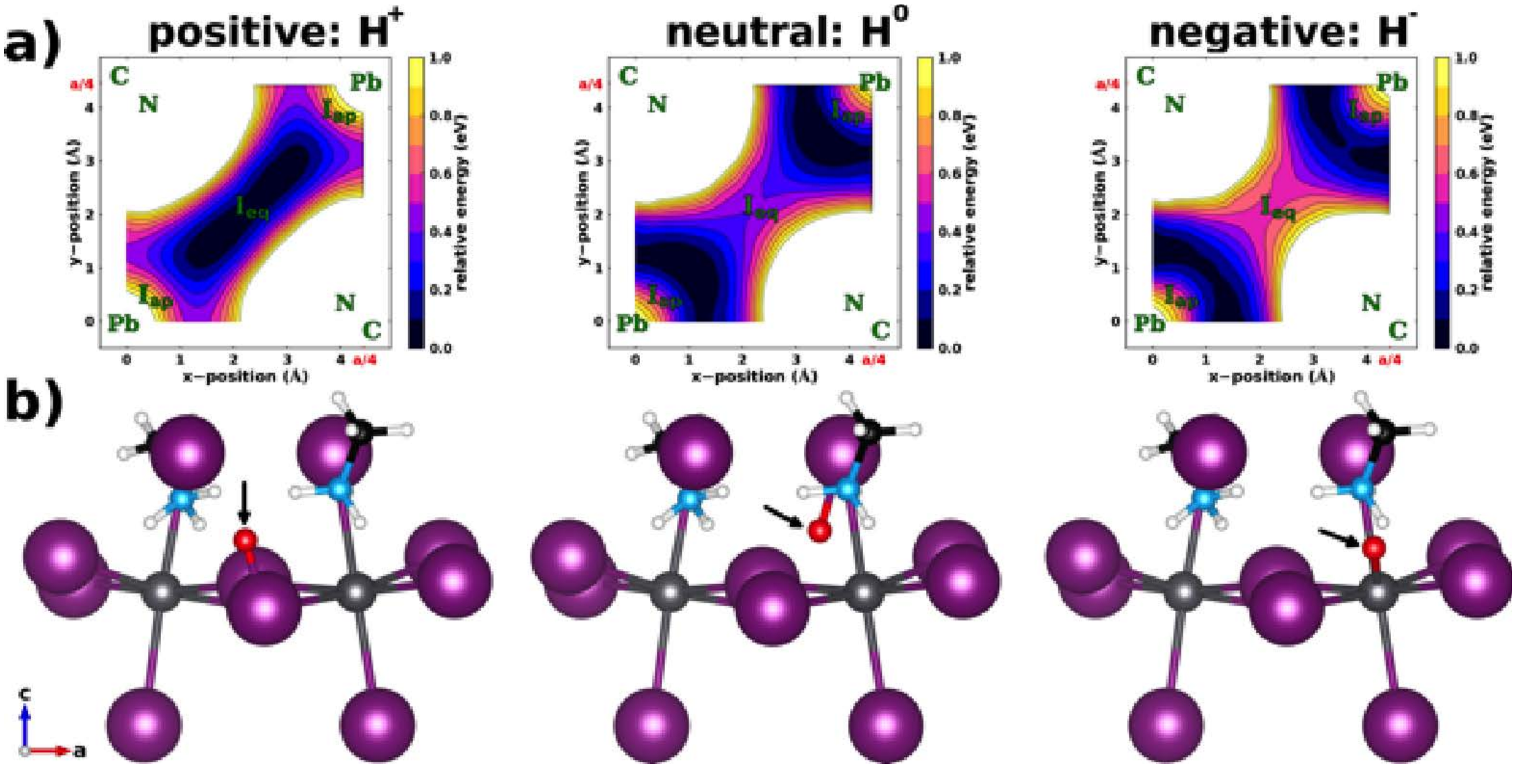
  H^+, H^0, H^-
- modeled by fixing the number of electrons per cell
- sample a slice of lateral adiabatic potential energy surface





D. A. Egger, L. Kronik, A. M. Rappe, *Angew. Chem. Int. Ed.* 2015, online

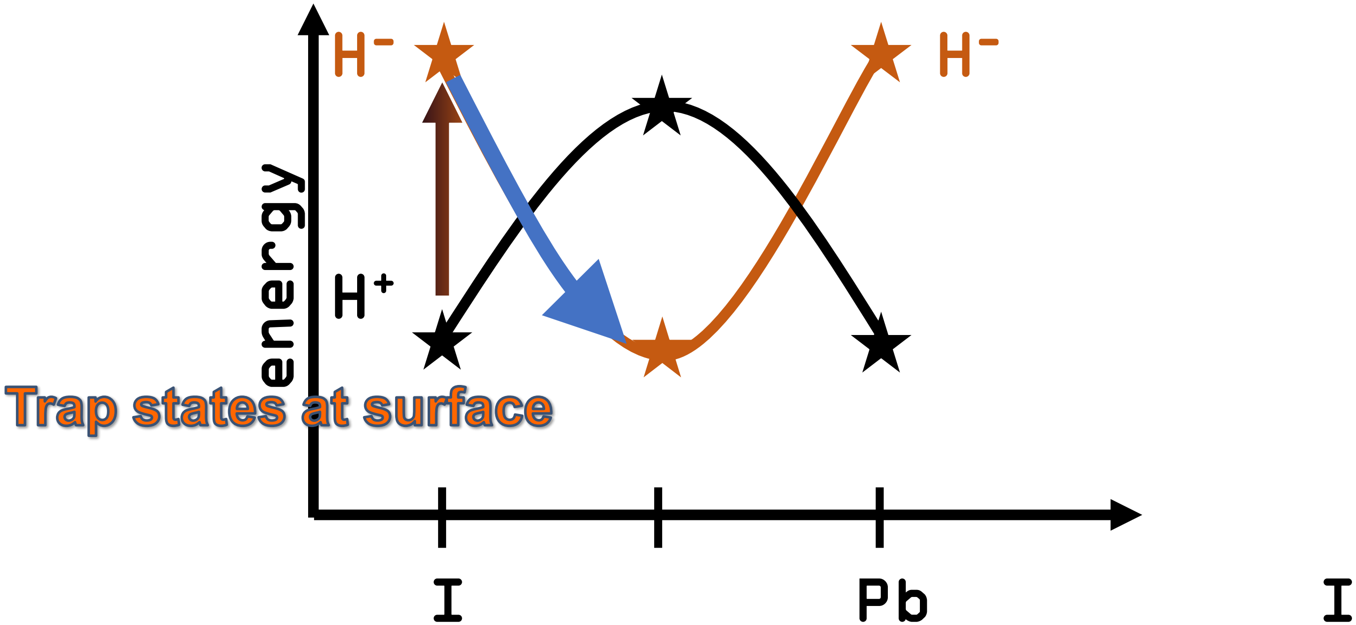
Adiabatic PES of Hydrogen in $MAPbI_3$



- All three hydrogenic defects are found to be repelled from the *A* site
- H^+ is stable in the vicinity of I
- H^0 is in an interstitial Pb-I site
- H^- is closer to the Pb site

