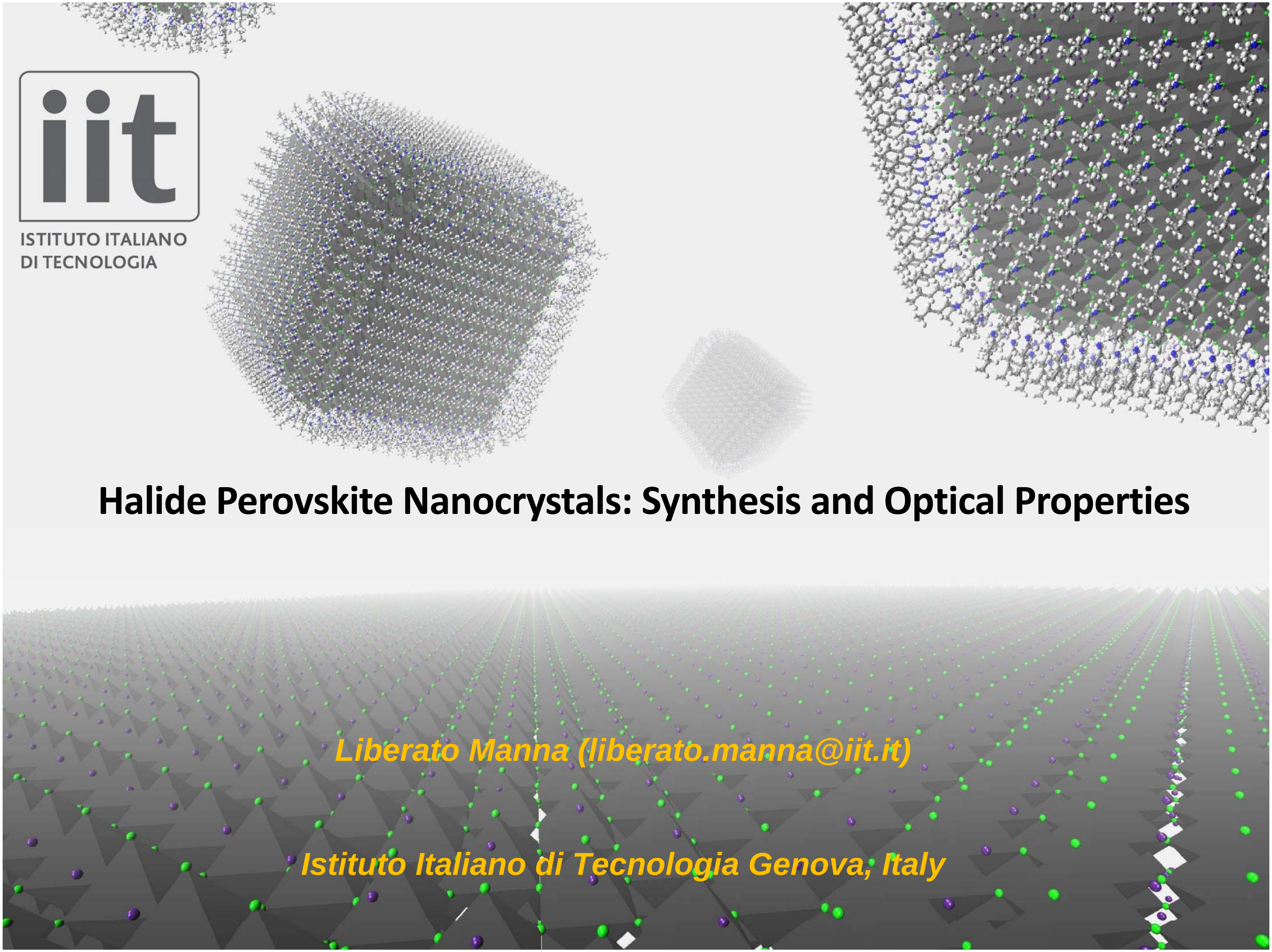


ISTITUTO ITALIANO
DI TECNOLOGIA

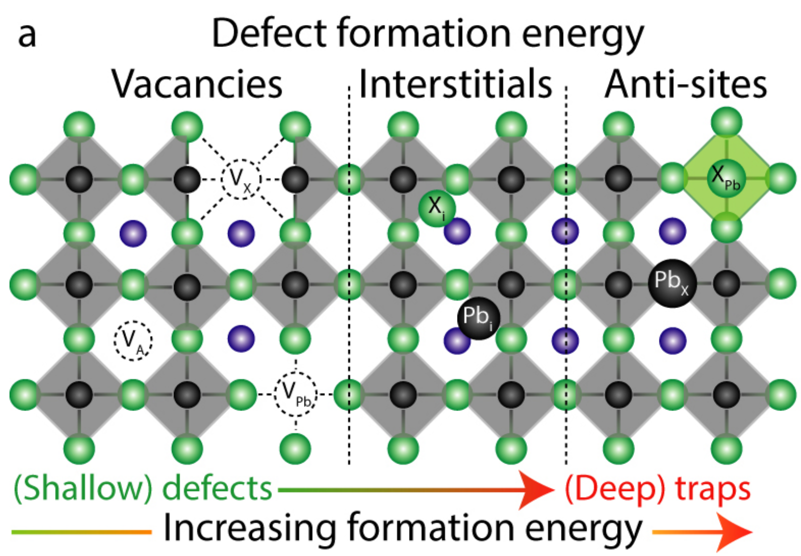
Halide Perovskite Nanocrystals: Synthesis and Optical Properties

Liberato Manna (liberato.manna@iit.it)

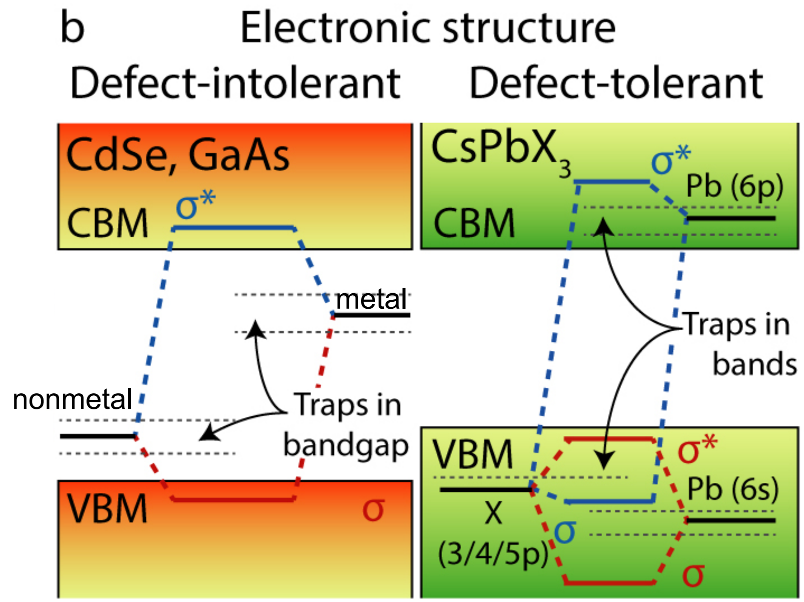
Istituto Italiano di Tecnologia Genova, Italy

Lead Halide Perovskites ($APbX_3$)

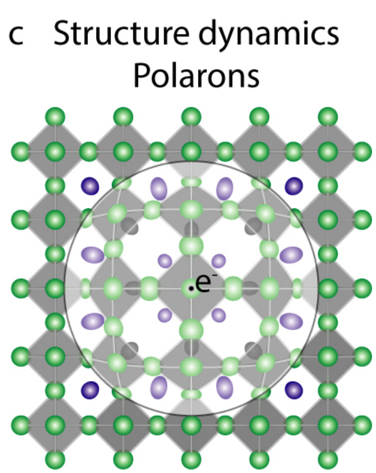
Hard to misplace ions in the structure



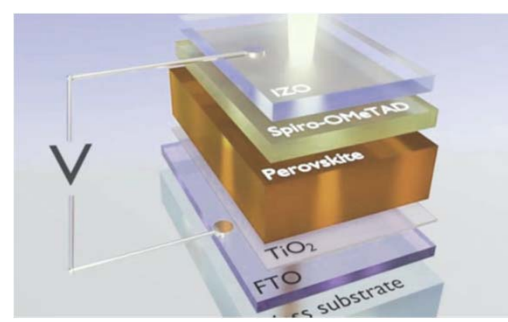
Hard to form mid-gap trap states



Reduced carrier scattering/recombination by the formation of polarons



Perovskite solar cells at 25.2% efficiency in 2019 in single-junction architectures



Akkerman, et al. *Nat. Mater.* **2018**, 17, 394-405; Shamsi et al., *Chem. Rev.* **2019**, 119, 3296–3348

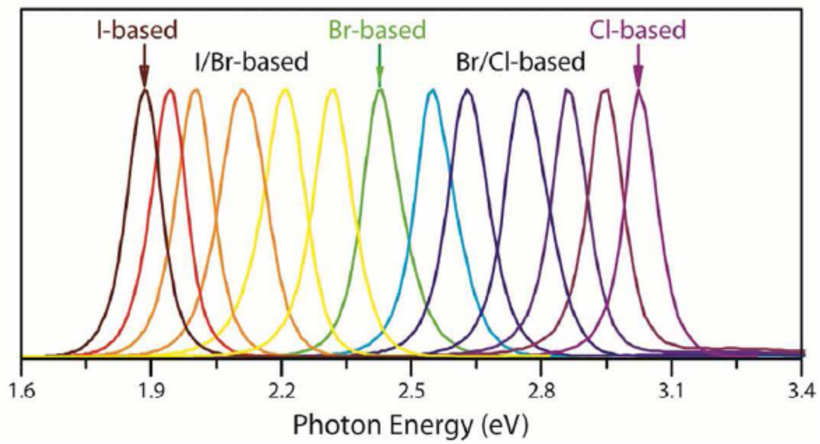
https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20190802.pdf

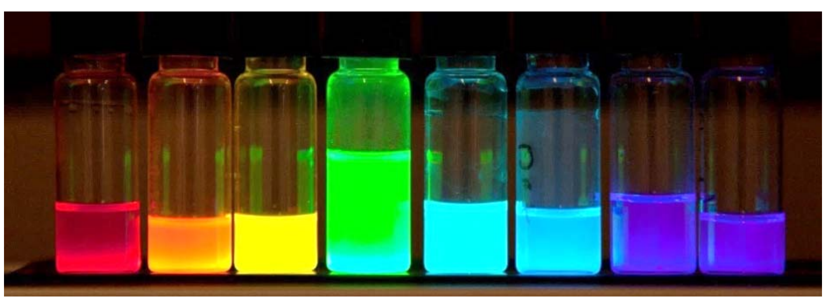
Lead Halide Perovskite ($APbX_3$) Nanocrystals

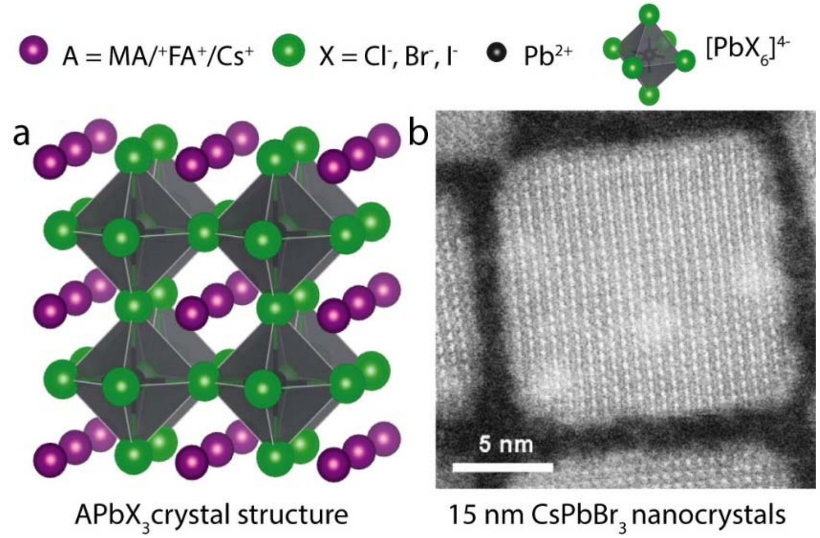
As in bulk crystals and thin films, properties are tunable by changing both the "A" cations and the X anions

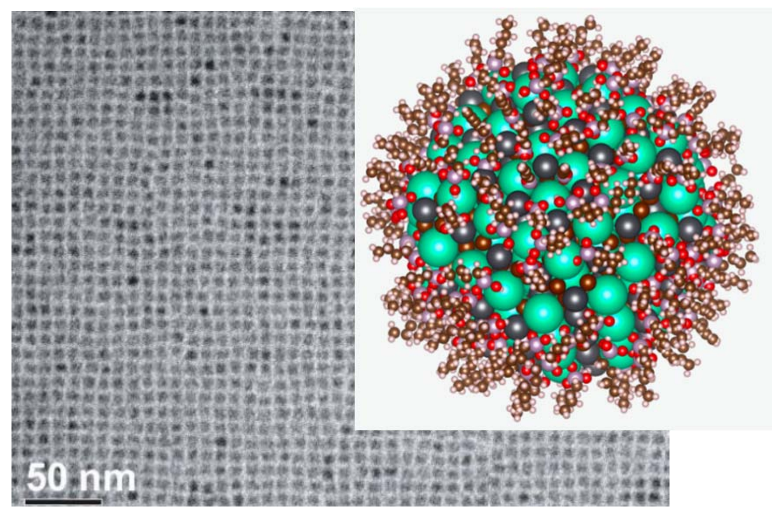
Nanocrystals (NCs), even more tunable in their properties *via* quantum confinement effects

