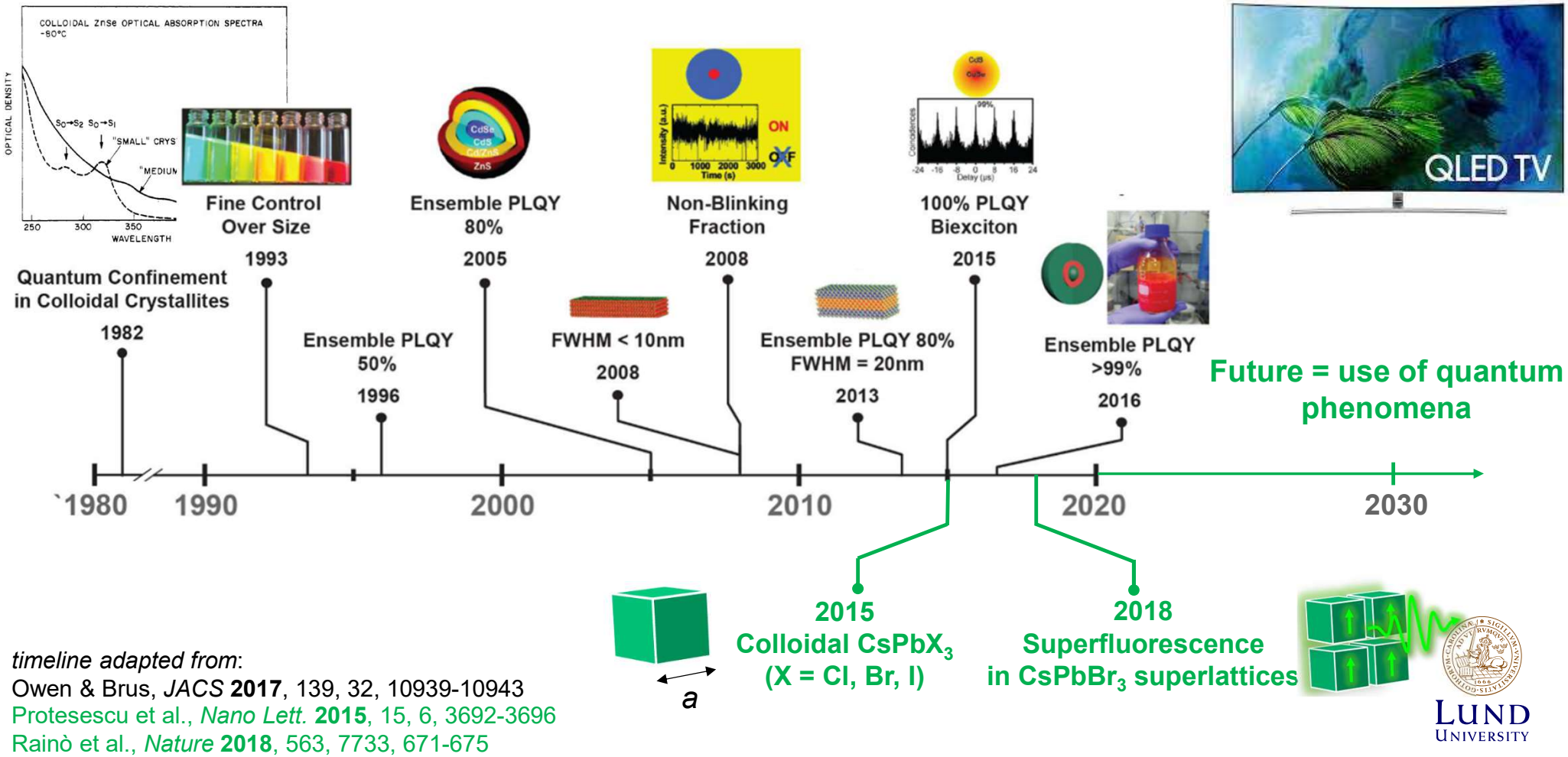
Collective X-ray Diffraction and Photoluminescence in Perovskite Nanocrystal Superlattices

DMITRY BARANOV, DIVISION OF CHEMICAL PHYSICS, LUND UNIVERSITY

KITP NANOASSEMBLY23 CONFERENCE
16 MAY 2023

Colloidal Semiconductor Nanocrystals



timeline adapted from:
Owen & Brus, *JACS* **2017**, 139, 32, 10939-10943
Protesescu et al., *Nano Lett.* **2015**, 15, 6, 3692-3696
Rainò et al., *Nature* **2018**, 563, 7733, 671-675

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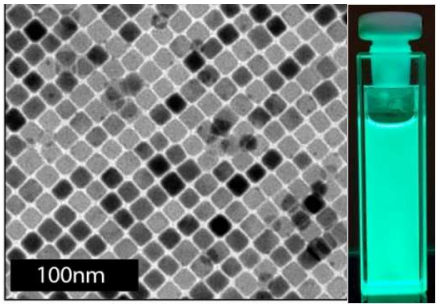
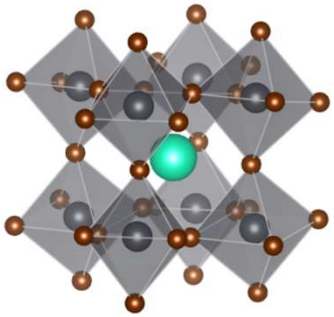
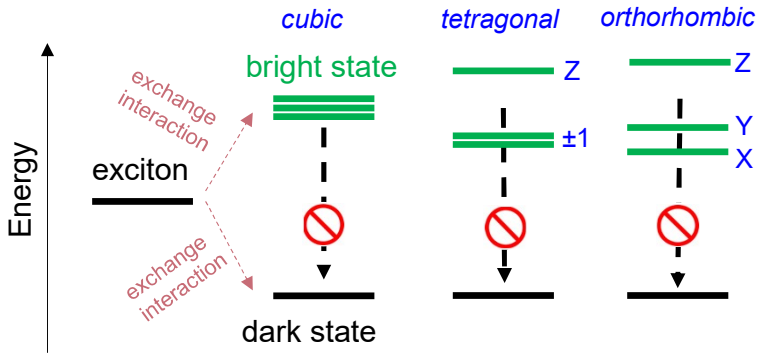
Lead Halide Perovskite Nanocrystals

