White Light Emission from 2D Layered Perovskites: Self-Trapped Exciton Mechanism

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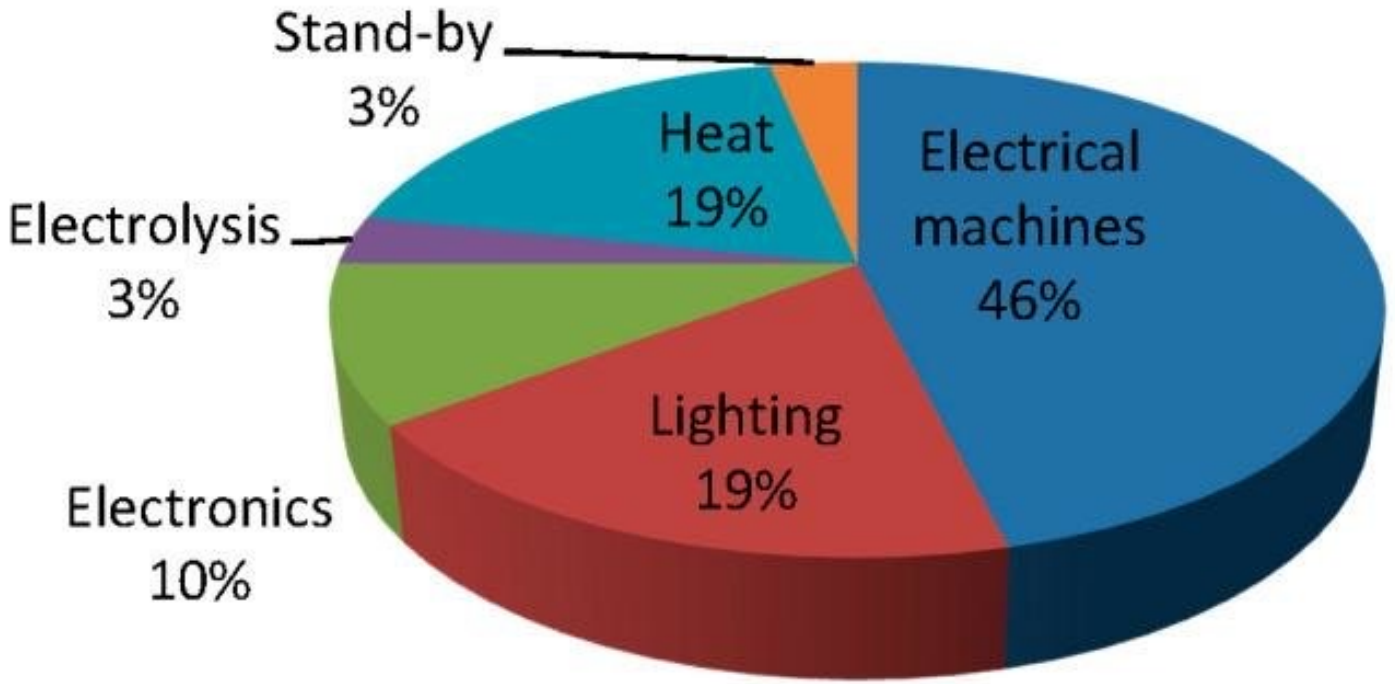
05/17/22

Ongoing Challenges in LED Lighting Industry

Producing **white light** is particularly challenging

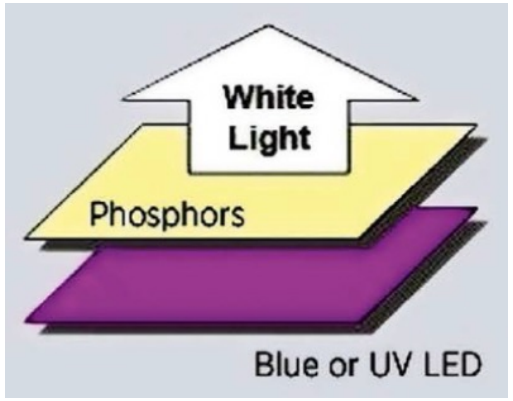


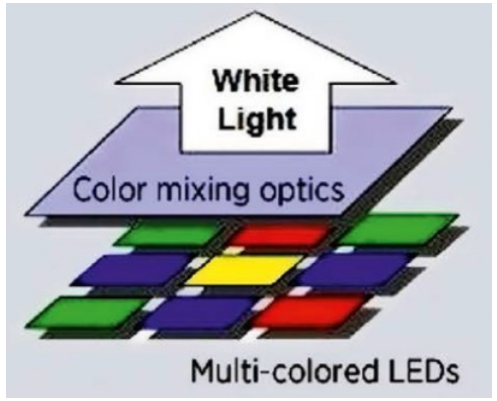
1. Efficiency
2. Color tone
3. Stability

Lei, G et al. "A Review of Design Optimization Methods for Electrical Machines" Energies, 10, 1962 (2017)