Good size and shape control, **high PLQY!**





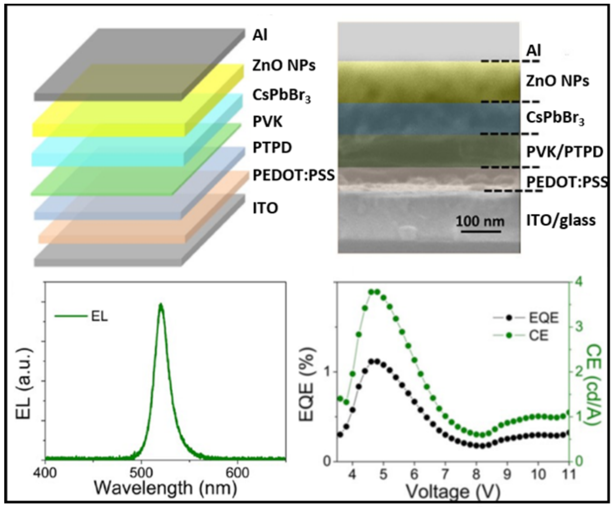




- L. Protesescu. *et al*. *Nano Letters* **15**, 3692-3696, **(2015)**
- Akkerman, et al., *Nat. Mater.* **2018**, 17, 394-405
- Shamsi, et al. *Chem. Rev.* **2019**, 119, 3296–3348

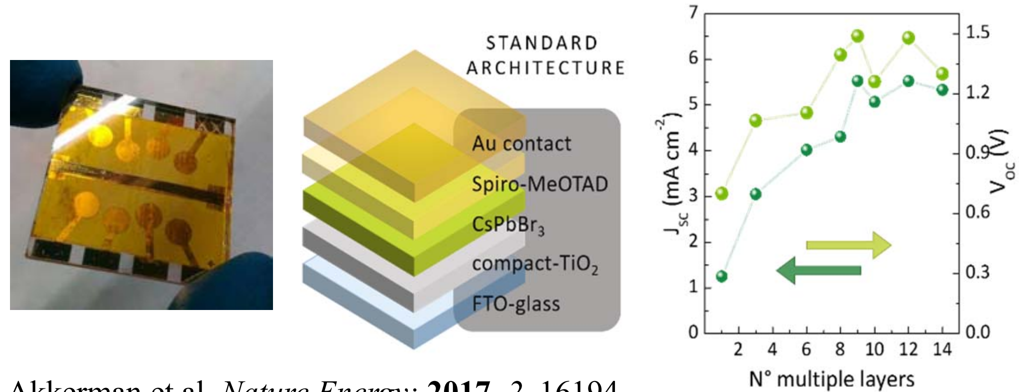
Lead Halide Perovskite Nanocrystals: Applications from our group/collaborations

Electroluminescent LEDs



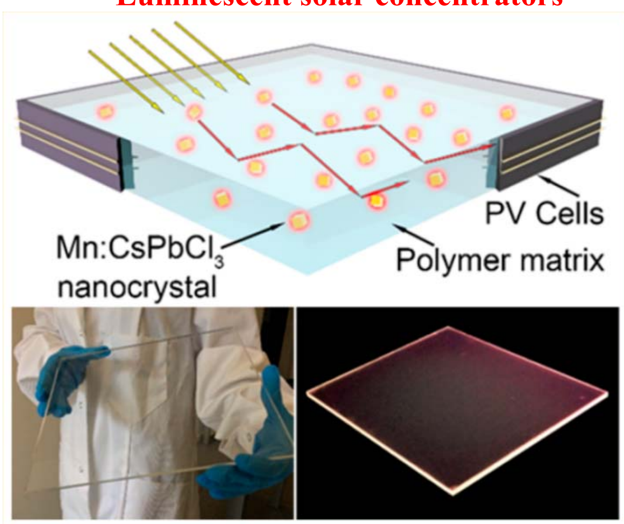
Shamsi, J. et al. *ACS Nano* **2017**, *11*, 10206-10213

Solar cells

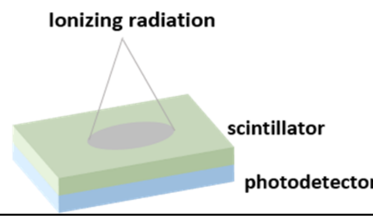


Akkerman et al. *Nature Energy:* **2017**, *2,* 16194

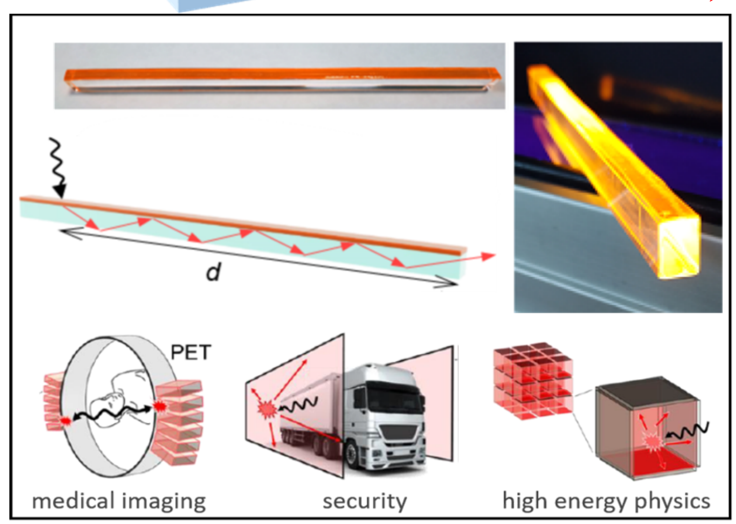
Luminescent solar concentrators



Meinardi, F. et al. *ACS Energy Lett.* **2017**, *2*, 2368-2377.

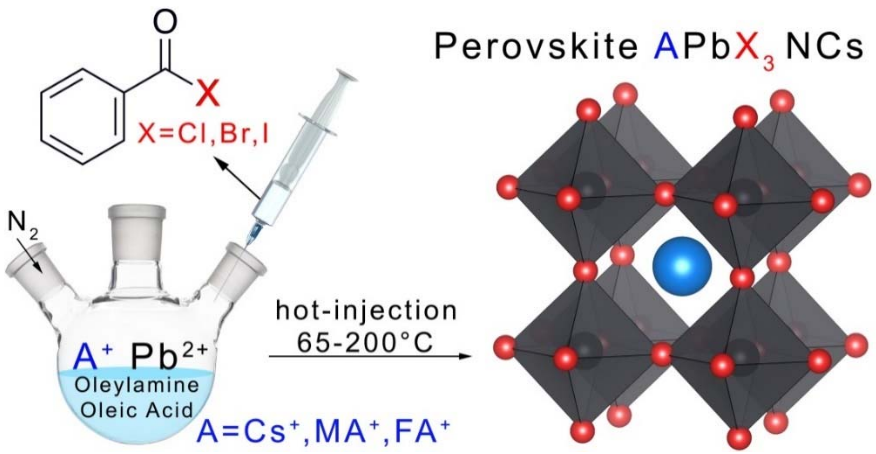


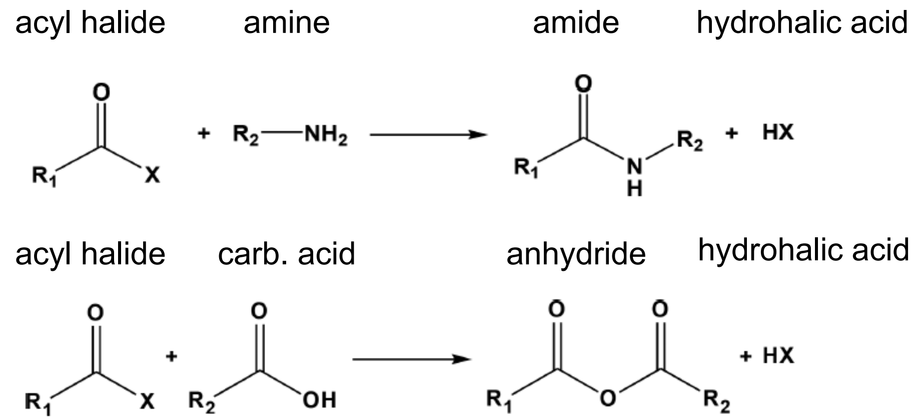
Scintillation Detectors (ns to sub-ns lifetimes)



Gandini, M.. et al. *Nature Nanotech.* **2020***, 15, 462–468*

Syntheses using Benzoyl Halides: <u>introducing Pb and X precursors separately!</u>

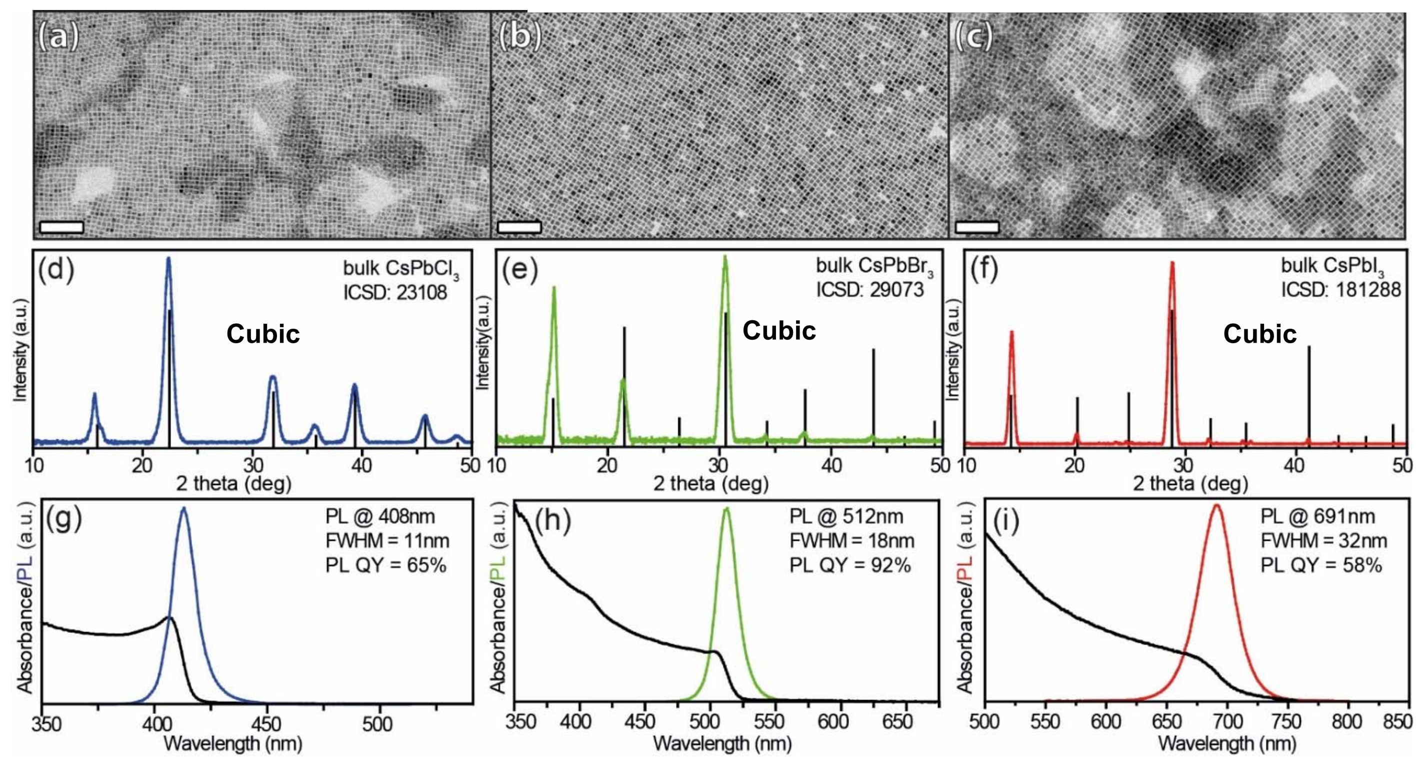




The amount of halide precursor introduced can be changed at wish!

