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Collective X-ray Diffraction and Photoluminescence in Perovskite Nanocrystal Superlattices

DMITRY BARANOV, DIVISION OF CHEMICAL PHYSICS, LUND UNIVERSITY

KITP NANOASSEMBLY23
28 APRIL, 2023



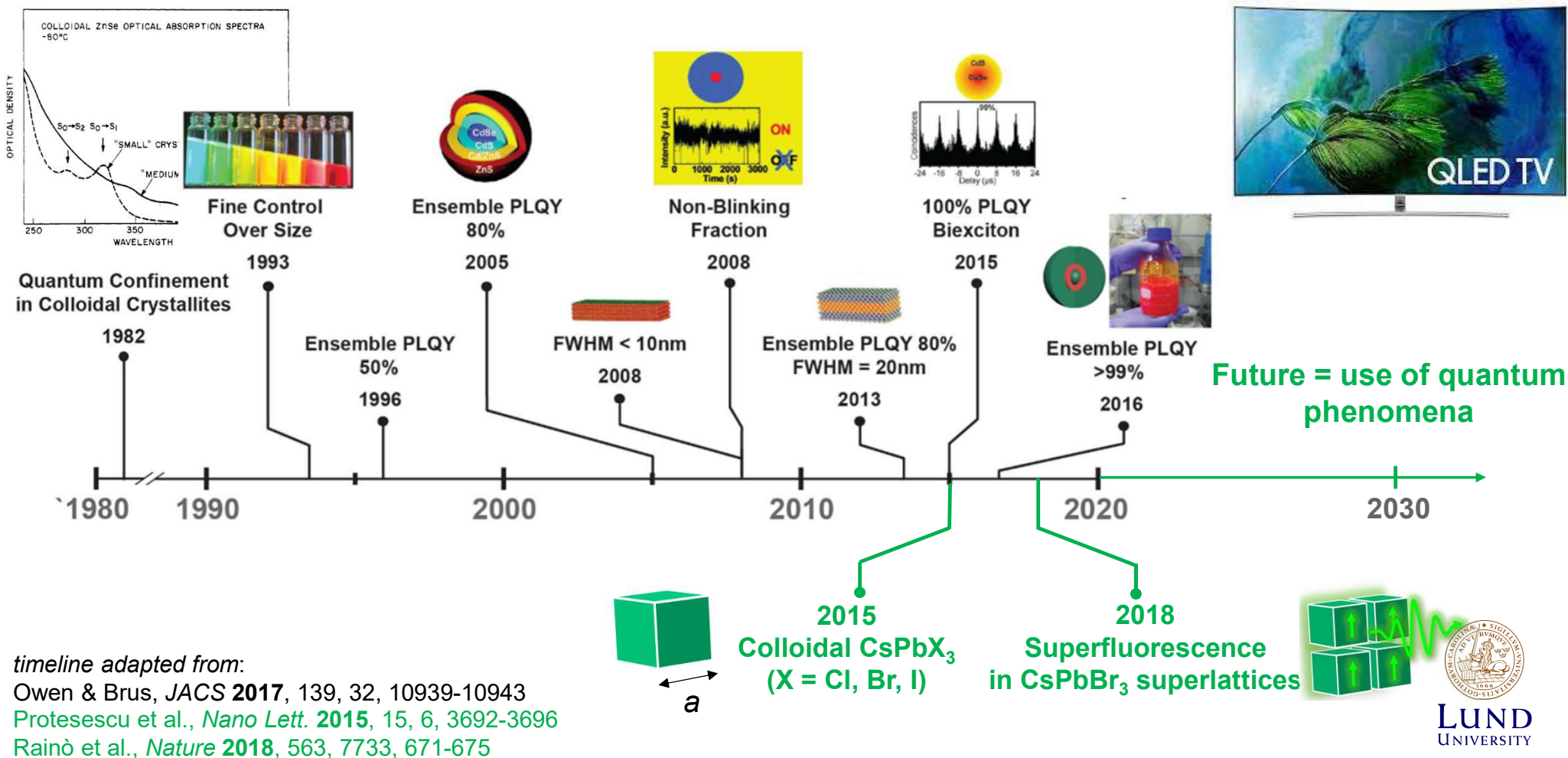
Central Questions

Why superlattices of perovskite nanocrystals are special?

Where does superfluorescence come from?

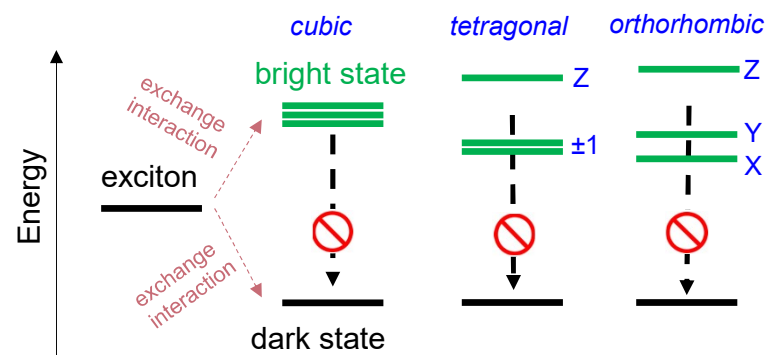
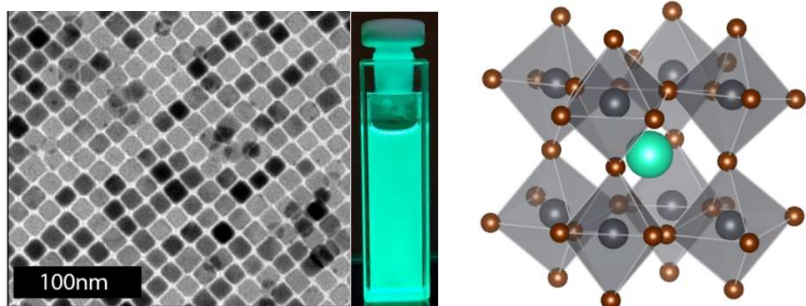


Colloidal Semiconductor Nanocrystals

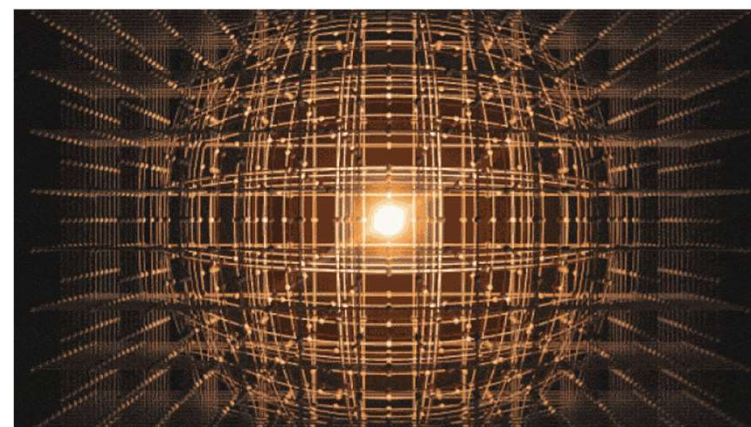
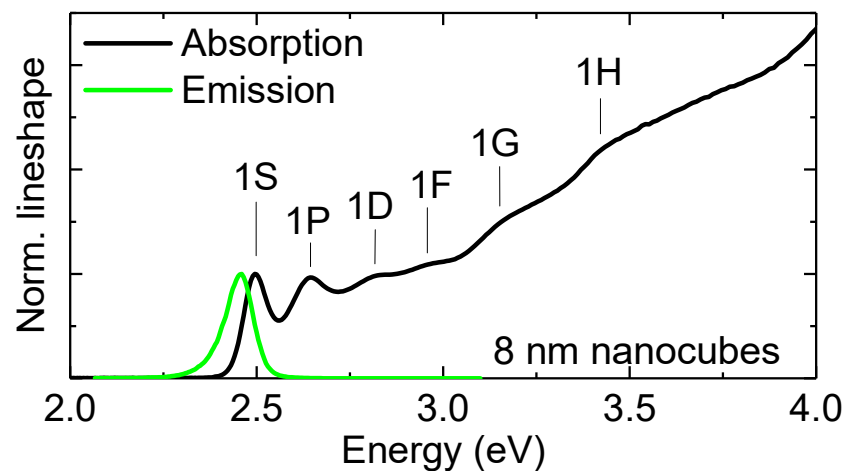


Lead Halide Perovskite Nanocrystals

CsPbBr_3



Efros, Even, Lounis, Sercel, and others

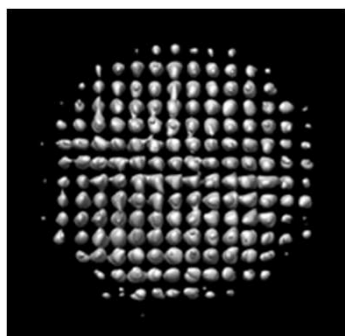


Guzelturk et al, *Nat. Mater.*, 2021, 20, 618-623

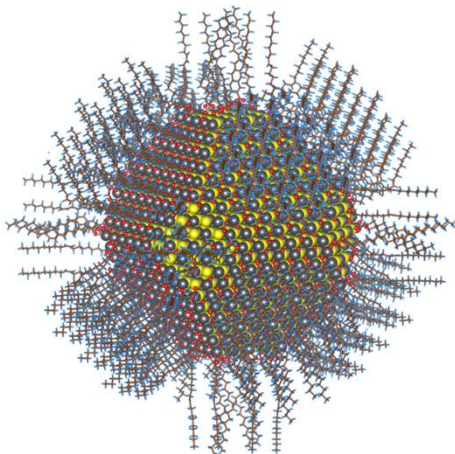


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Nanocrystal Superlattices



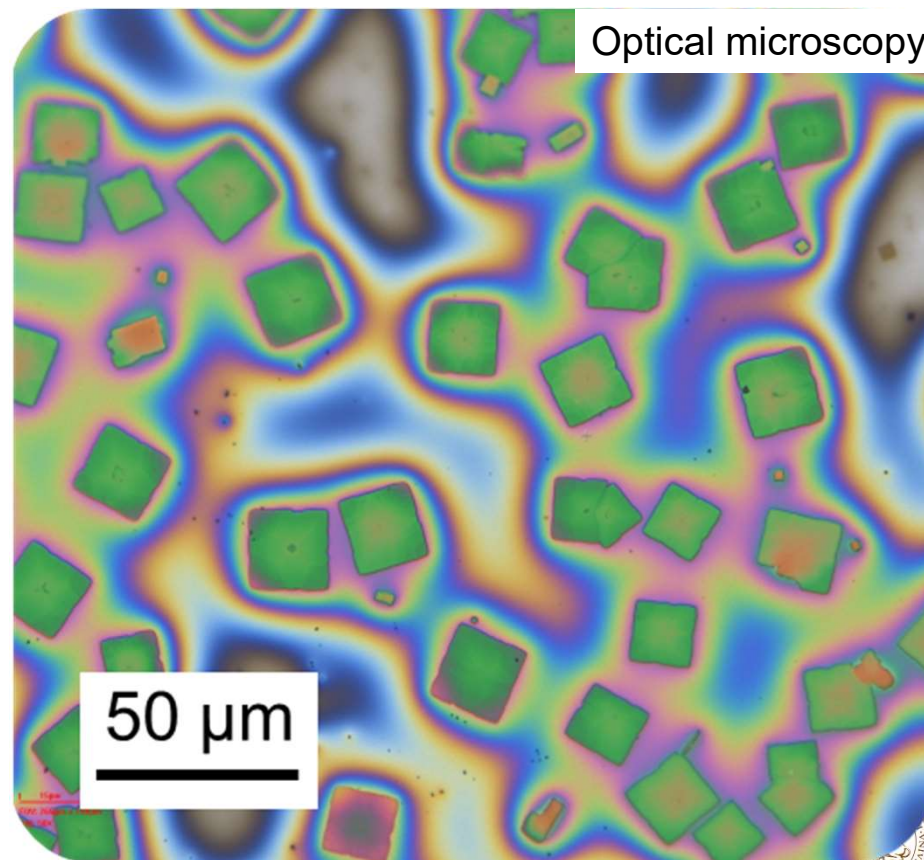
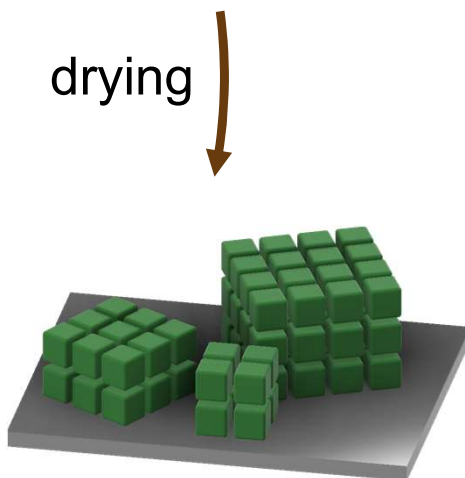
Pt nanocrystal (Berkeley Lab)



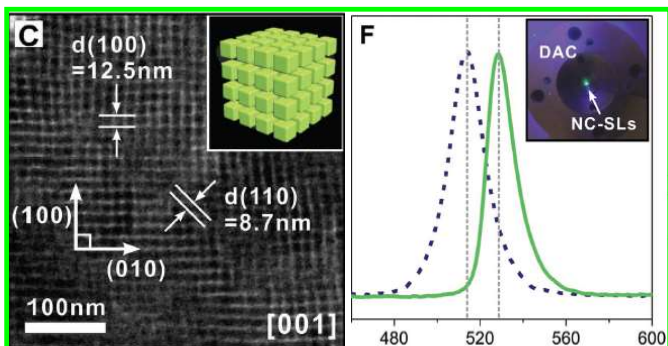
PbS, Zherebetsky et al., *Science* 2014



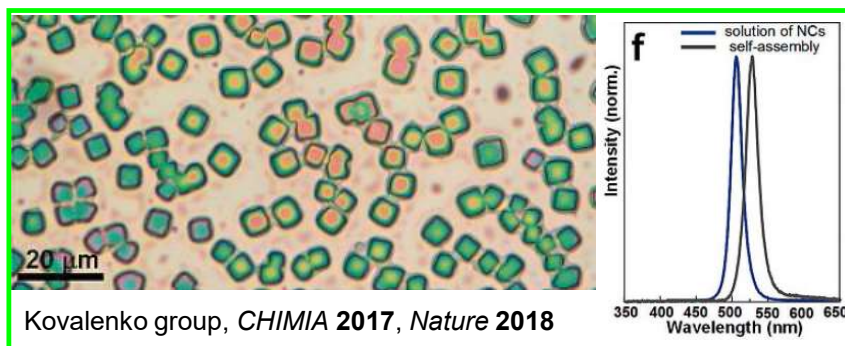
drying



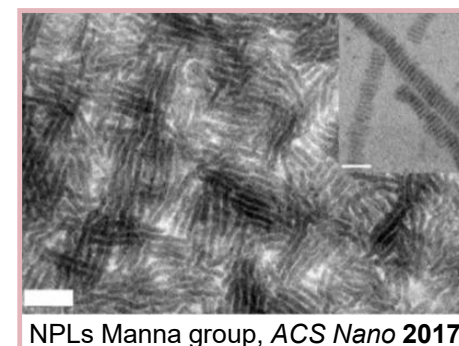
Early Nanocrystal Superlattices of CsPbBr₃



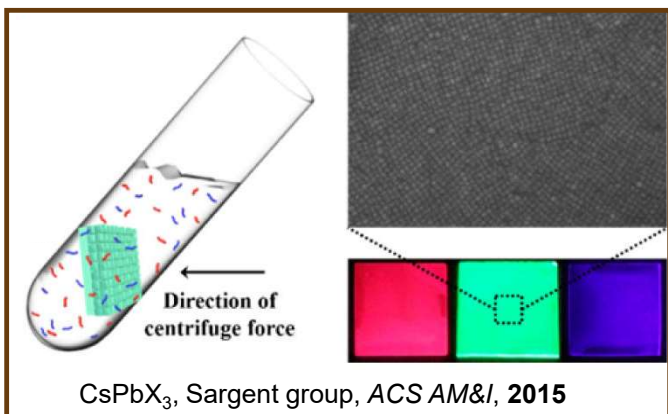
CsPbBr₃ nanocubes, solvent evaporation, Nagaoka et al, *Adv. Mater.* **2017**



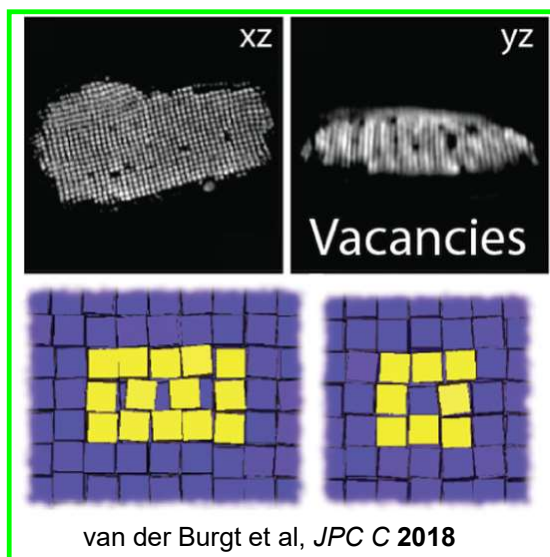
Kovalenko group, *CHIMIA* **2017**, *Nature* **2018**



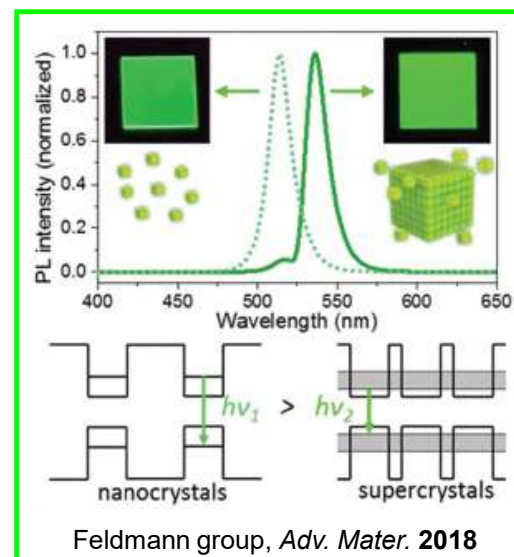
NPLs Manna group, *ACS Nano* **2017**



CsPbX₃, Sargent group, *ACS AM&I*, **2015**



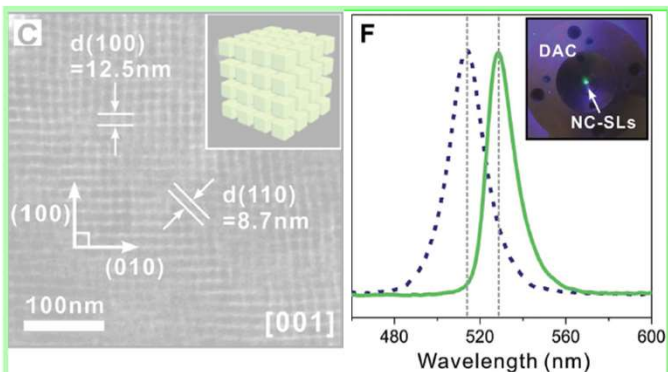
van der Burgt et al, *JPC C* **2018**



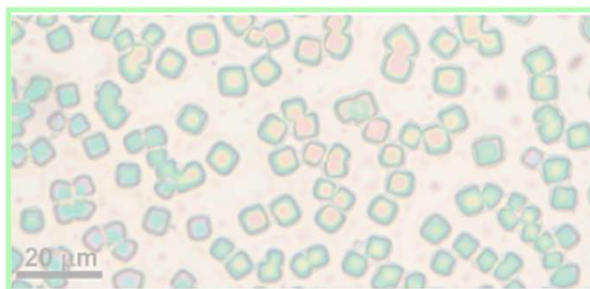
Feldmann group, *Adv. Mater.* **2018**



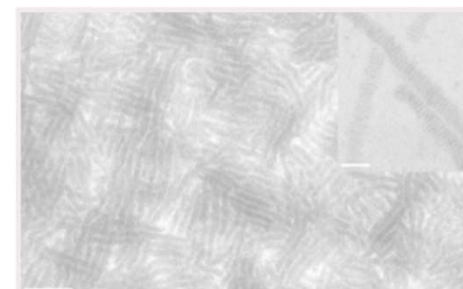
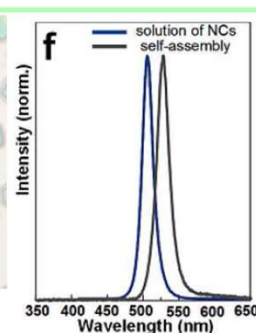
Early Nanocrystal Superlattices of CsPbBr₃