Ionic character $MAPbI_3$

Ionization enhanced hydrogen migration



- **Bourgoin-Corbett mechanism:**[1] interstitial migrates via successive changes of its charge state
- Similar mechanism relevant for Si-interstitials in Si[2,3] → might be relevant for other defect types too

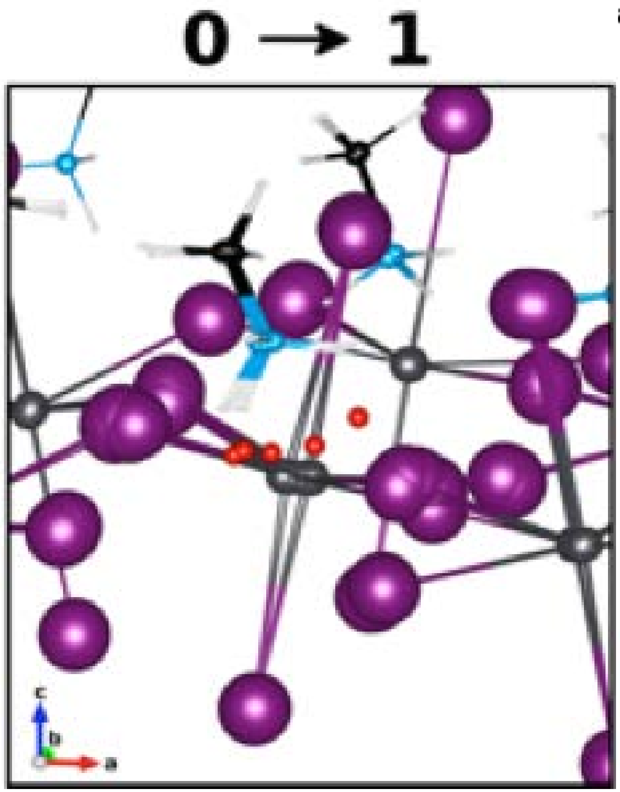
[1] Bourgoin & Corbett, *Phys. Lett.* 38A, 2 (1971)

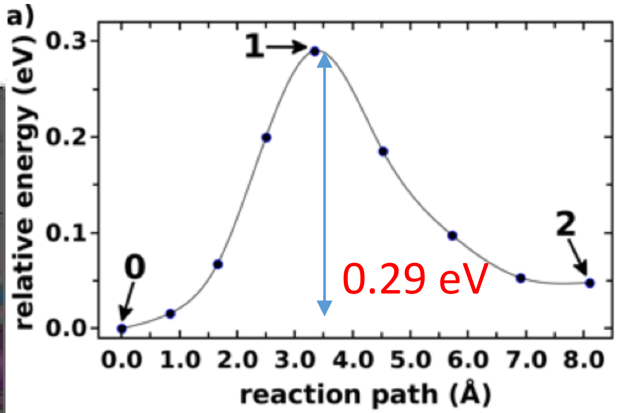
[2] Bar-Yam and Joannopoulos, *Phys. Rev. Lett.* 52, 1129 (1984);

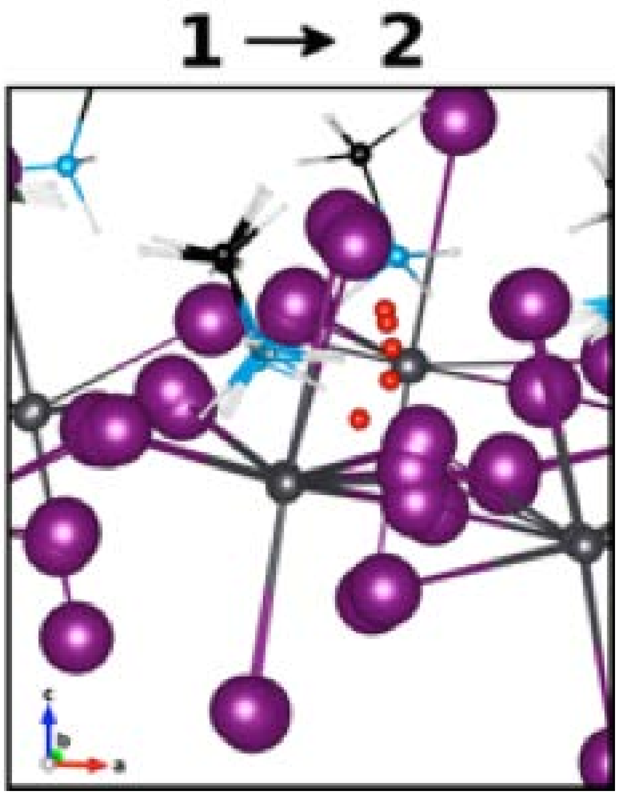
[3] Car *et al.*, *Phys. Rev. Lett.* 52, 1814 (1984)

Minimum energy path for H^+ in $MAPbI_3$

Proton migration between equatorial iodines in $MAPbI_3$







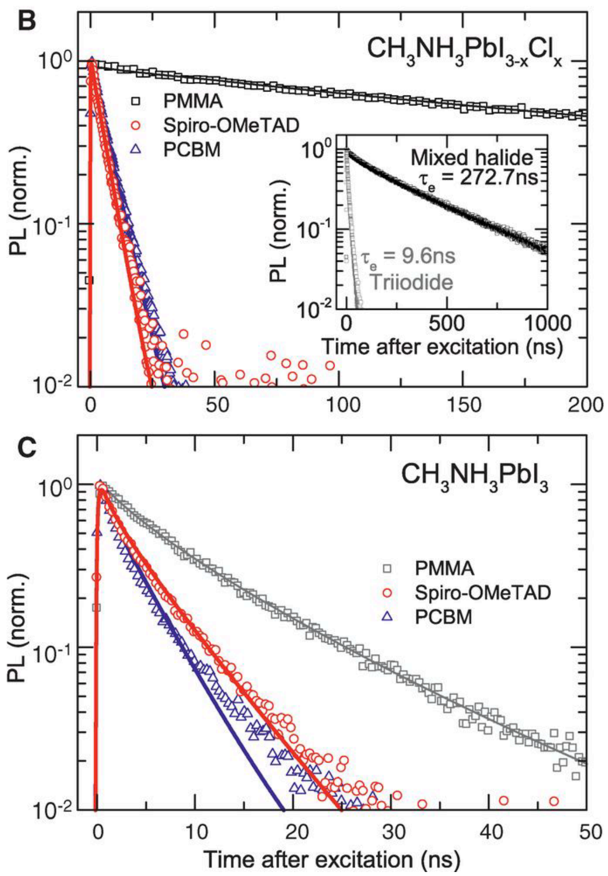
- Overall proton migration is enhanced by successive displacements of iodide atoms.
- The energy barriers for iodide-iodide H^+ transfer can even be **as low as 0.17 eV** if proton migration between different I sites is considered