Halide-rich NCs are synthesized

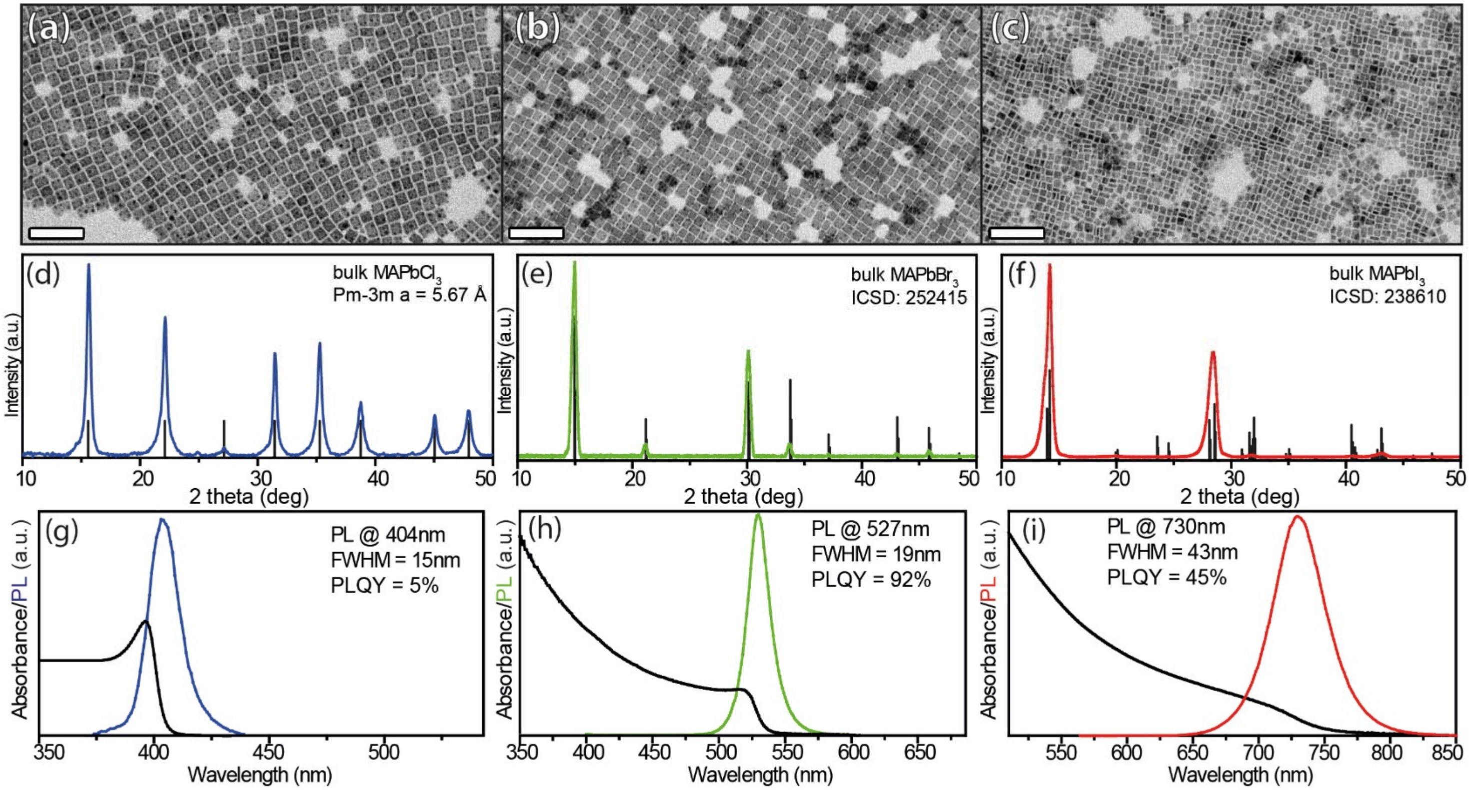
Phase pure $CsPbX_3$



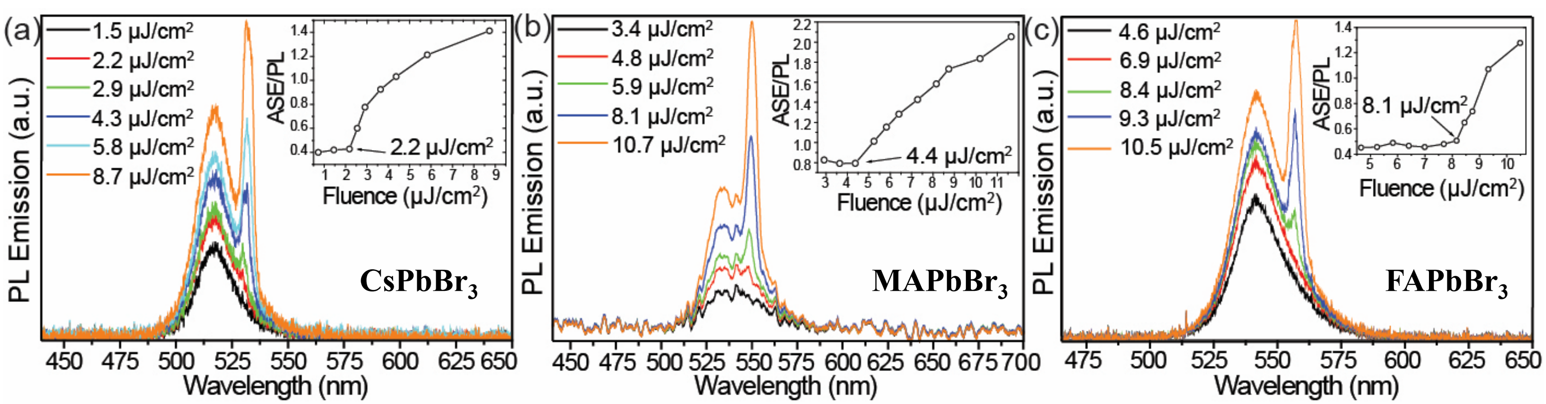
M. Imran et al. J. Am. Chem. Soc. ***2018****, 140, 2656−2664*

Phase pure $MAPbX_3$ NCs

Works also for $FAPbX_3$ NCs

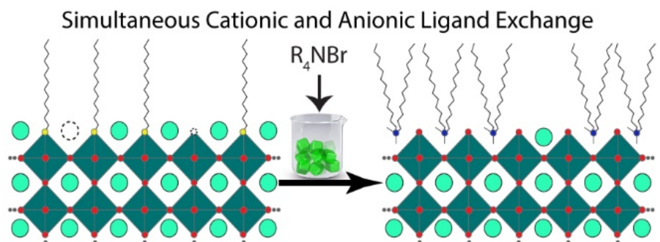


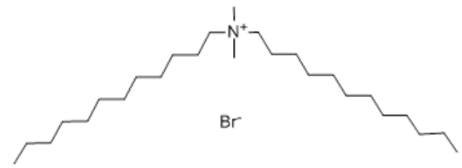
Low threshold for amplified spontaneous emission (ASE) in $APbBr_3$ NC films



M. Imran et al. J. Am. Chem. Soc. ***2018****, 140, 2656−2664*

Right ligands are important in stabilizing nanocrystals

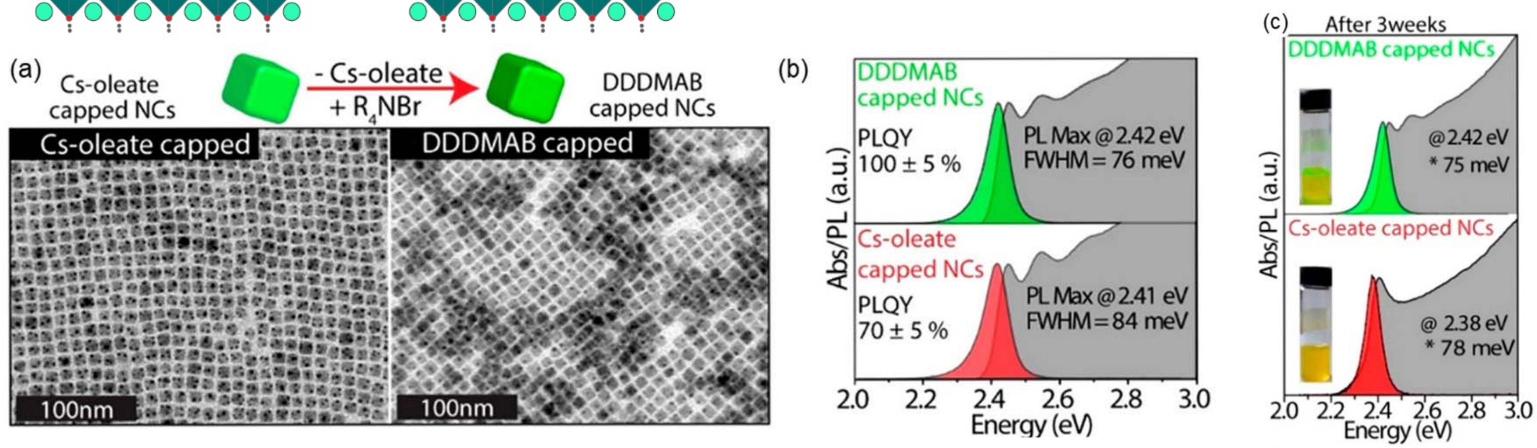




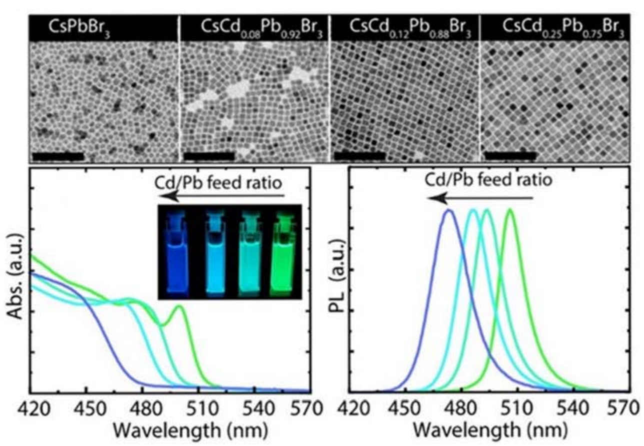
DDDMAB: didodecyl-dimethyl ammonium bromide

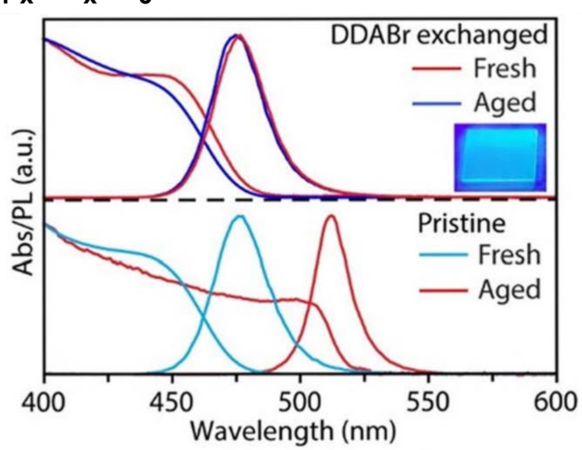
Preservation of PLQY

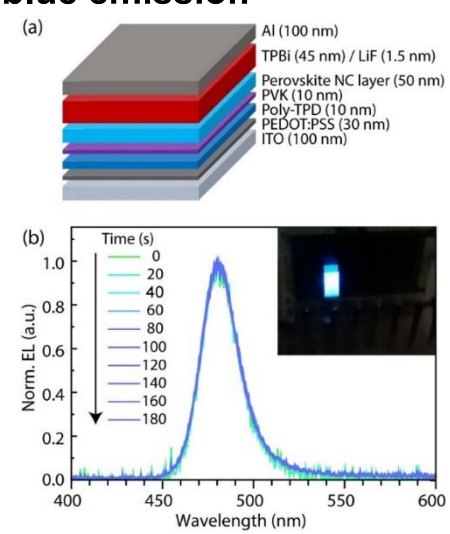
$CsPbBr_3$



Same ligand exchange, but for $CsPb_{1-x}Cd_xBr_3$: Preservation of PLQY and blue emission