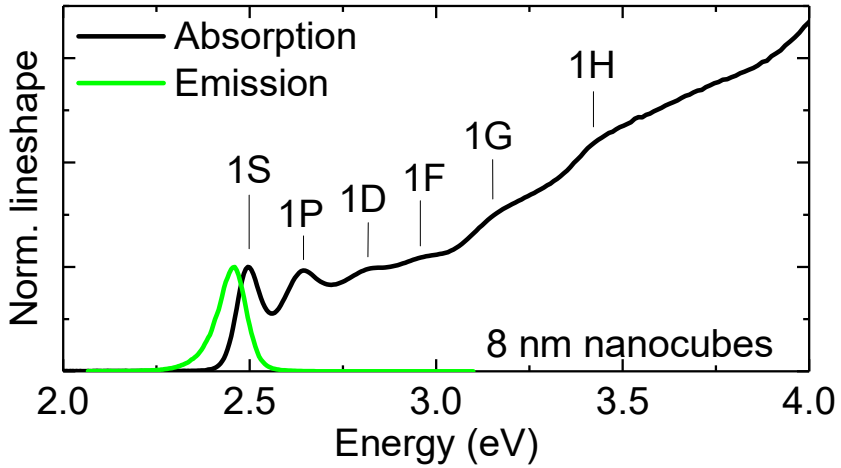
$CsPbBr_3$

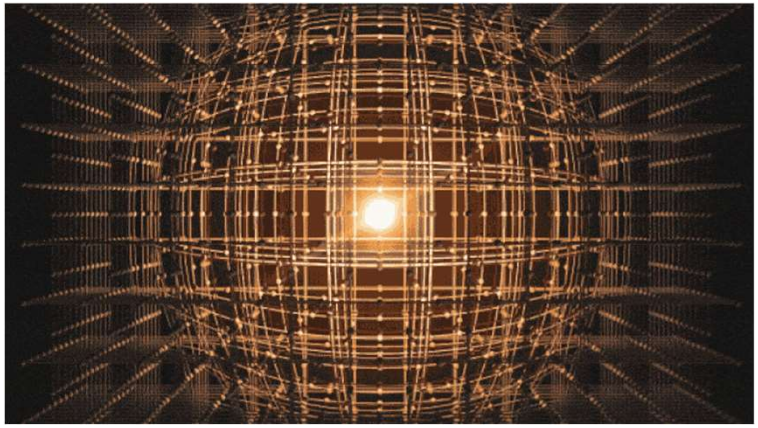






Efros, Even, Lounis, Sercel, and others





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

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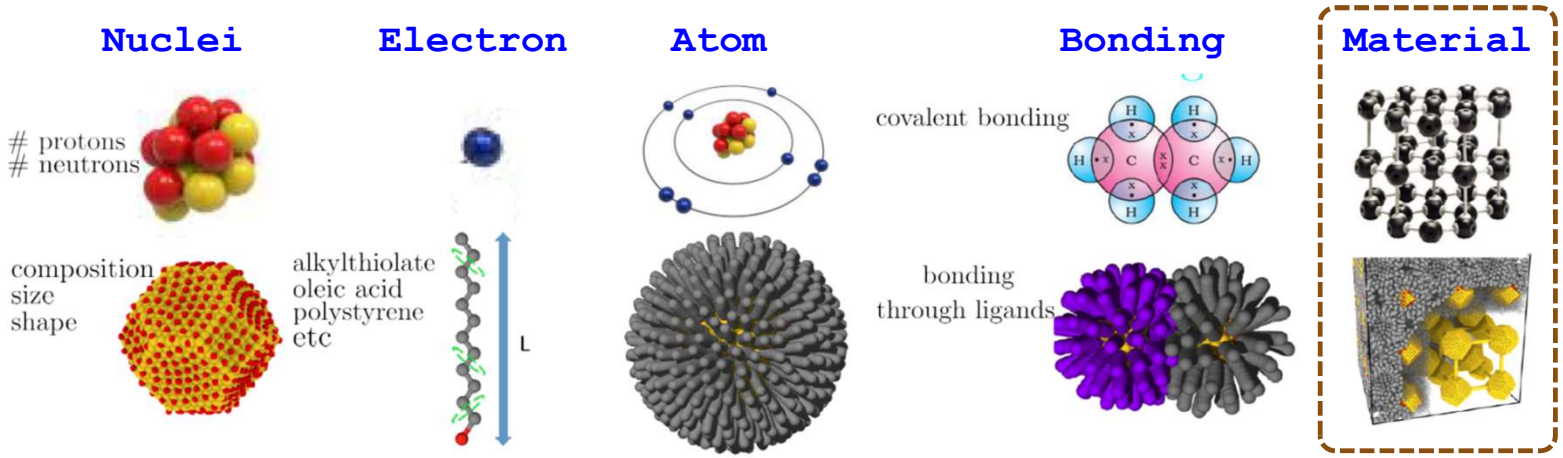
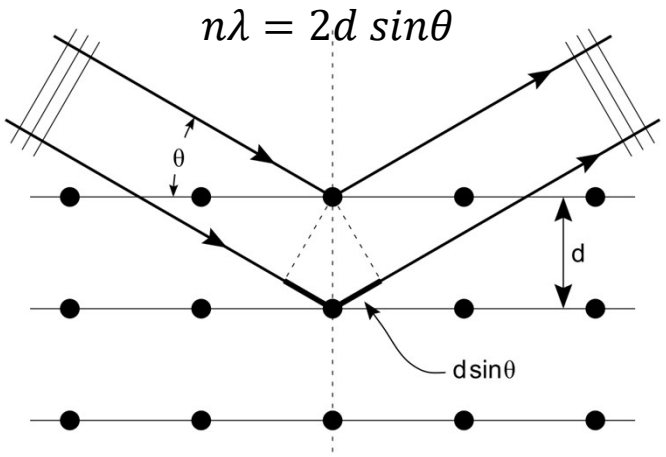
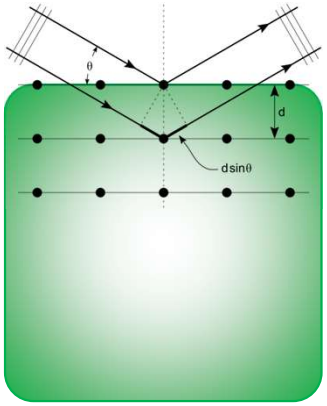
Artificial Atoms and Collective Effects

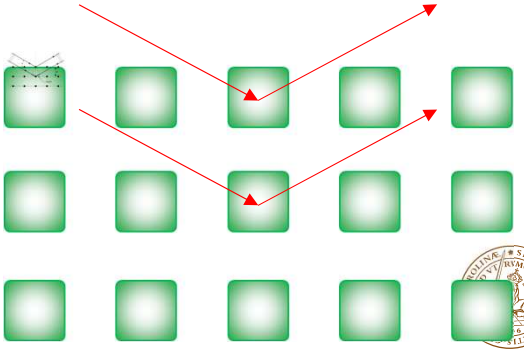
KITP
Nanoassembly23
conceptual
framework
Figure 1





Angstroms

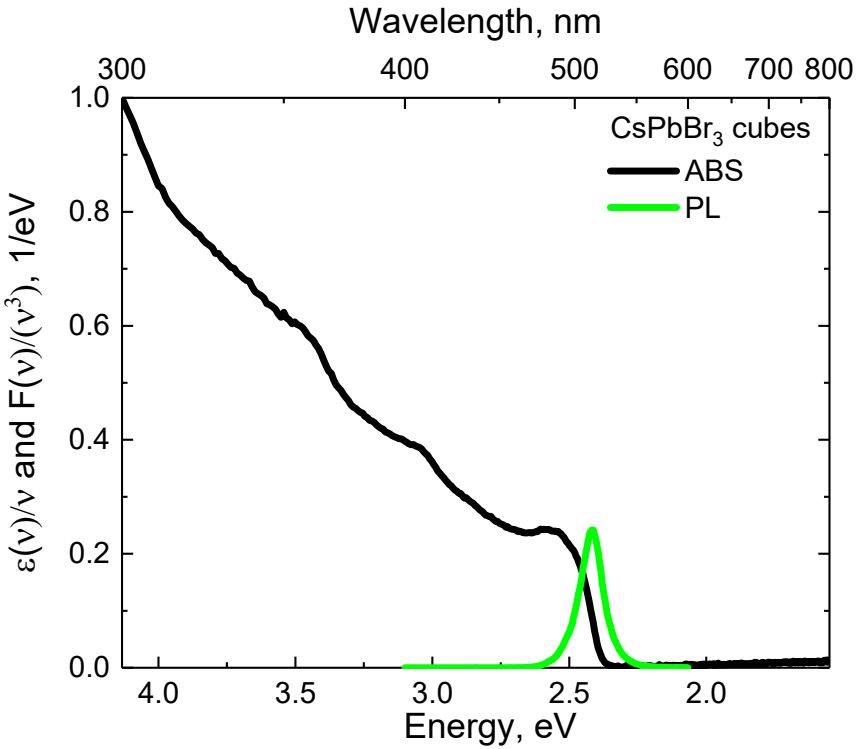


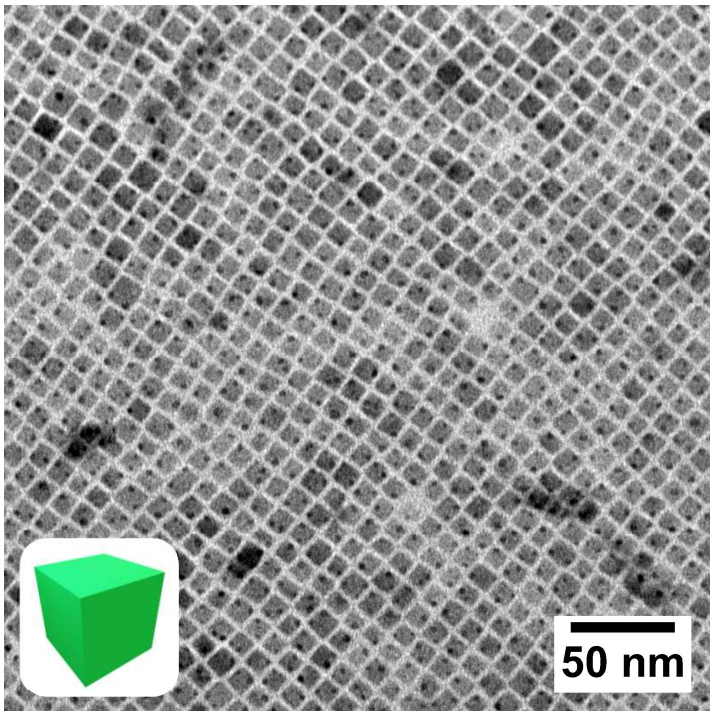


Nanometers

8-10 nm $CsPbBr_3$ Nanocubes

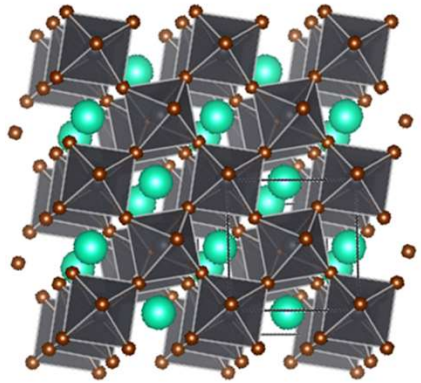
$PbBr_2 + C_{17}H_{33}COOCs + C_{18}H_{35}NH_2 \rightarrow \mathbf{CsPbBr_3}$ + by-products





$C_{18}H_{35}NH_3^+ Br^-$

dynamic



dynamic

$C_{17}H_{33}COO^- Cs^+$

Protesescu et al., *Nano Lett*, 15 (6), 3692-3696, **2015**
Almeida et al., *ACS Nano*, 12 (2), 1704-1711, **2018**