Observation of Long Carrier Lifetimes

L_D =1069 nm
τ = 273 ns

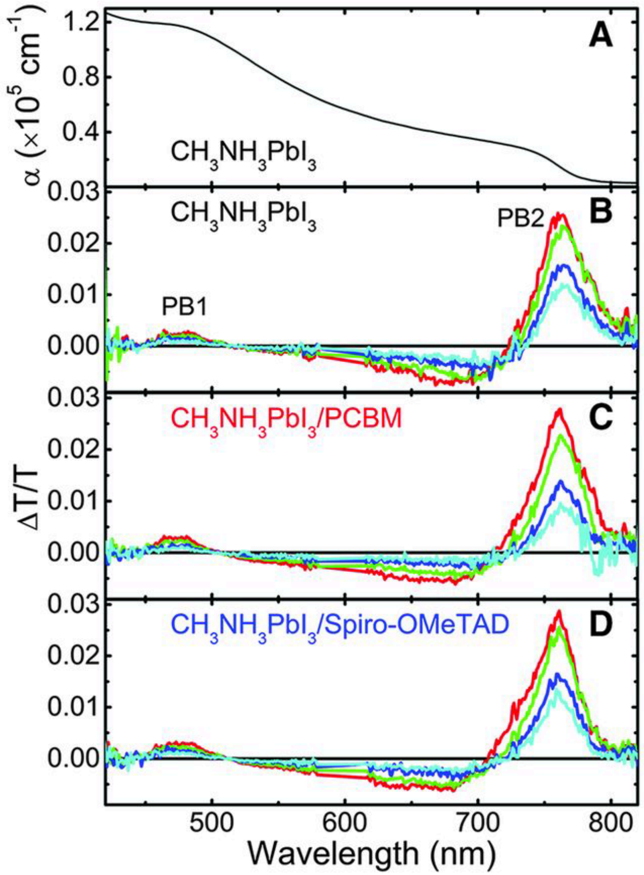
L_D =129 nm
τ = 9.6 ns

Photoluminescence



Science 342, 341 (2013)

Transient Absorption

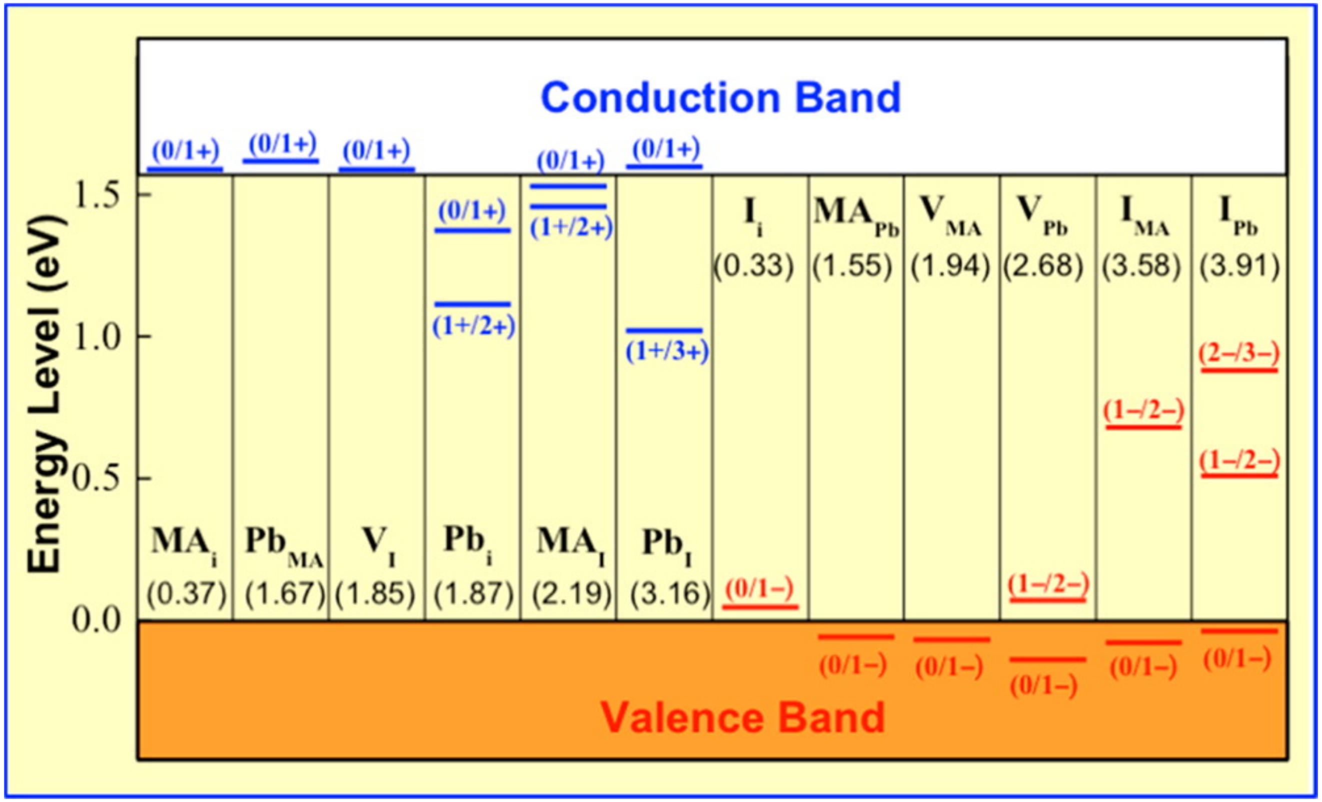


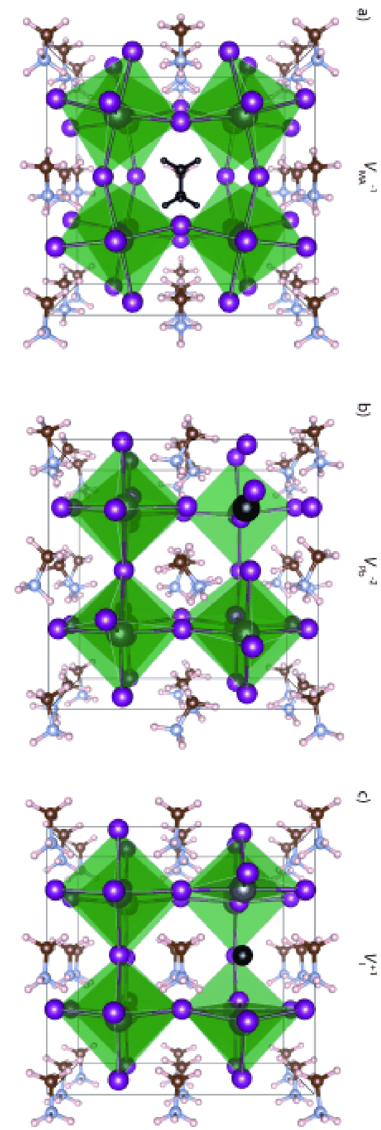
Legend: 1ps 100 ps 500 ps 1 ns

Science 342, 344 (2013)