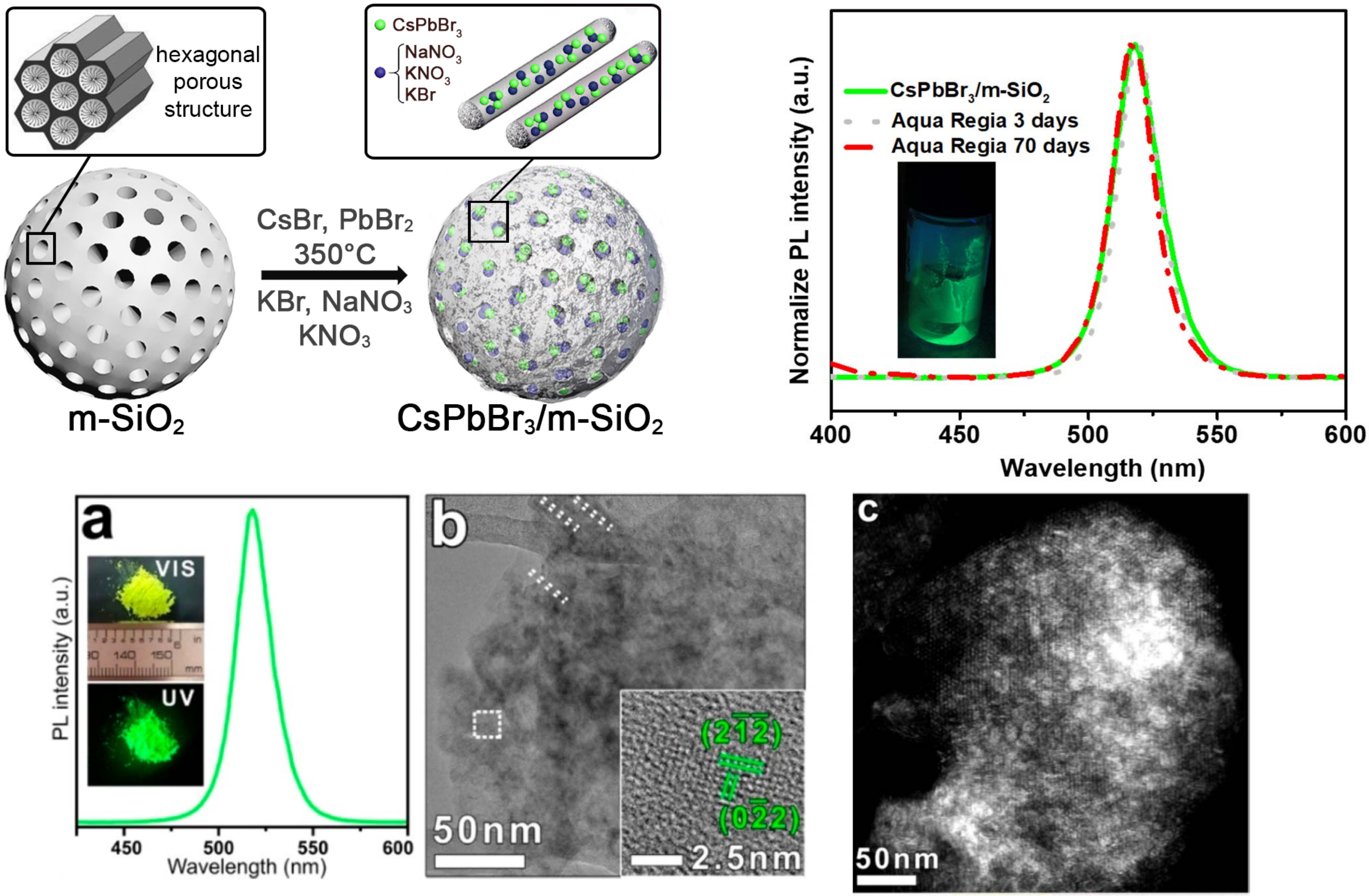






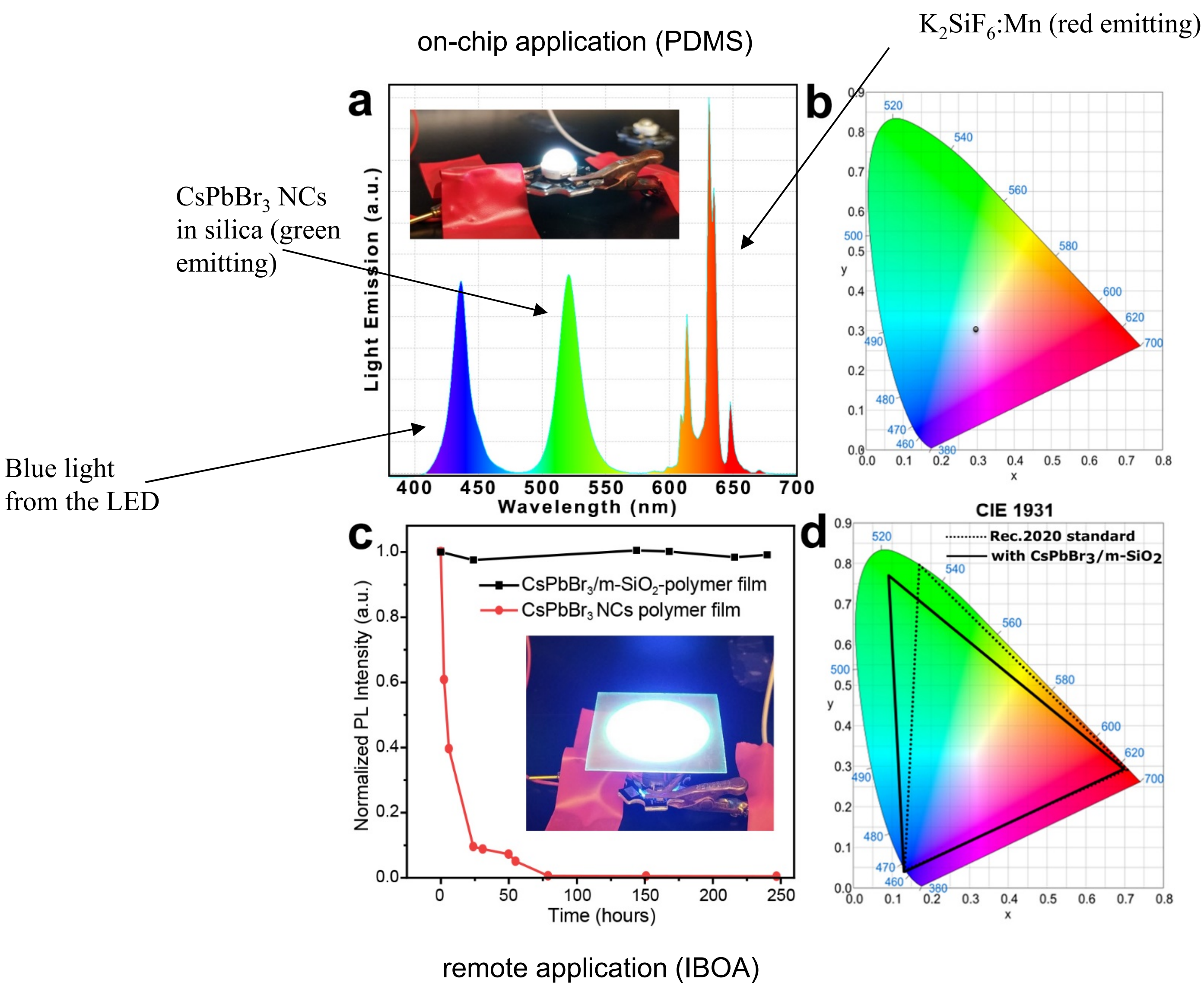
M. Imran et al. *ACS Energy Lett.* **2019,** 4, 819–824
M. Imran et al. *Chem. Mater.* **2020**, 32, 24, 10641–10652

Robust silica-halide perovskite nanocomposites grown in molten salts



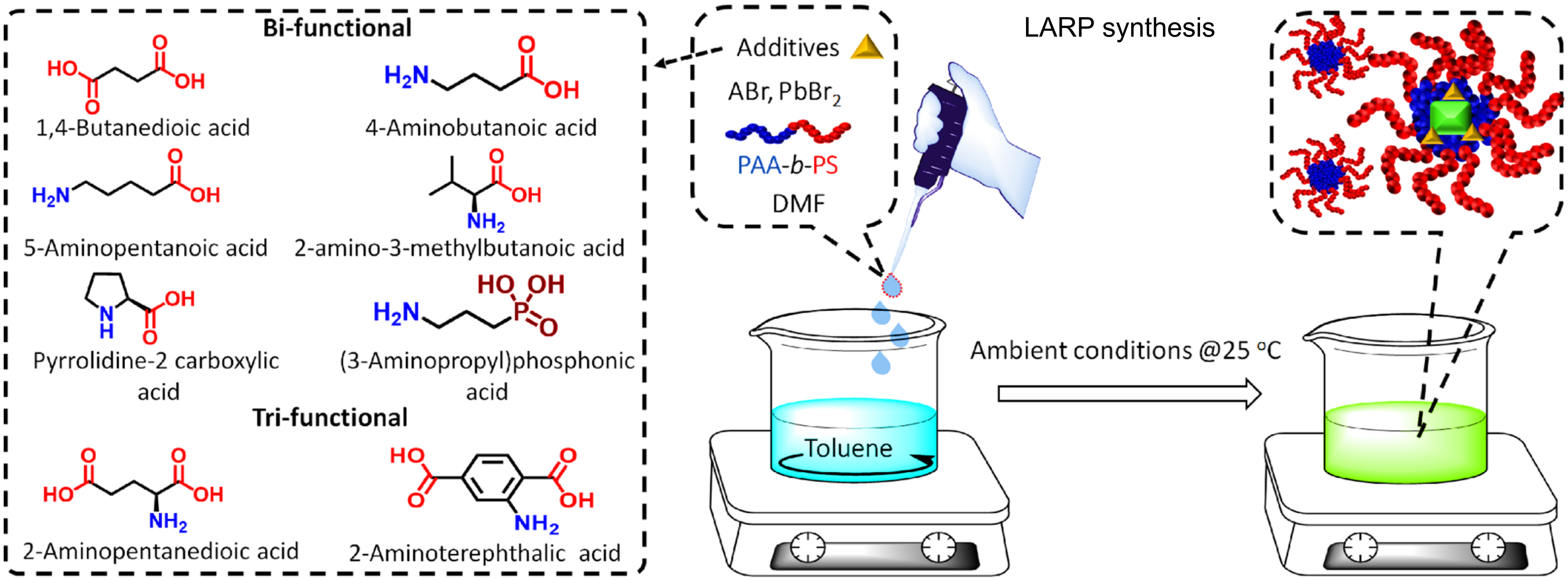
Mai, N. A. et al. ACS Energy Lett. ***2021****, 6, 900−907*

Robust silica-halide perovskite nanocomposites grown in molten salts



Mai, N. A. et al. ACS Energy Lett. ***2021****, 6, 900−907*

Polymer-Encapsulated $APbX_3$ Nanocrystals



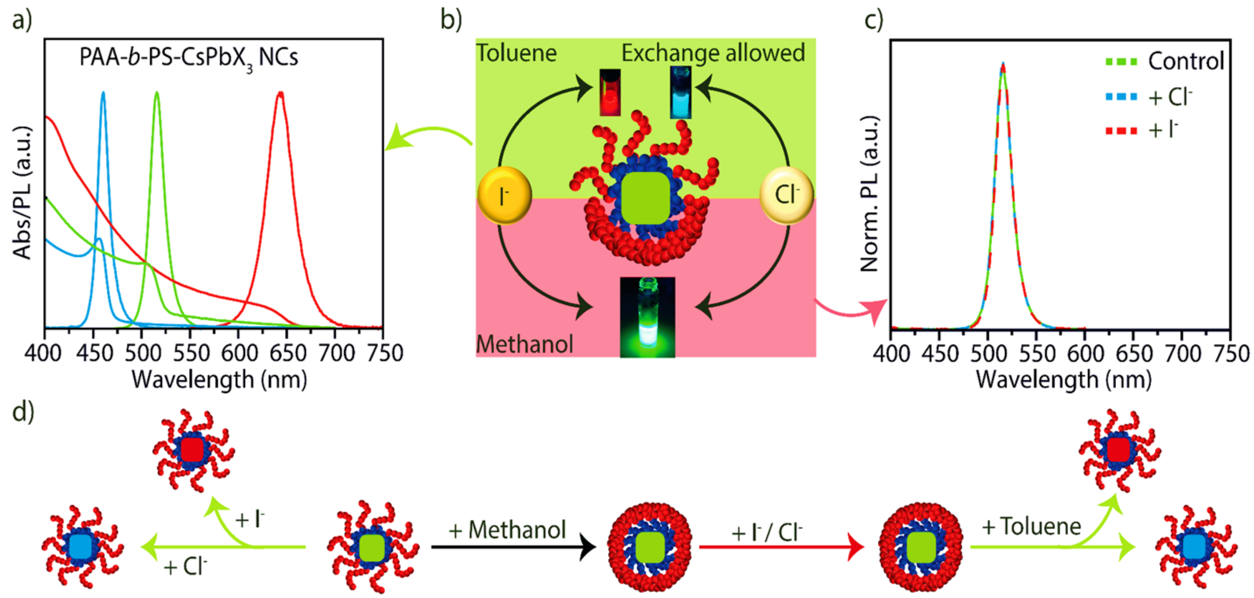
poly(acrylic acid)-block-polystyrene (PAA-b-PS)

PAA core and PS outer shell

M. Imran et al. ***ACS Energy Lett.*** *2021, 6, 2844−2853*

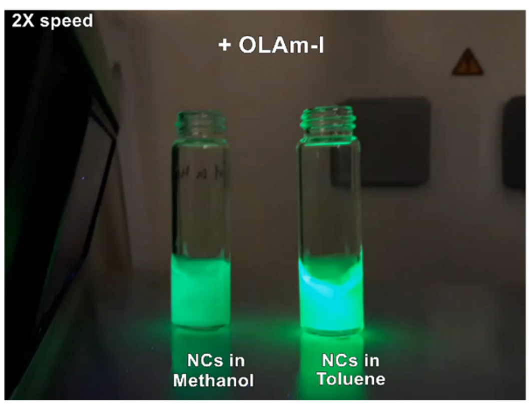
Switchable Anion Exchange

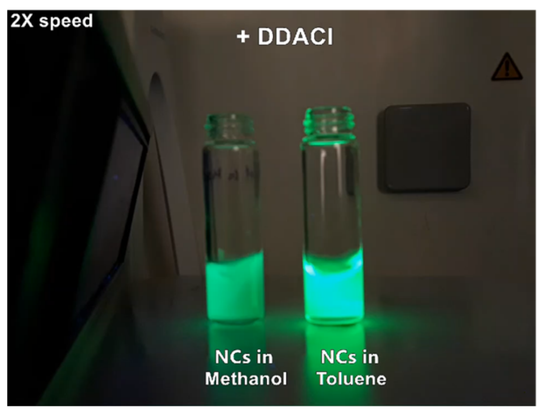
Toluene: Anion exchange on (polymer in coil state)

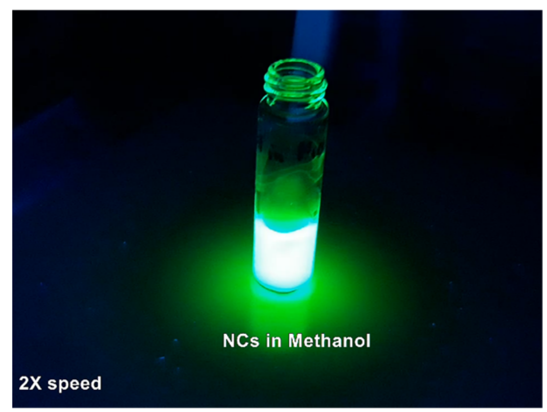


Methanol: Anion exchange off (polymer in globule state)