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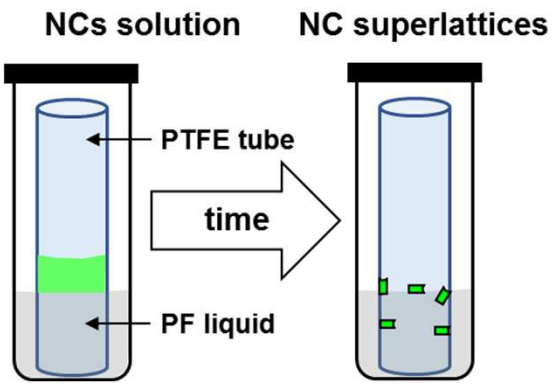
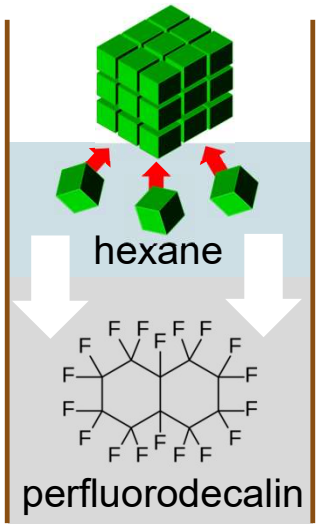
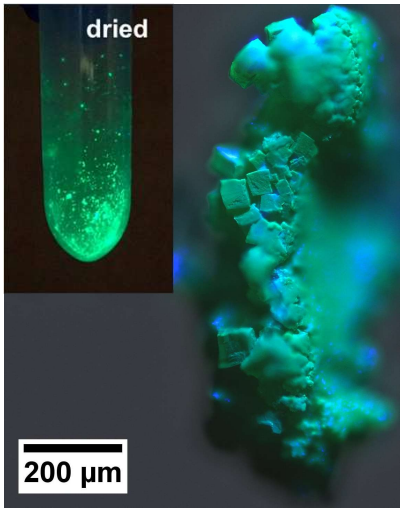
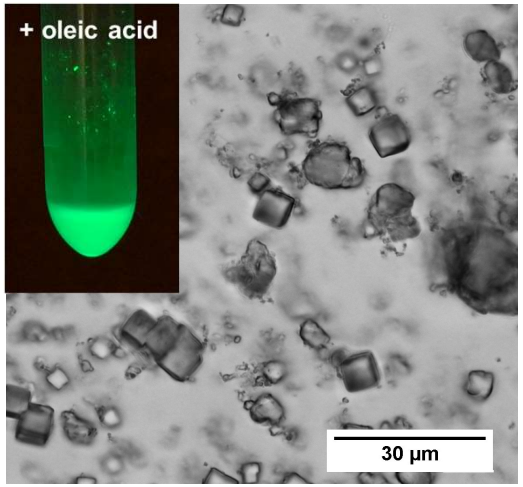
Superlattices by Solvent Removal

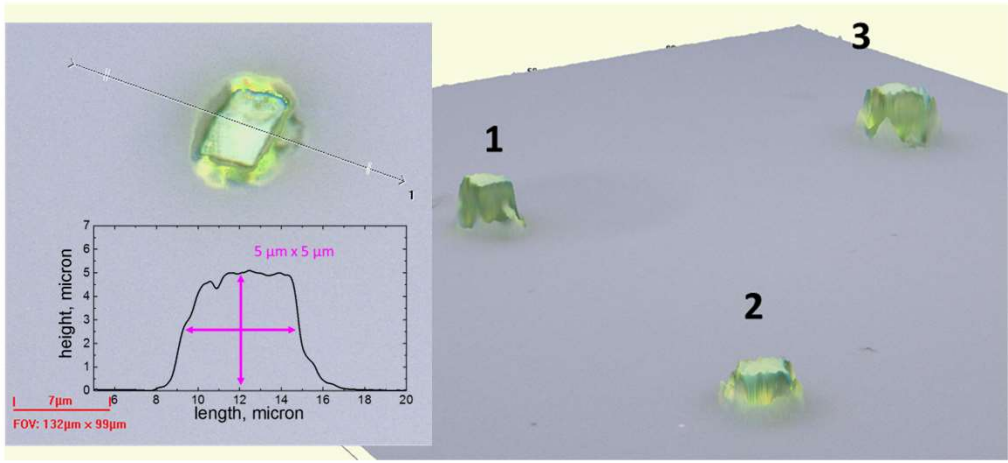


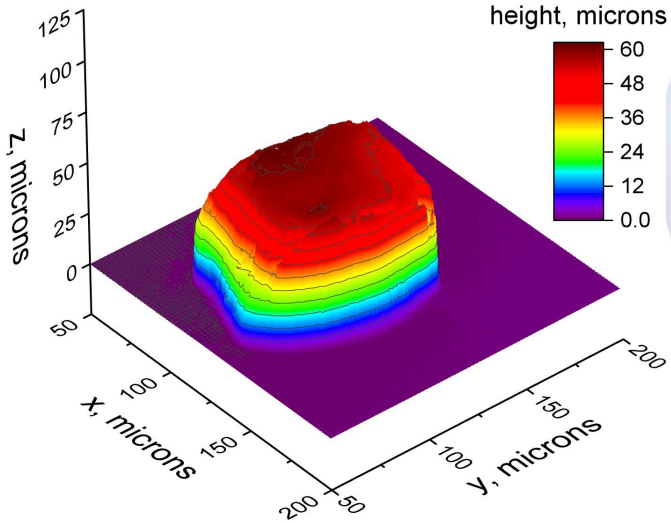


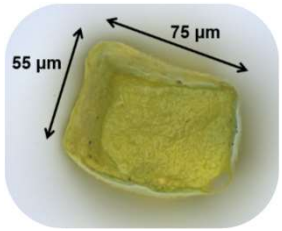
DB et al, *JPC Lett* **2019**











~ 10^{11} NCs

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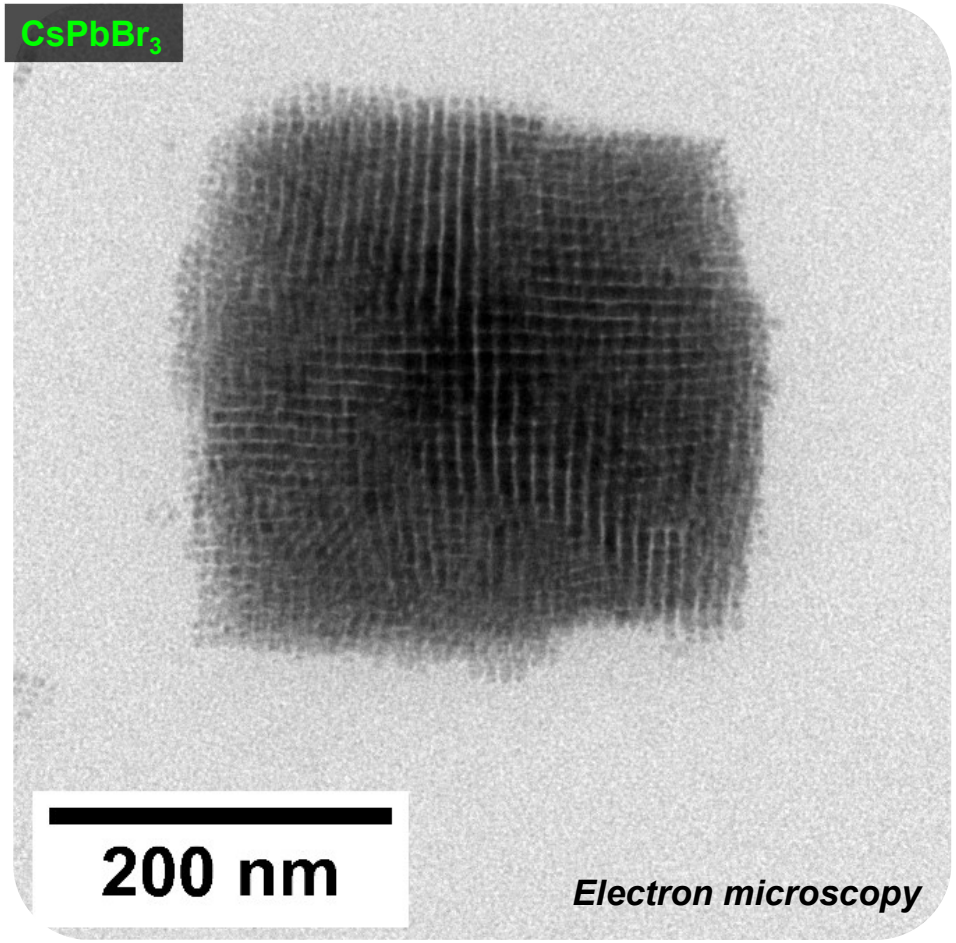
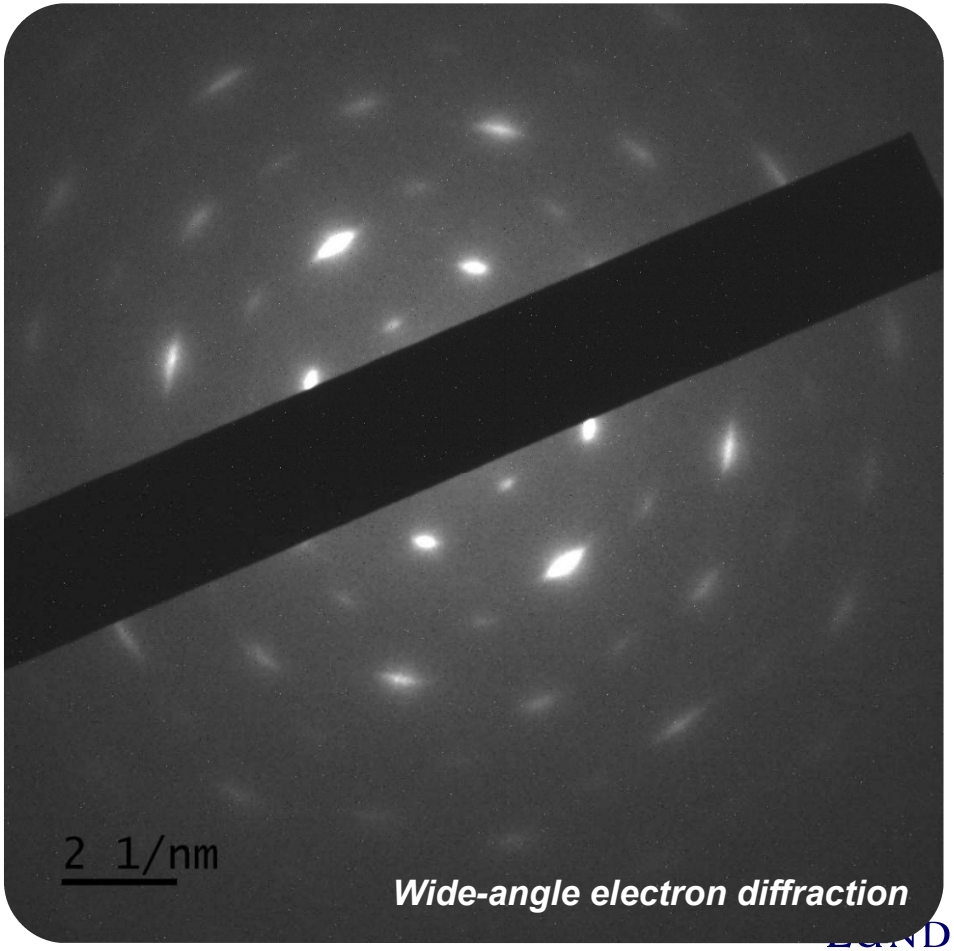
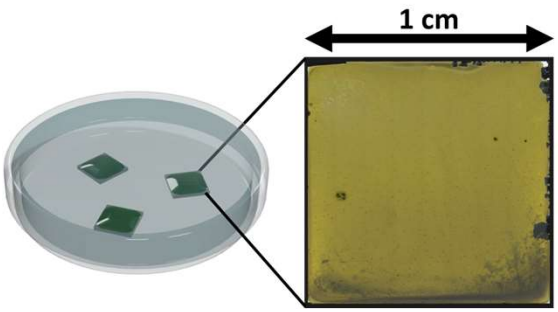
Well-ordered in Electron Diffraction