Techniques for Producing White Light

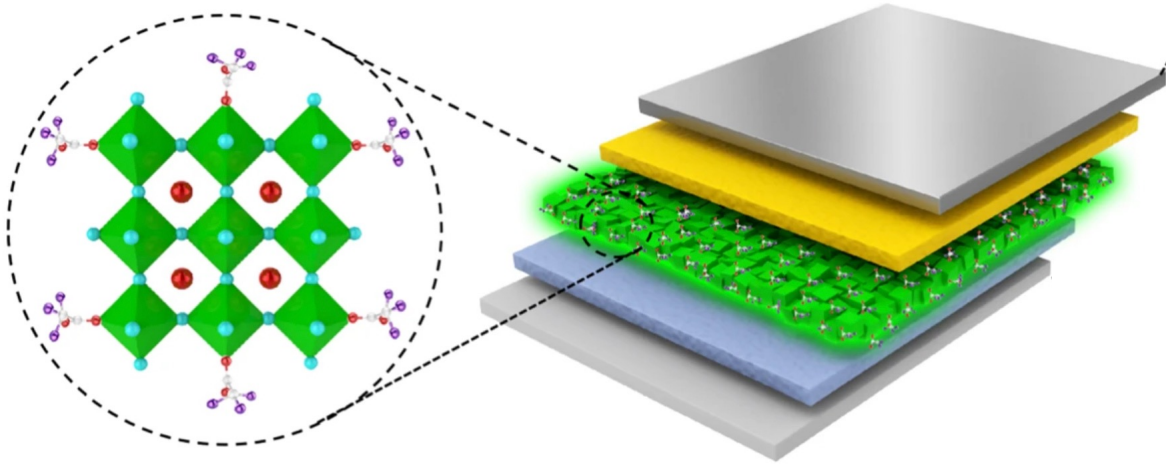
Current LED sources of white light





1. Poor color quality
2. Lowered efficiency

Alternative intrinsic sources of white light

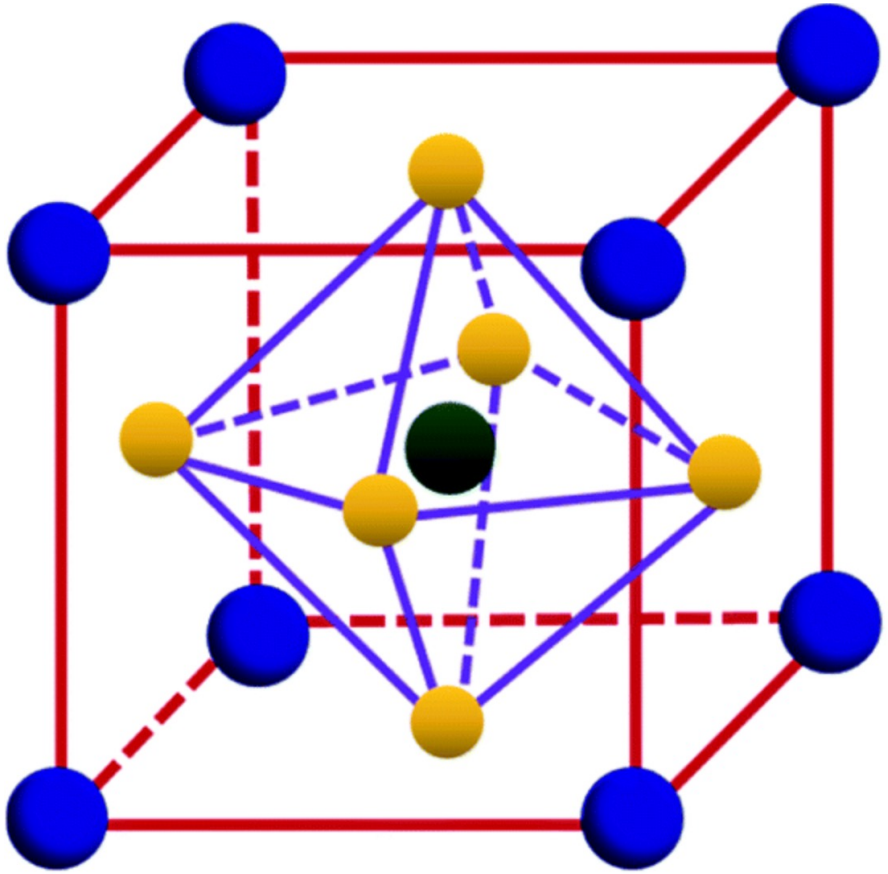


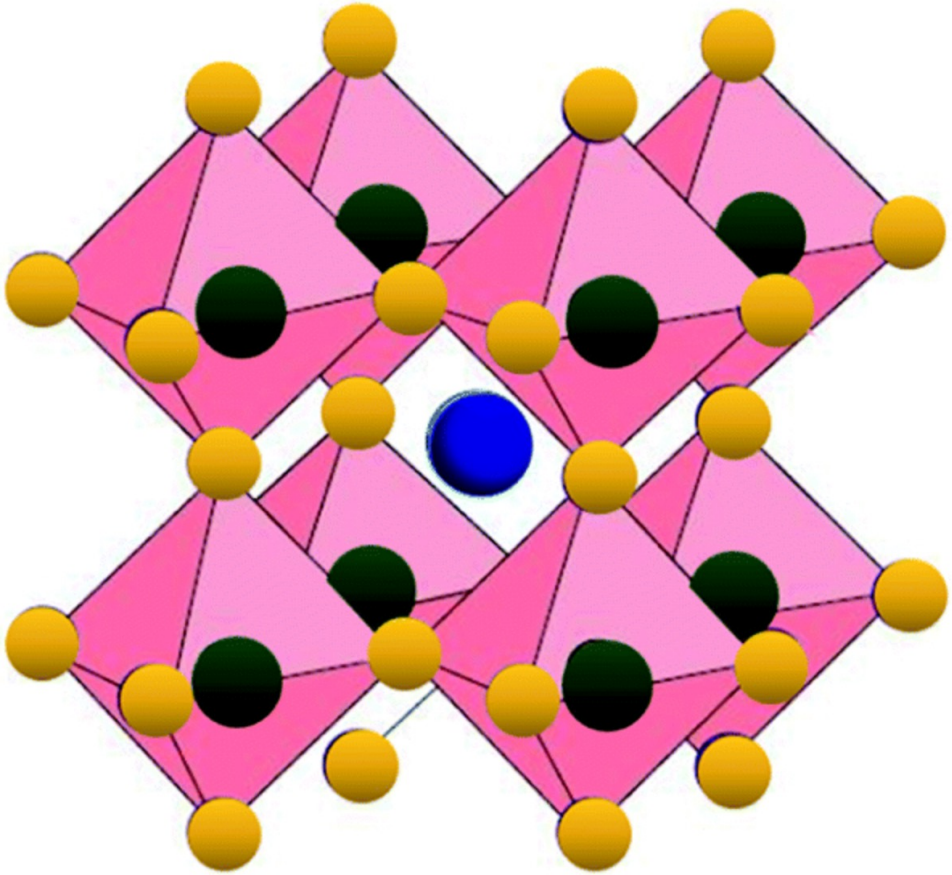
2D hybrid metal halide perovskites are a prime candidate

Figure 1a,b: "Solid-State Lighting: LED Basics" *Office of Energy Efficiency & Renewable Energy*

Figure 2: "New approach improving stability and optical properties of perovskite film" City University of Hong Kong (2019)

Structure of a 3D Perovskite

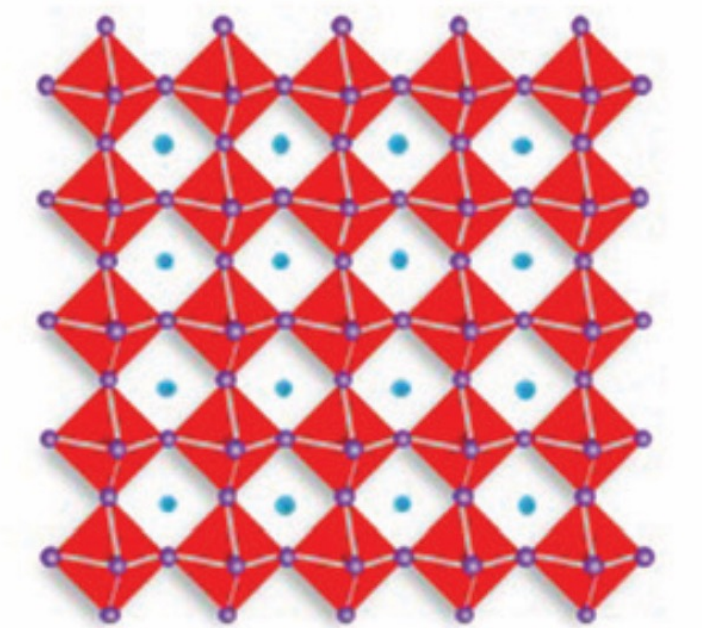




ABX_3

Yi et al. "Will organic-inorganic hybrid halide lead perovskites be eliminated from optoelectronic applications?" Nanoscale Adv. 1, 1276-1289 (2019)