CsPbBr₃ nanocubes, solvent evaporation, Nagaoka et al, *Adv. Mater.* 2017



Kovalenko group, *CHIMIA* 2017, *Nature* 2018



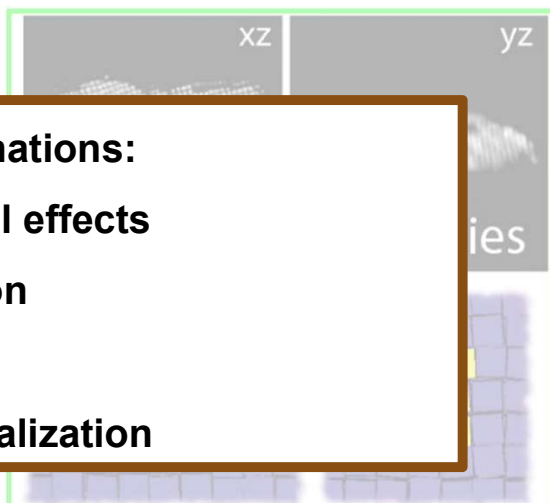
NPLs Manna group, *ACS Nano* 2017



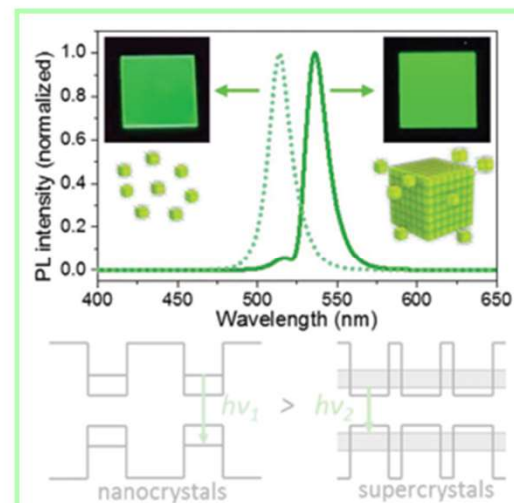
CsPbX₃, Sargent group, *ACS AM&I*, 2015

Proposed explanations:

- Environmental effects
- Self-absorption
- Coalescence
- Exciton delocalization



van der Burgt et al, *JPC C* 2018



Feldmann group, *Adv. Mater.* 2018



Syntheses of High-Quality CsPbBr₃ Nanocrystals

2015, ETH PbBr ₂ in oleylamine (OLA) and oleic acid (OA) + Cs-oleate	(1 st generation);
2018, IIT, UW Cs,Pb-oleates + Benzoyl-X / TMS-X (X = Cl, Br, I), OA & OLA	(2 nd generation);
2018, ETH PbBr ₂ + Cs-oleate, zwitterionic ligands	(3 rd generation);
2018, IIT 2 nd generation + R ₂ NH => shape-pure nanocubes	(4 th generation);
2018, ETH, UC Berkeley 1 st generation + Lewis bases for PLQY	(5 th generation);
2019, IIT 2 nd generation + R ₂ R' ₂ N ⁺ X ⁻ for PLQY & stability	(6 th generation);
2018-2022, amines → phosphines, carboxylates → phosphonates	(7 th generation);
+ variations (e.g., ZnX ₂ , TOP-X, NBS, @lecithin, @zwitterionic polymers)	(n th generation);

References:

[1^o] Protesescu et al., *Nano Lett.*, 15 (6), 3692-3696, **2015**

[1^o] Almeida et al., *ACS Nano*, 12 (2), 1704-1711, **2018**

[2^o] Imran et al., *J. Am. Chem. Soc.*, 140 (7), 2656-2664, **2018**

[2^o] Creutz et al., *Nano Lett.*, 18 (2), 1118-1123, **2018**

[3^o] Krieg et al., *ACS Energy Lett.*, 3, 614-646, **2018**

[4^o] Imran et al., *Nano Lett.*, 18 (12), 7822-7831, **2018**

[5^o] Bodnarchuk et al., *ACS Energy Lett.*, 4, 63-74, **2018**

[5^o] Nenon et al., *JACS*, 140 (50), 17760-17772, **2018**

[6^o] Imran et al., *ACS Energy Lett.*, 4, 819-824, **2019**

[7^o] Almeida et al., *JACS*, 140 (44), 14878-14886, **2018**

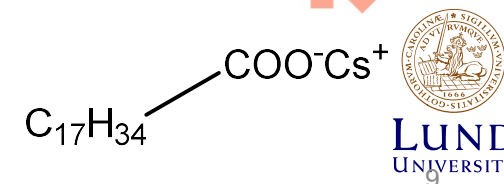
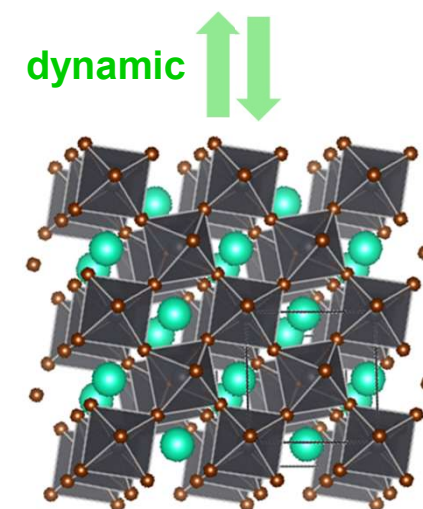
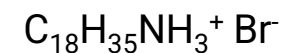
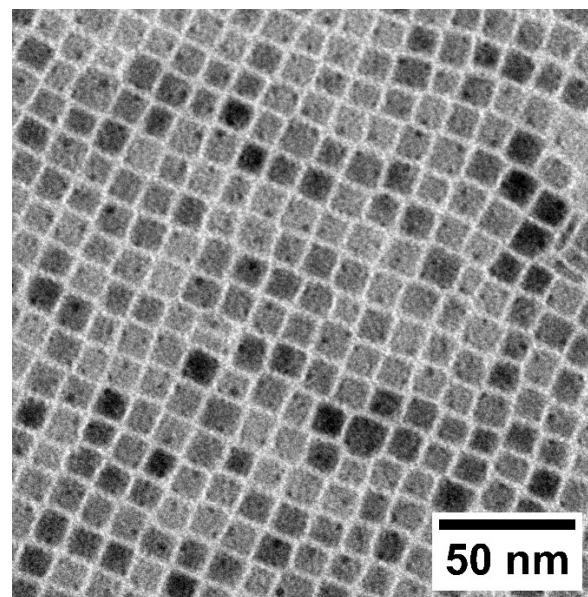
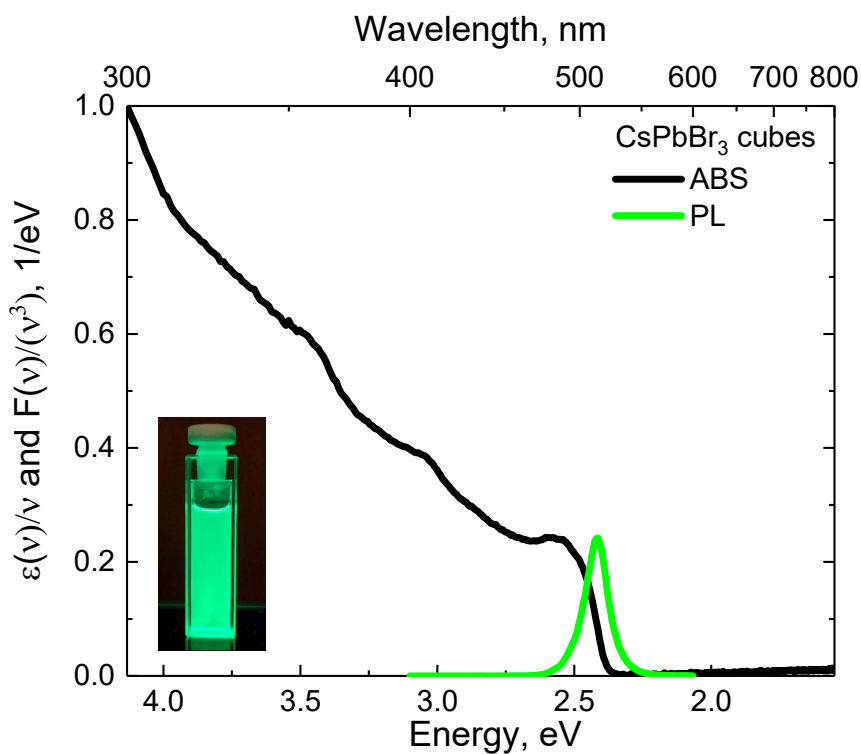
[7^o] Zhang et al., *Chem. Mater.*, 31 (21), 9140-9147, **2019**

[7^o] Akkerman et al., *Science*, 377 (6613), 1406-1412, **2022**



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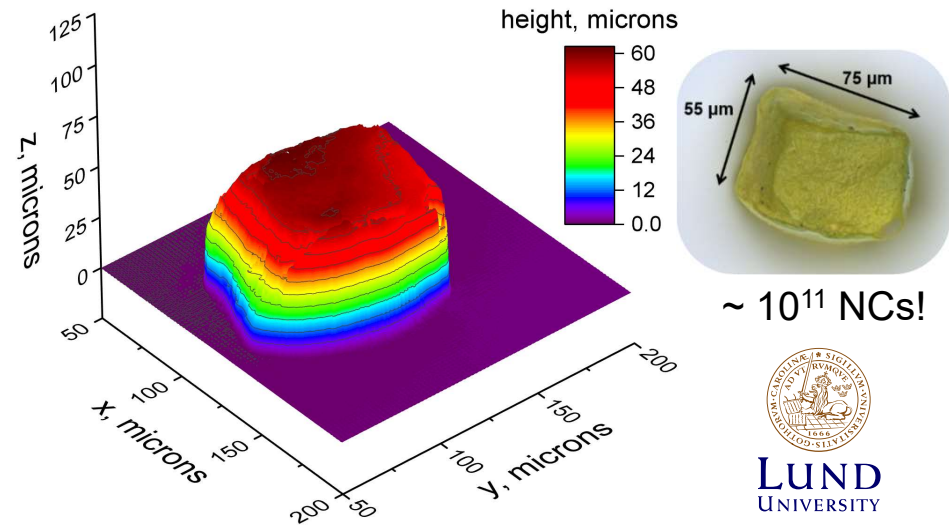
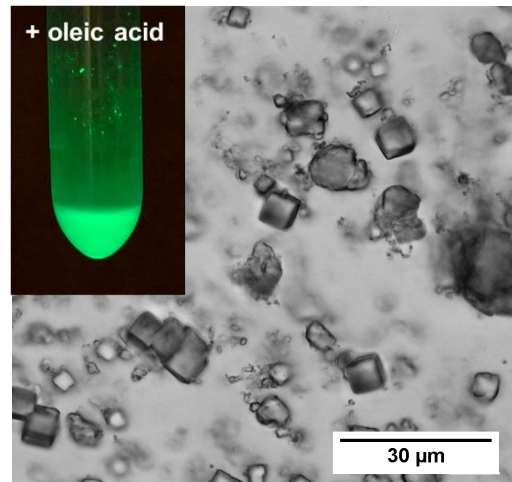
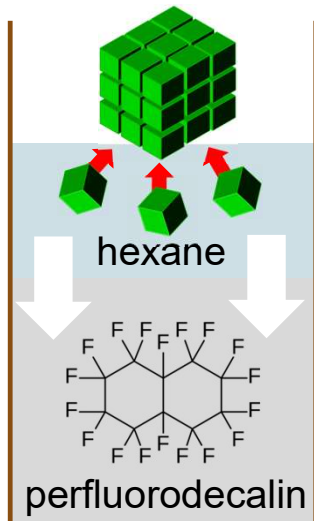
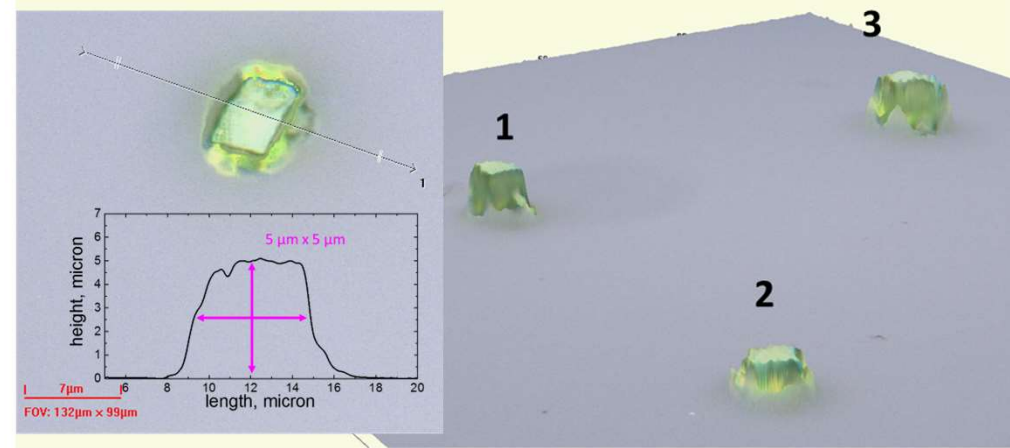
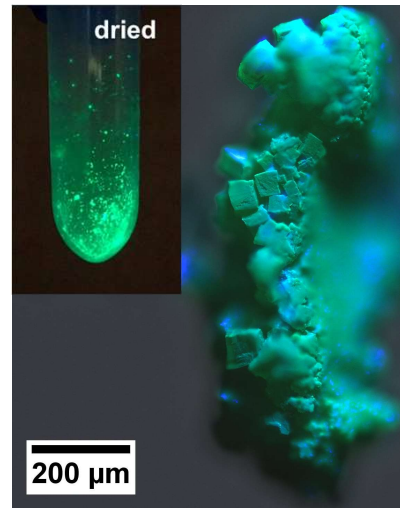
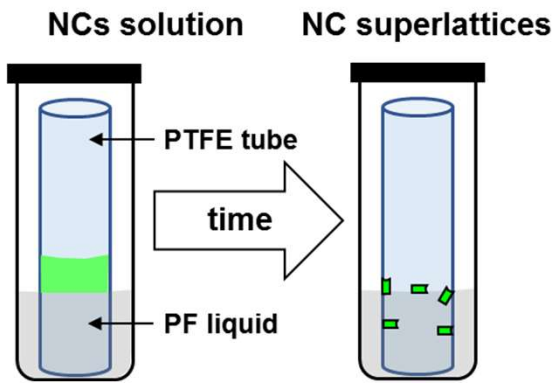
10 nm CsPbBr₃ Nanocubes (1st Generation)



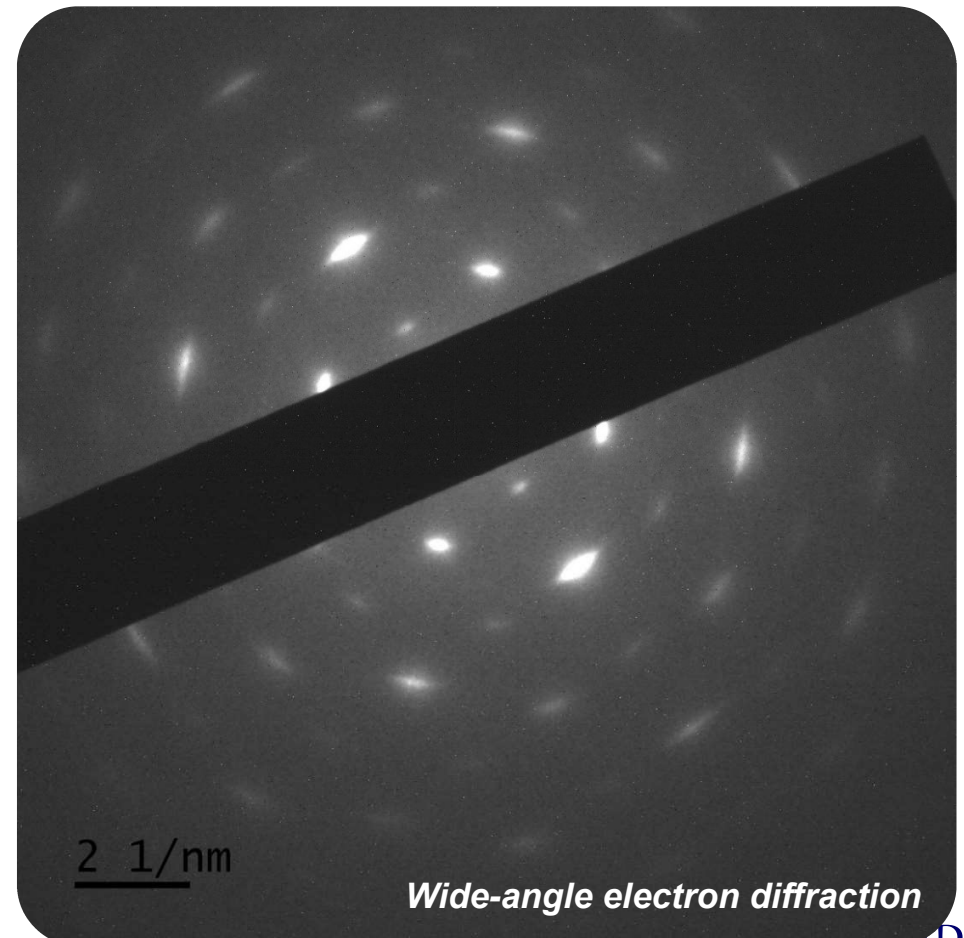
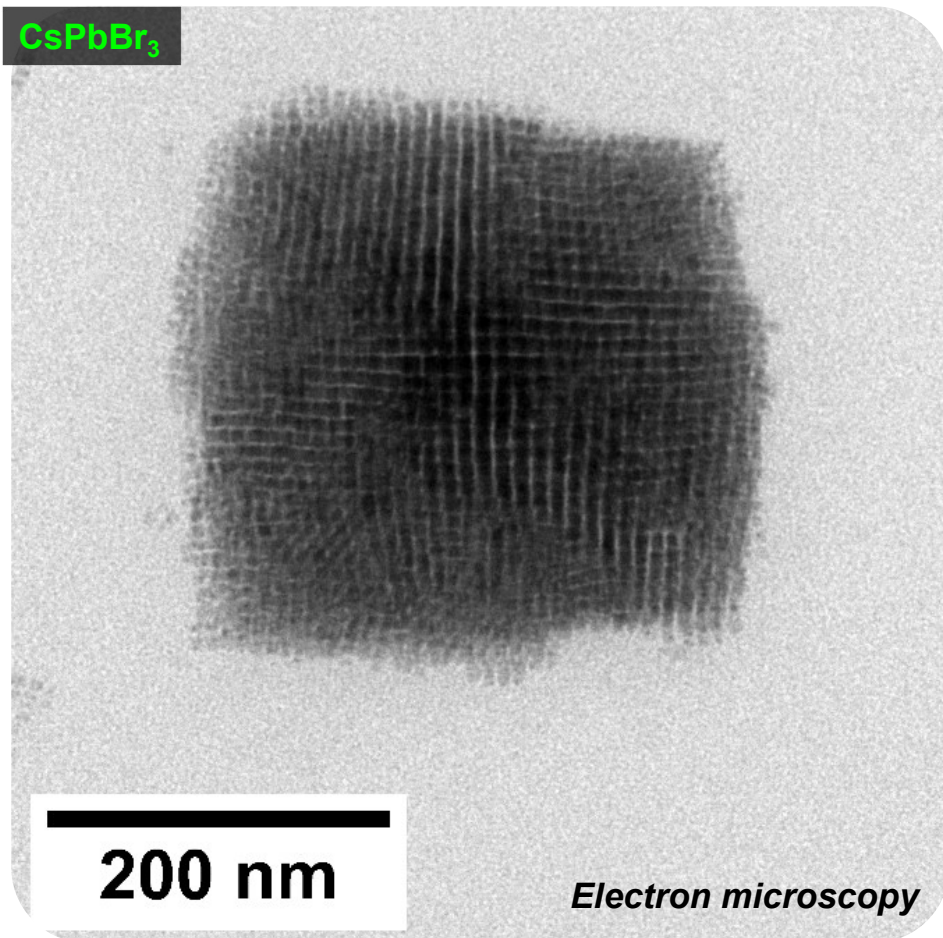
Protesescu et al., *Nano Lett*, 15 (6), 3692-3696, 2015