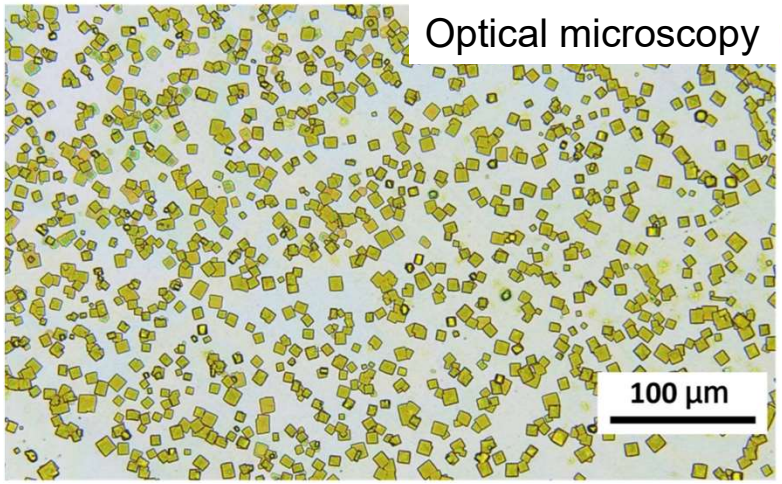
Assembly by Solvent Evaporation

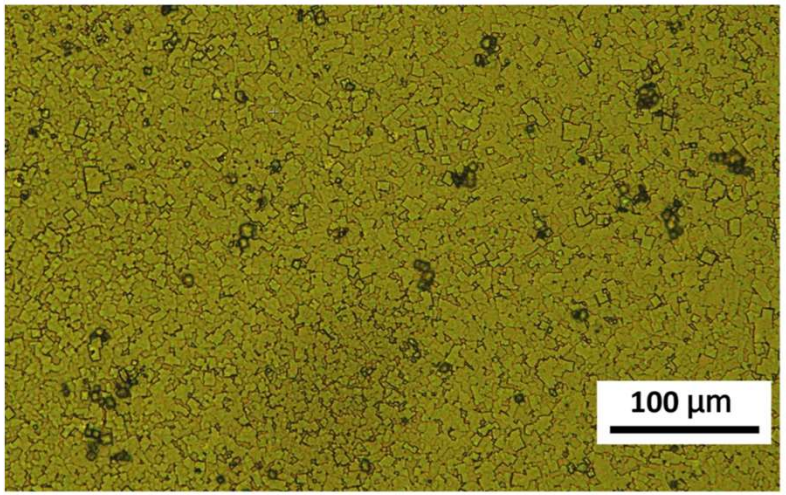


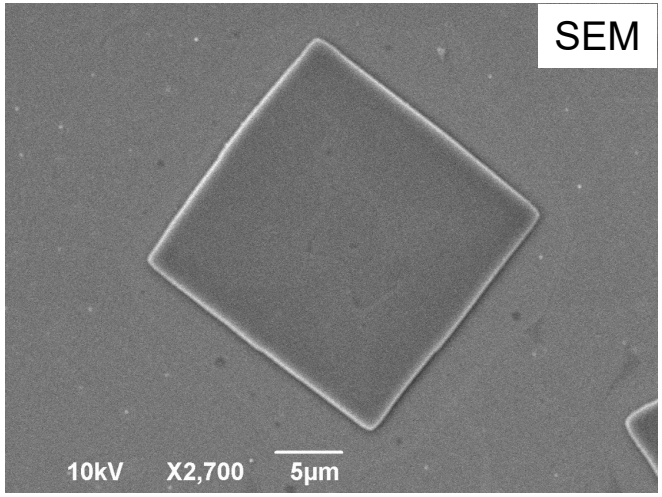
$[CsPbBr_3]_{NC} \approx 0.8\text{-}1\ \mu M$

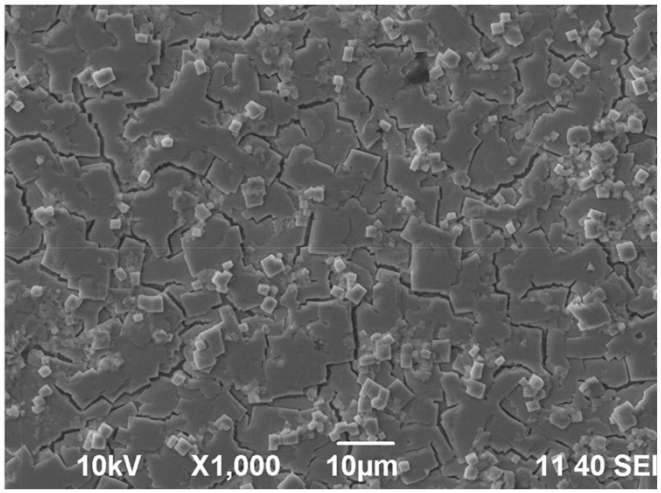
Solvents:
Toluene (*b.p.*111 °C)
Tetrachloroethylene (b.p. 121 °C)