3D Perovskite vs. 2D Layered Perovskite



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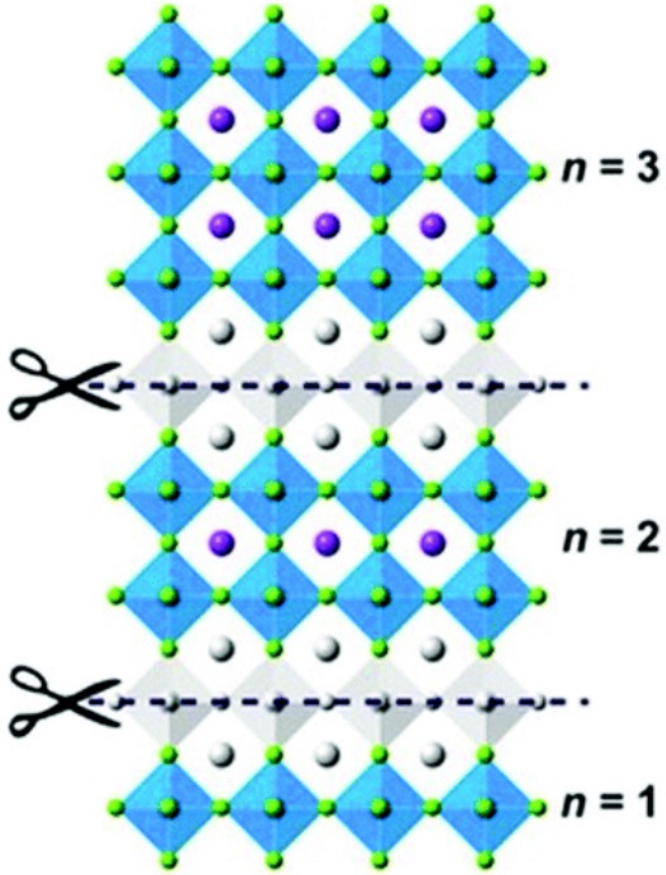
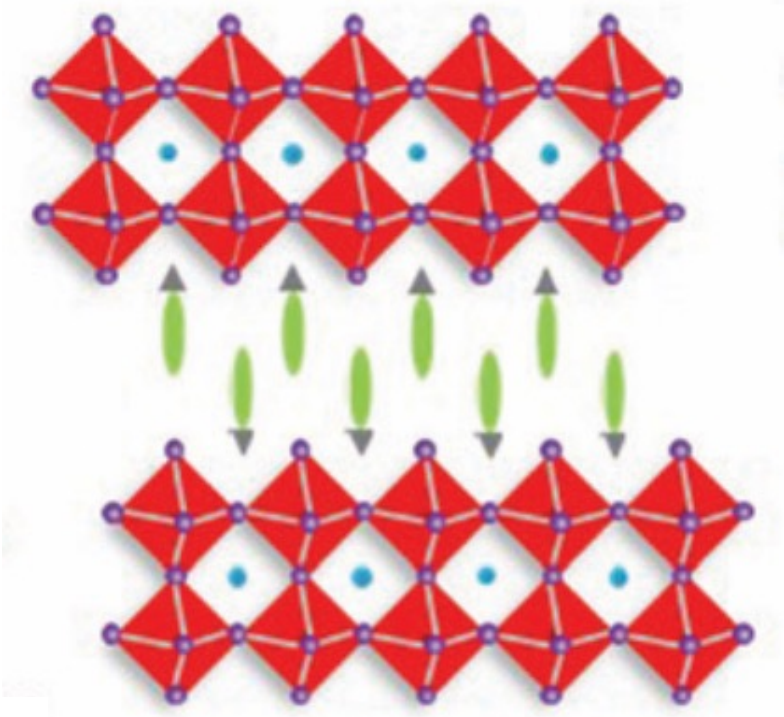


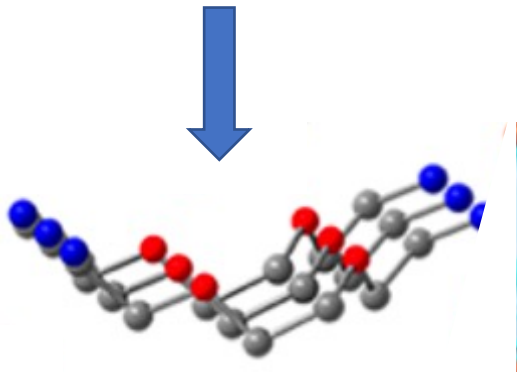


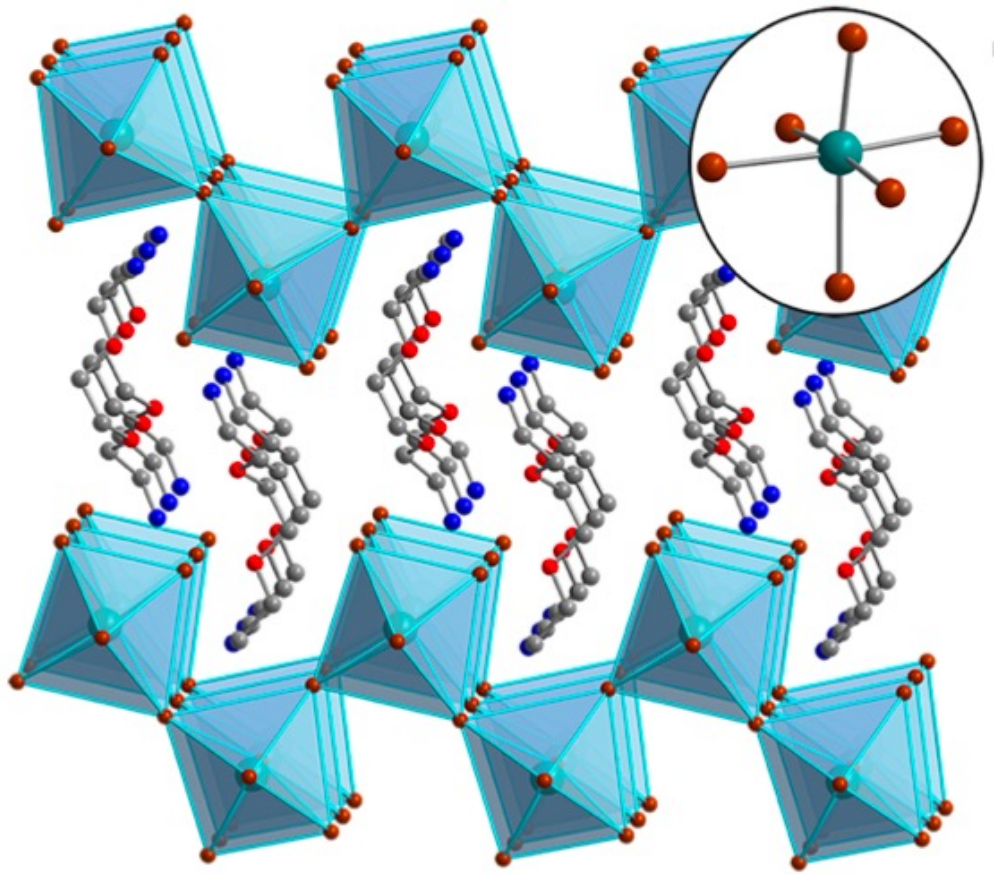
$(A')_m(A)_{n-1}B_nX_{3n+1}$

Zhang, F *et al.* "Advances in two-dimensional organic-inorganic hybrid perovskites", *Energy & Environmental Science* 13, 1154-1186 (2020)