Almeida et al., *ACS Nano*, 12 (2), 1704-1711, 2018

Superlattices by Solvent Removal

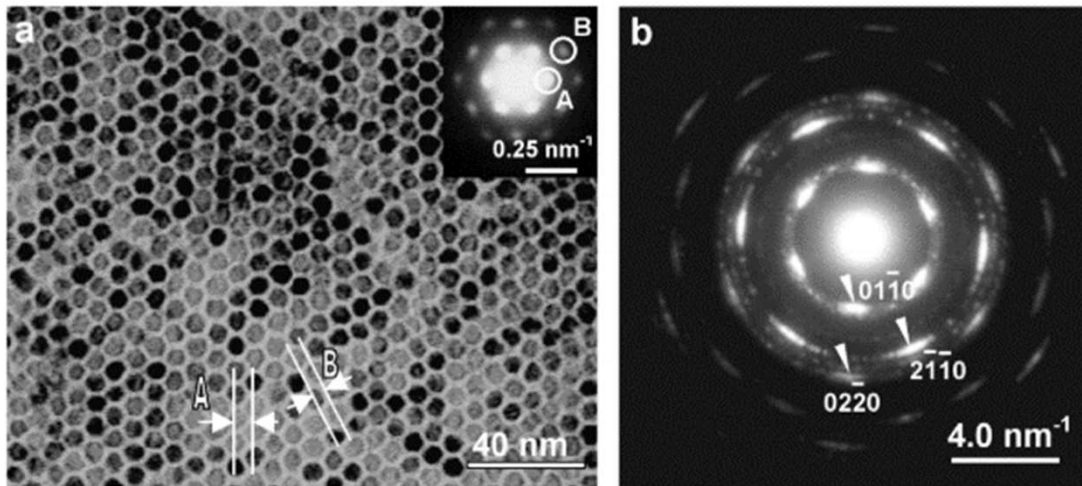


Well-ordered in Electron Diffraction



Well-ordered in Electron Diffraction

CsPbBr₃



Assembly of CdSe nanocrystals

Kang et al., *Phil. Mag. Lett.*, 2003, 83, 569

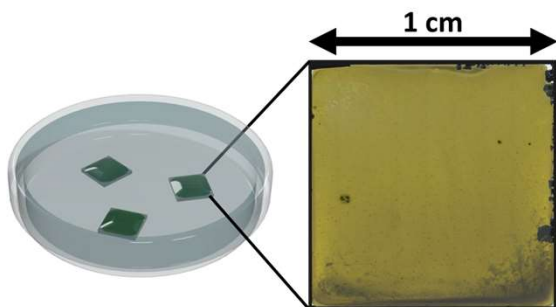
200 nm

Electron microscopy

$2 \frac{1}{\text{nm}}$

Wide-angle electron diffraction

Assembly by Solvent Evaporation



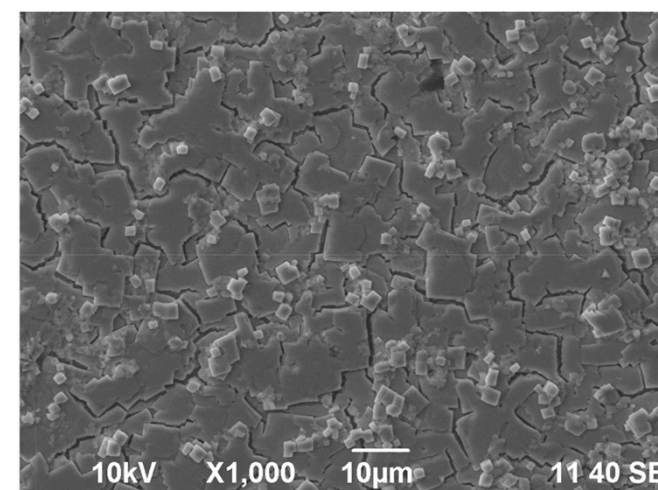
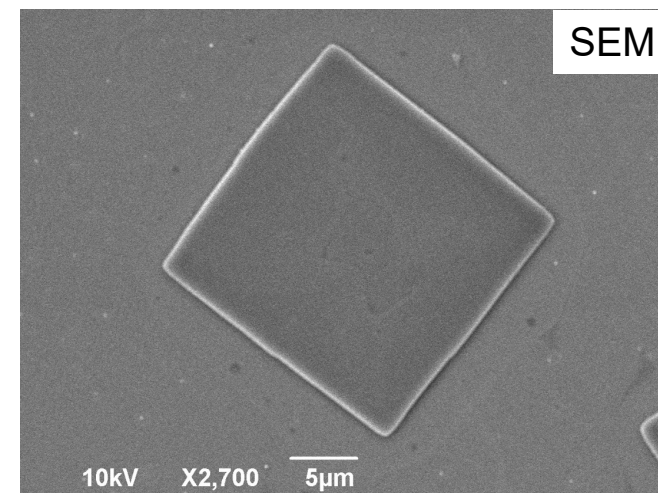
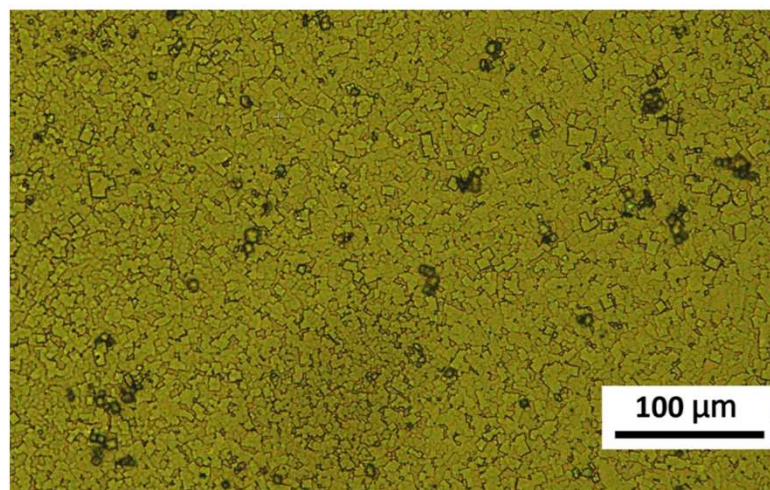
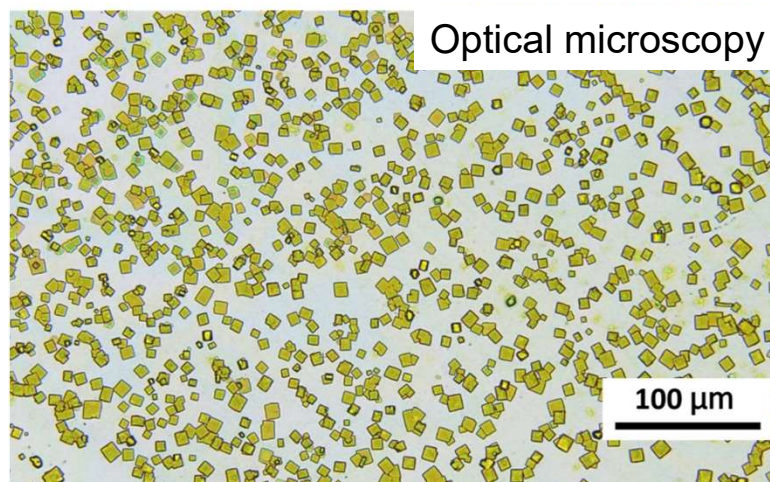
$[\text{CsPbBr}_3]_{\text{NC}} \approx 0.8\text{-}1 \mu\text{M}$

Solvents:

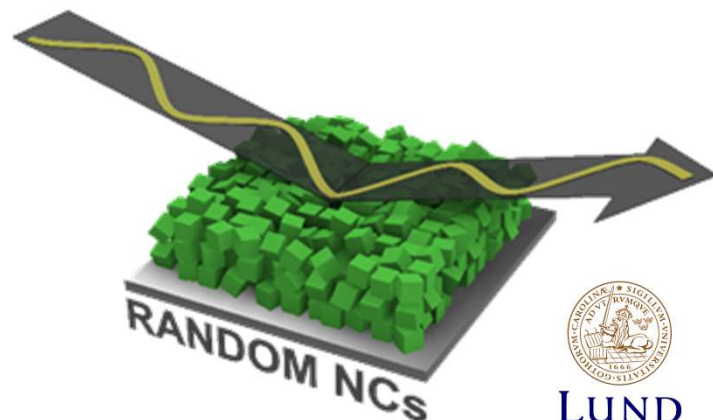
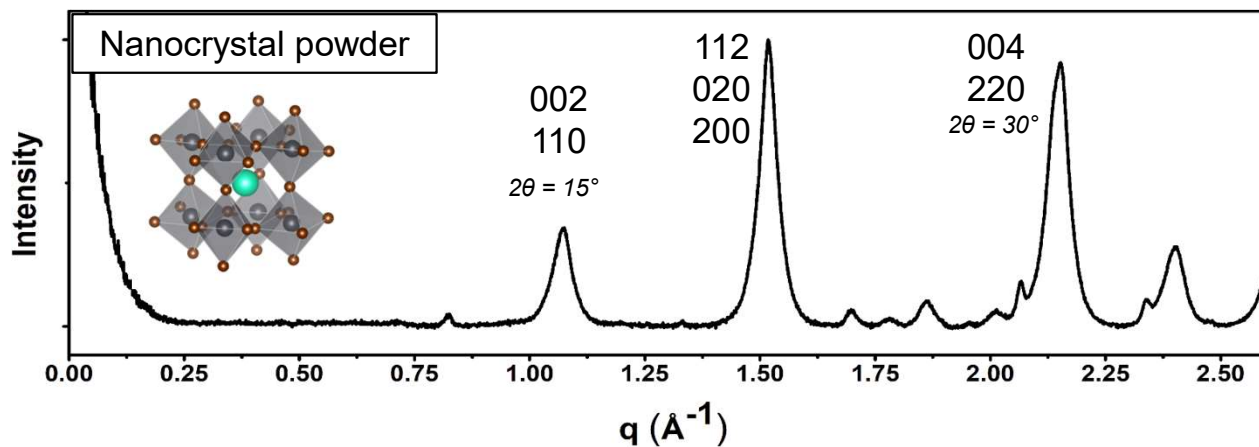
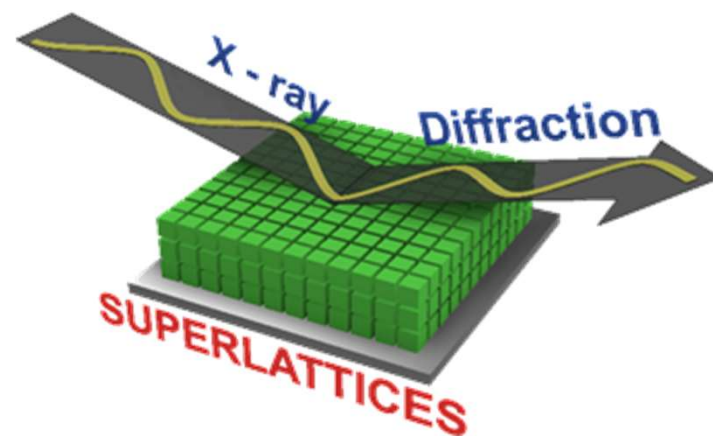
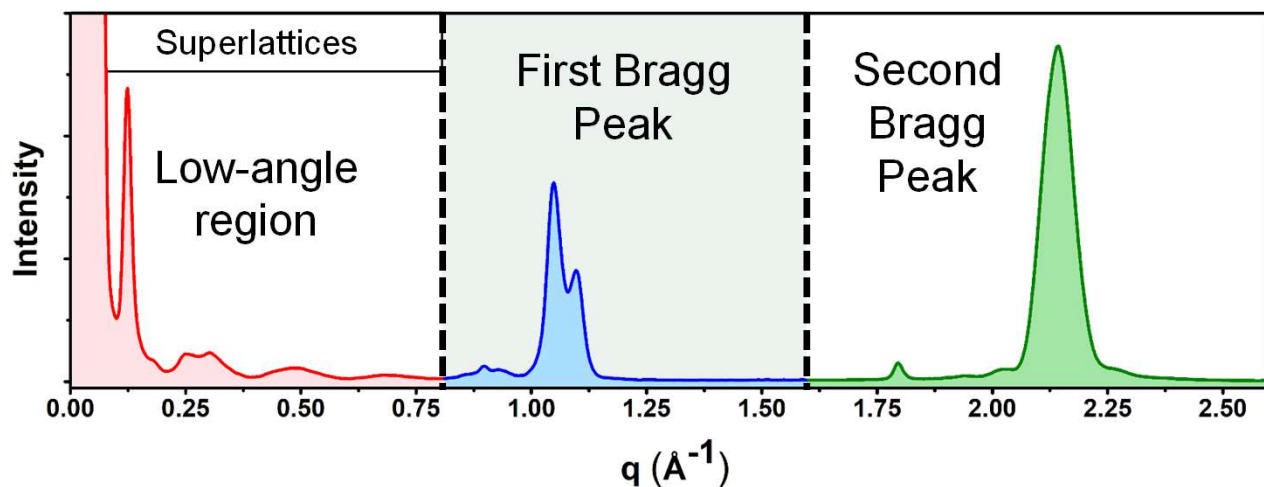
Toluene (*b.p.* 111 °C)

Tetrachloroethylene (*b.p.* 121 °C)

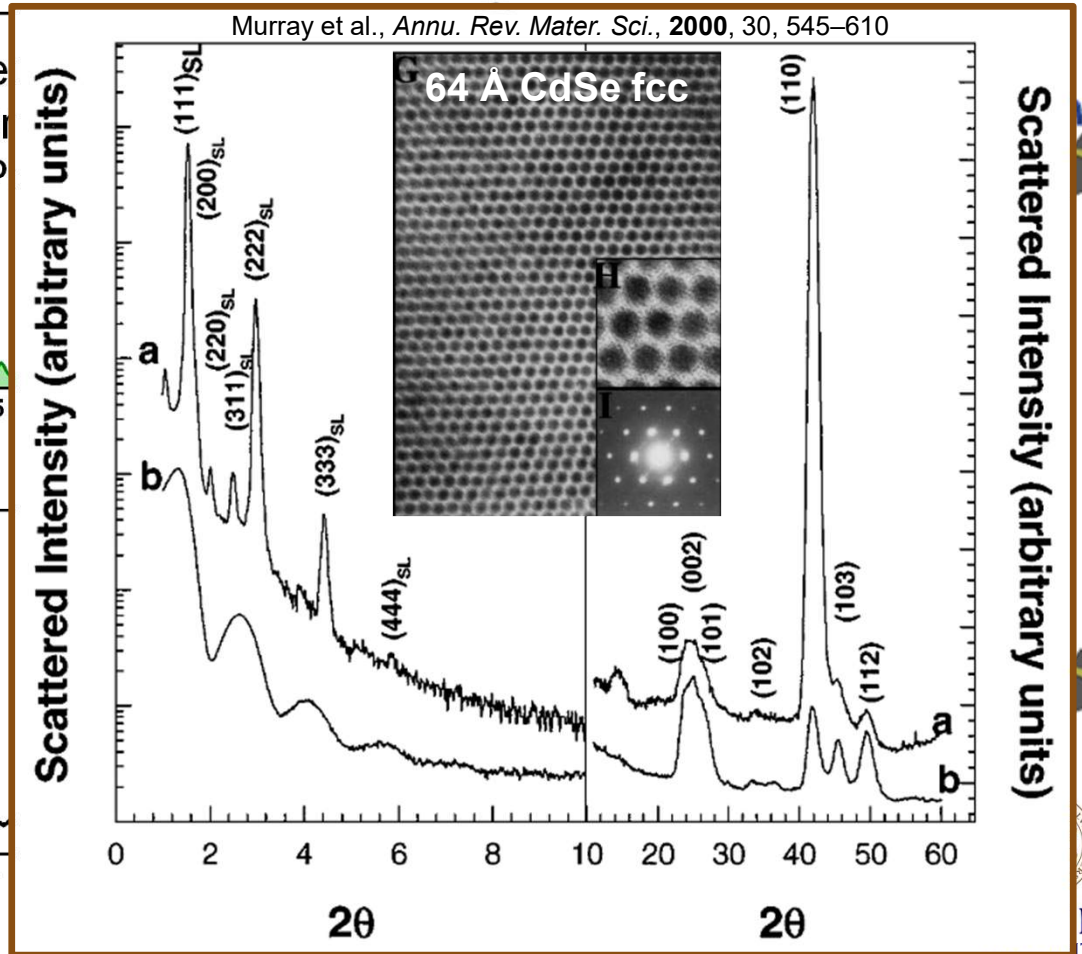
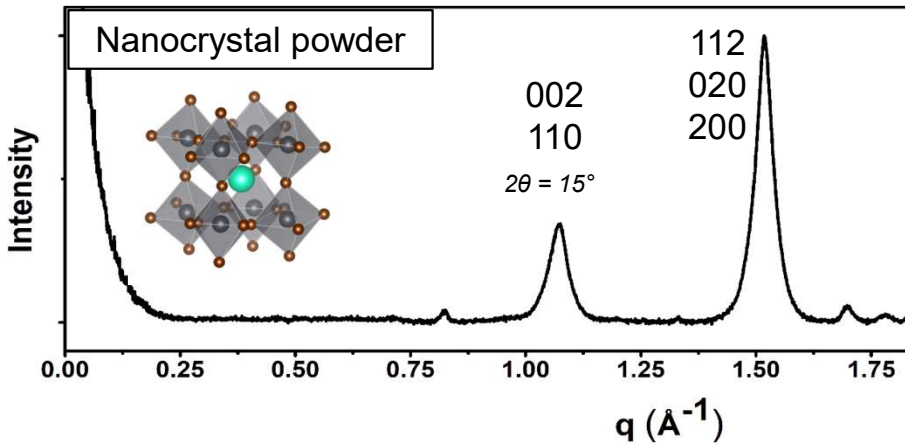
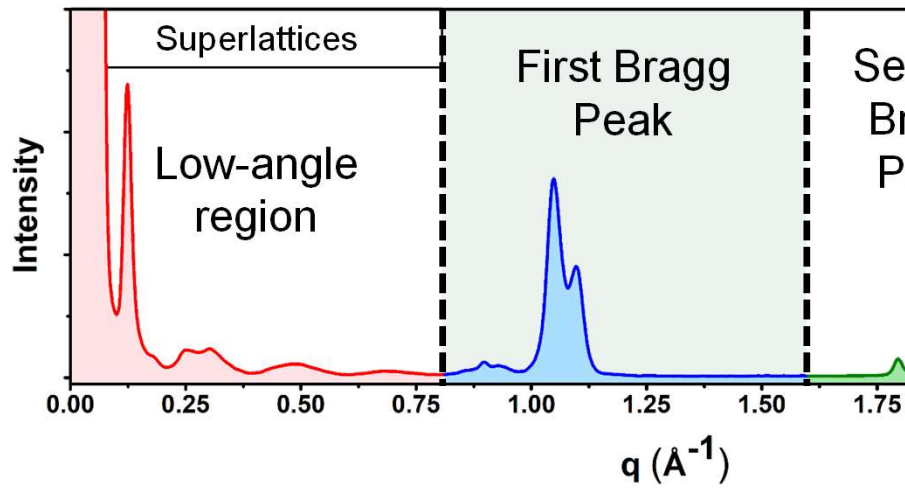
Evaporation takes 2-12 hours, depending on the amount of liquid.