PAA core and PS outer shell





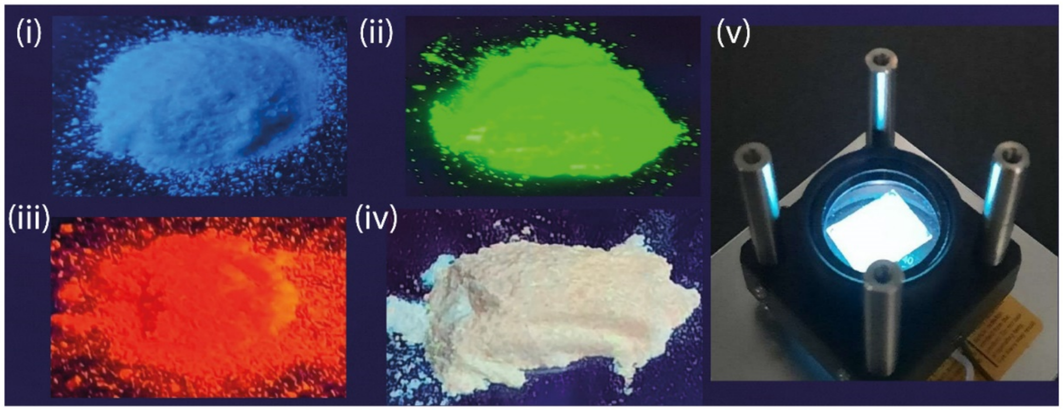


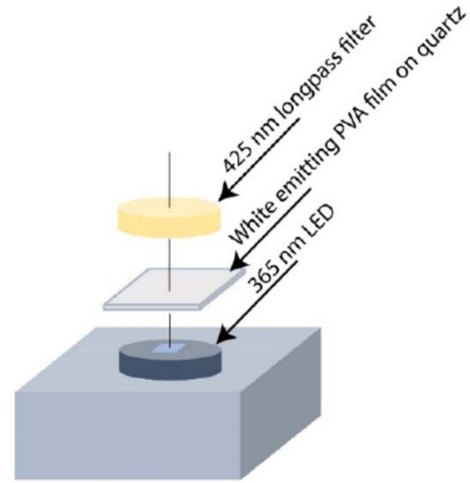
M. Imran et al. ***ACS Energy Lett.*** *2021, 6, 2844−2853*

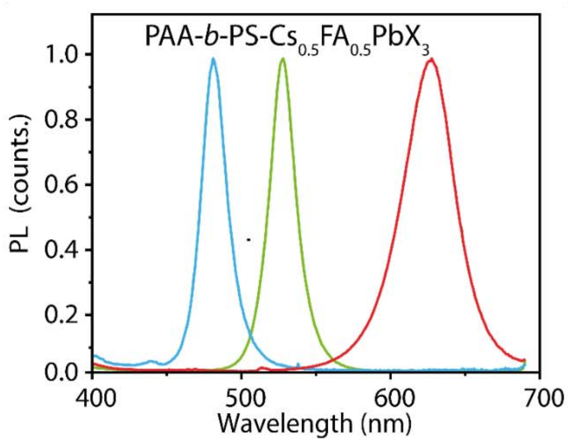
Switchable Anion Exchange in Polymer-Encapsulated $APbX_3$ Nanocrystals Delivers Stable All-Perovskite White Emitters

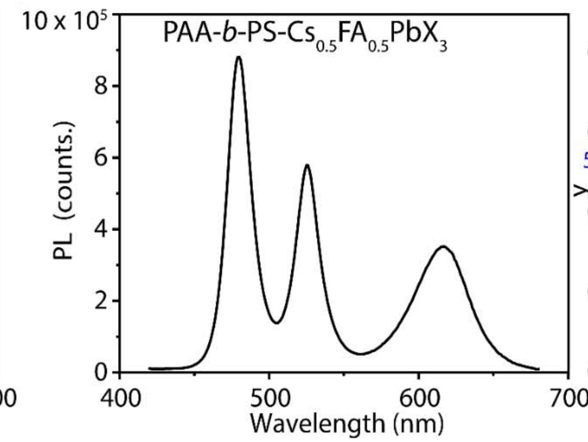
$Cs_{0.5}FA_{0.5}PbX_3$NCs

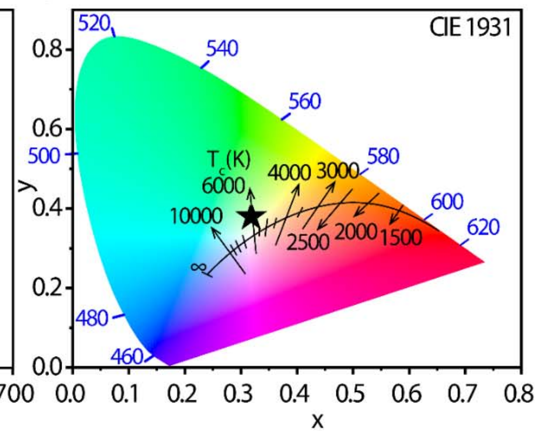
Samples mixed with PMMA, dried, milled and (iv-v) mixed









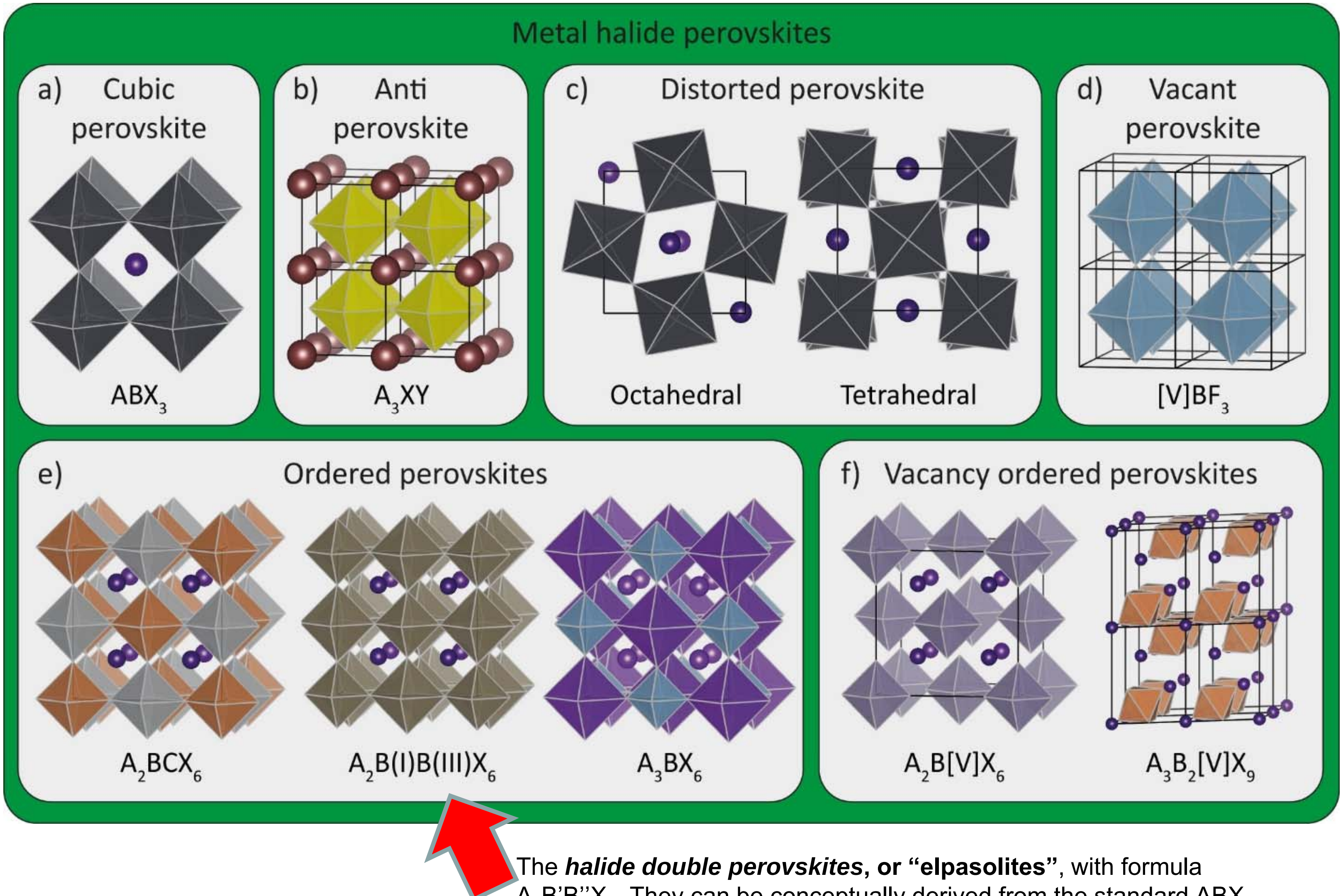


Ball milling

Film (ball milled powders + poly(vinylalcohol))

M. Imran et al. ***ACS Energy Lett.*** *2021, 6, 2844−2853*

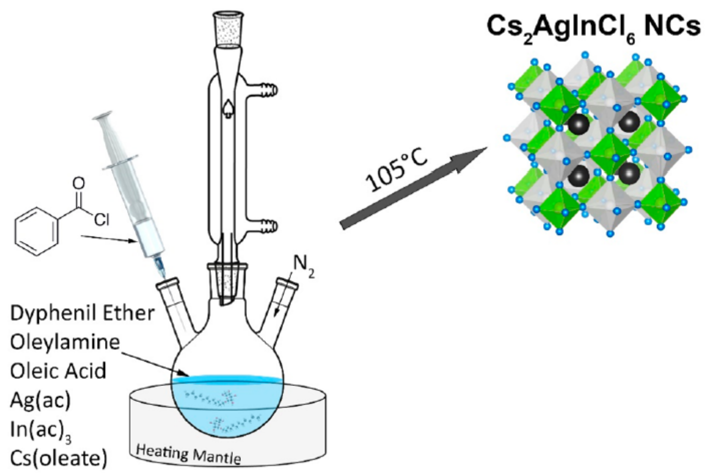
Different Halide Perovskites

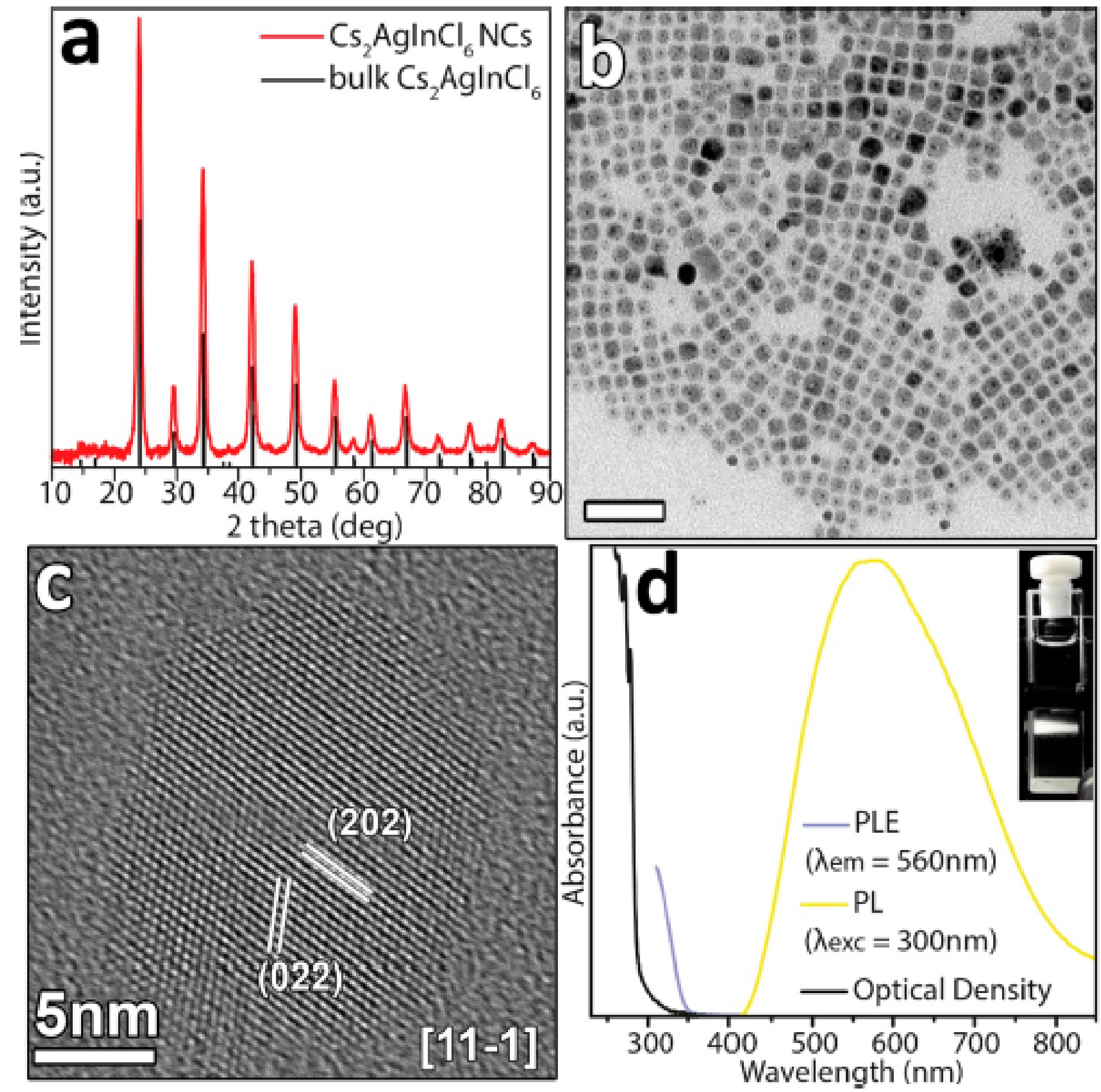


The ***halide double perovskites*, or "elpasolites"**, with formula $A_2B'B''X_6$. They can be conceptually derived from the standard ABX_3 halide perovskite structure by replacing two B^{2+} cations with one monovalent (B') and one trivalent (B'') cation;