Structure of 2D Hybrid Halide Perovskites

EDBE = H_2N O O NH_2

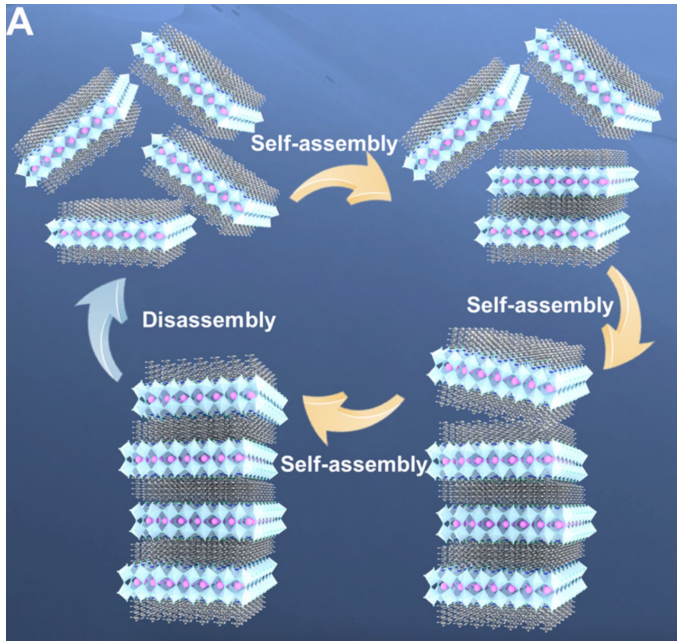




$(EDBE)PbBr_4$

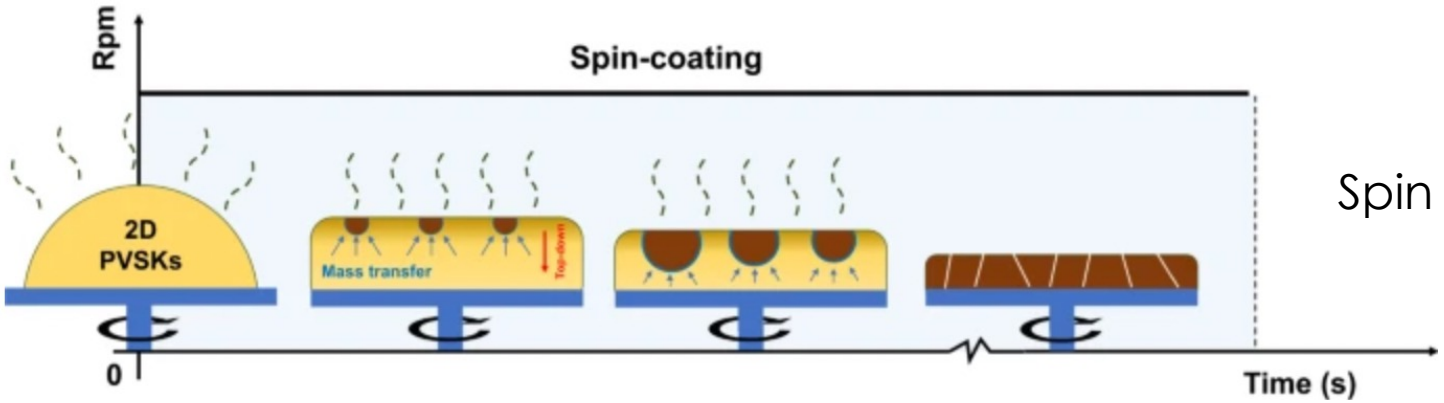
Dohner, E et. al. "Intrinsic White-Light Emission from Layered Hybrid Perovskites", *J. Am. Chem. Soc.* 136, 38, 13154-13157 (2014)

Synthetic Route to Layered Hybrid Perovskites



2D layered perovskites self-assemble

- **Hydrogen bonding** interactions

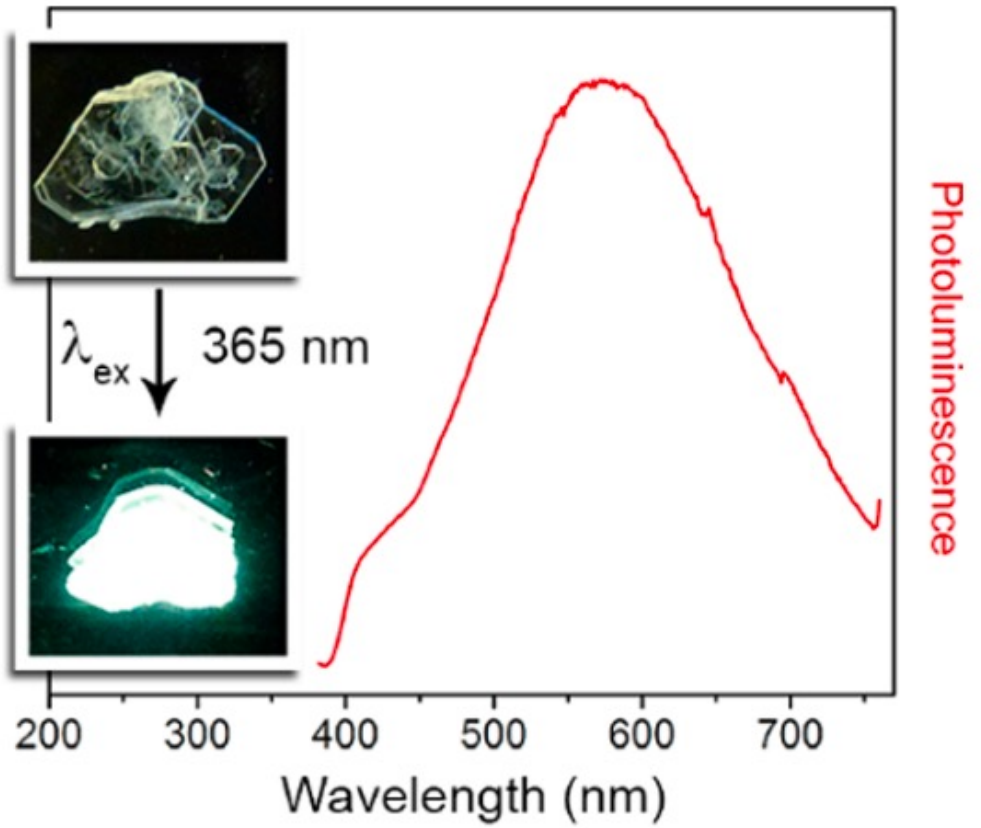


Spin coating self-assembly for thin films

Figure 1: Liu Y et al. "Self-Assembly of Two-Dimensional Perovskite Nanosheet Building Blocks into Ordered Ruddlesden-Popper Perovskite Phase" J. Am. Chem. Soc. 141,33, 13028-13032 (2019)

Figure 2: Yan, Y et al. "Implementing an intermittent spin-coating strategy to enable bottom-up crystallization in layered halide perovskites", *nature communications*, 12, 6603 (2021)

2D Hybrid Perovskites Produce Broadband Emission



Emission spectra of (EDBE)$PbBr_4$

Proposed Mechanism for Broad Emission:

Formation of **self-trapped excitons**

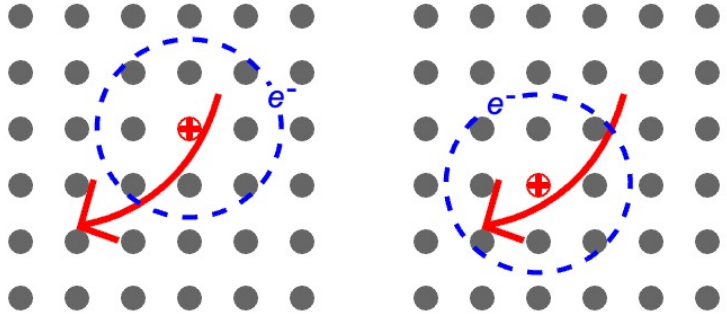
Karunadasa, H *et al.* "White Light Emission from Layered Halide Perovskites. *Acc. Chem. Res.*", 51, 619-627 (2018)

Distinguishing Between Excitons

Exciton: Bound state of an electron and hole that forms upon excitation

Free Exciton: Delocalized exciton that can move through the crystal

- Typically associated with narrow emission



Trapped Exciton: Exciton trapped in a low potential well by local lattice distortions

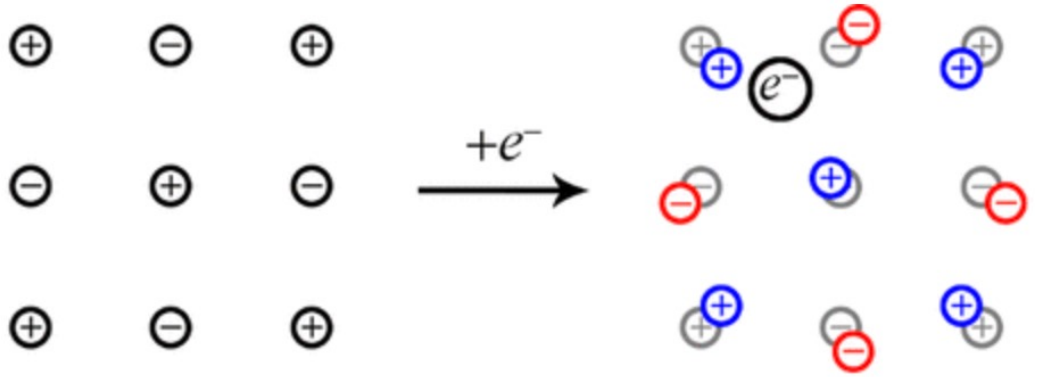
- Lattice distortion can be transient or permanent defect in lattice
- Often associated with broad emission

"Exciton" https://en.wikipedia.org/wiki/Exciton

Excitons Can Cause Lattice Distortions

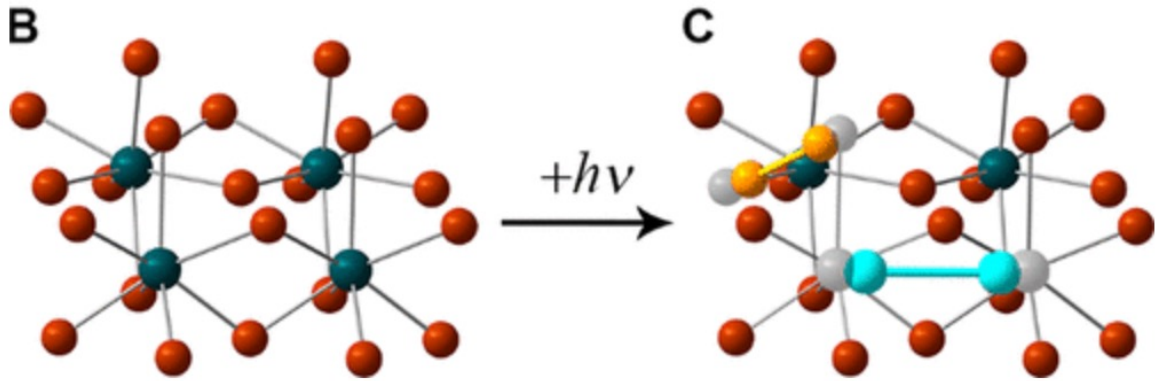
STEs behave like small **polarons**

Polarons: charge carriers that displace neighboring ions in the lattice



Excitons can also displace lattice:

- In 2D perovskite, organics create "softer lattice"
- More susceptible to distorting