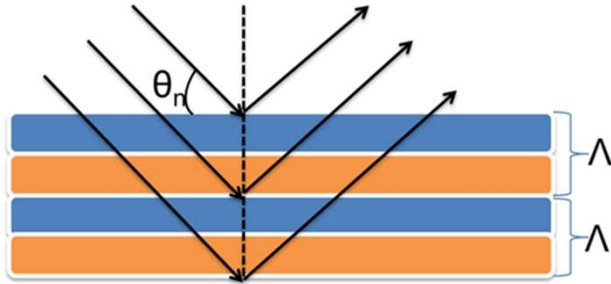
Wide-Angle X-Ray Diffraction



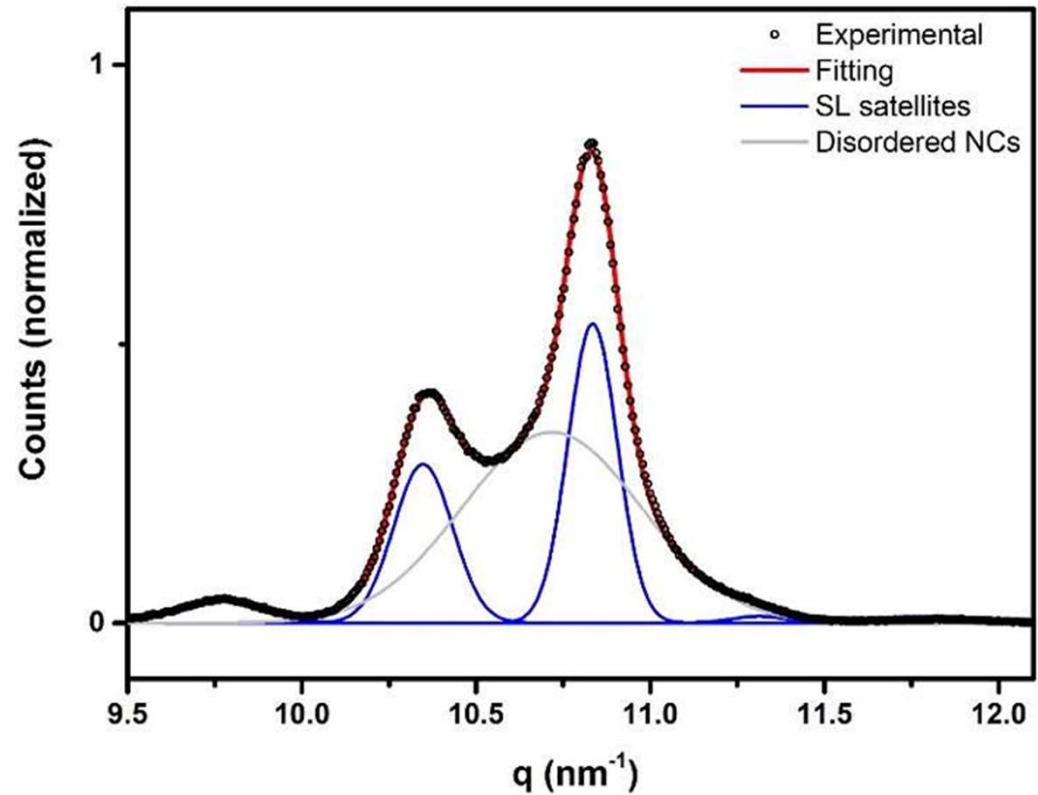
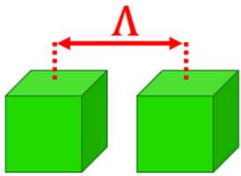
Wide-Angle X-Ray Diffraction



Superlattice Satellites of the 1st Bragg Peak

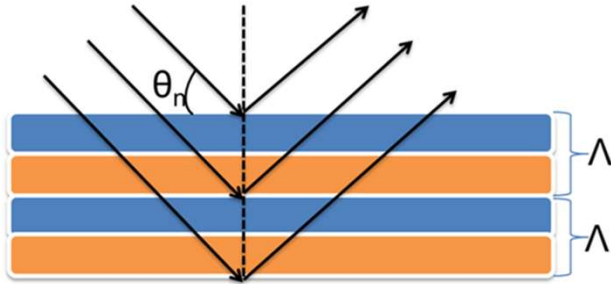


$$q_n = \frac{2\pi n}{\Lambda}$$

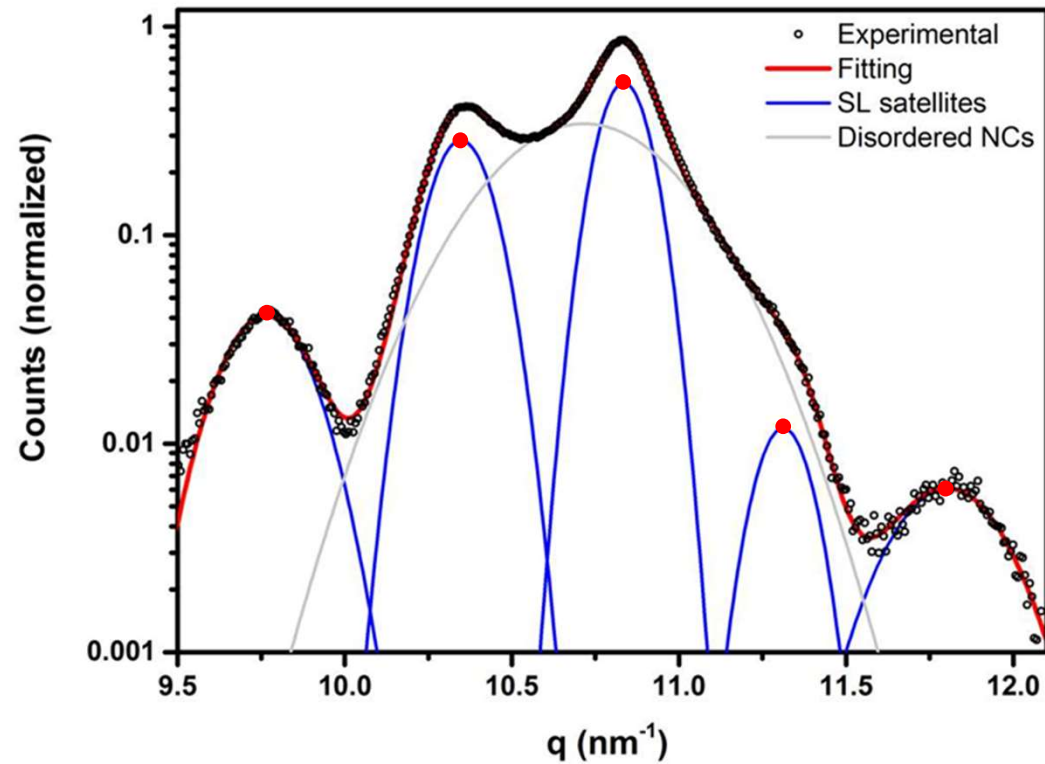
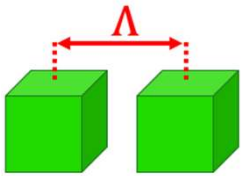


Schuller, *Phys. Rev. Lett.*, **1980**, 44, 24, 1597-1600
Toso, DB, Giannini, Manna, *ACS Mater. Lett.* **2019**, 1, 2, 272-276

Superlattice Satellites of the 1st Bragg Peak



$$q_n = \frac{2\pi n}{\Lambda}$$

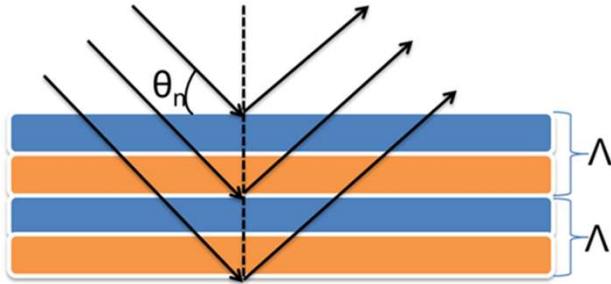


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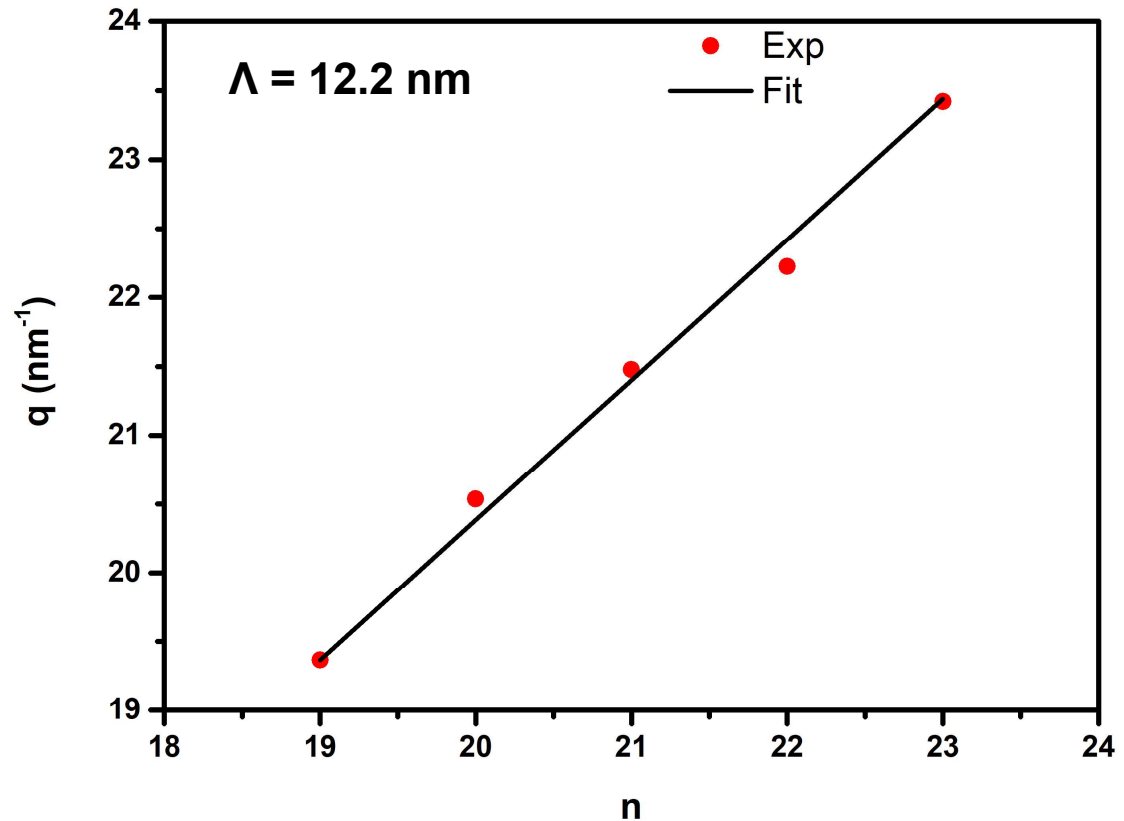
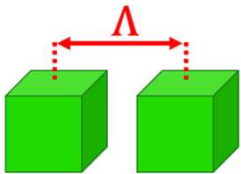


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Superlattice Satellites of the 1st Bragg Peak



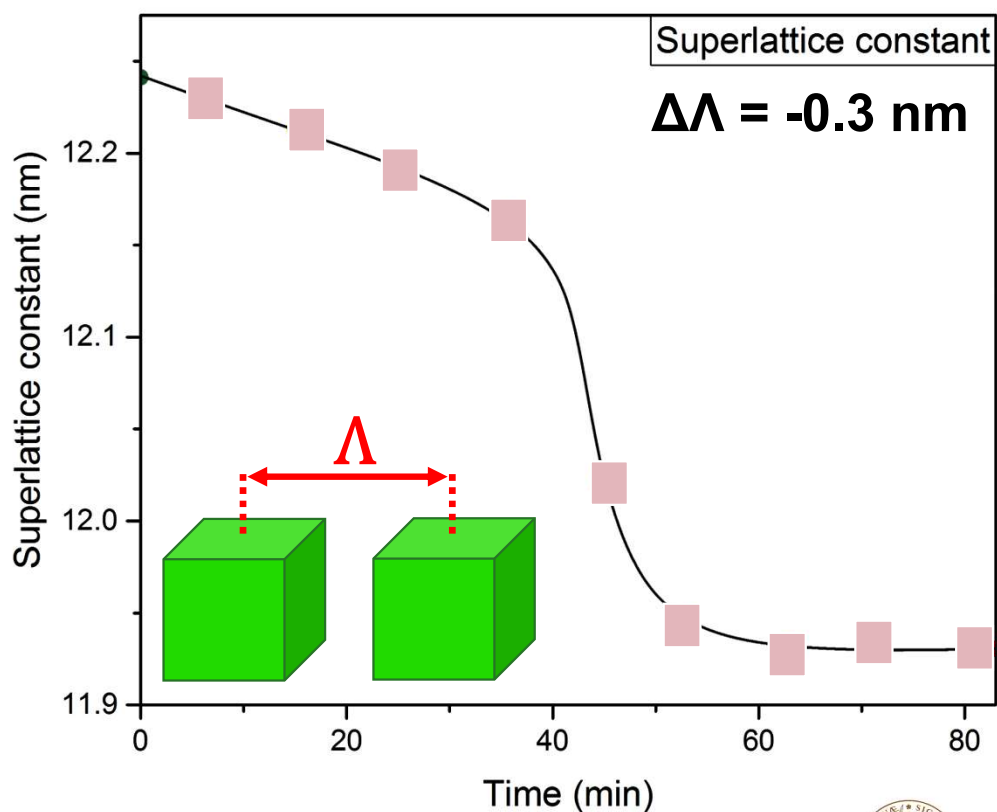
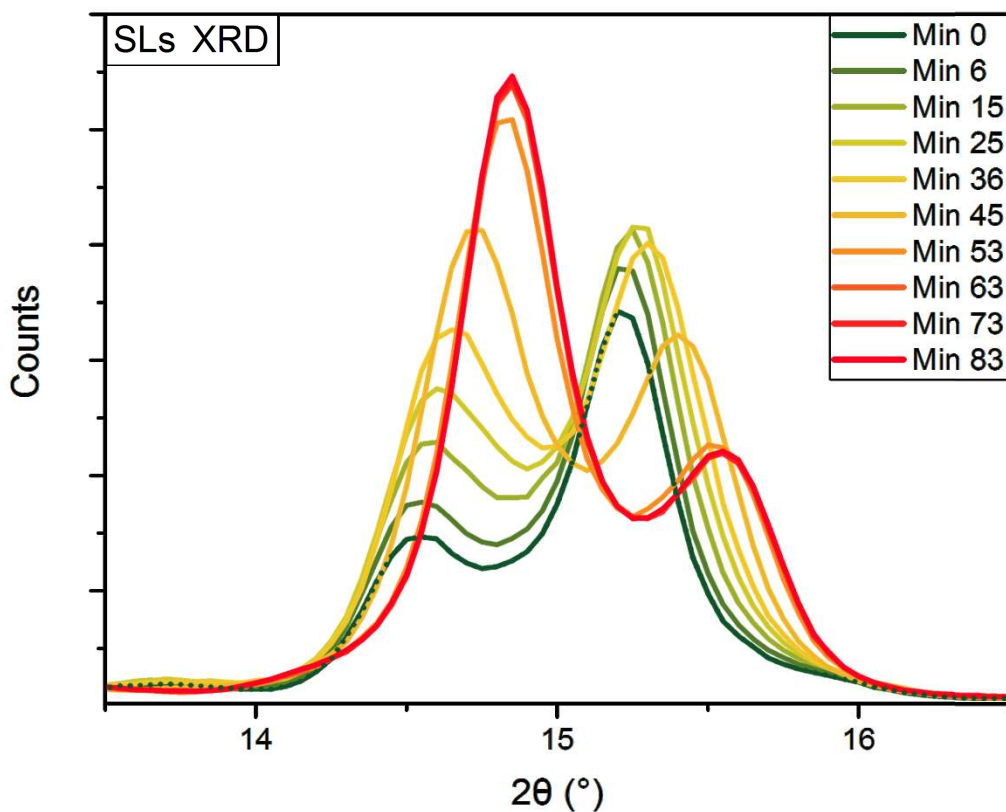
$$q_n = \frac{2\pi n}{\Lambda}$$



Schuller, *Phys. Rev. Lett.*, **1980**, 44, 24, 1597-1600
Toso, DB, Giannini, Manna, *ACS Mater. Lett.* **2019**, 1, 2, 272-276

From TEM of monolayers:
11.5-12.6 nm center-to-center distance

Tracking Effect of Vacuum



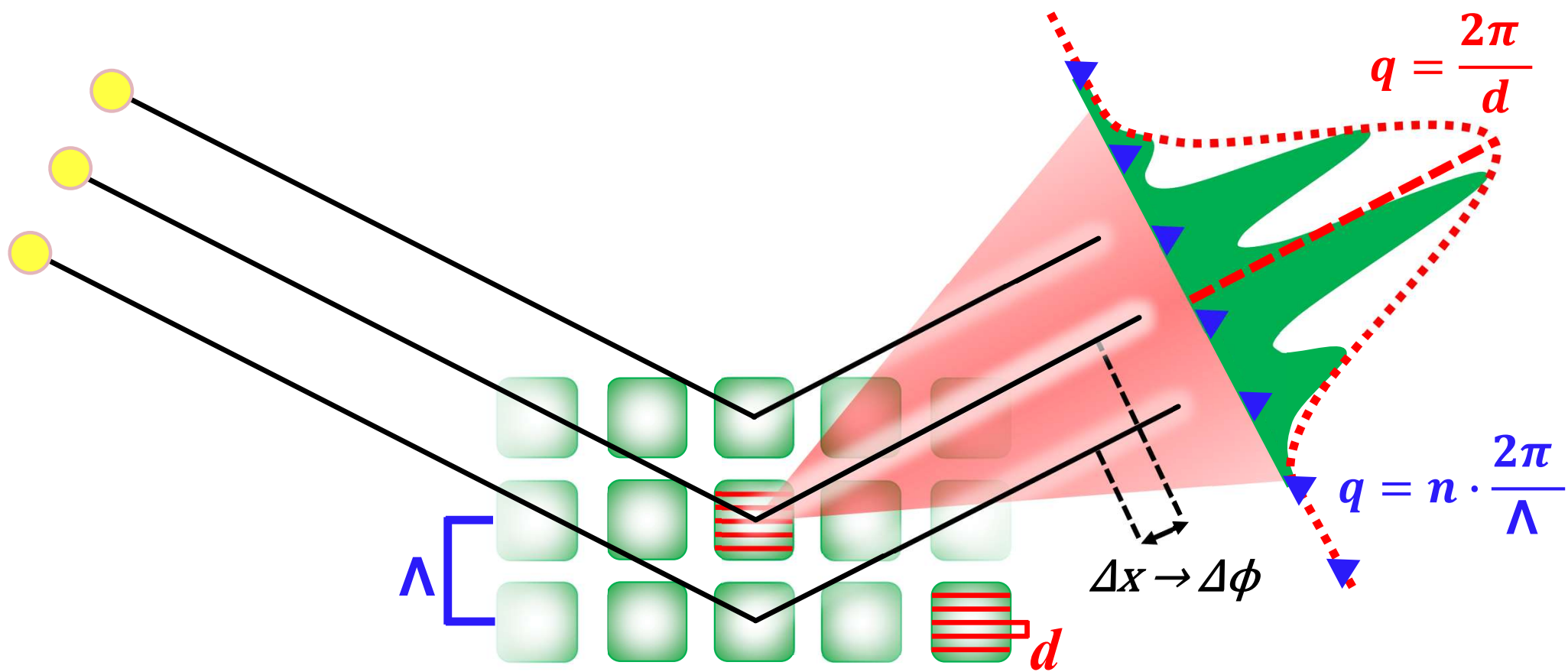
Toso, DB, Giannini, Manna, *ACS Mater. Lett.* **2019**, 1, 2, 272-276

0.3 nm = 3 Å is approx. the size of tetrachloroethylene (C_2Cl_4)