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

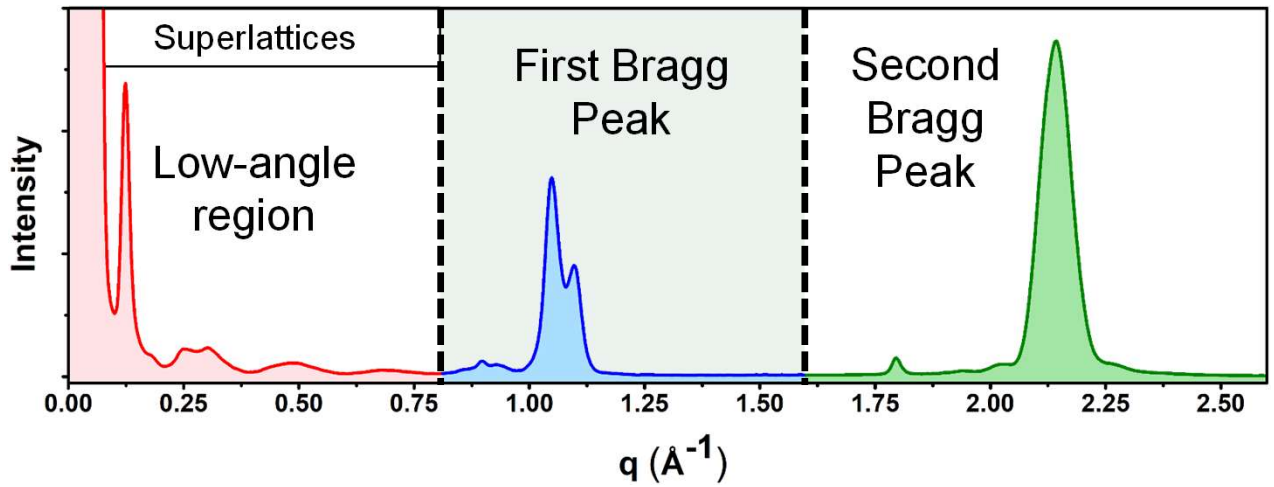


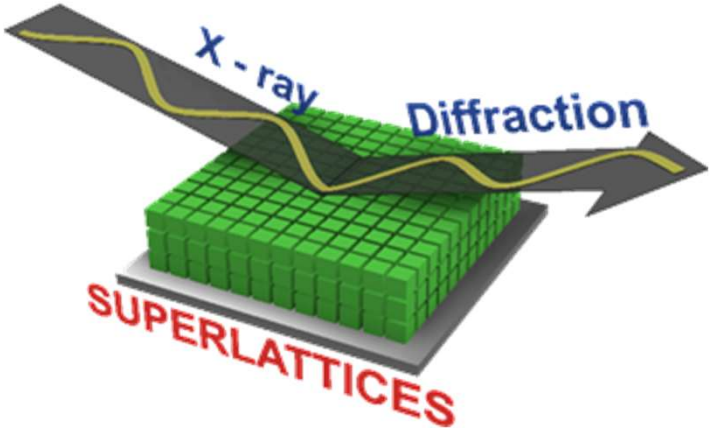


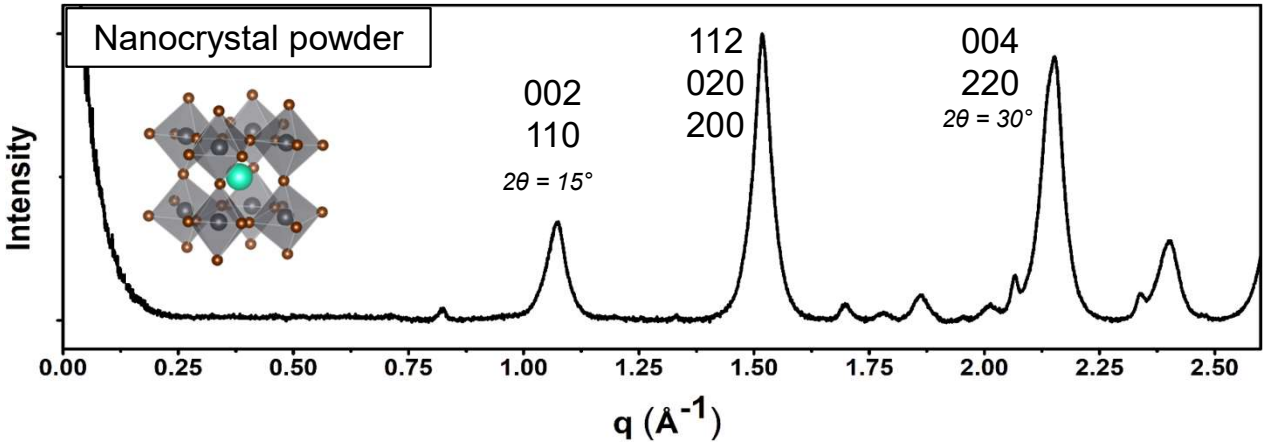


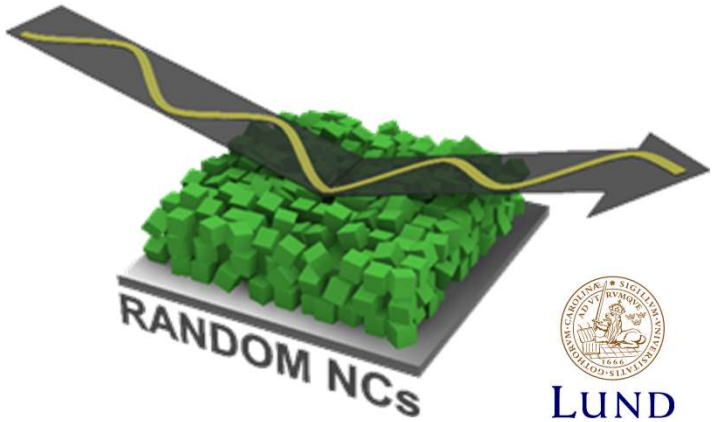


Wide-Angle X-Ray Diffraction









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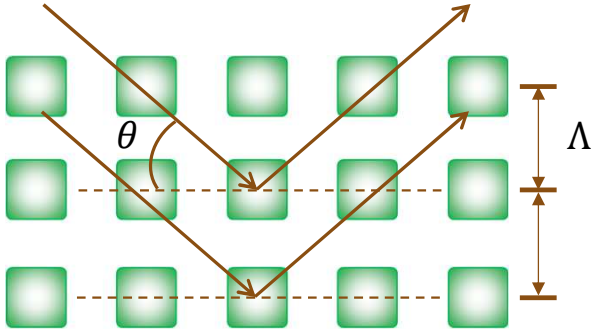
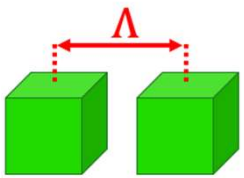
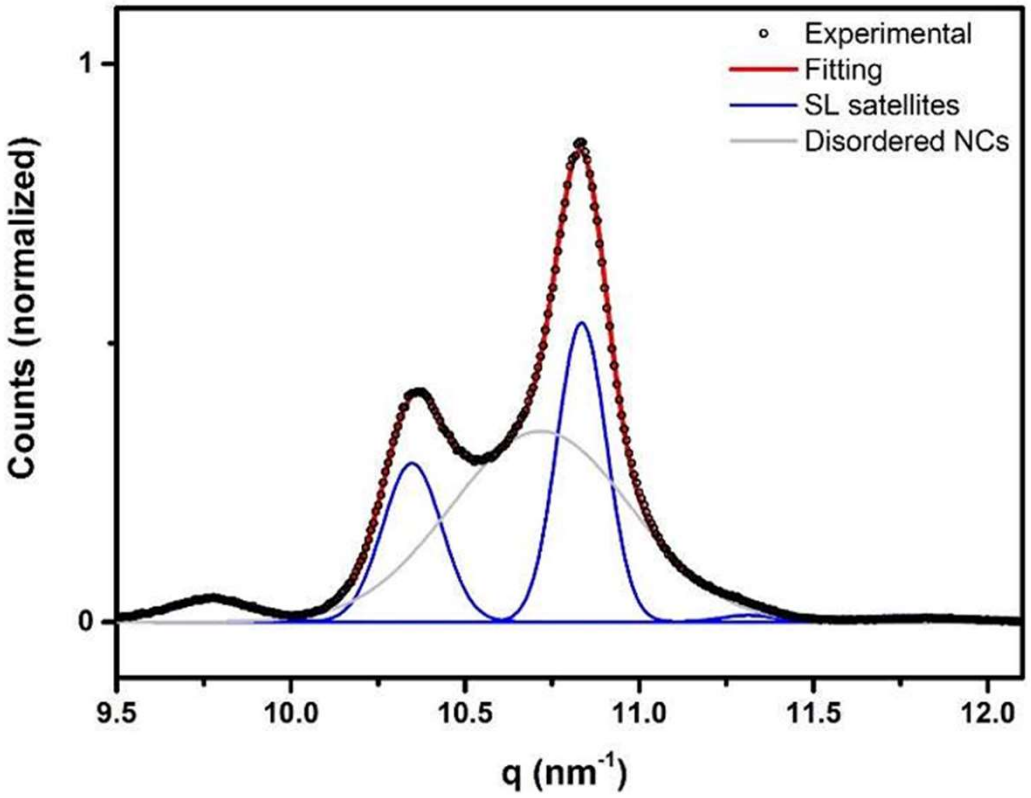
Superlattice Satellites of the 1st Bragg Peak



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





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

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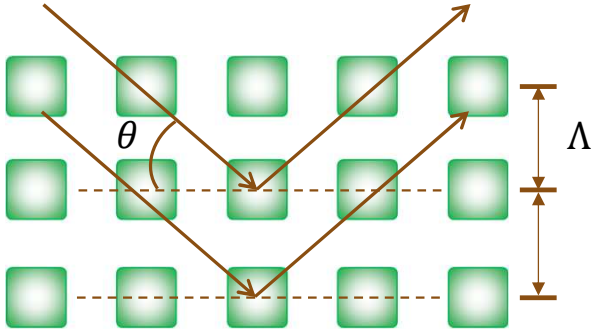
Superlattice Satellites of the 1st Bragg Peak



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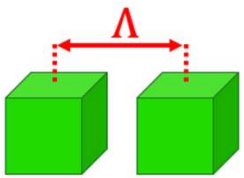