Explanation of Long Carrier Lifetimes (1)

- Defects with favorable formation energies have shallow levels → **Electronically benign**





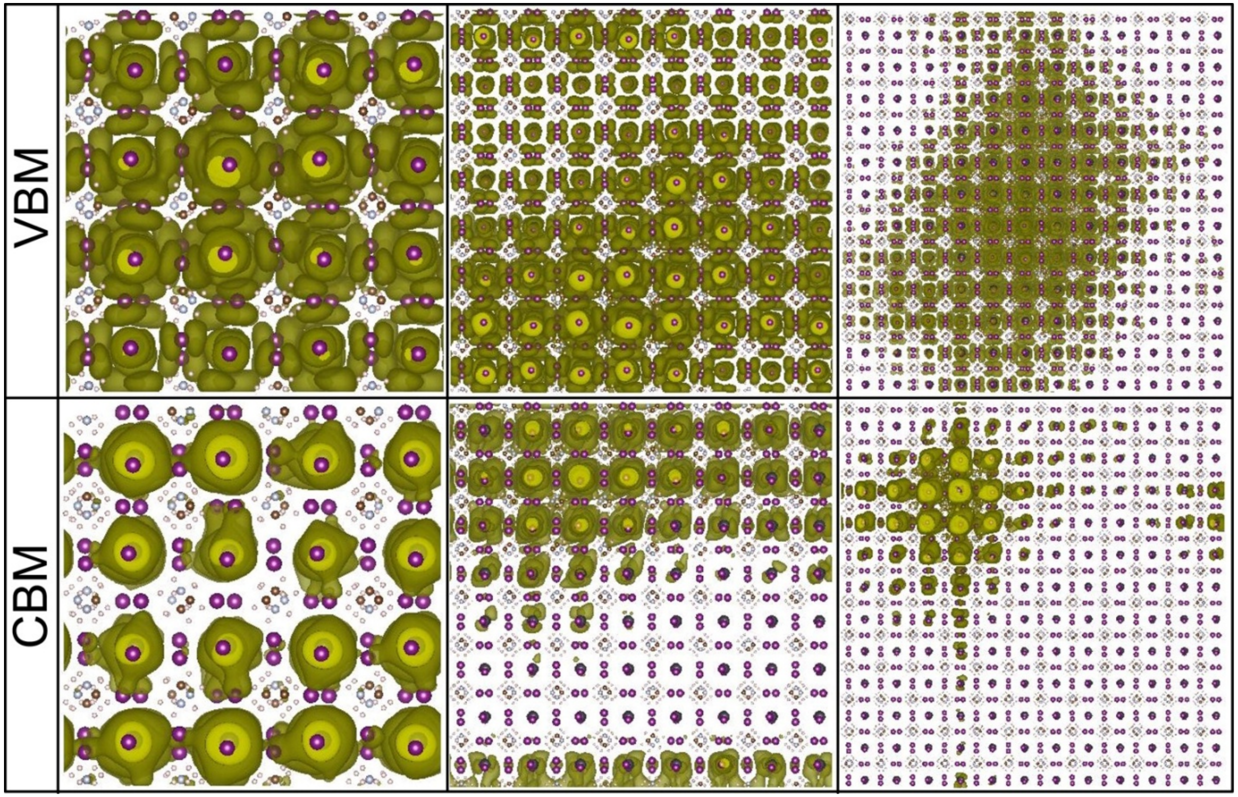
Adv. Mater. 26, 4653 (2014)

J. Phys. Chem. C, 119 , 5253 (2015)

Angew. Chem. 54, 1791 (2015)

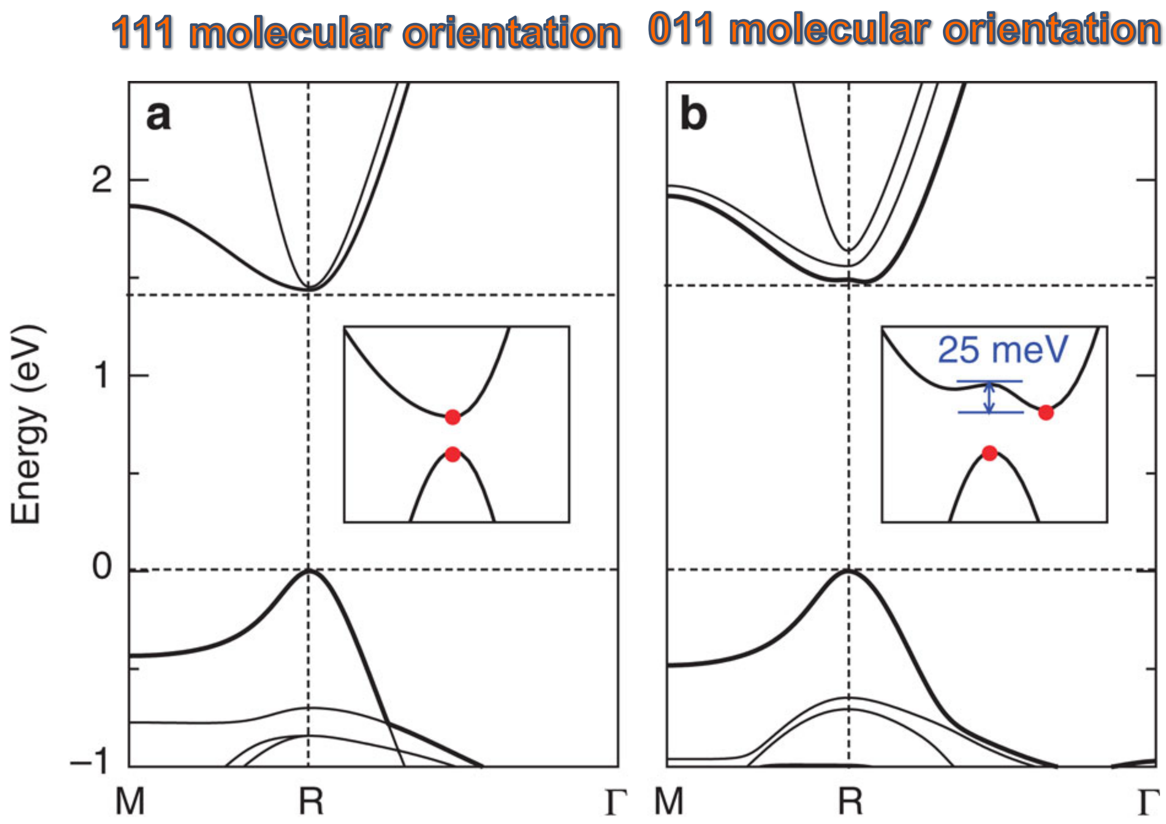
Explanation of Long Carrier Lifetimes (2)