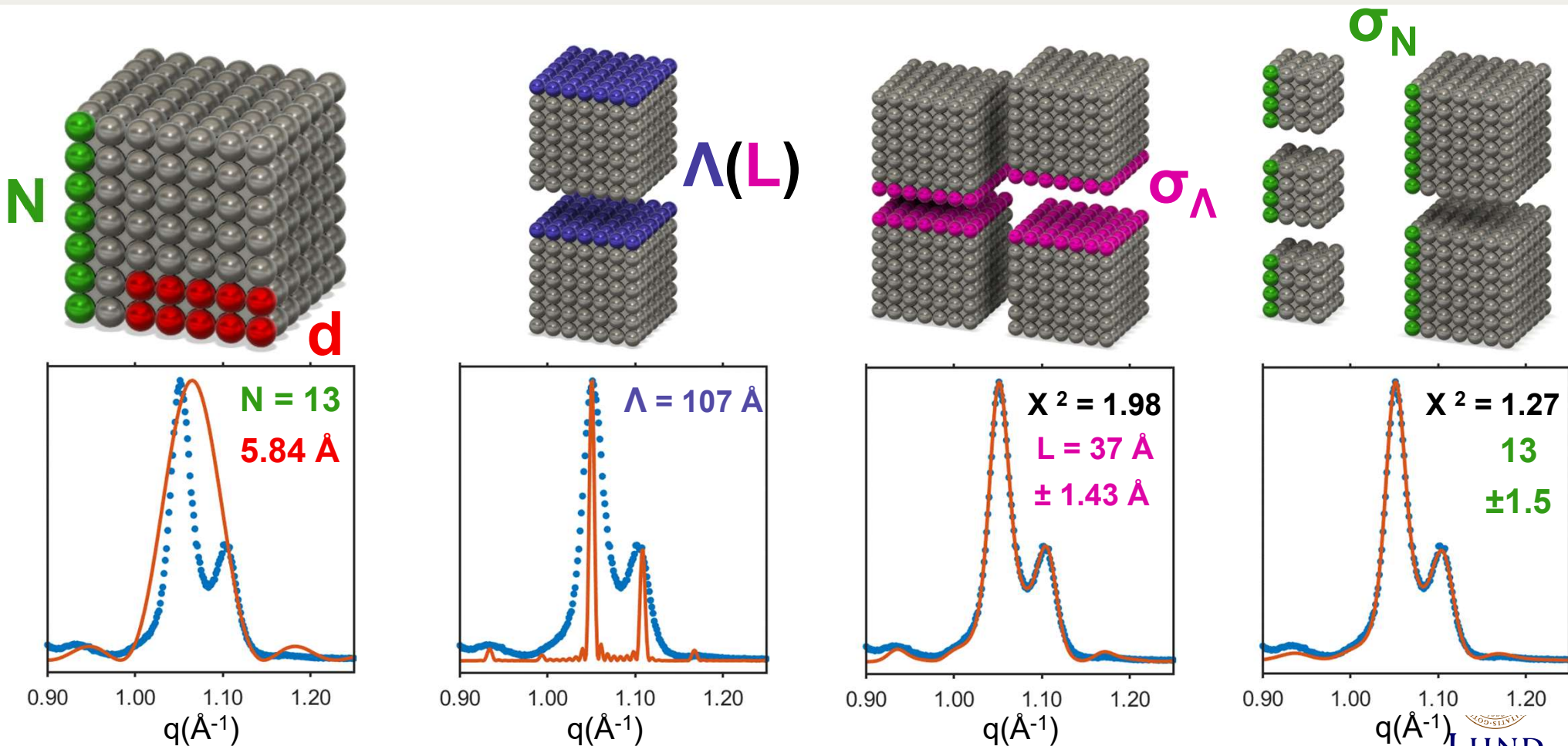


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Physical Picture of Superlattice Diffraction

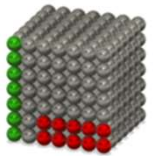
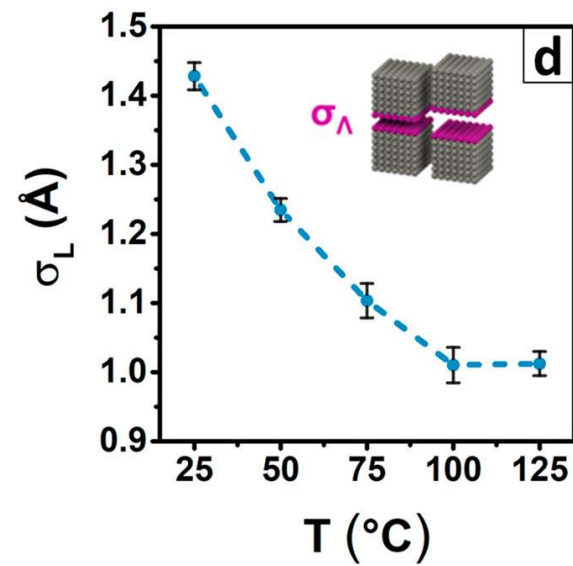
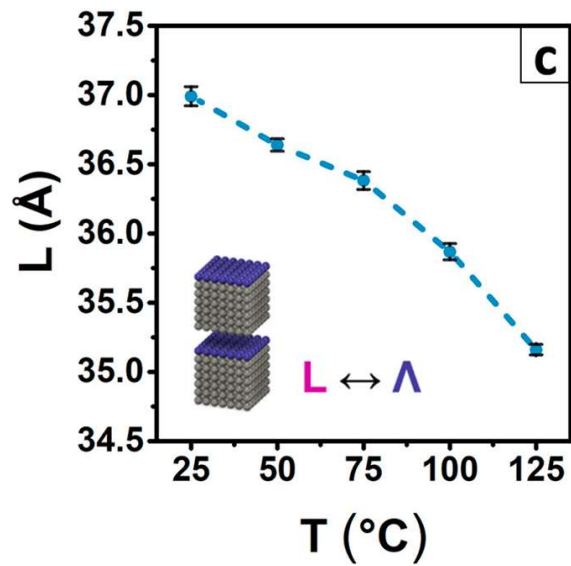
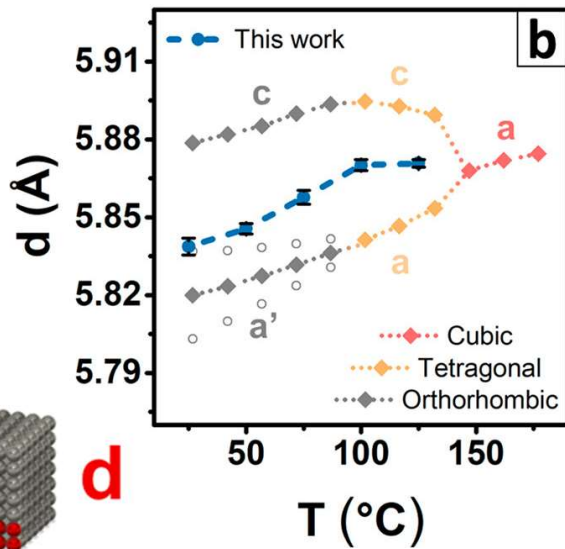
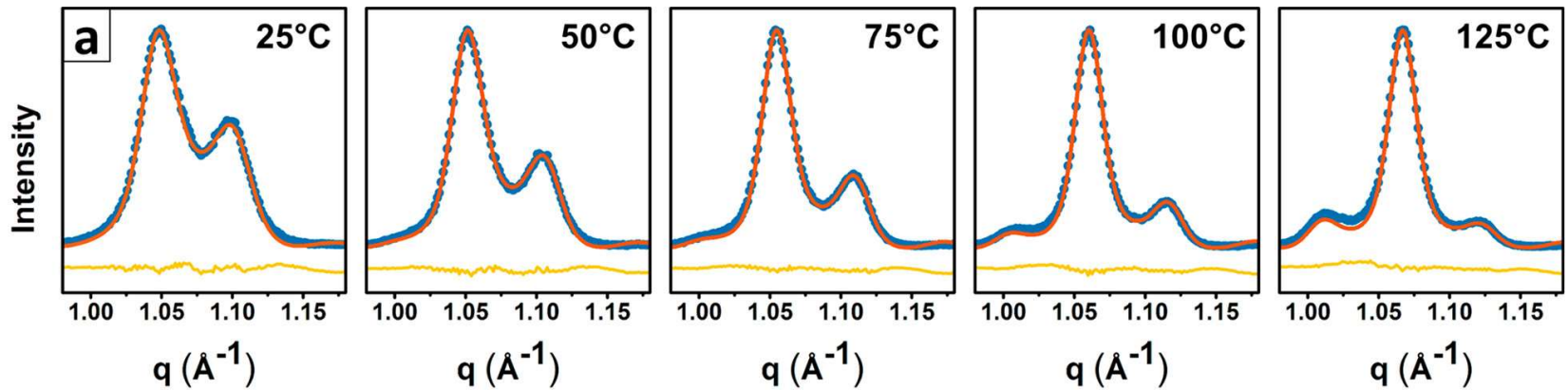
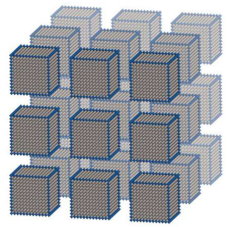


Quantitative Structural Refinement



Toso, DB et al, *ACS Nano* **2021**, 15, 4, 6243-6256; model based on Fullerton et al., *Phys. Rev. B*, **1992**, 45, 16, 9292-9310

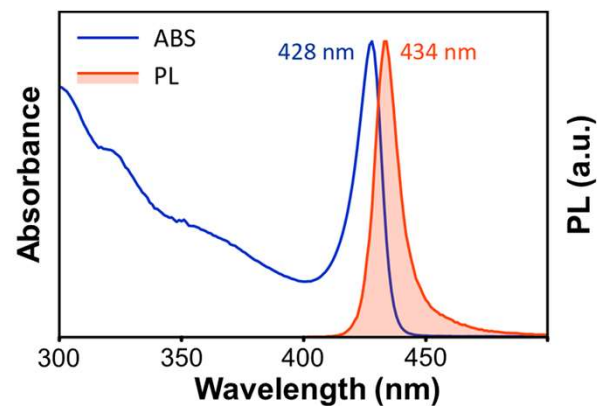
Quantifying Effect of Temperature on Superlattices



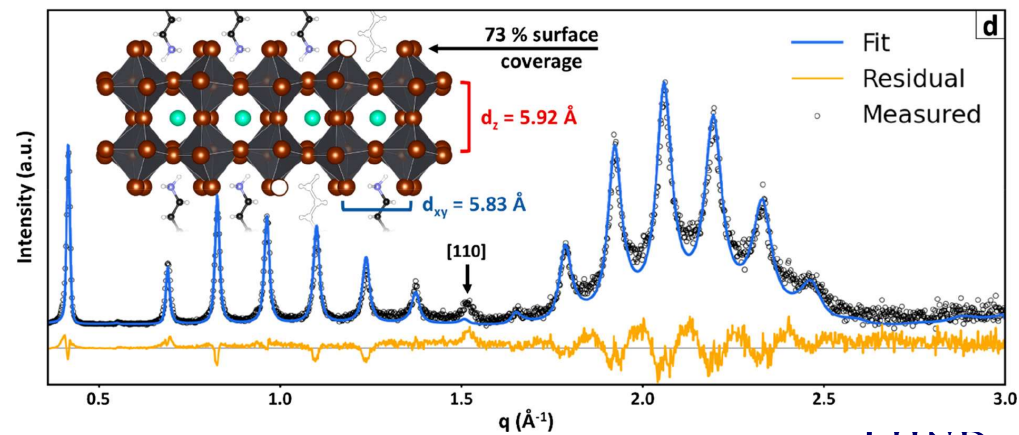
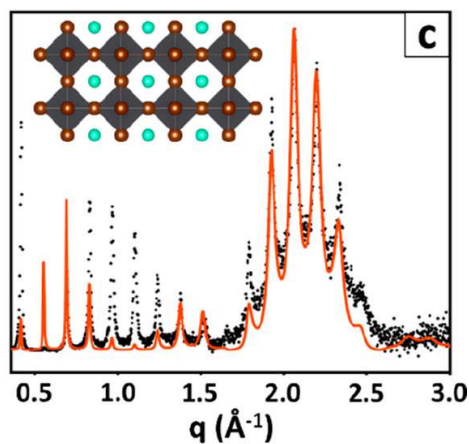
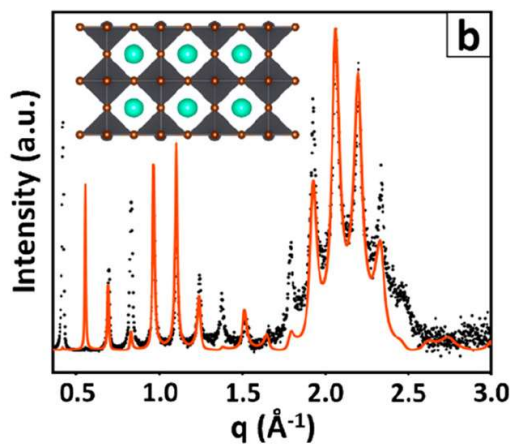
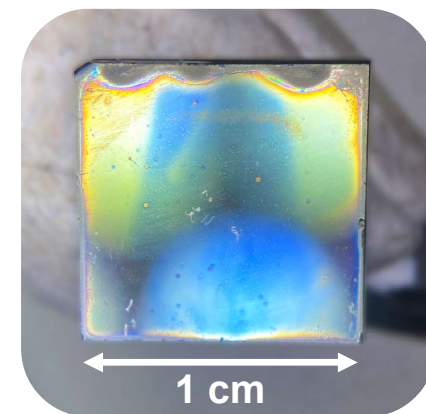
Refining Surface Passivation of Nanoplatelets



2-Monolayer Cs-Pb-Br Nanoplatelets

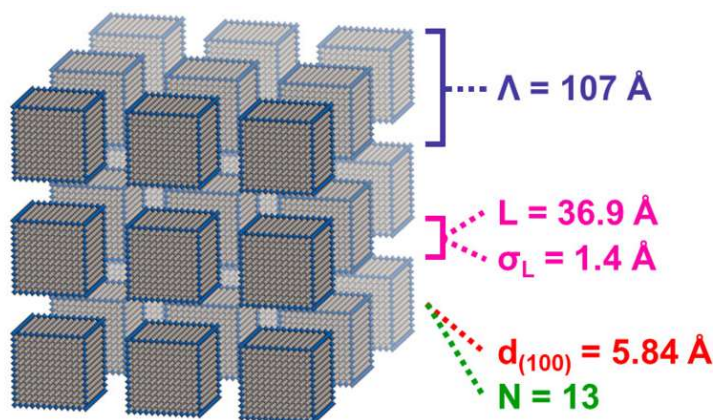


Nanoplatelet Superlattices

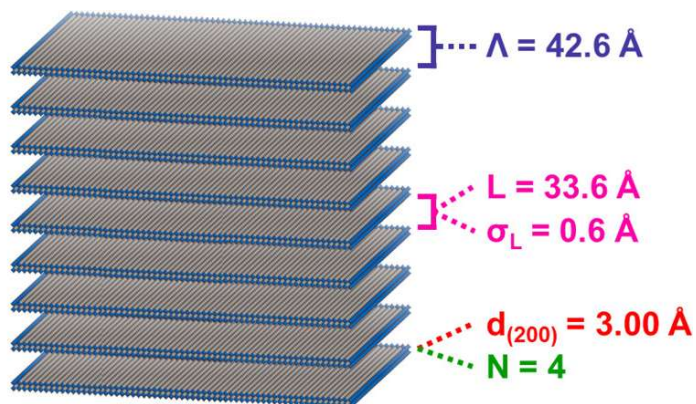


Quantification of Structural Parameters

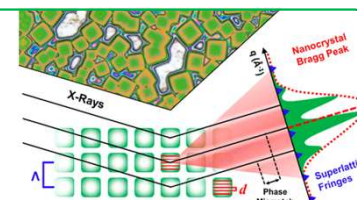
CsPbBr₃ nanocubes



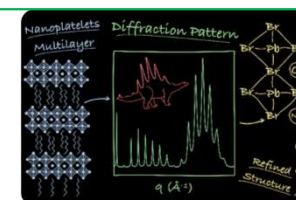
nanoplatelets



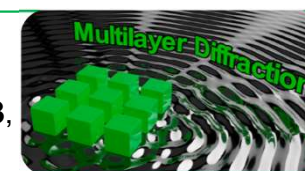
Toso, Baranov et al.
ACS Nano **2021**,
 15, 4, 6243–6256



Toso, Baranov et al.
ACS Nano **2021**,
 15, 12, 20341–20352



Toso, Baranov, Filippi,
 Giannini, Manna
Acc. Chem. Res. **2023**,
 56, 1, 66-76



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Diffraction and Interference

$$R_1 = A_1 \cos(\omega_1 t + \phi_1)$$

$$R_2 = A_2 \cos(\omega_2 t + \phi_2)$$

...

$$R_n = A_n \cos(\omega_n t + \phi_n)$$

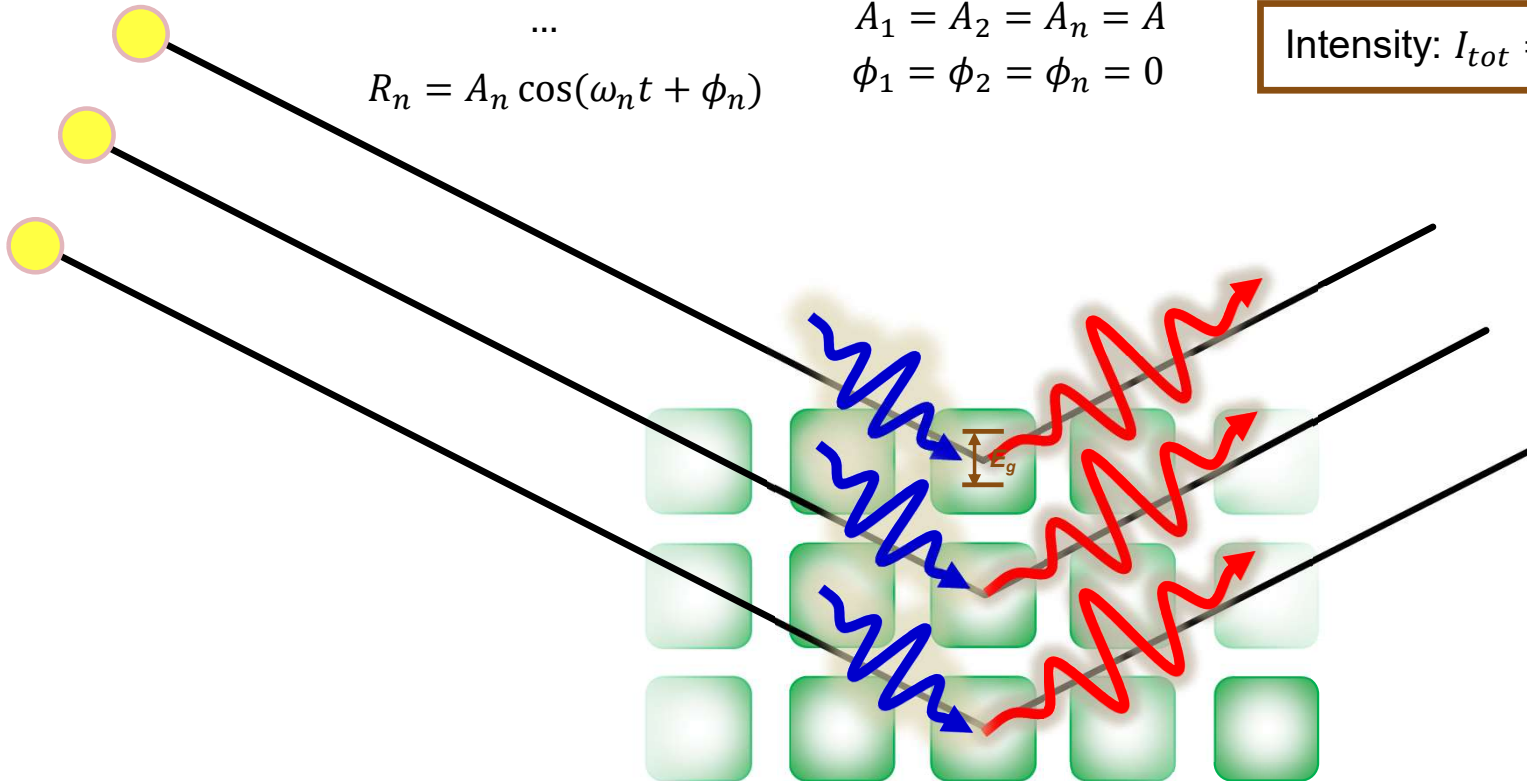
$$\omega_1 = \omega_2 = \omega_n = \omega$$