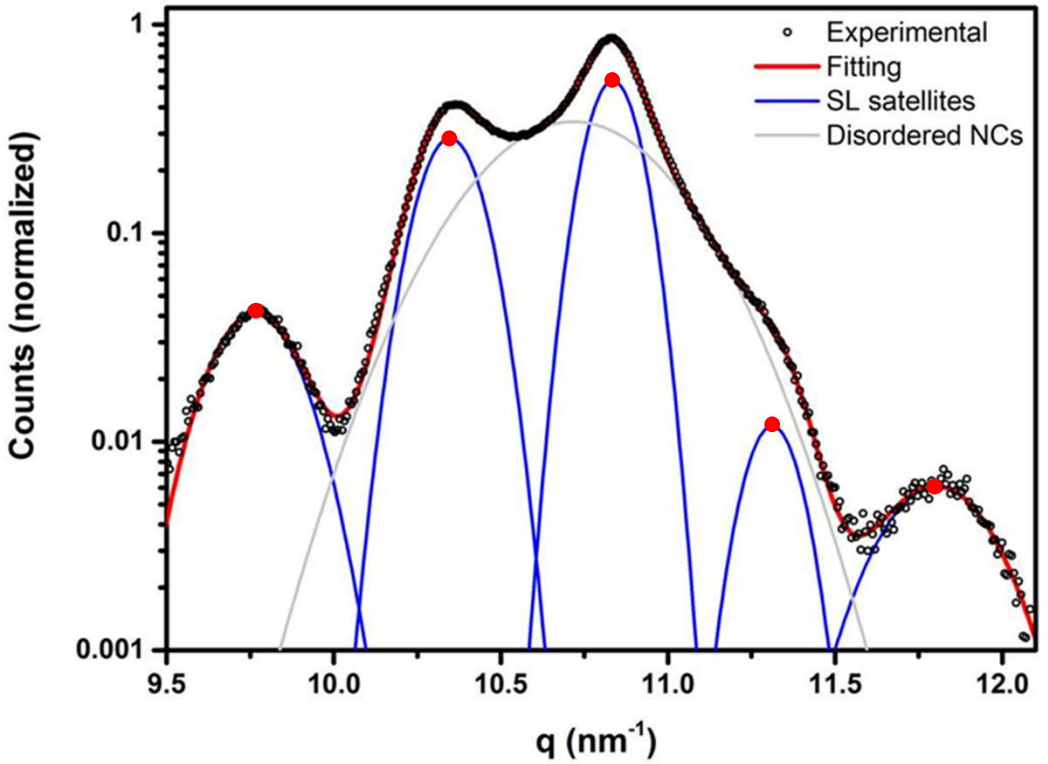

Schuller, *Phys. Rev. Lett.*, **1980**, 44, 24, 1597-1600
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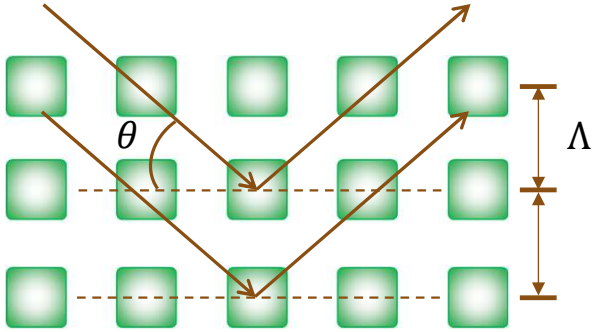
Superlattice Satellites of the 1st Bragg Peak



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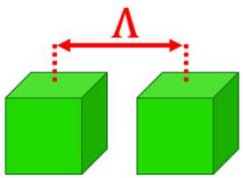

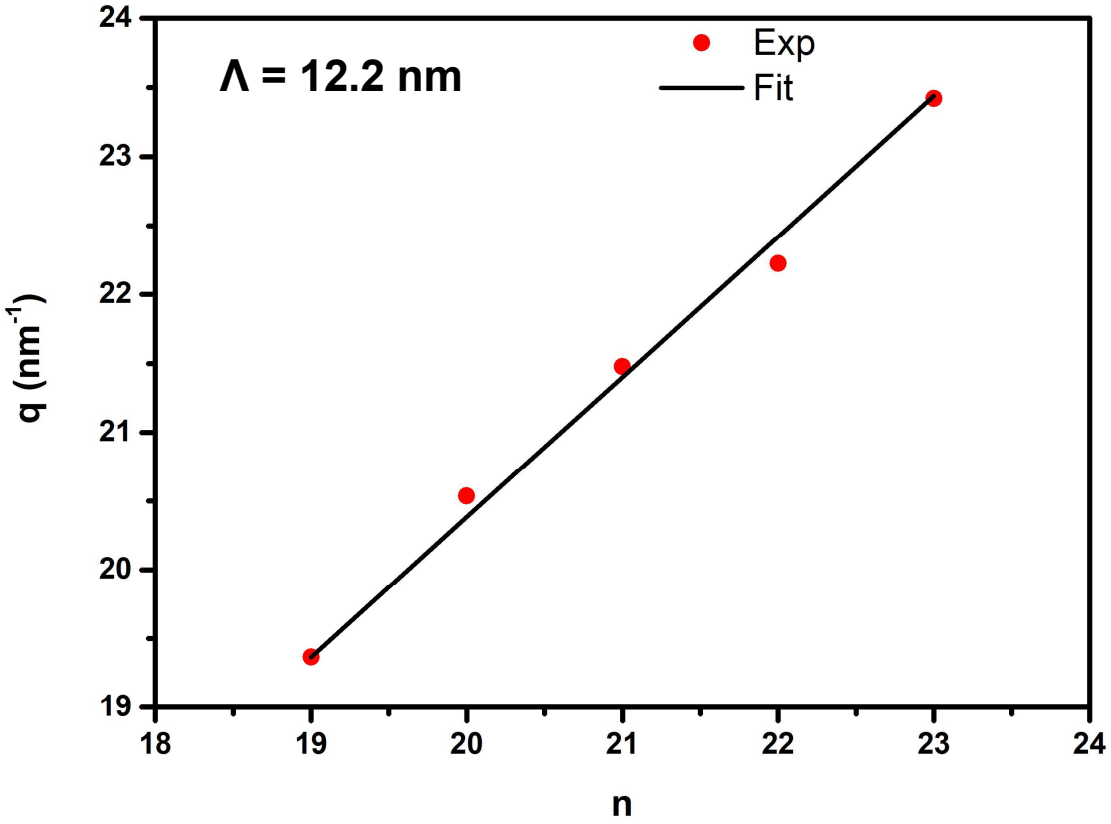

From TEM of monolayers:
11.5-12.6 nm center-to-center distance

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

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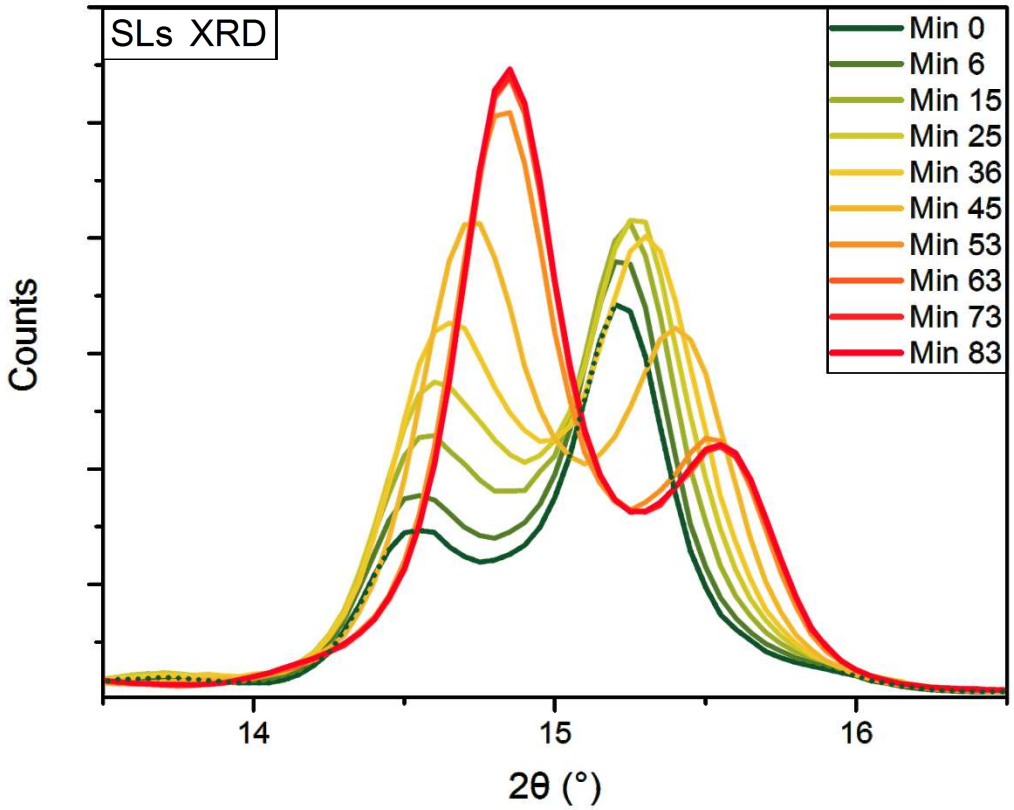
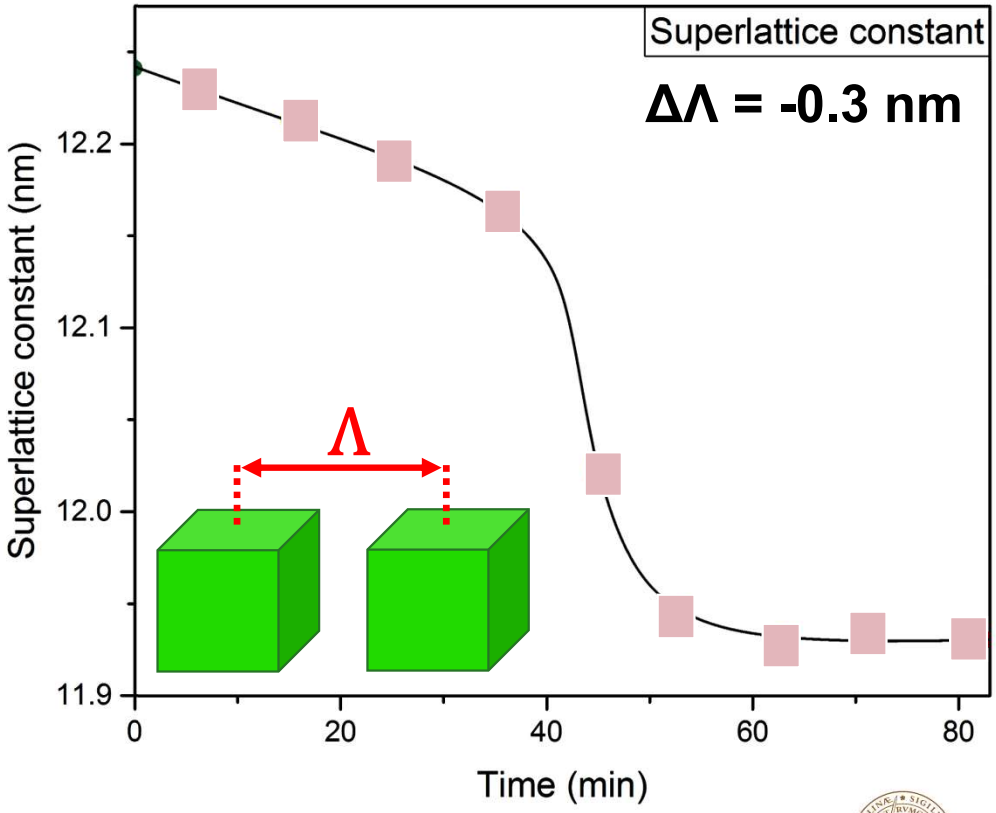
Drying Superlattice in Vacuum