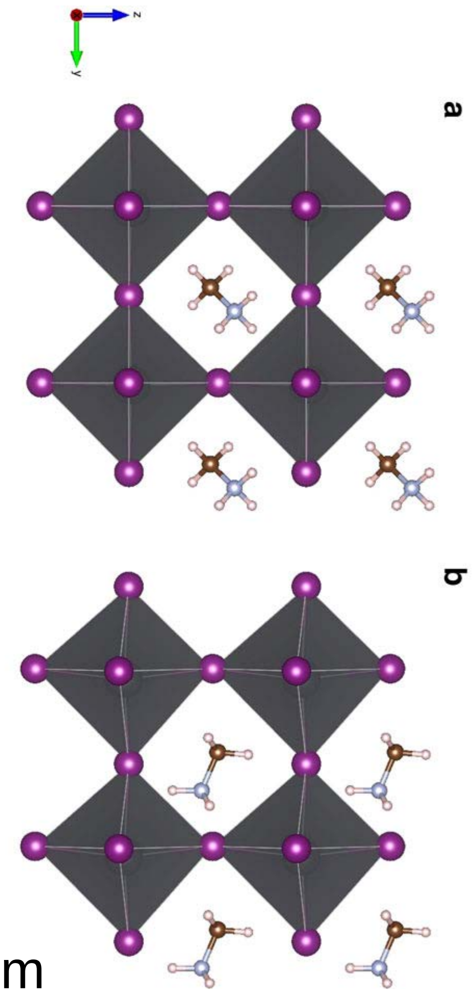
- Charge separation induced by **long range potential fluctuations** associated with molecular orientational disorder.
- Large scale DFT calculations suggest that the localization length is **40 – 60 nm.**



Nano Lett. 15, 248 (2015)

Explanation of Long Carrier Lifetimes (3)



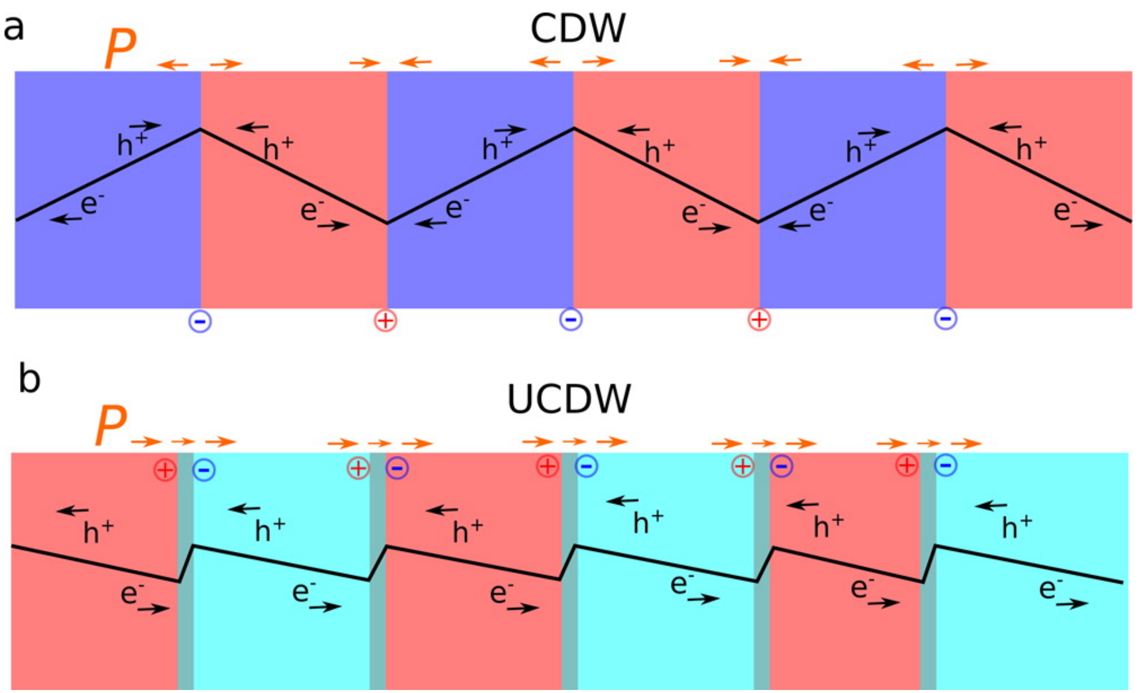


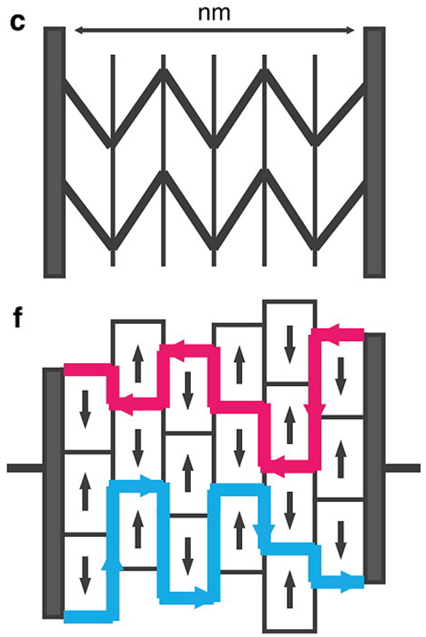
- Dynamical band gap: CBM position fluctuates at room temperature

Nat. Comm. 6, 7026 (2015)

Domain Walls and Carrier Lifetimes

- Potential steps from domain walls aid carrier separation
- Carriers move along potential maxima in multi-domain samples