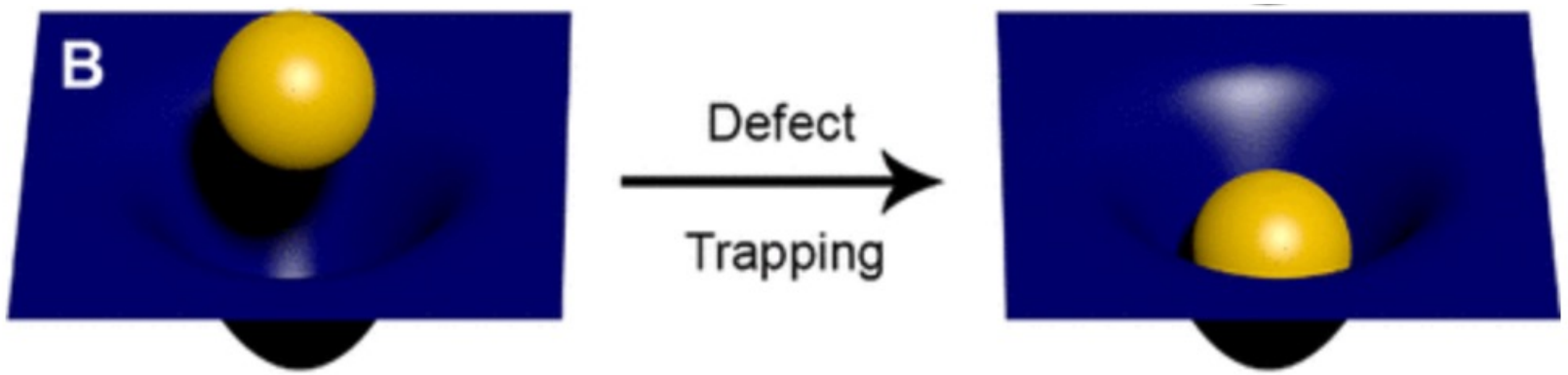


$PbBr_4$ lattice

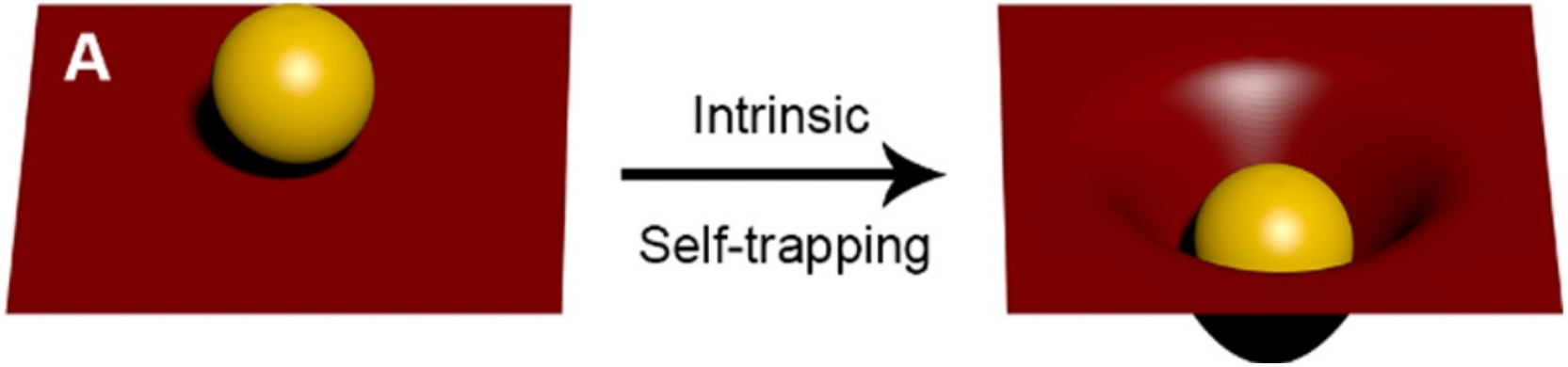
Figures 1, 2: Karunadasa, H *et al.* White Light Emission from Layered Halide Perovskites. *Acc. Chem. Res.*, 51, 619-627 (2018)

Defect Trapping vs Intrinsic Self-Trapping

Defect Trapping: Exciton is trapped in a low potential state by a permanent defect in lattice

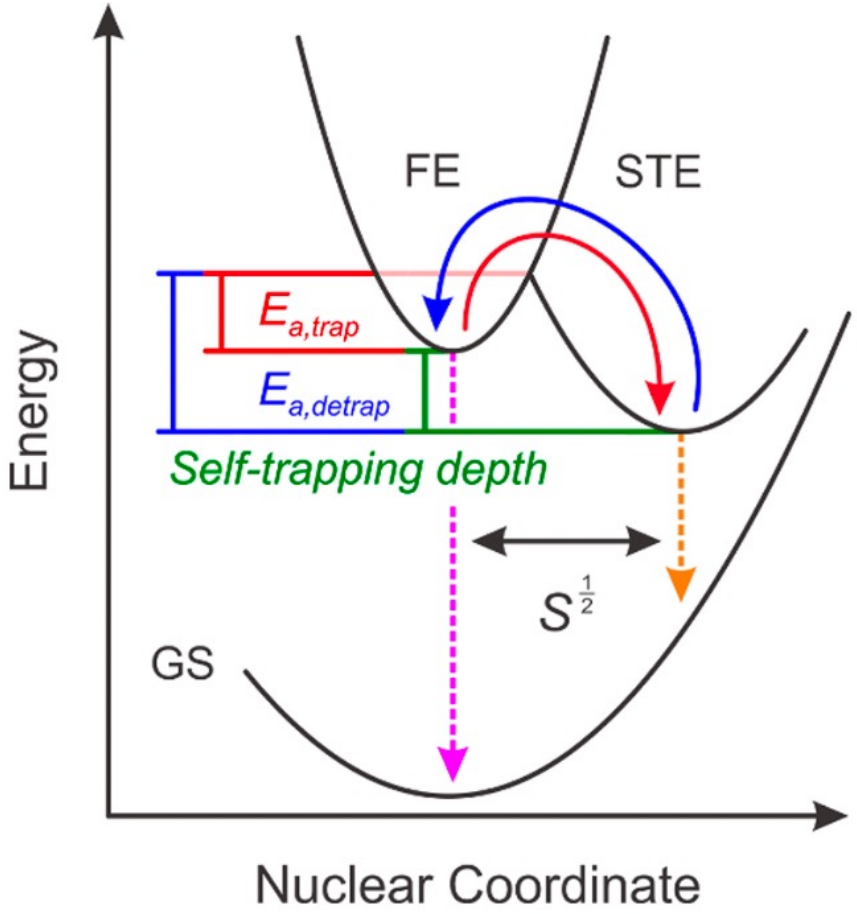


Self-Trapping: Exciton formation causes lattice distortion and then becomes trapped in a low potential state by the distorted lattice

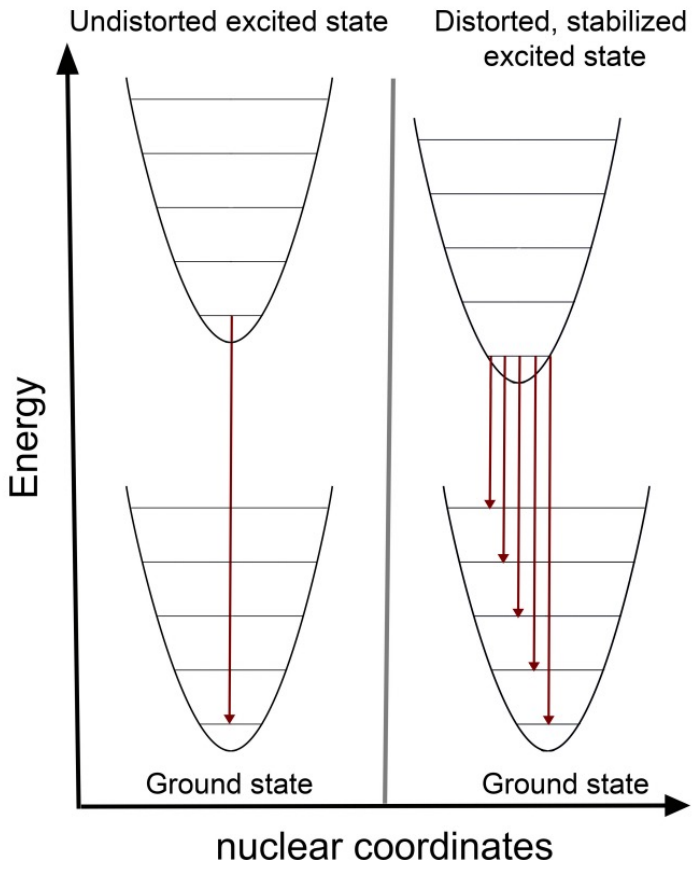


Figures 1, 2: Karunadasa, H *et al.* White Light Emission from Layered Halide Perovskites. *Acc. Chem. Res.*, 51, 619-627 (2018)