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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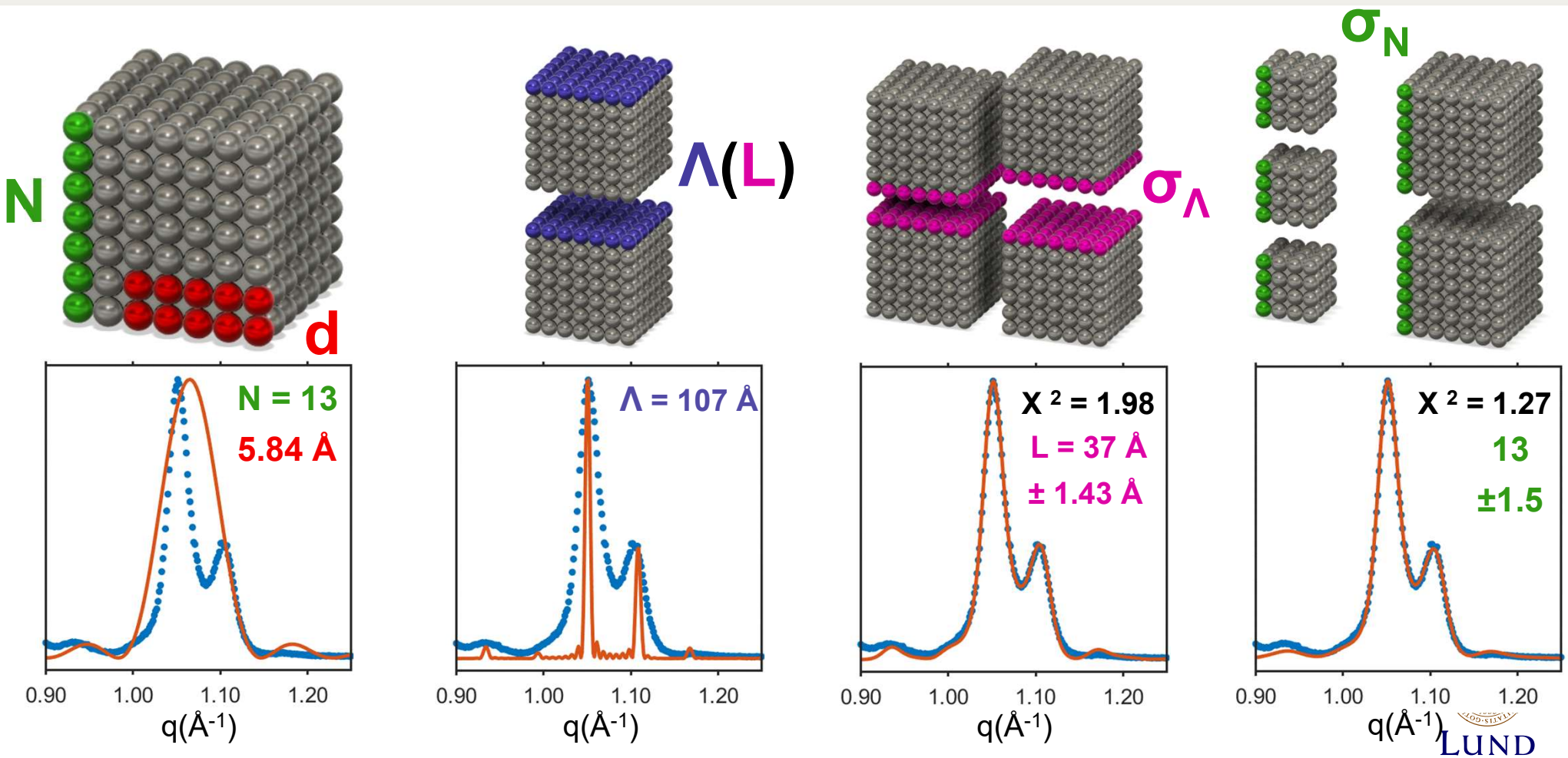
Physical Picture of Superlattice Diffraction

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

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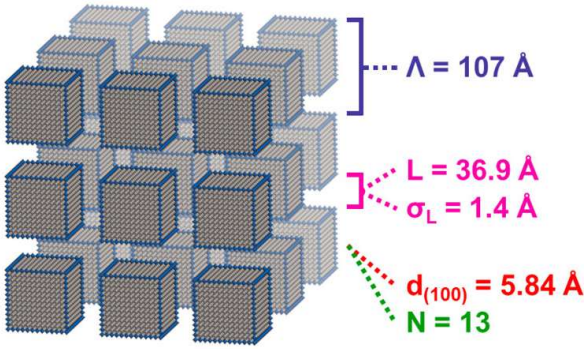
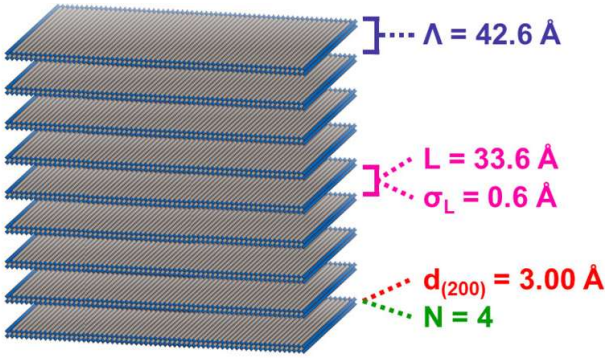
Quantification of Structural Parameters

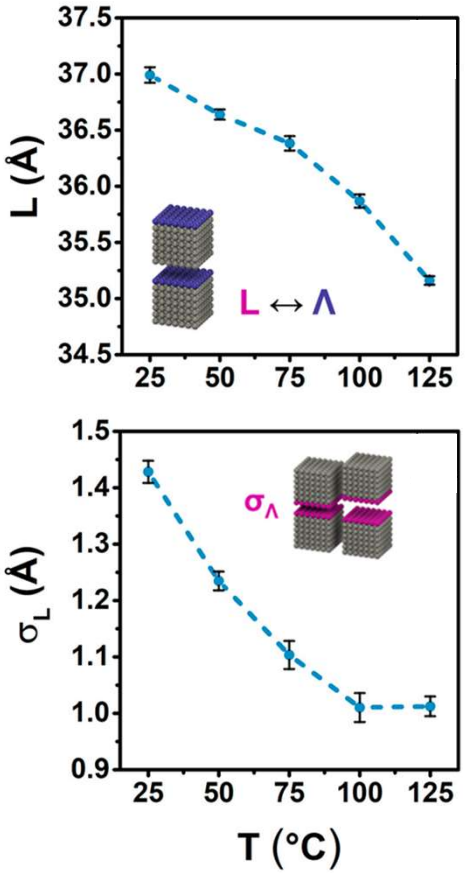
$CsPbBr_3$ nanocubes



$CsPbBr_3$ nanoplatelets



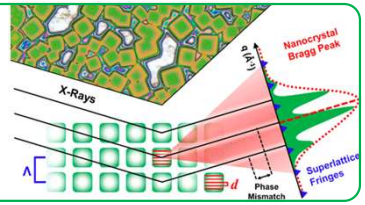
Tracking changes



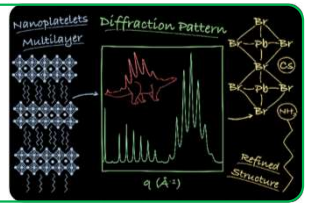
Open-source code (and exp. data)

jupyter python™ zenodo

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



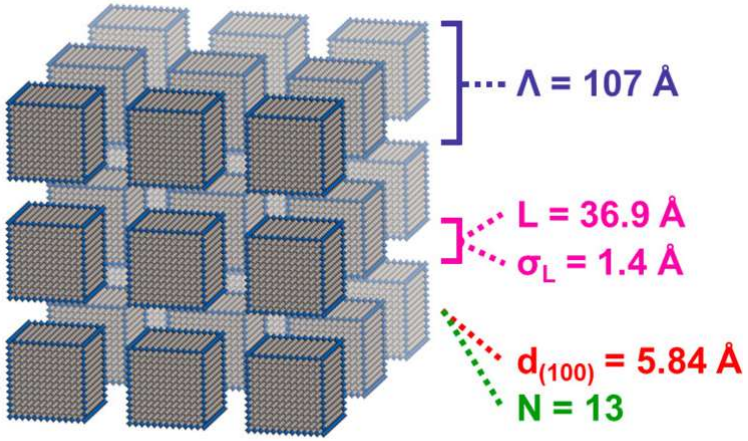
Toso et al.
ACS Nano **2021**,
15, 12, 20341–20352