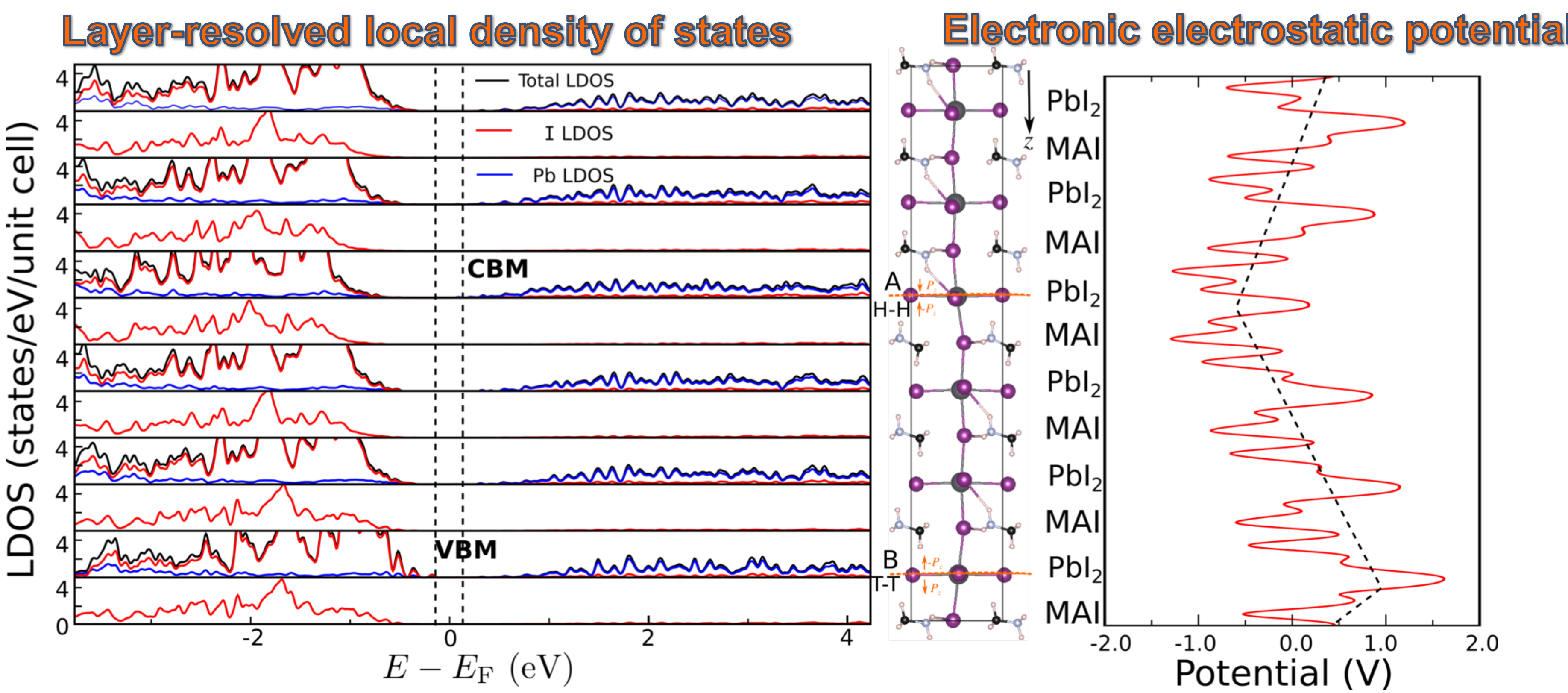


J. Phys. Chem. Lett., 6, 693 (2015)

Nano Lett. 14, 2584 (2014)

Domain wall → Polarization gradient → Built-in electric field

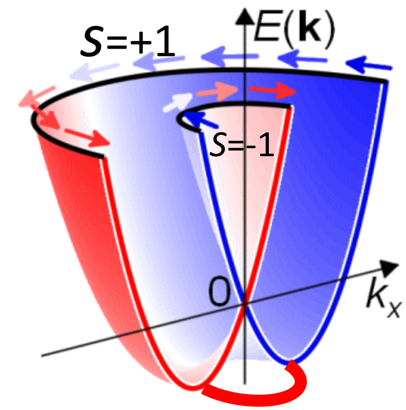
Domain Walls and Carrier Lifetimes



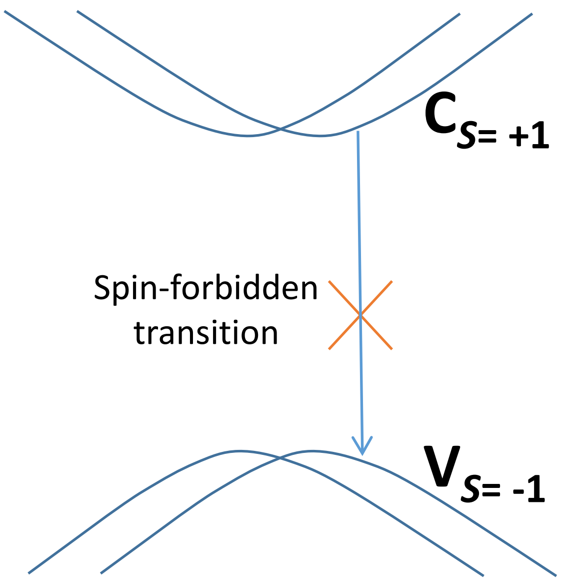
- CBM is located at domain wall A: P_z components meeting with a head-to-head configuration
- VBM is located at domain wall B: P_z components meeting with a tail-to-tail configuration

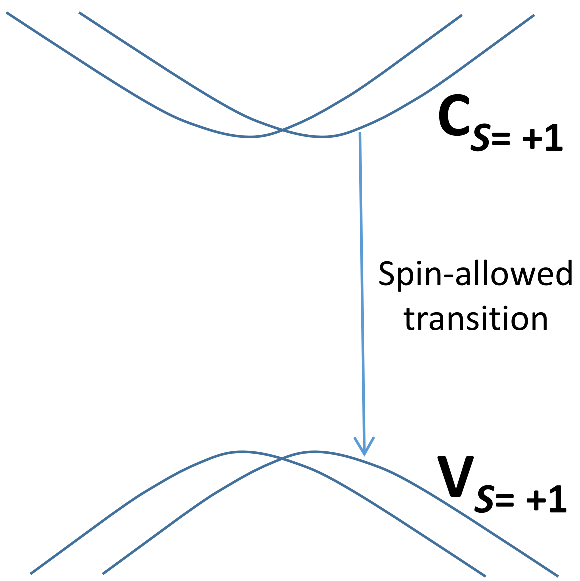
S. Liu et al., J. Phys. Chem. Lett., 6, 693 (2015)