$$A_1 = A_2 = A_n = A$$

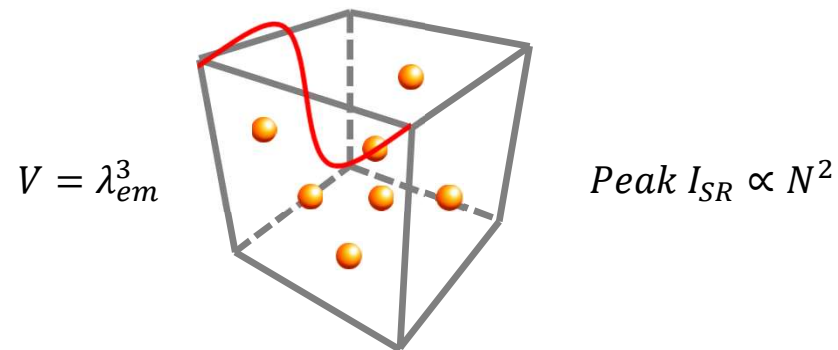
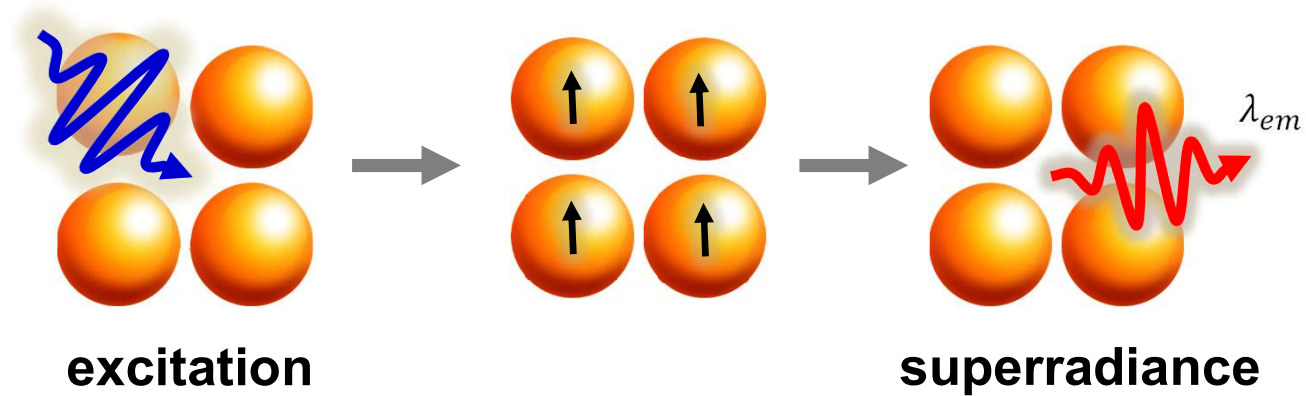
$$\phi_1 = \phi_2 = \phi_n = 0$$

$$\text{Amplitude: } R_{tot} = nA \cos(\omega t)$$

$$\text{Intensity: } I_{tot} = R_{tot}^2 = n^2 A^2 [\cos(\omega t)]^2$$

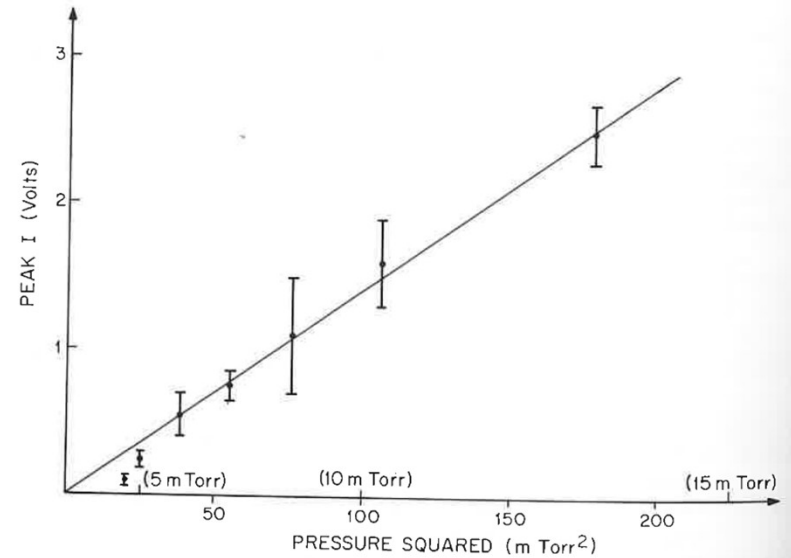
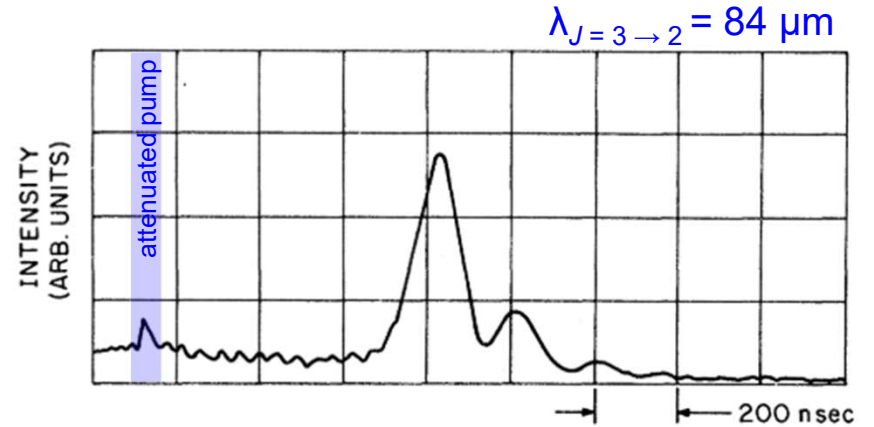
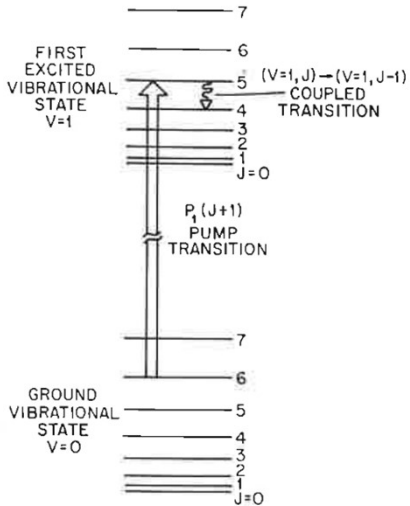
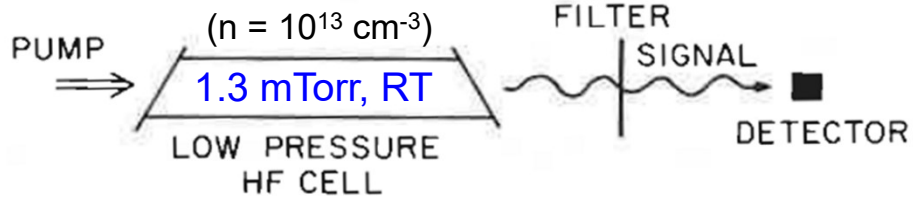


Dicke Superradiance, 1954



Dicke, *Phys. Rev.*, 93 (1), 1954

Experiment with HF gas, 1972

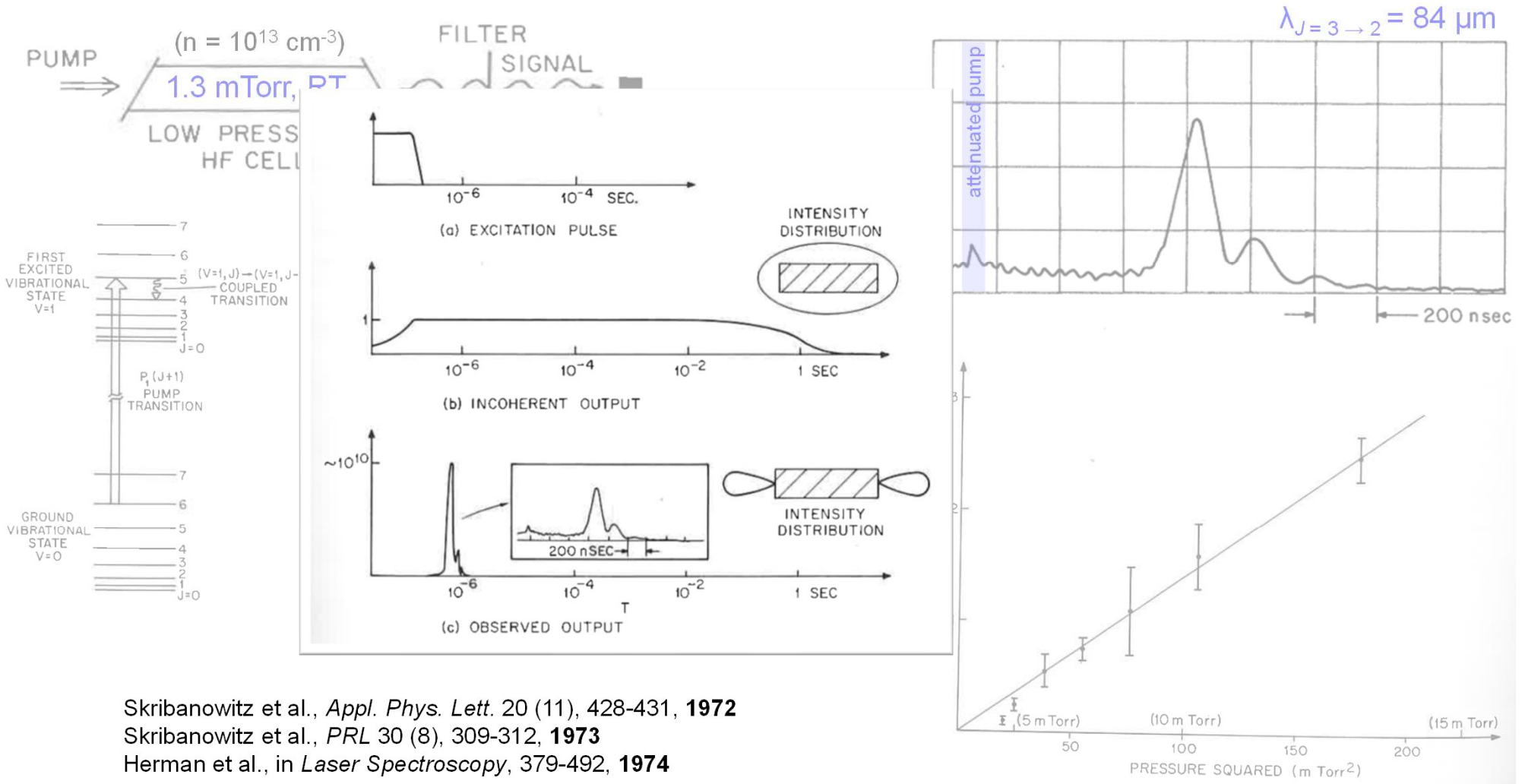


Skribanowitz et al., *Appl. Phys. Lett.* 20 (11), 428-431, 1972

Skribanowitz et al., *PRL* 30 (8), 309-312, 1973

Herman et al., in *Laser Spectroscopy*, 379-492, 1974

Experiment with HF gas, 1972

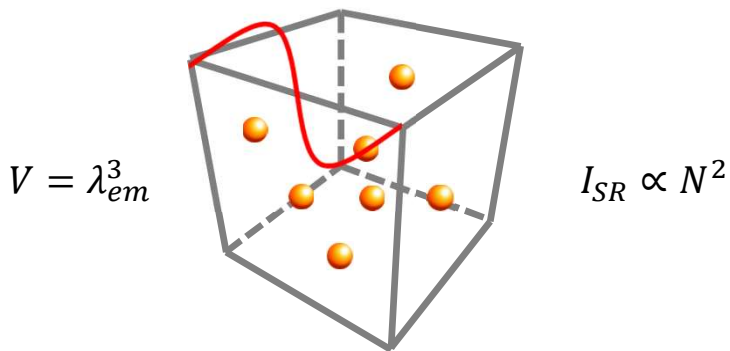
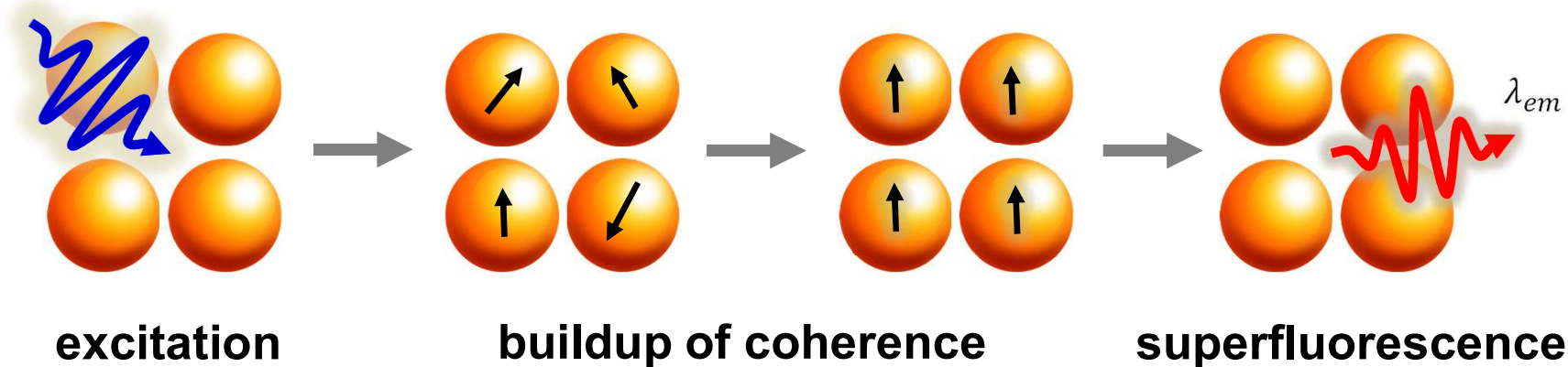


Skribanowitz et al., *Appl. Phys. Lett.* 20 (11), 428-431, 1972

Skribanowitz et al., *PRL* 30 (8), 309-312, 1973

Herman et al., in *Laser Spectroscopy*, 379-492, 1974

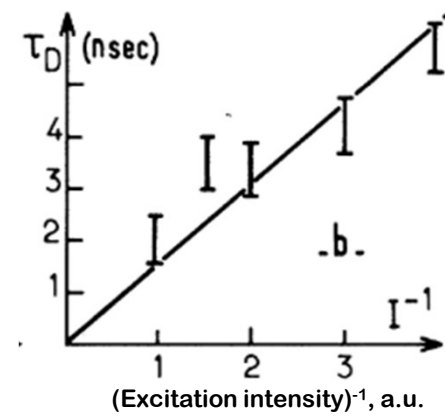
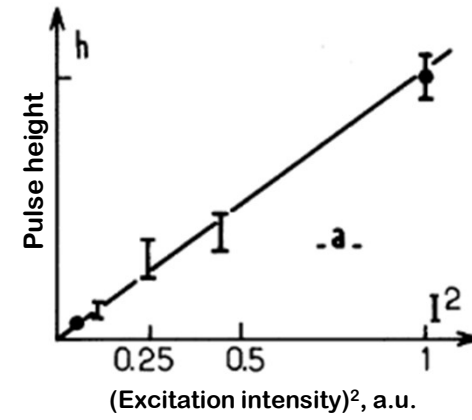
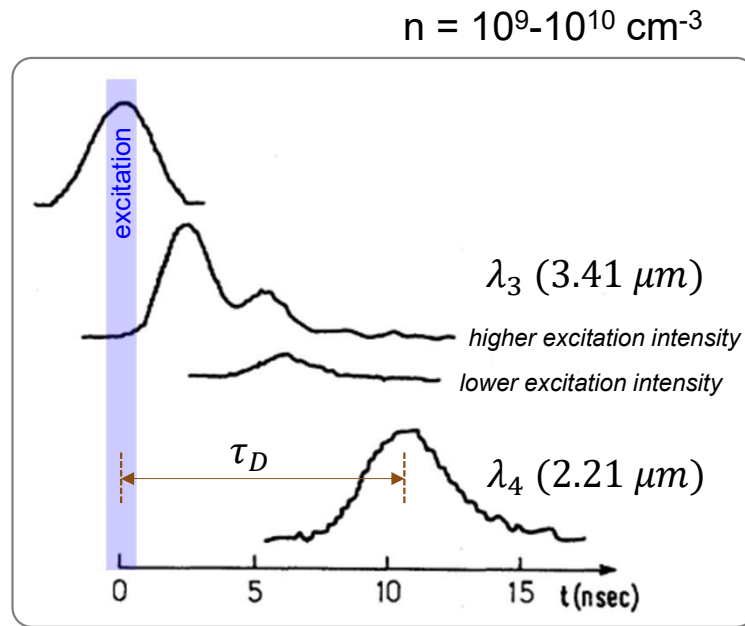
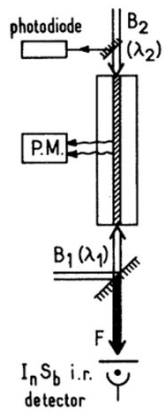
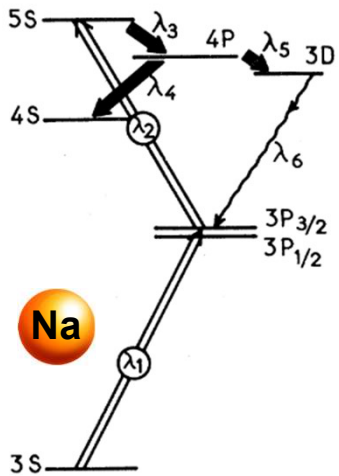
Superfluorescence, 1975



Bonifacio and Lugiato, *Phys. Rev. A*, 11 (5), 1975

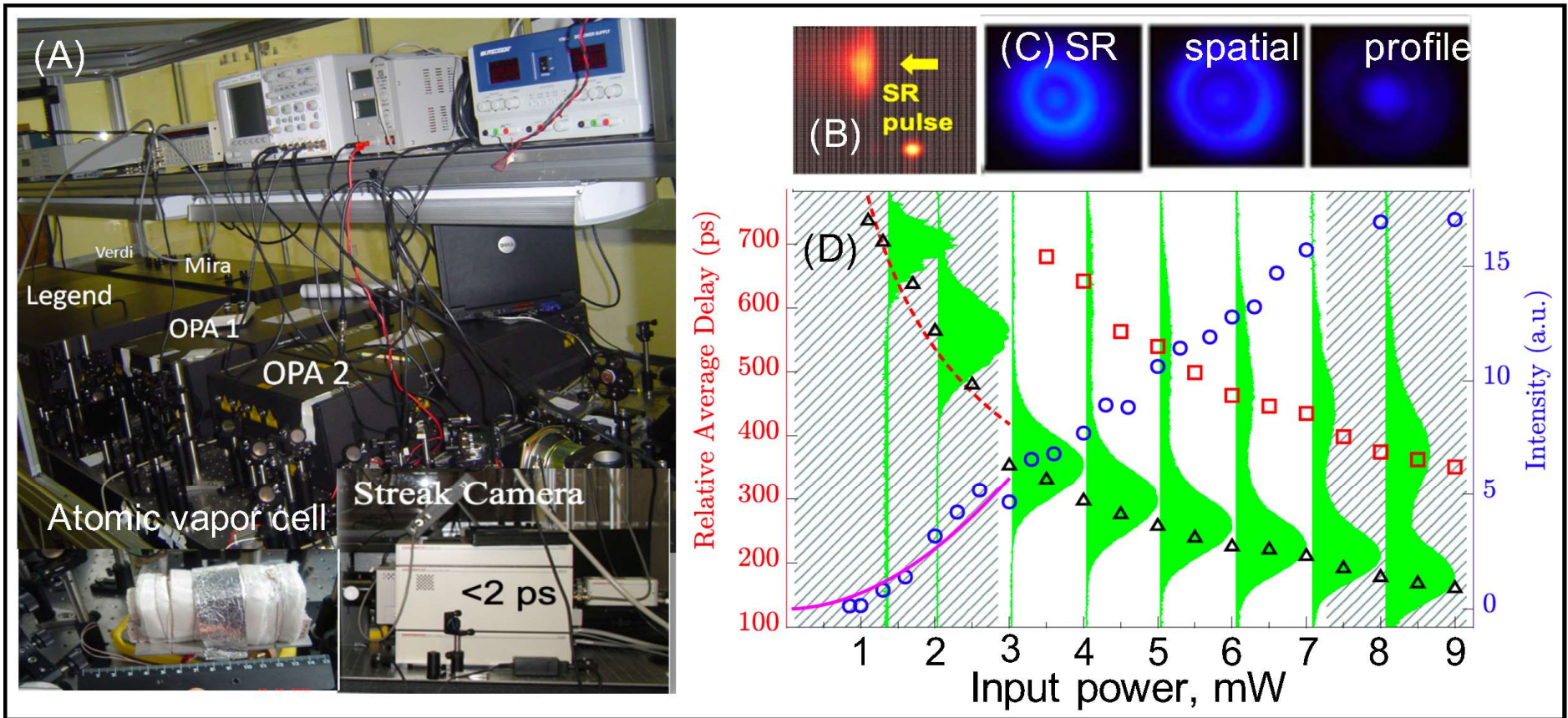


Experiment with Na vapor, 1976



Gross et al., *Phys. Rev. Lett.*, 36 (17), 1035-1038, 1976

Recent experiments with Rb vapor



Ariunbold, *Processes* 10 (9), 1885, 2022
Ariunbold et al., *Phys. Rev. A.*, 82, 043421, 2010