Self-Trapped Excitons and Broad Emission



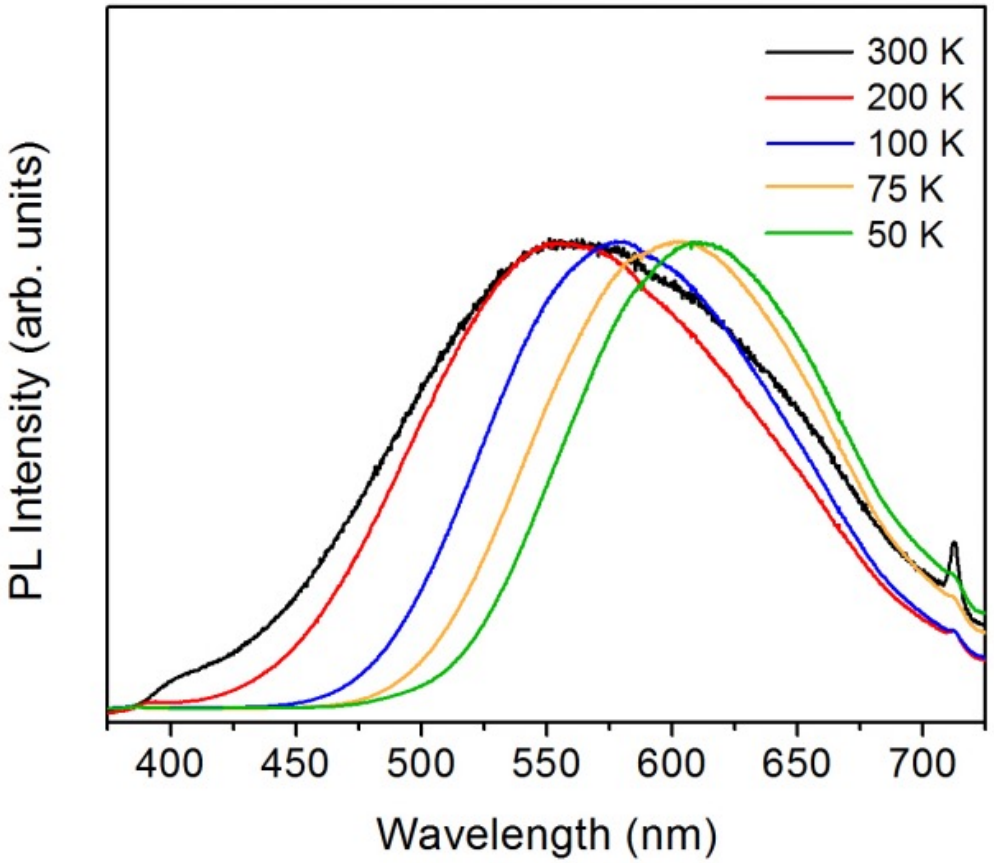
Self trapped exciton state is distorted from free exciton state



Distorted state results in range of emission wavelengths

Figures 1, 2: Karunadasa, H *et al.* White Light Emission from Layered Halide Perovskites. *Acc. Chem. Res.*, 51, 619-627 (2018)

Evidence for Self-Trapped Exciton Formation



PL spectrum of (EDBE)[$PbBr_4$]

- Decrease in temperature = more narrow emission
- Due to decrease in vibrations and less phonon coupling

Evidence is not complete…

Dohner, E et. al. Intrinsic White-Light Emission from Layered Hybrid Perovskites, *J. Am. Chem. Soc.* 136, 38, 13154-13157 (2014)

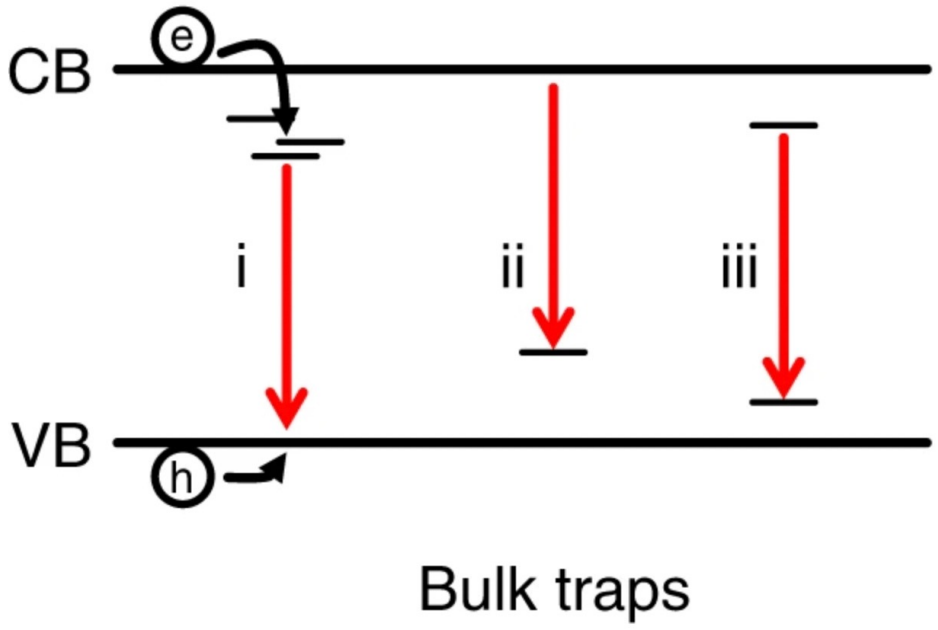
Defects May be Responsible for Broad Emission

$(PEA)_2PbI_4$:

Iodine vacancies cause broad emission

Evidence:

- Broad emission not observed for different synthetic routes

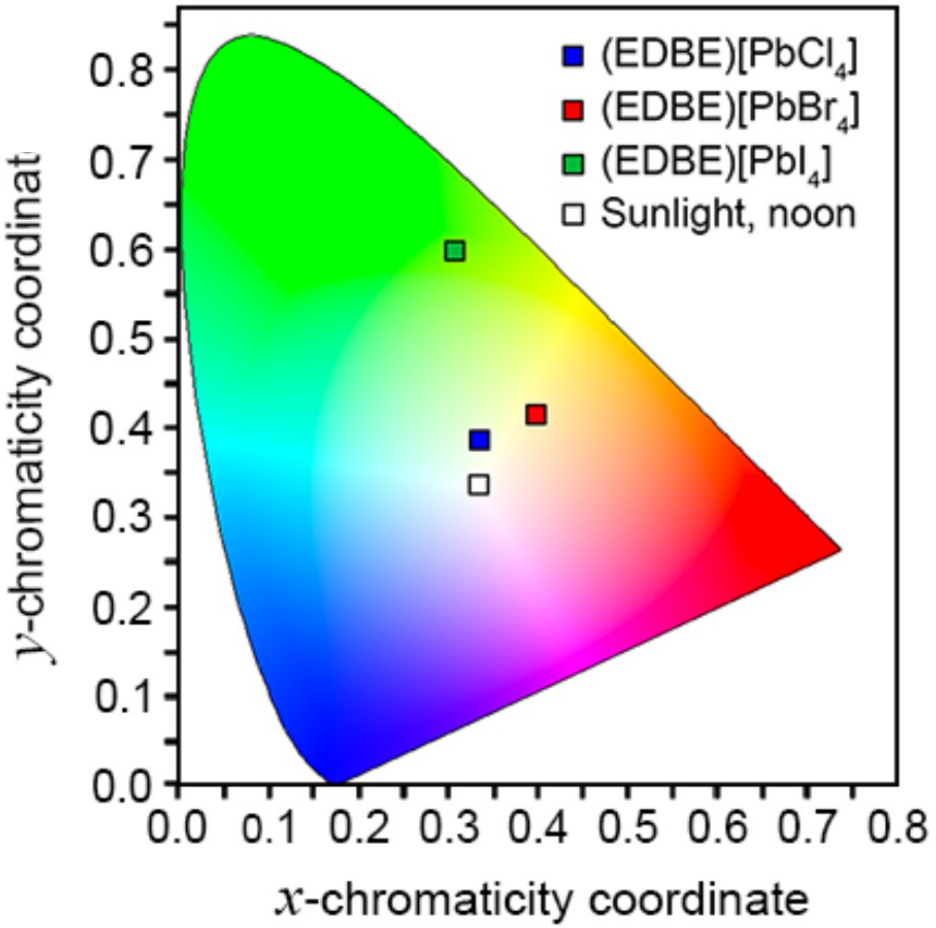


Defect induced in-gap trap states

Kahmann, S. Tekenlenburg, E. Duim, H. Kamming, M. Loi, M. "Extrinsic nature of the broad photoluminescence in lead iodide-based Ruddlesden-Popper perovskites" Nature Communications, 11, 2344 (2020)