Q. Akkerman and L. Manna, "What defines a Halide Perovskite?", ACS Energy Lett. ***2020****, 2020, 5, 2, 604-610*

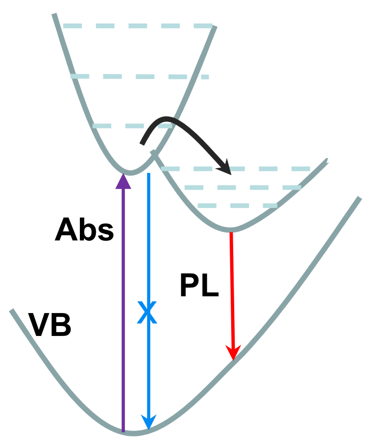
Benzoyl chlorides for the synthesis of double perovskite nanocrystals





Emission from a Self-trapped exciton

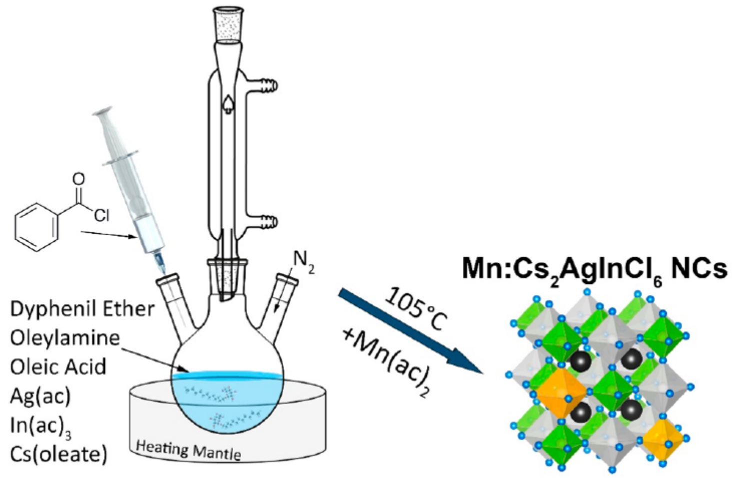
Weak and broad PL (PLQY 1.6%)

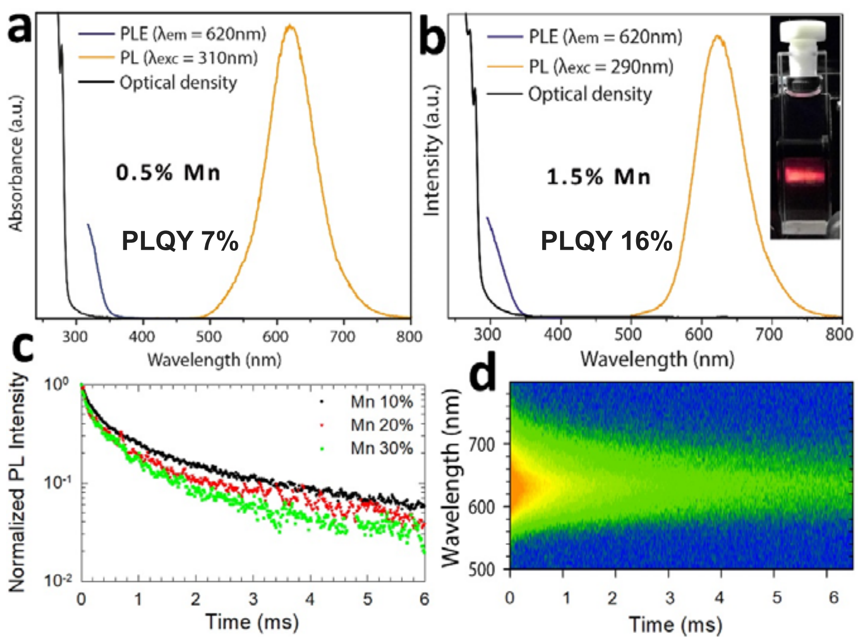


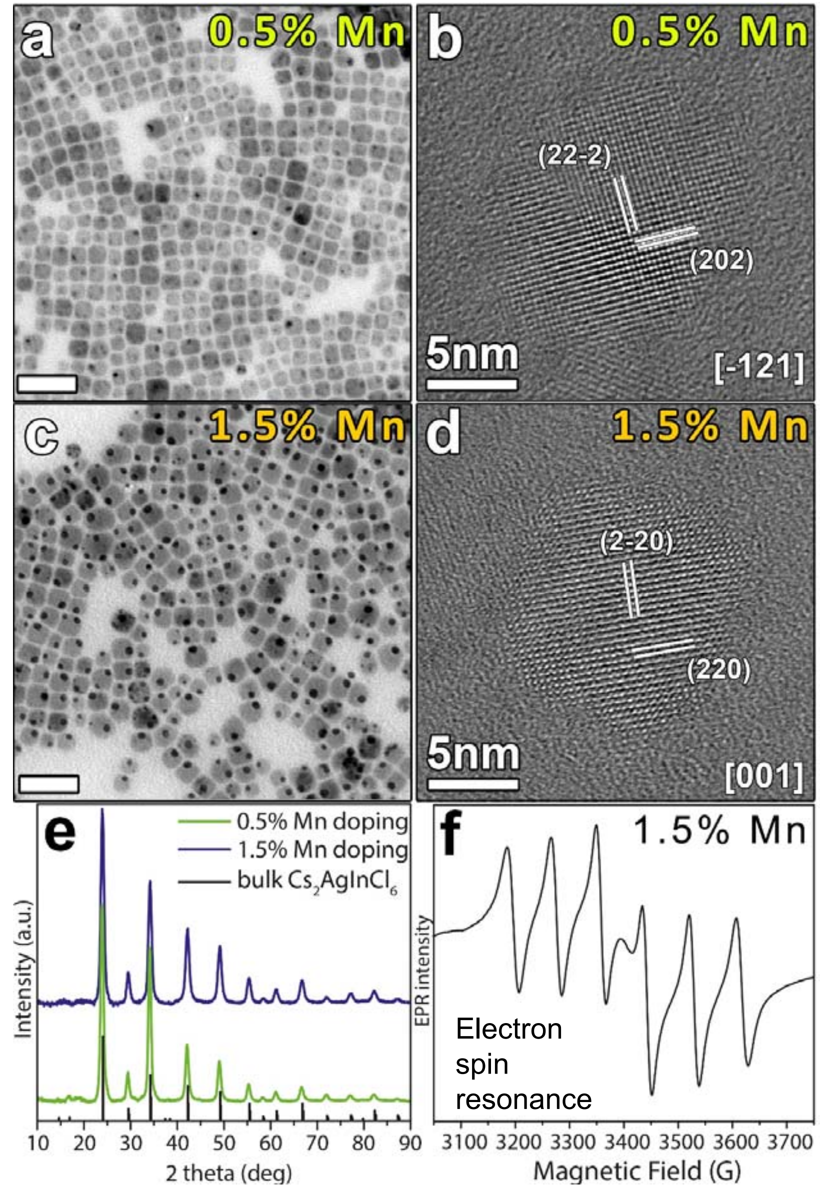
Adapted from M. Cong et al. Sci. Bull. ***2020****, 65, 1078-1084*

F. Locardi et al. J. Am. Chem. Soc. ***2018****, 140,12989−12995*

Benzoyl chlorides for the synthesis of double perovskite nanocrystals



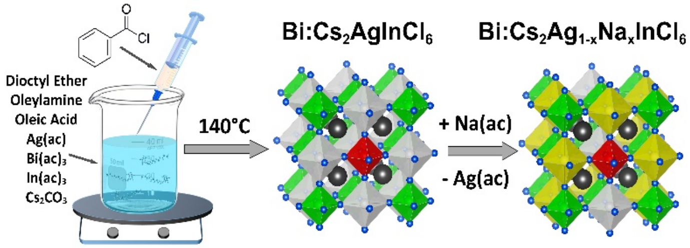




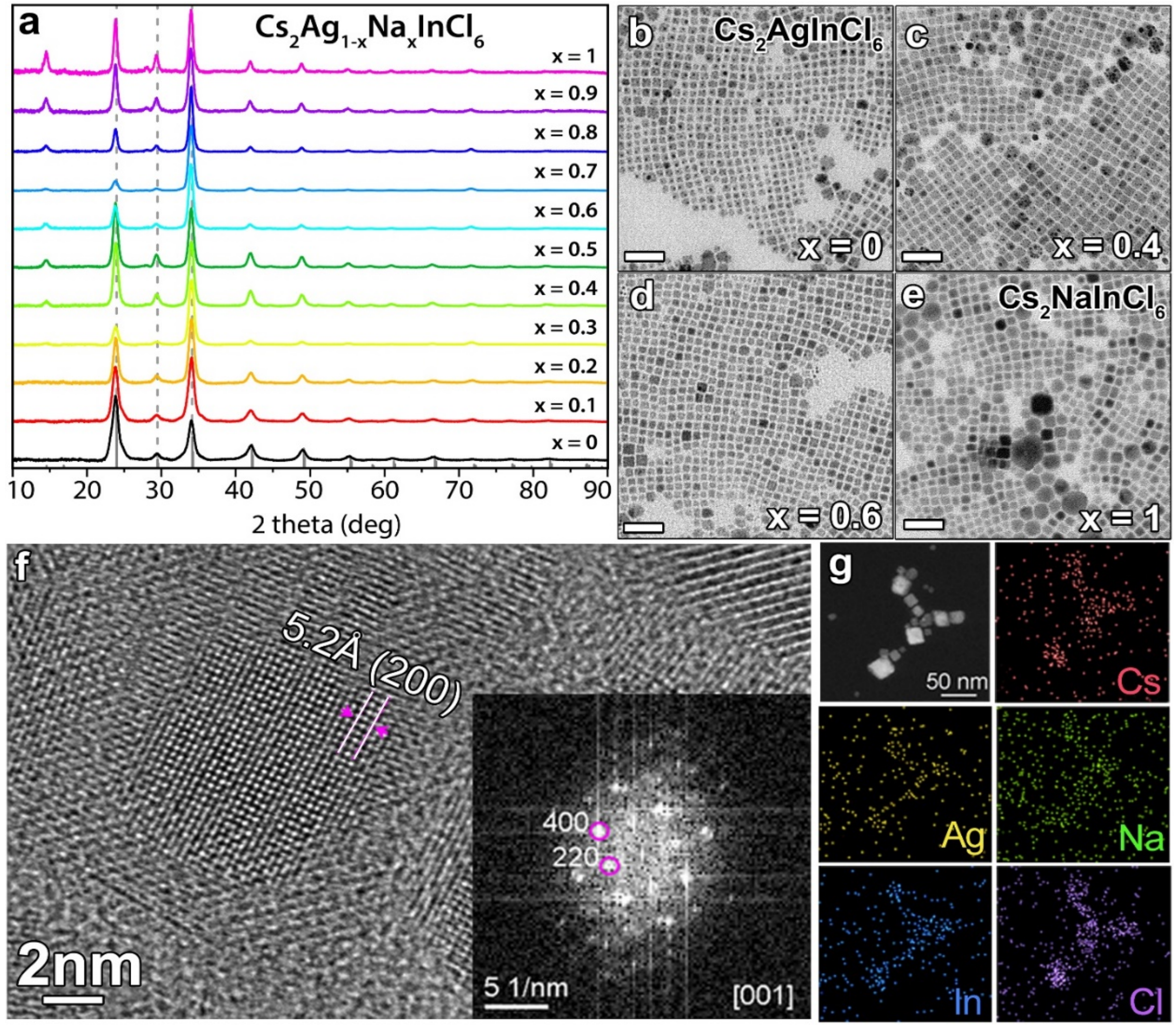
Orange emission due to $^6T_1 \rightarrow {}^6A_1$ Transitions of Mn^{2+} dopants

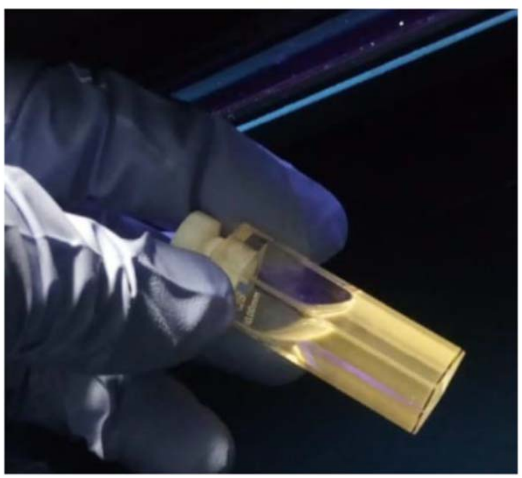
F. Locardi et al. J. Am. Chem. Soc. ***2018****, 140,12989−12995*