Spin Effects on Carrier Lifetimes



Favorable and unfavorable spin helicities





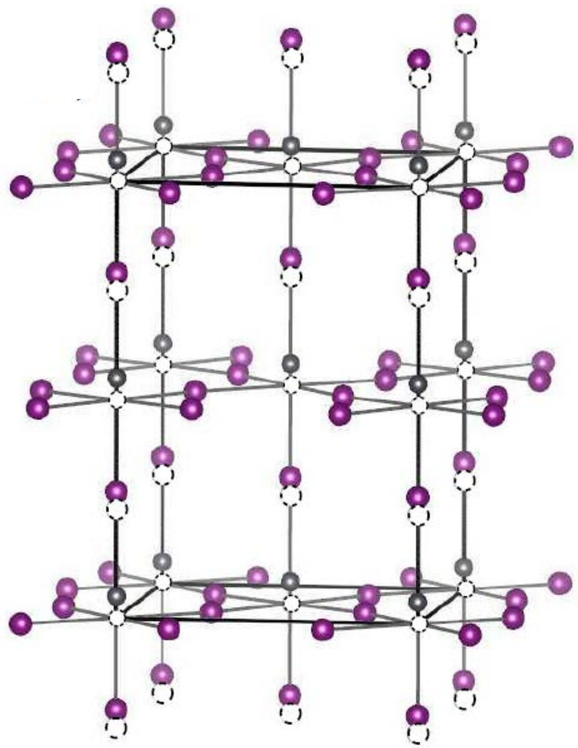
Favorable spin helicity

Unfavorable spin helicity

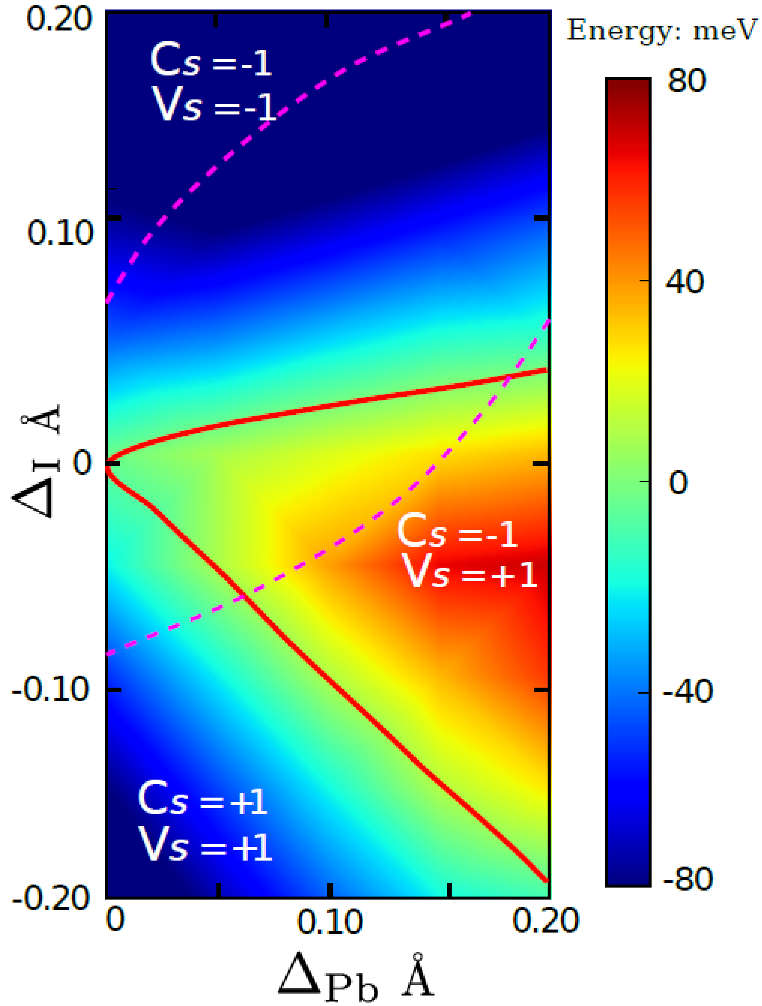
Spin helicity can be controlled by structural distortions

Spin Effects on Carrier Lifetimes

Space group: *I4cm*, Room temperature



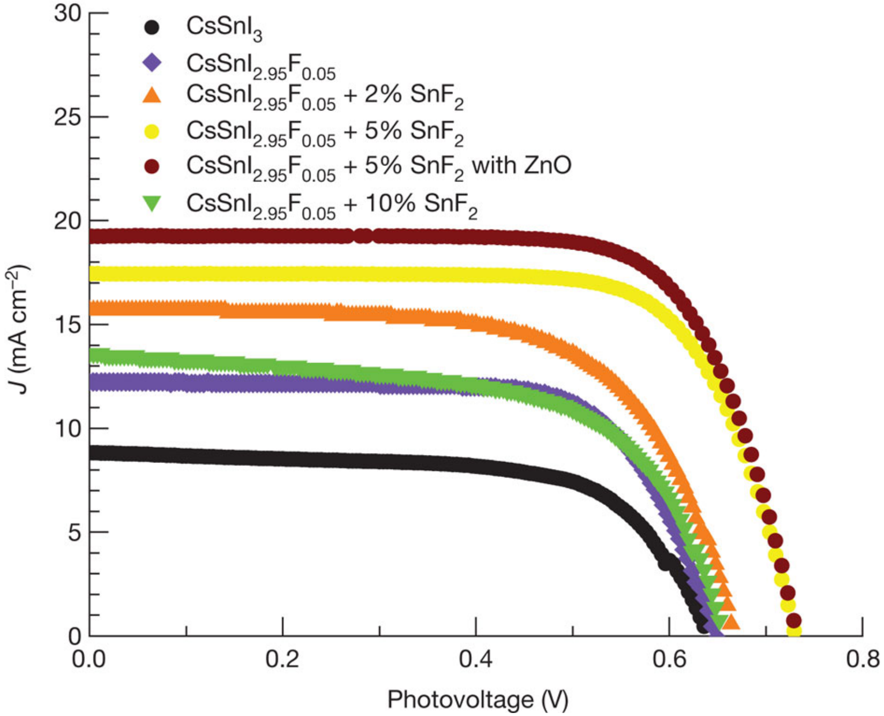
- Pb displacements give rise to favorable spin helicity



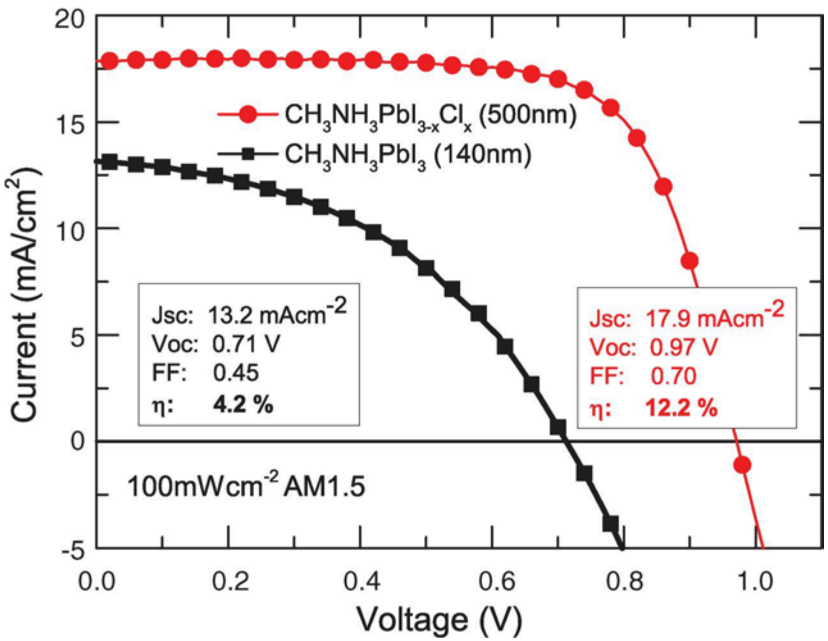
F. Zheng et al, submitted (2015)

Materials design: Halide Substitution

- Halide substitution has significant impact on efficiencies
- What are the materials design principles?
  - Theoretical guidance is needed.