White Light Emission is Highly Tunable in 2D Perovskites

Altering halogen component shifts wavelength of light on spectrum



Sunlight (0.33,0.33)

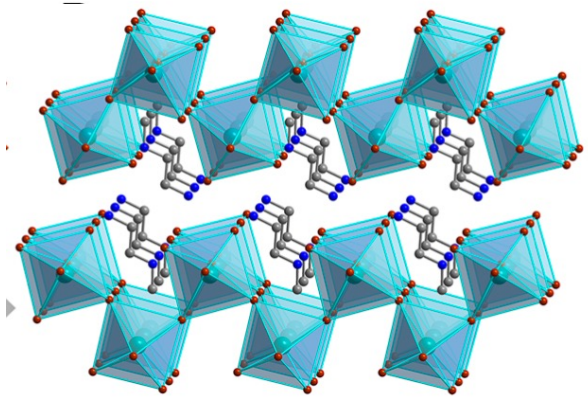
- More electronegative halides = higher energy emission
- Chlorine compound is more blue-shifted

Dohner, E et. al. Intrinsic White-Light Emission from Layered Hybrid Perovskites, *J. Am. Chem. Soc.* 136, 38, 13154-13157 (2014)

Efficiencies Need to be Improved

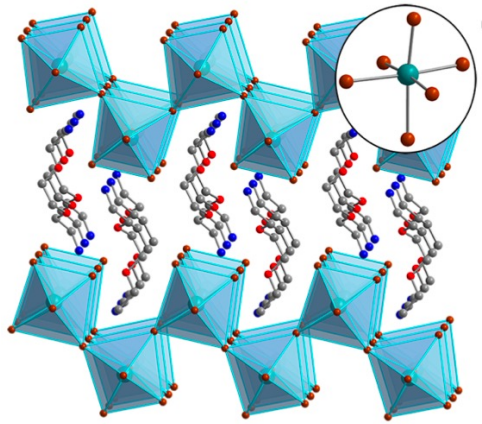
$$\text{PLQY} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

Generation 1 2D Hybrid Halide: (N-MEDA)$[PbBr_4]$



PLQY = 1.5%

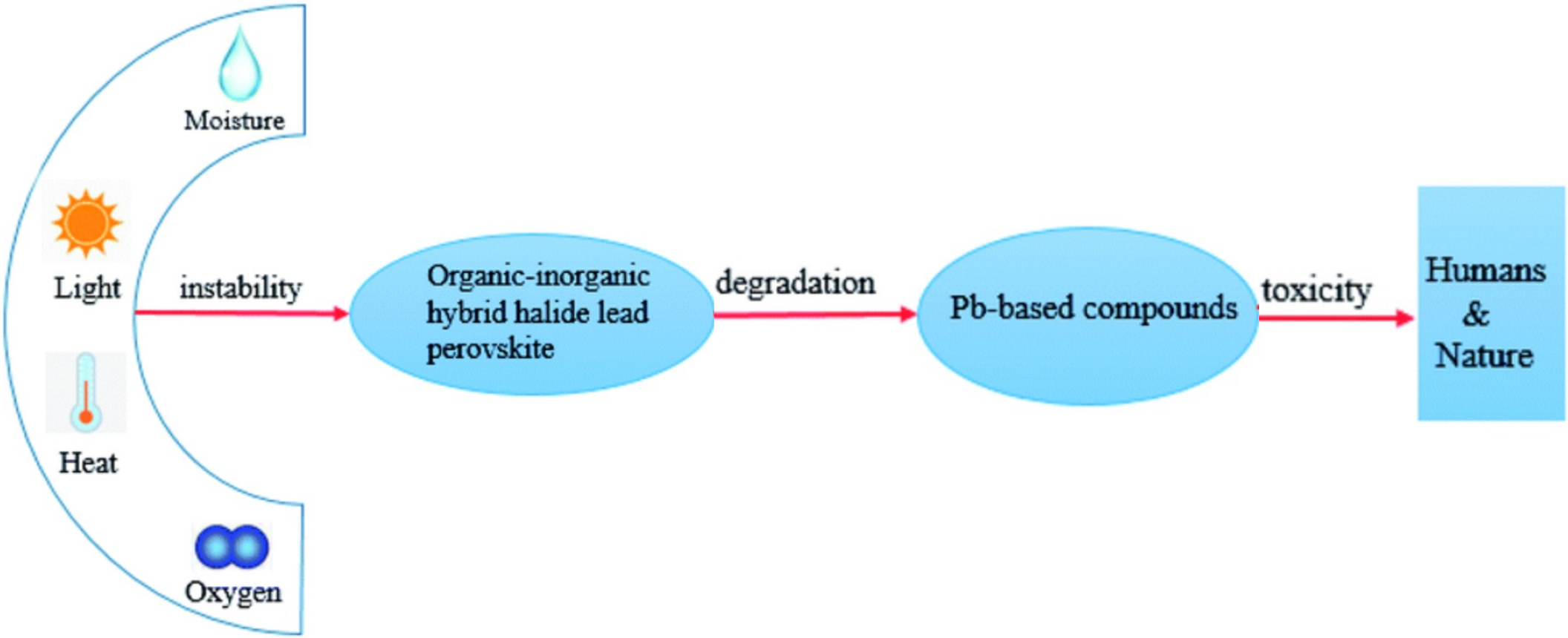
Generation 2 2D Hybrid Halides: (EDBE)$[PbBr_4]$



PLQY = 9%

Figure 1: Dohner, E et al. Self-Assembly of Broadband White-Light Emitters, *J. Am. Chem. Soc.* 136, 5, 1718-1721 (2014)
Figure 2: Dohner, E et. al. Intrinsic White-Light Emission from Layered Hybrid Perovskites, *J. Am. Chem. Soc.* 136, 38, 13154-13157 (2014)

Other Concerns with Hybrid Lead Halide Perovskites



Yi, J. et al. "Will organic-inorganic hybrid halide perovskites be eliminated from optoelectronic applications" *Nanoscale Advances*, 1, 1276-1289 (2019)

Key Takeaways

- 2D hybrid structure promotes exciton-phonon coupling and self-trapped exciton formation
- Broad emission is generally attributed to self-trapped excitons
- Intermediate trap states or extrinsic defects could also cause broad emission in certain 2D materials
- 2D Layered perovskites require a higher efficiency and improved stability to be practical.

References

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Questions?