Superfluorescence in CsPbBr₃ Nanocrystals

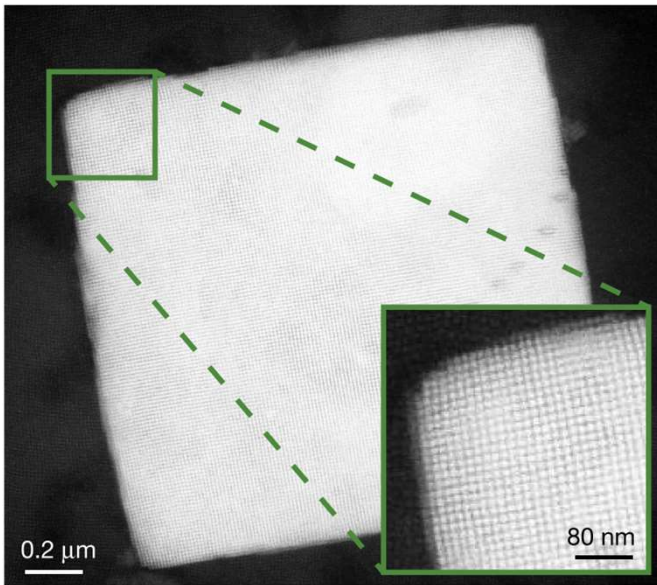
CsPbBr₃ nanocubes (1st Generation)

Letter | Published: 07 November 2018

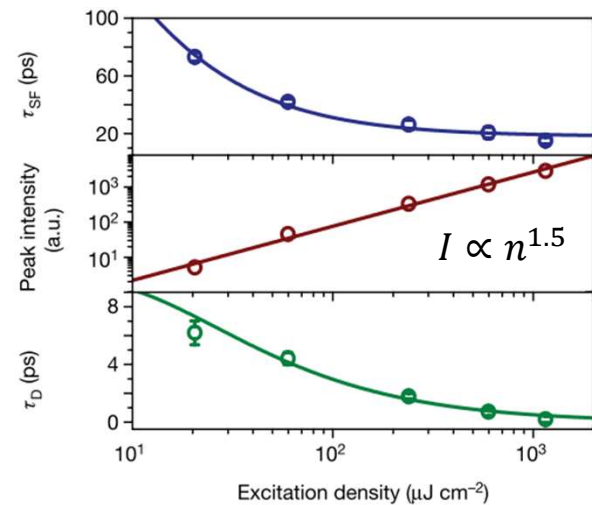
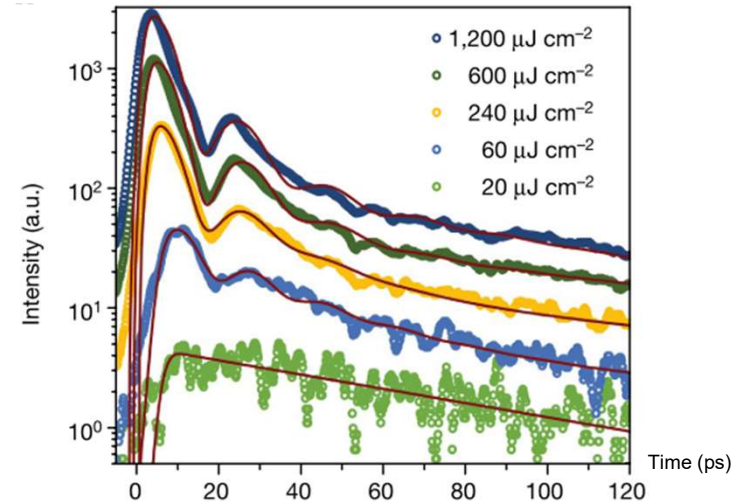
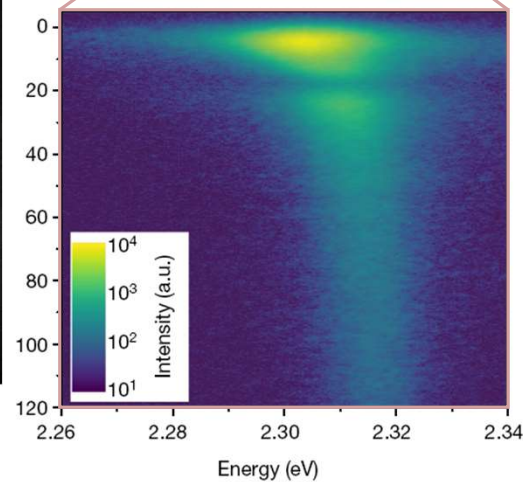
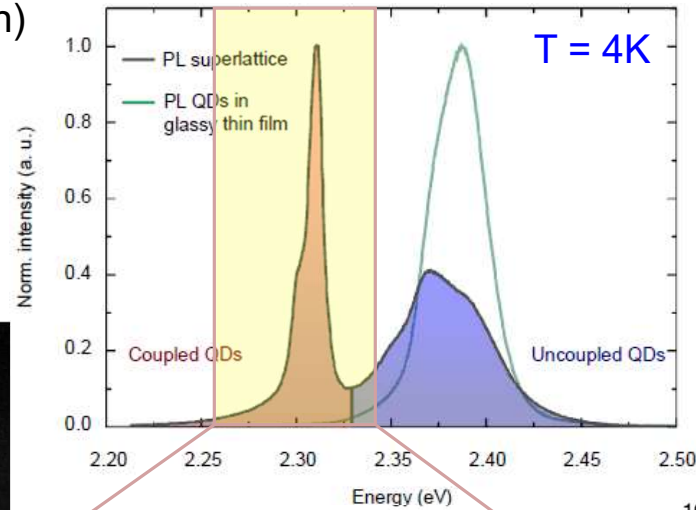
Superfluorescence from lead halide perovskite quantum dot superlattices

Gabriele Rainò, Michael A. Becker, Maryna I. Bodnarchuk, Rainer F. Mahrt, Maksym V. Kovalenko & Thilo Stöferle

Nature 563, 671–675 (2018) | Cite this article

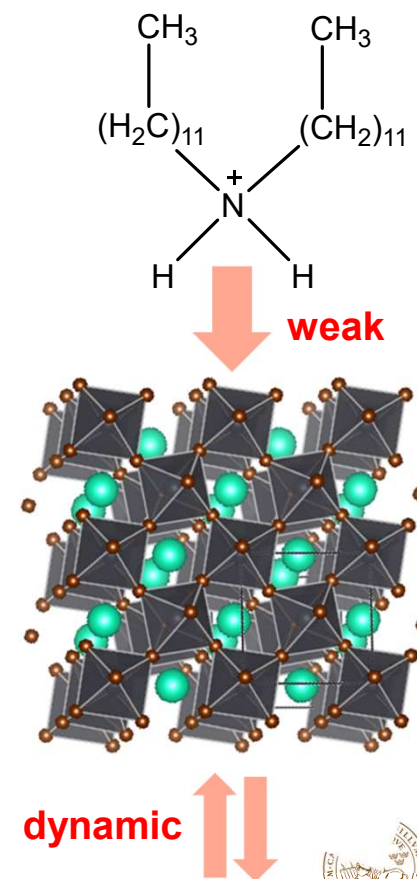
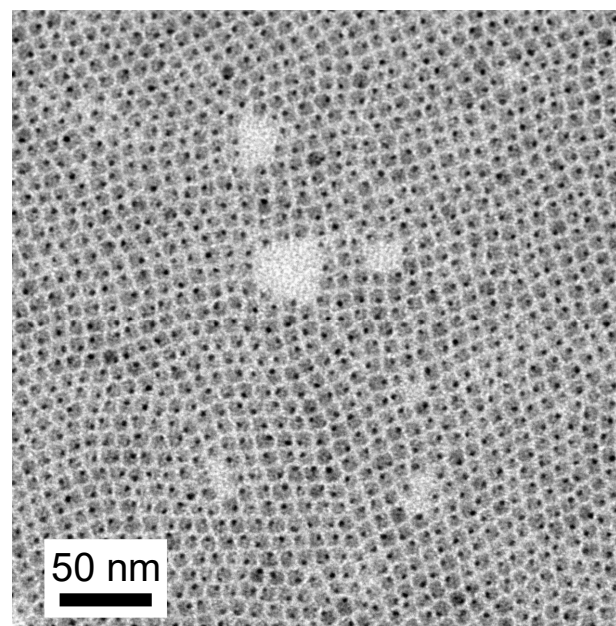
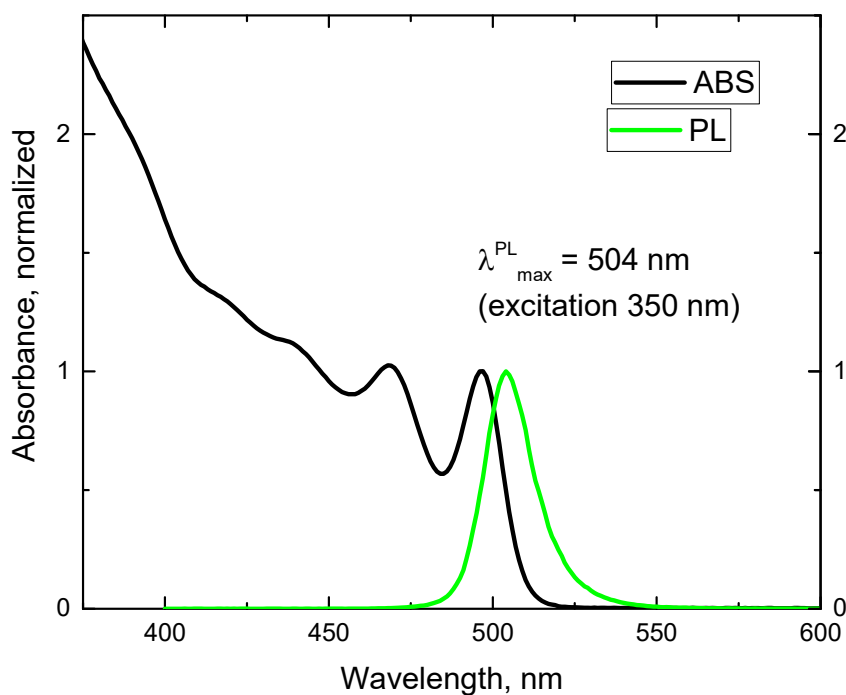
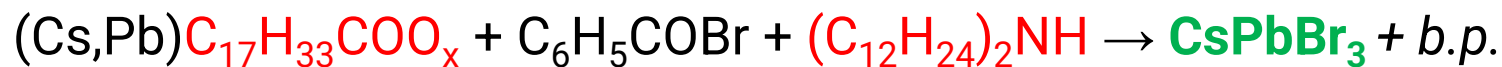


Excitation: 3.06 eV exc, CW of 50 ps, 40 MHz
Streak: 3.1 eV exc, 100-200 fs, 1 kHz



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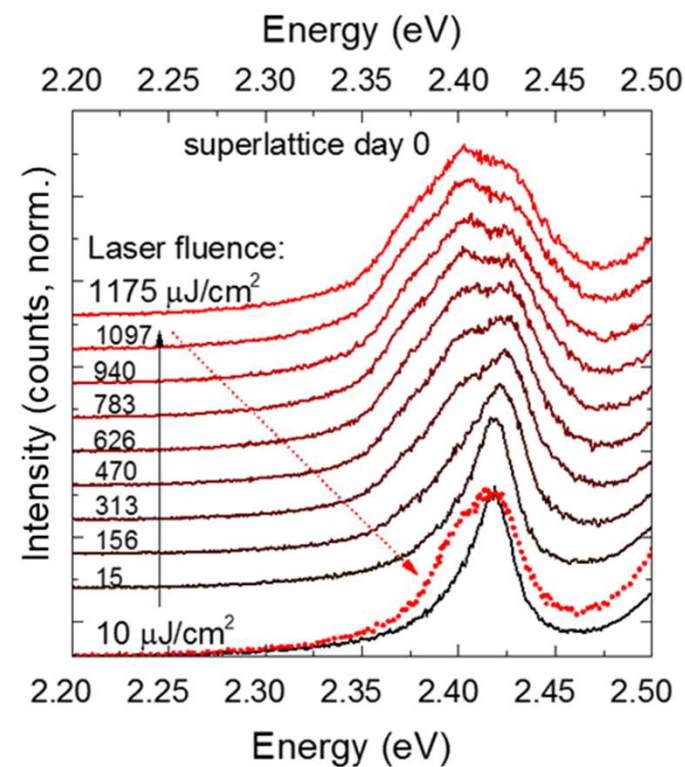
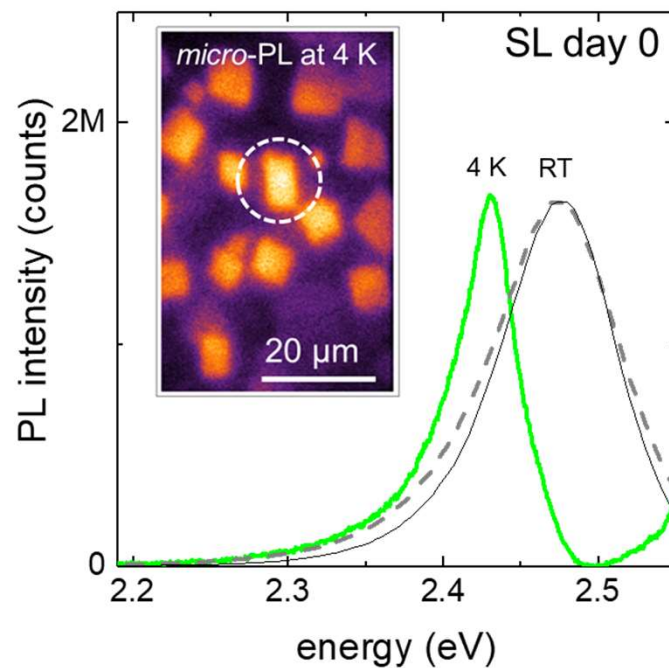
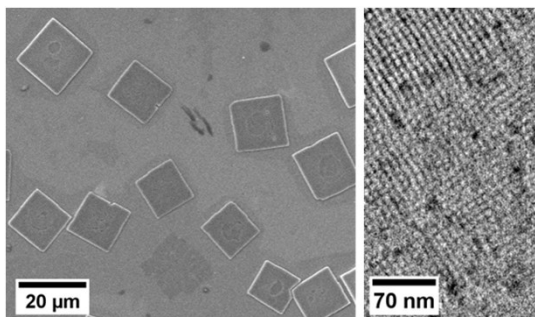
8 nm CsPbBr₃ nanocubes (4th Generation)



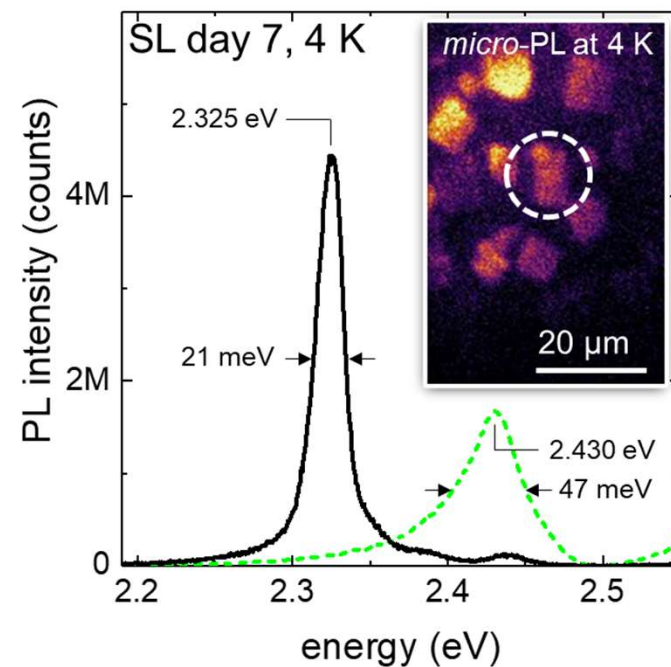
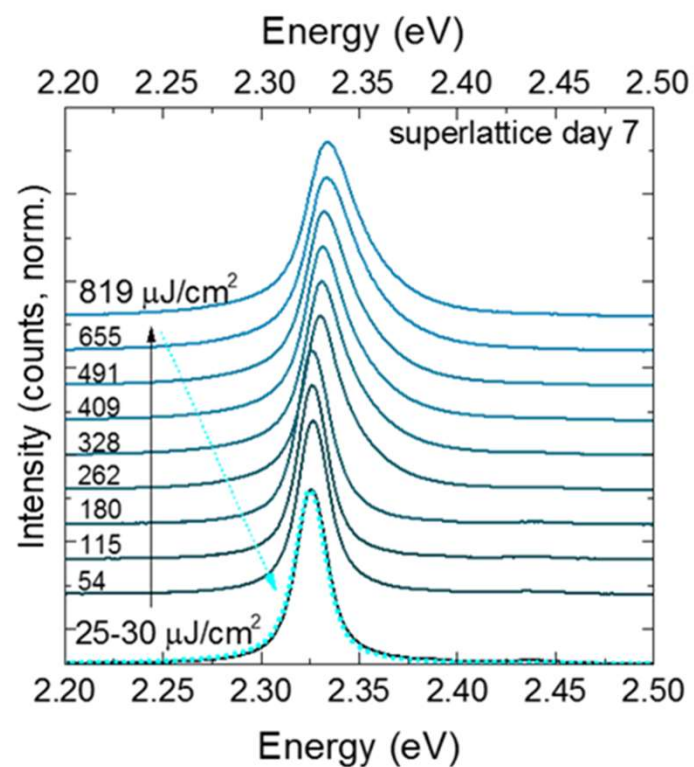
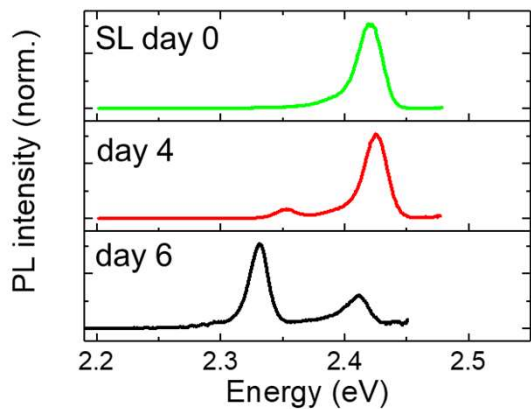
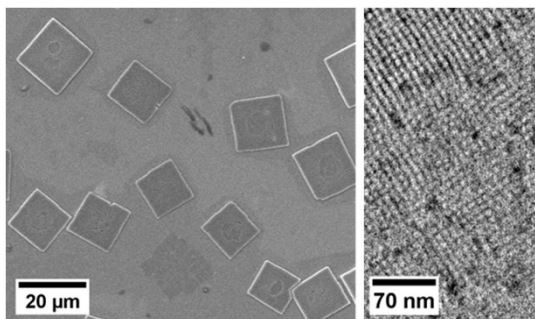
Imran et al., *J. Am. Chem. Soc.*, 140 (7), 2656-2664, **2018**