Emissive Double Perovskite Bi-doped $Cs_2Ag_{1-x}Na_xInCl_6$ Nanocrystals



Bi doping fixed at 0.5%

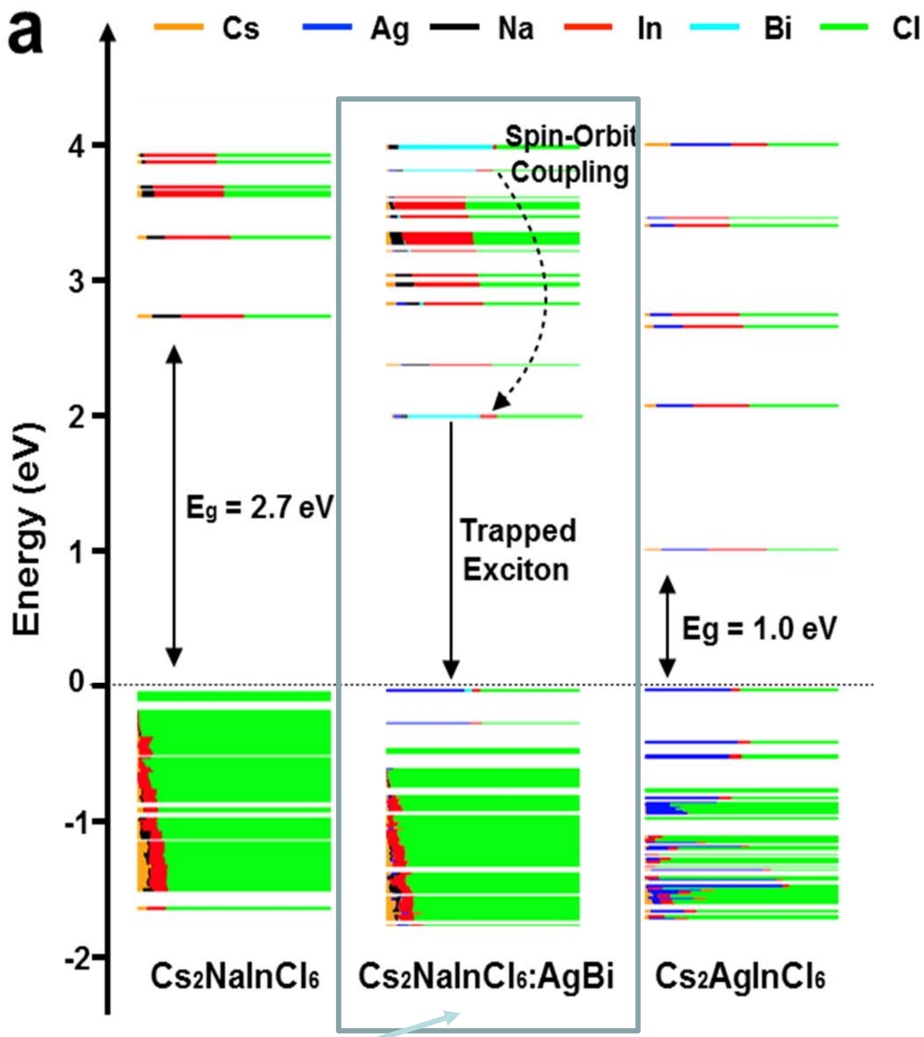




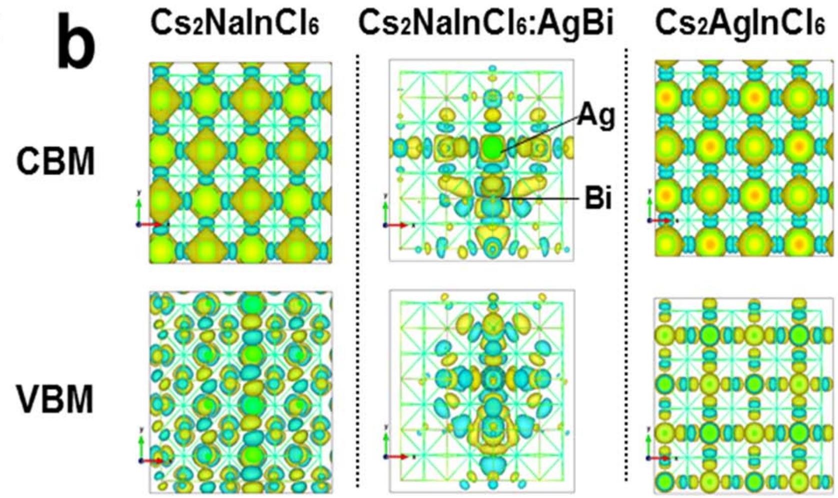
Corresponding bulk crystals reported by Sargent's group in Nature 563, 541–545 (2018), *showing up to 86% PLQY*

F. Locardi et al. ACS Energy Lett. ***2019****, 4, 1976−1982*

Emissive Double Perovskite Bi-doped $Cs_2Ag_{1-x}Na_xInCl_6$ Nanocrystals

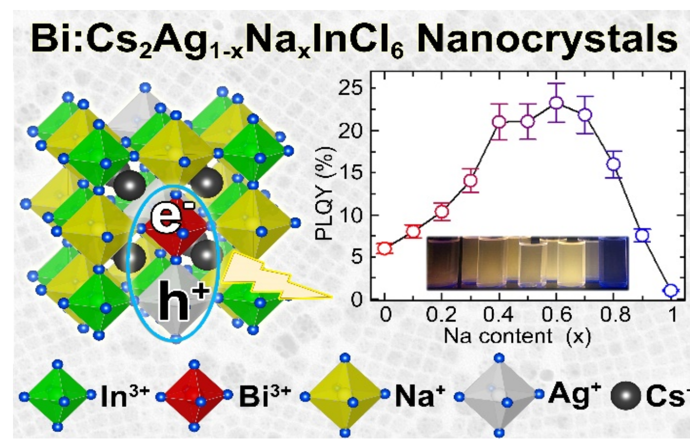


Replacing one Na^+ ion with one Ag^+ ion, and one In^{3+} with one Bi^{3+} ion at the center of the supercell of $Cs_2NaInCl_6$



Mid-gap localized states

CBM and VBM formed by delocalized states

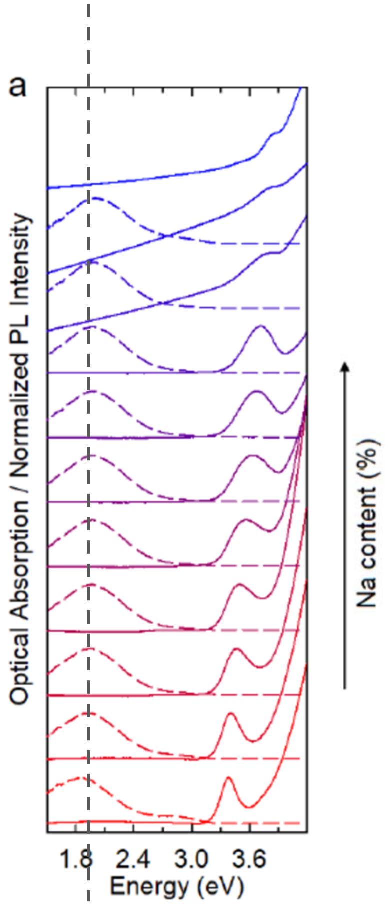


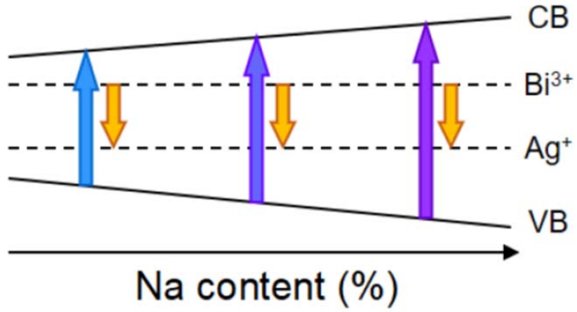
Maximum PLQY 22%

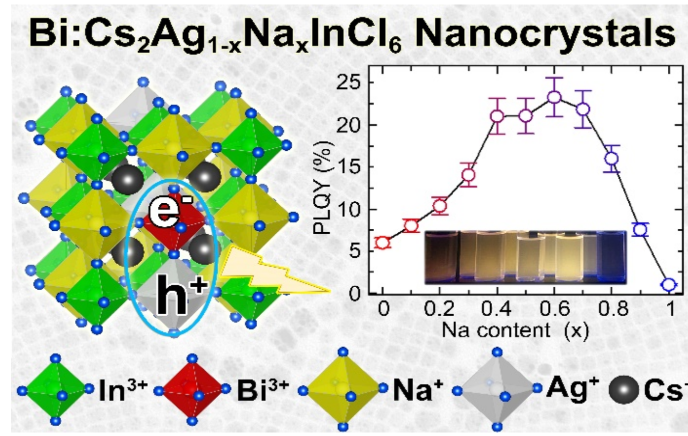
F. Locardi et al. ACS Energy Lett. ***2019****, 4, 1976−1982*

Emissive Double Perovskite Bi-doped $Cs_2Ag_{1-x}Na_xInCl_6$ Nanocrystals

PL peak position almost unchanged with Na content (%)

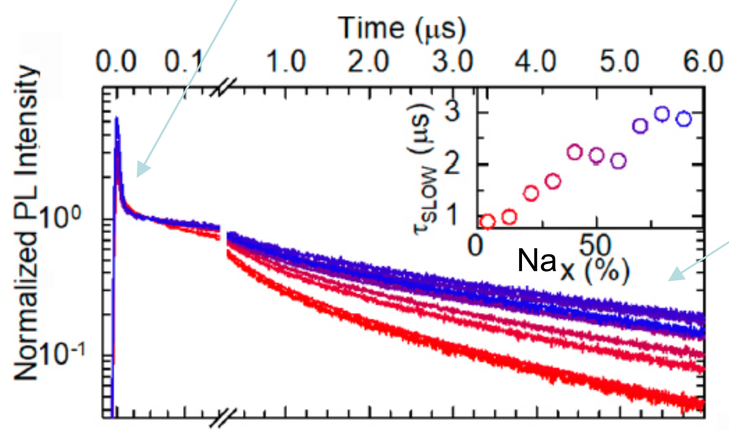






Fast non-radiative losses

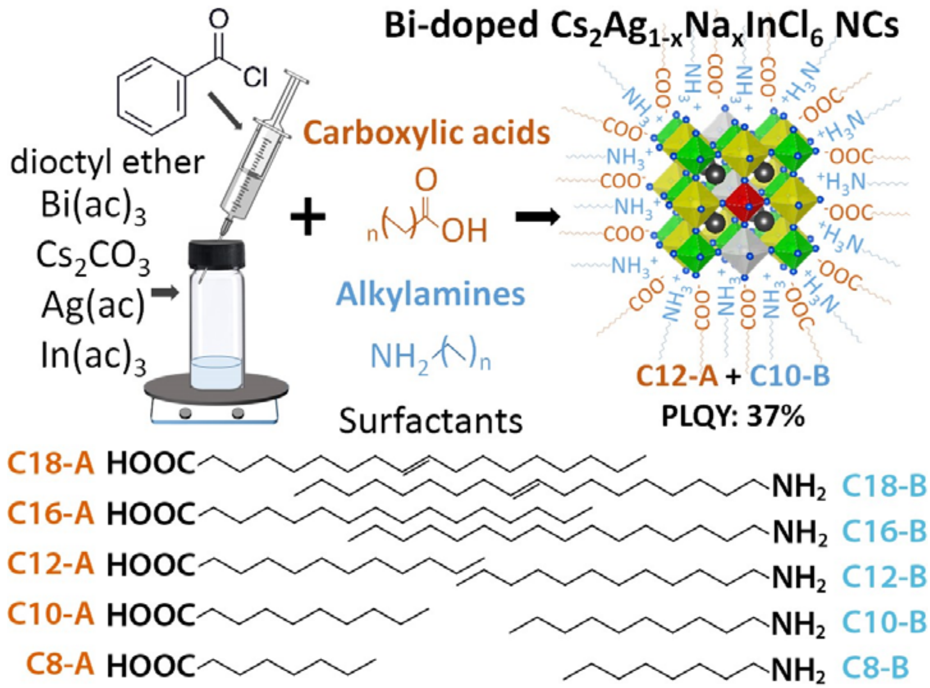
Long-lived emission from trapped exciton