Chung et al., *Nature* 485,486 (2012)

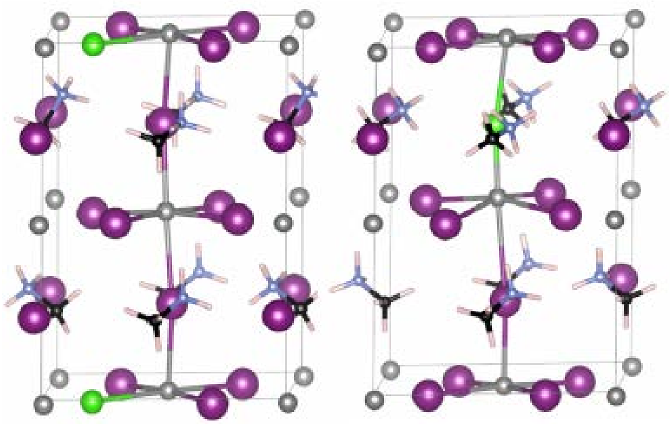


Stranks et al., *Science* 342, 341 (2013)

Materials design: Halide Substitution

Atomic structure of $CH_3NH3PbI_{3-x}Cl_x$

Equatorial Substitution

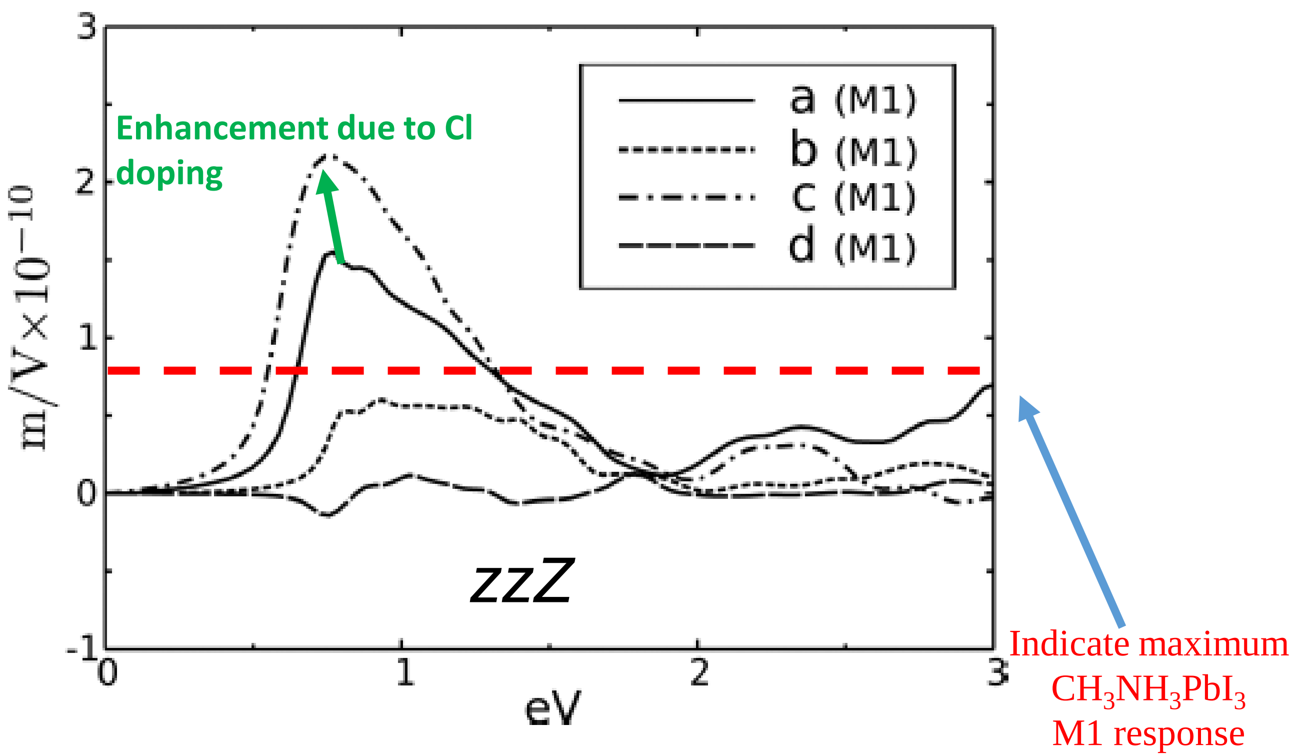


Apical Substitution

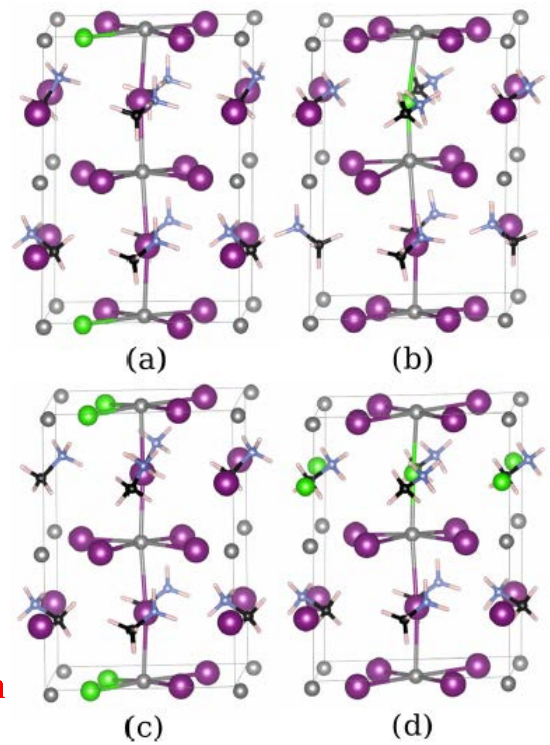
Structure	$\|P_z\|$ ($\mu C/cm^2$)	Band Gap, SOC (eV)
$CH_3NH_3PbI_3$	5.0	0.69
$CH_3NH_3PbI_{3-x}Cl_x$, equatorial	6.2	0.83
$CH_3NH_3PbI_{3-x}Cl_x$, apical	4.4	0.84

J. Phys. Chem. Lett. 6, 31 (2015)

Glass coefficient response of $MAPbI_{3-x}Cl_x$ M1 Structures (polar)



M1: net dipole along z



- Cl substitution increases response in some cases
- Equatorial site substitution gives larger response

Summary

- Ferroelectricity in OMHPs is in debate:
  - Experimental setup may strongly affect the ferroelectricity
  - *A* site molecular dynamics is important for understanding the ferroelectricity
  - Bulk photovoltaic effect in polar order has higher magnitude than $BiFeO_3$, which may explain the large V_{oc}.

- Origin of *J*/*V* hysteresis is still unknown:
  - Ion migration may play an important role in *J*/*V* hysteresis
  - Hydrogen migration in $MAPbI_3$ is studied systematically

- Intrinsic reason of long carrier lifetime:
  - Low defect density; disordered dynamics of molecules; …
  - Domain and domain wall can help separate carriers
  - Rashba spin helicity plays a significant role in explaining long carrier lifetime

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- Domain walls: S.Liu, F.Zheng, N.Z.Koocher, H.Takenaka, F.Wang
- H Diffusion: D. Egger, L. Kronik
- Rashba/lifetime: F.Zheng, L.Z.Tan, S. Liu

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