Imran et al., *Nano Lett.*, 18 (12), 7822-7831, **2018**

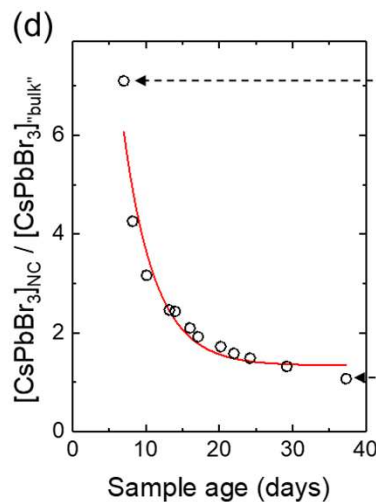
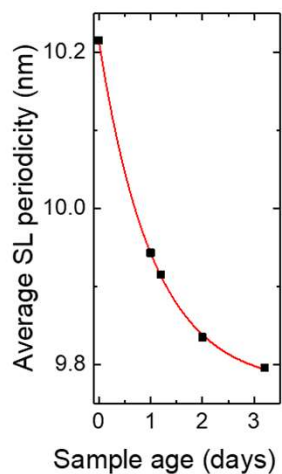
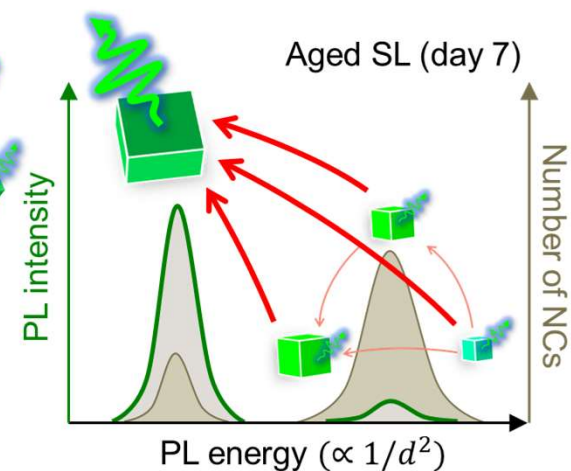
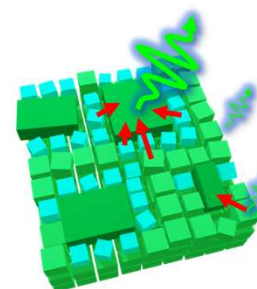
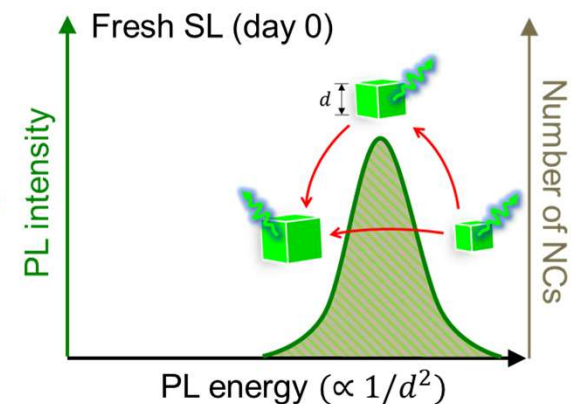
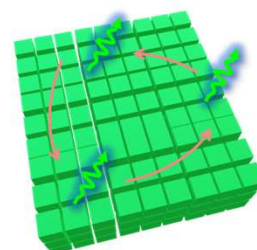
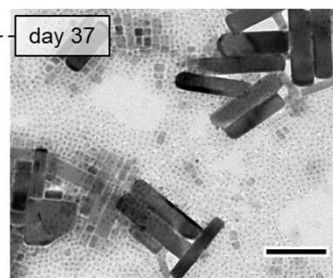
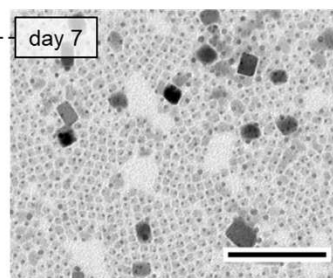
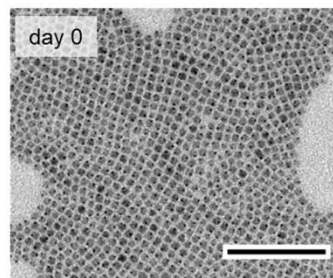
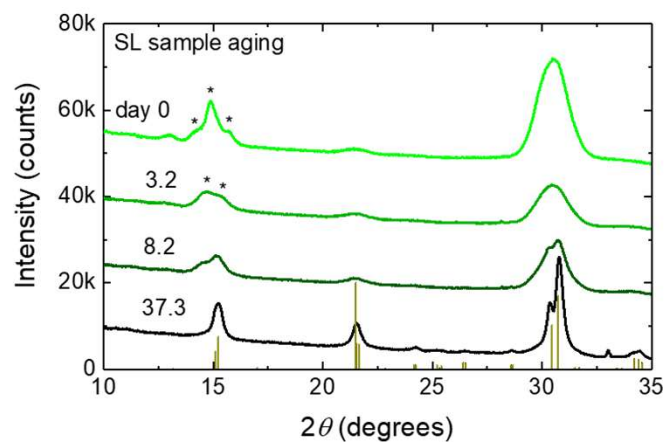
Looking for Cooperative Emission



Looking for Cooperative Emission

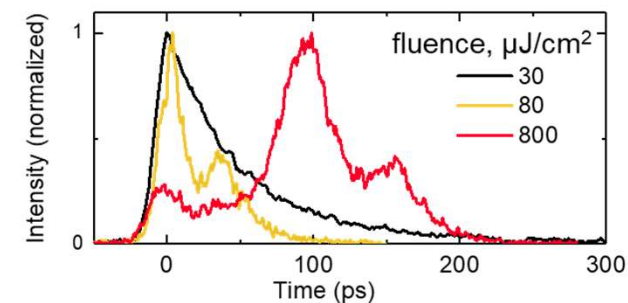
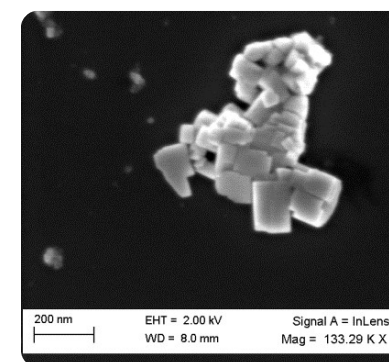
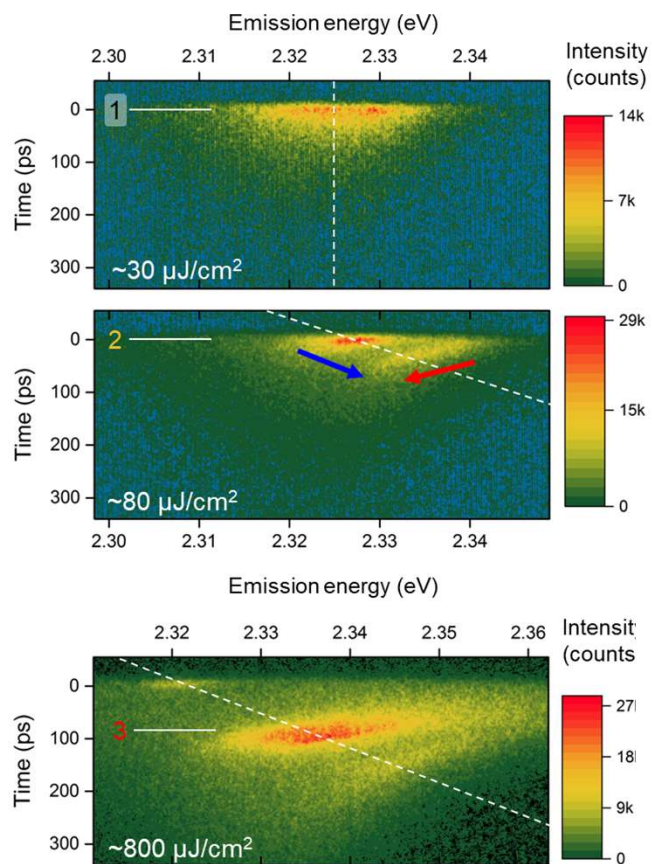
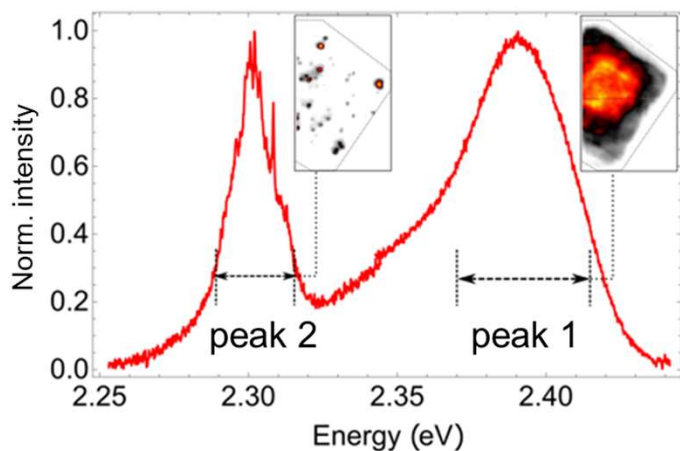
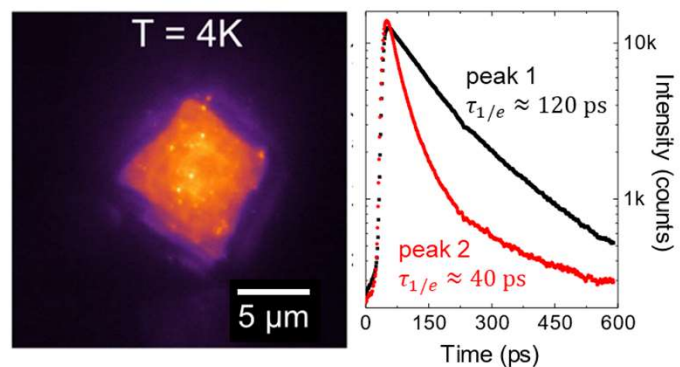
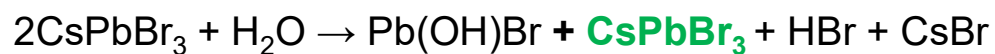


Coalescence of CsPbBr₃ Nanocubes



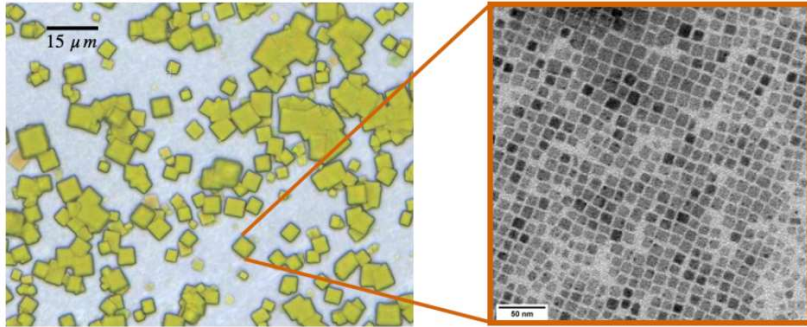
Possible Superfluorescence, Case 1

CsPbBr₃ nanocubes (4th Generation)

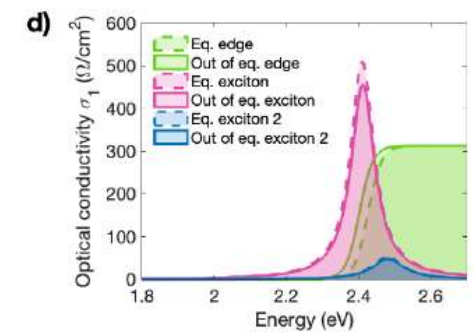
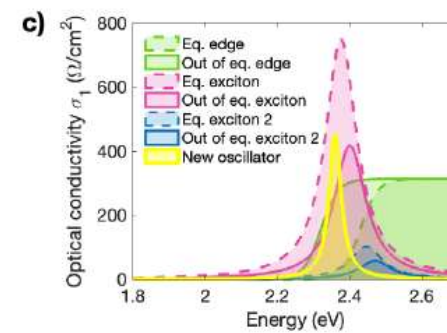
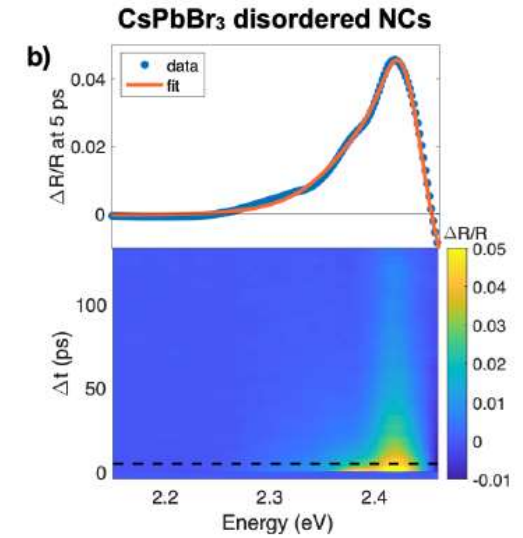
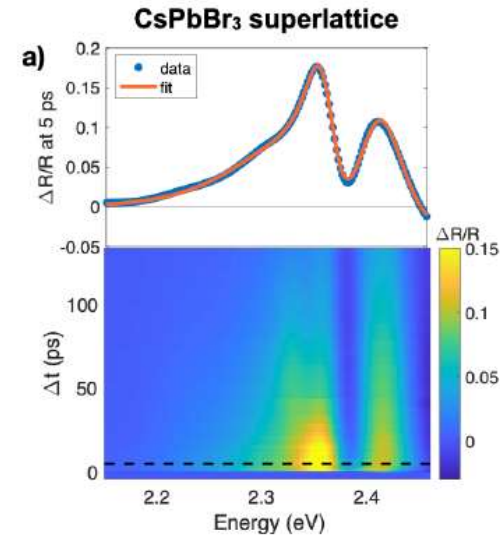
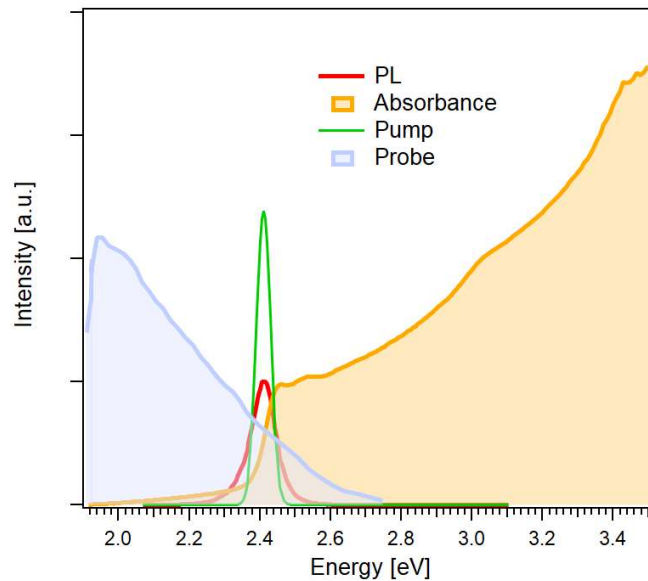


Possible Superfluorescence, Case 2

CsPbBr₃ nanocubes (1st Generation)



90 days old (vacuum), no signs of coalescence

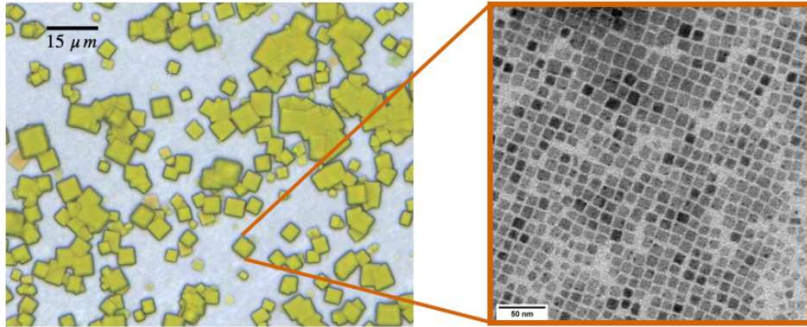


Miloch et al., *arXiv*, **2023**, 2303.08791

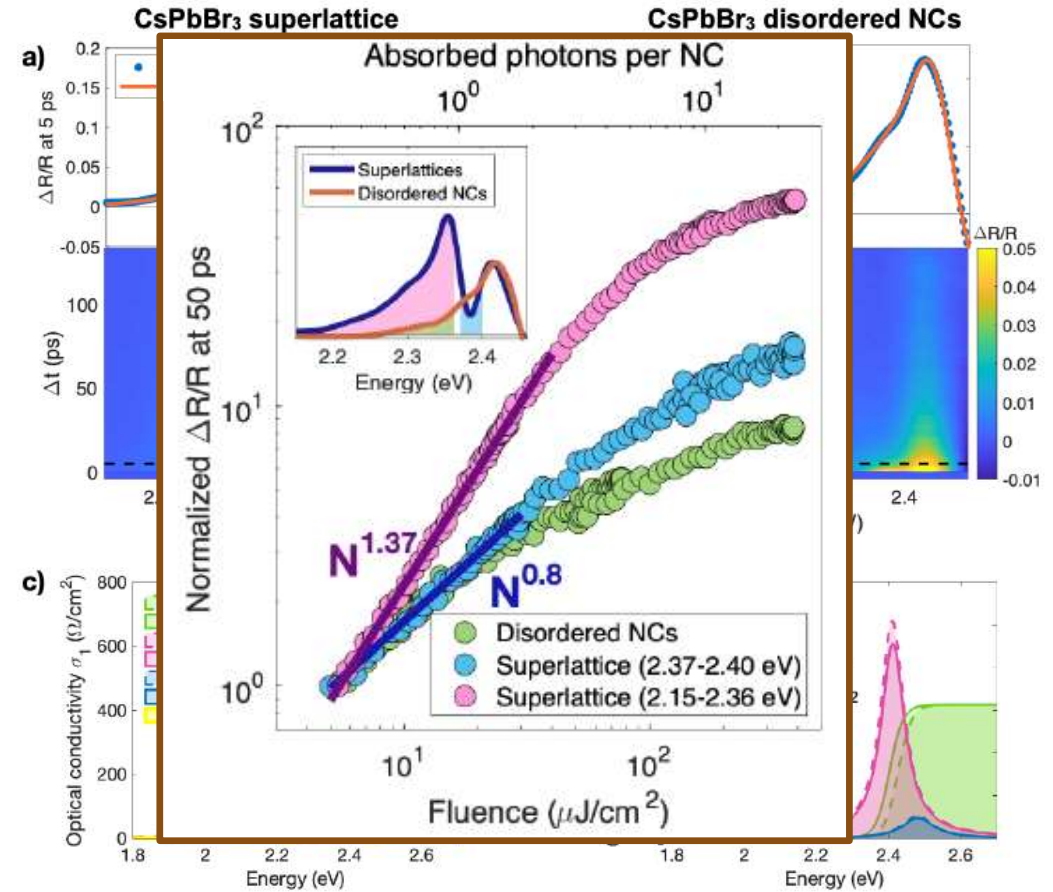
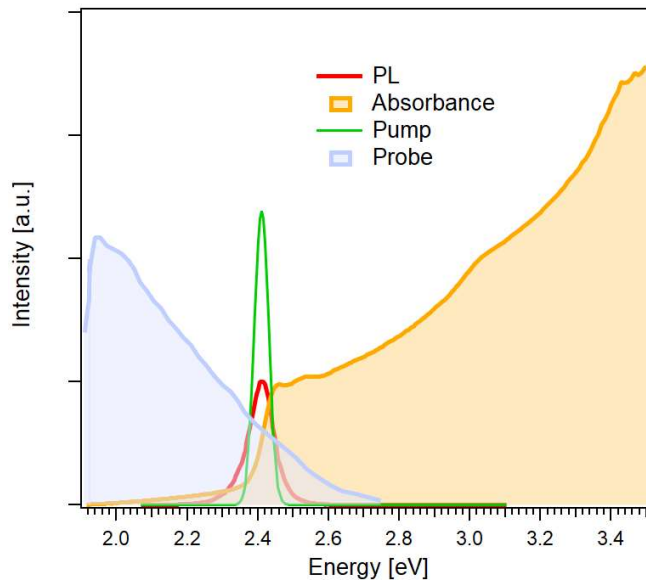
TR at T = 17 K in Aged Superlattices (w Giannetti Group @Brescia)

Possible Superfluorescence, Case 2

CsPbBr₃ nanocubes (1st Generation)



90 days old (vacuum), no signs of coalescence



Miloch et al., *arXiv*, **2023**, 2303.08791

TR at T = 17 K in Aged Superlattices (w Giannetti Group @Brescia)

Conclusions

What makes superlattices of these nanocrystals special?

Where does superfluorescence come from?





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