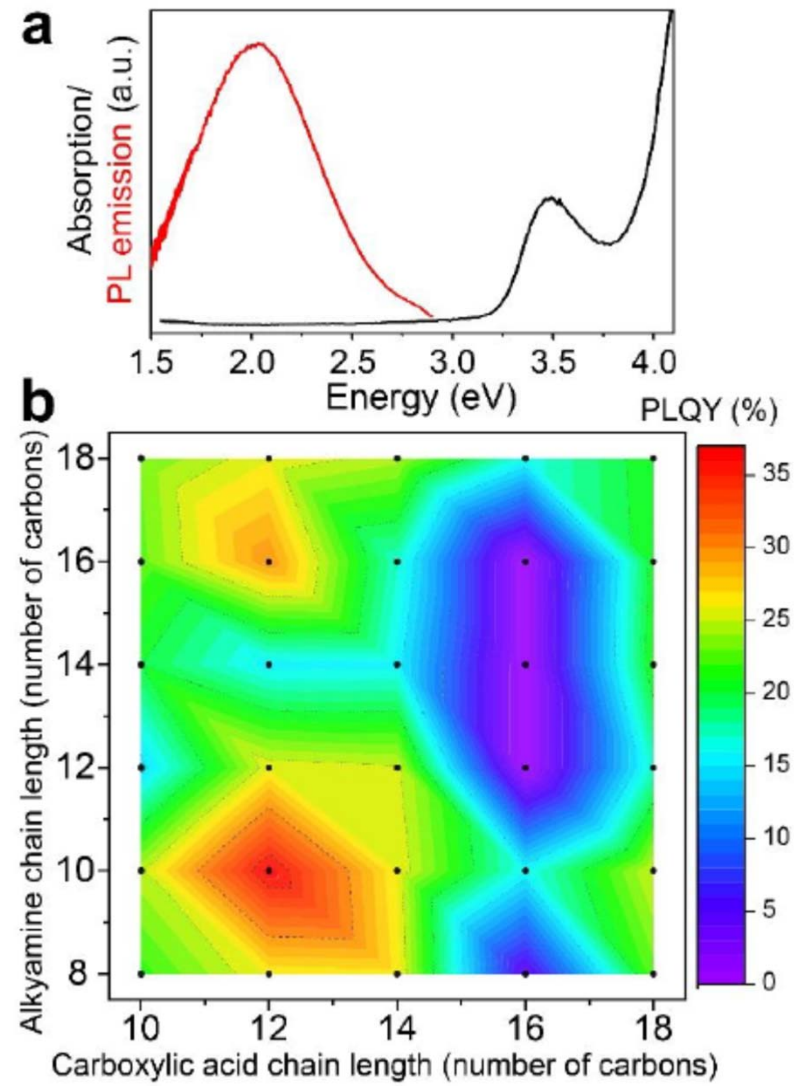


Higher %Na (lower %Ag) corresponds to longer lifetime: Na ions remove the less efficient non-radiative pathways

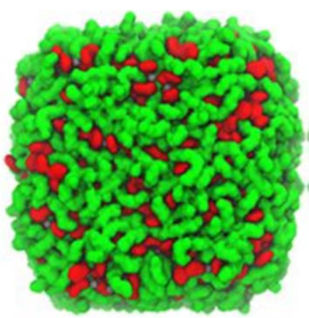
F. Locardi et al. ACS Energy Lett. ***2019****, 4, 1976−1982*

Surface passivation is critical to achieve high PL QY in double perovskite NCs



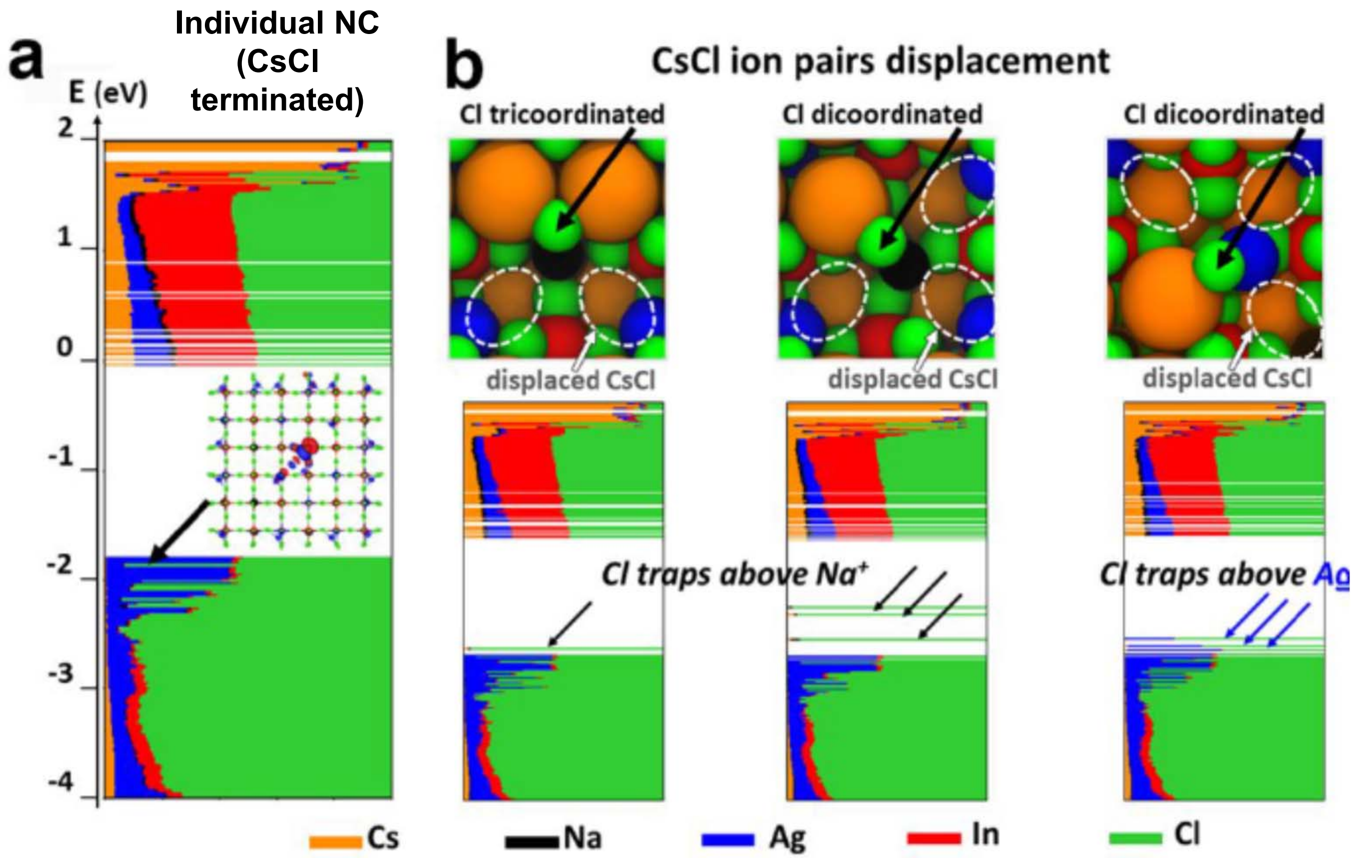


According to NMR, both carboxylic acids and amines are present and intermixed on the surface of double perovskite nanocrystals



B. Zhang, at al. ACS Mater. Lett. ***2020****, 2, 11, 1442–1449*

Surface passivation is critical to achieve high PL QY in double perovskite NCs

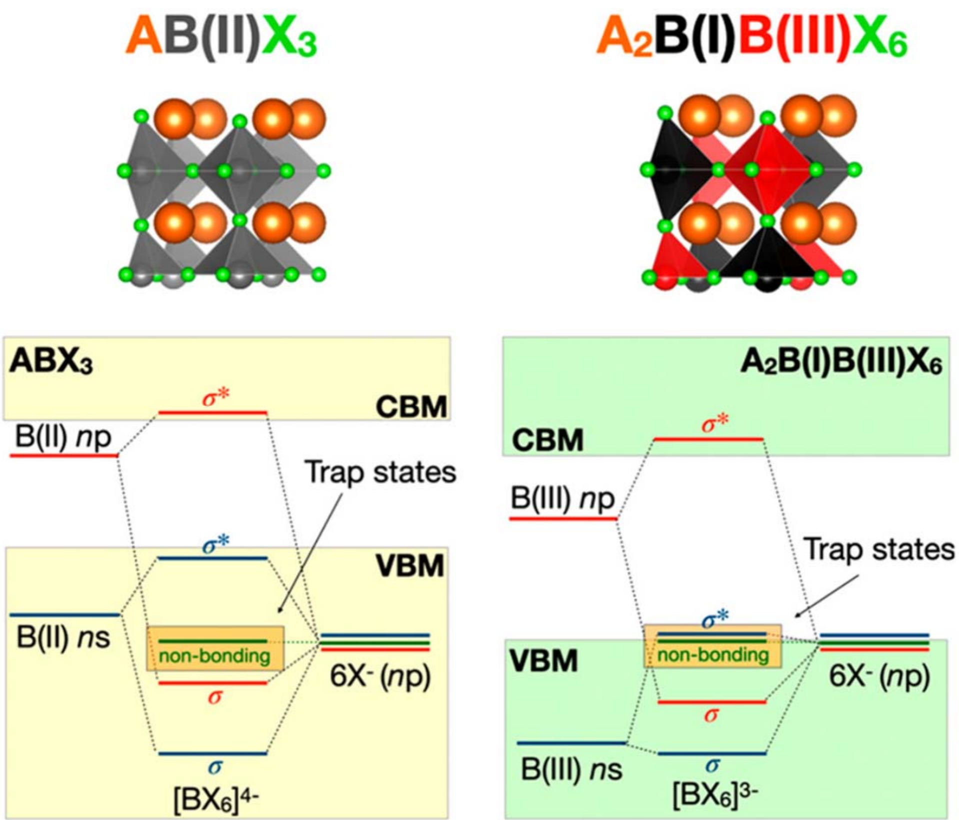


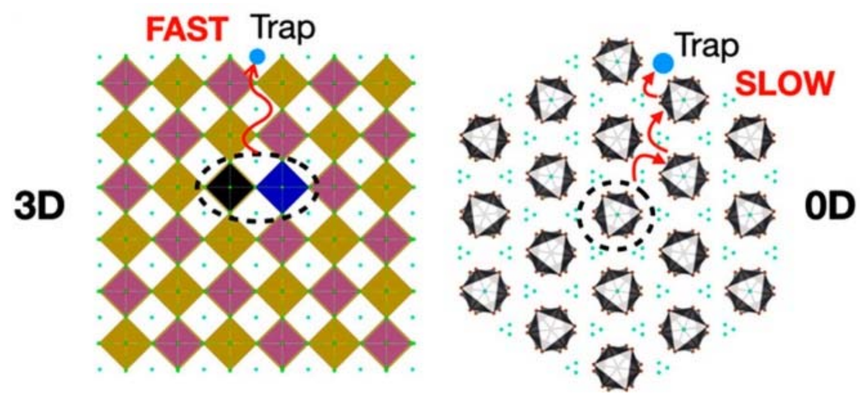
The displacement of CsCl ion pairs from the surface of the NCs simulates a partial decapping of the NCs

Deep states inside the band gap are easily formed in this material

B. Zhang, at al. ACS Mater. Lett. ***2020****, 2, 11, 1442–1449*

Surface Tolerance: AB(II)X_3 Perovskites versus Double Perovskites and 0D systems





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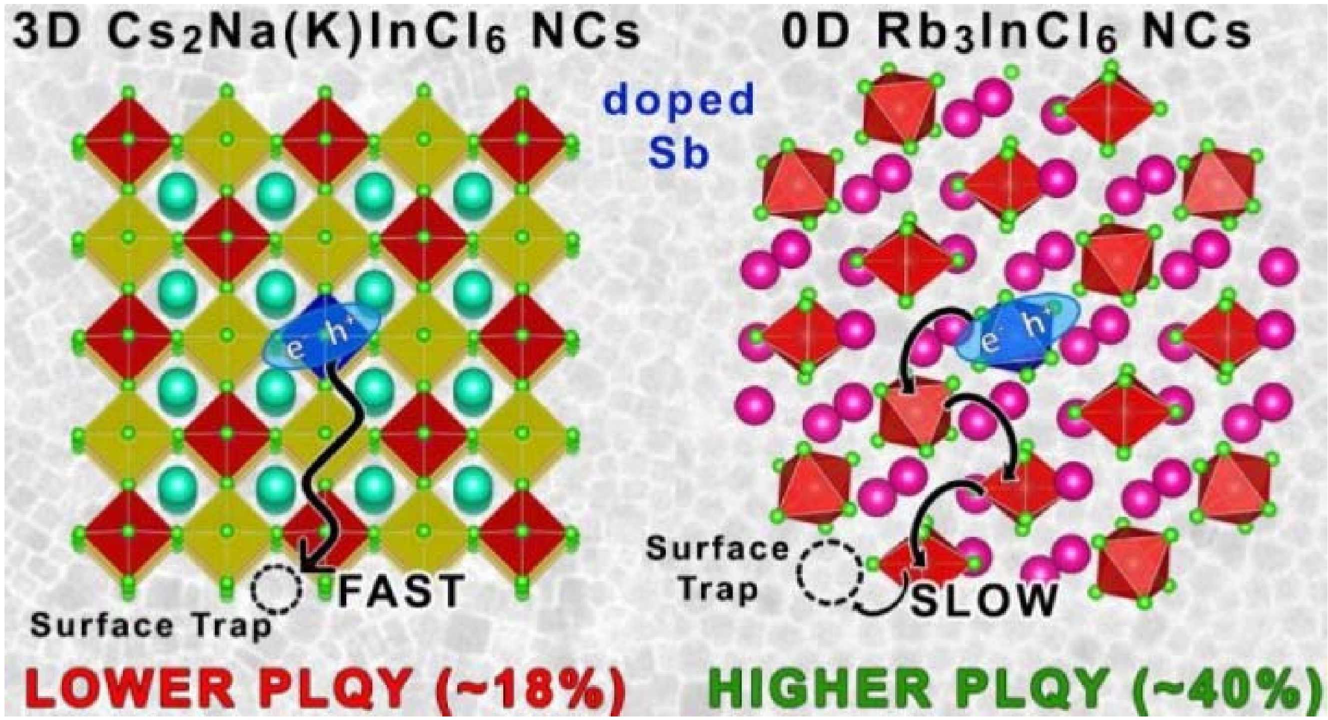

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