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

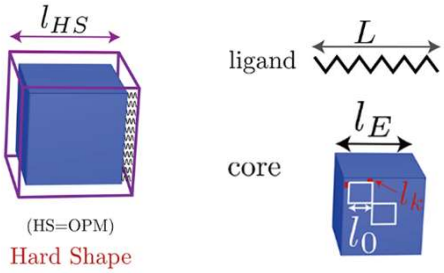
Comparison with Model

$CsPbBr_3$ nanocubes



Ligand: oleylamine (C18)
Surface coverage: unknown

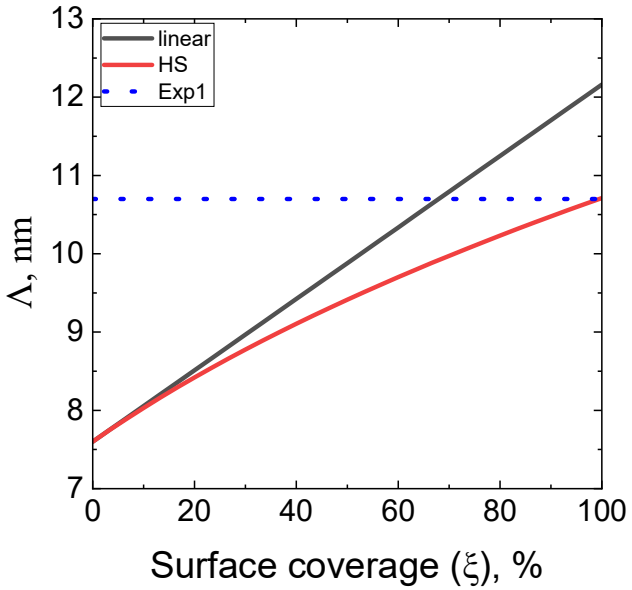
Exp1: Toso et al., *ACS Nano* **2021**, 15, 4, 6243-6256



$$\frac{L}{l_E} = \lambda$$

$$l_{HS} = l_E + 2\xi L$$

$$l_{HS} = l_E(1 + 6\xi\lambda)^{1/3}$$



Hallstrom et al., *ACS Nano* **2023**, 17, 8, 7219-7228

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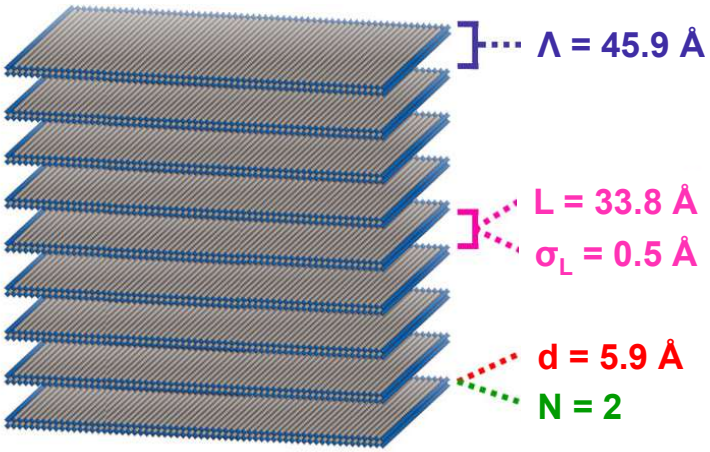
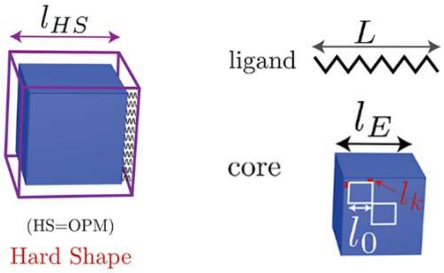
Comparison with Model

$CsPbBr_3$ nanoplatelets



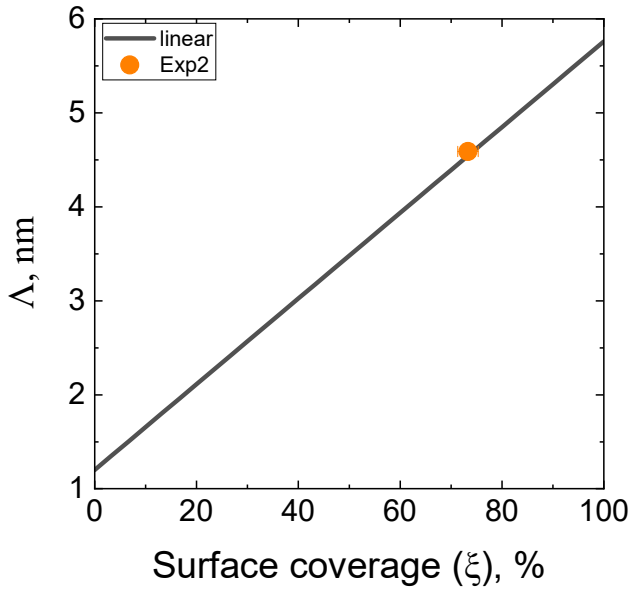
Ligand: oleylamine (C18)
Surface coverage: $73 \pm 2\%$

Exp 2: Toso et al., *ACS Nano* **2021**, 15, 12, 20341-20352



$$\frac{L}{l_E} \ll 1$$

$$l_{HS} = l_E + 2\xi L$$



Hallstrom et al., *ACS Nano* **2023**, 17, 8, 7219-7228

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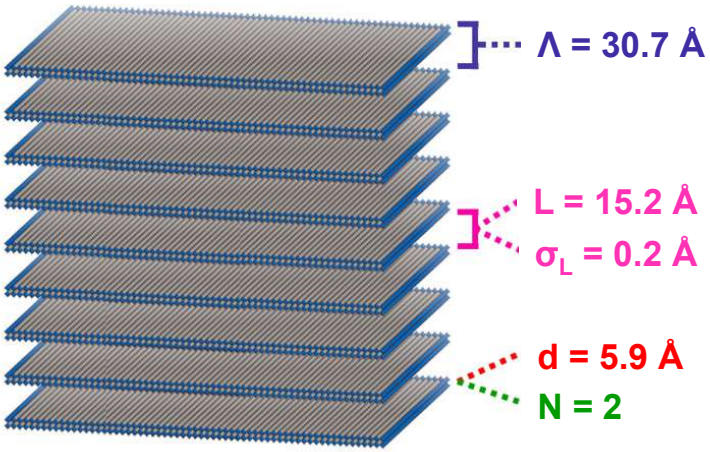
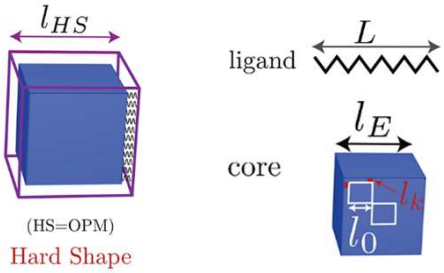
Comparison with Model

$CsPbBr_3$ nanoplatelets

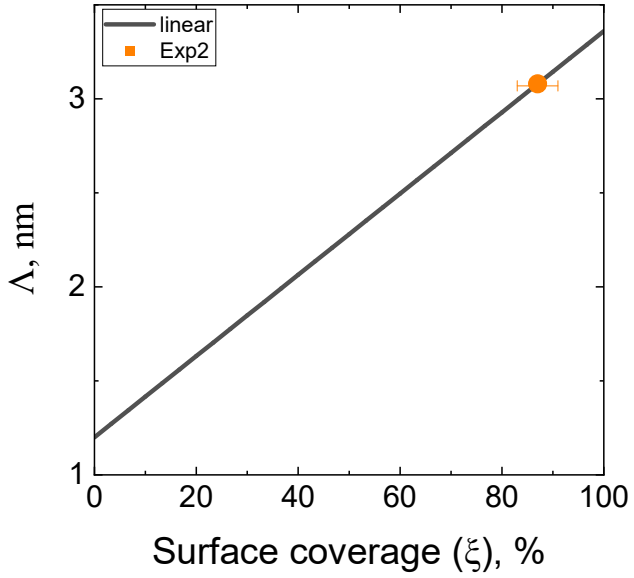


Ligand: octylamine (C8)
Surface coverage: $87 \pm 4\%$



$$\frac{L}{l_E} \ll 1$$

$$l_{HS} = l_E + 2\xi L$$



Exp 2: Toso et al., *ACS Nano* **2021**, 15, 12, 20341-20352

Hallstrom et al., *ACS Nano* **2023**, 17, 8, 7219-7228

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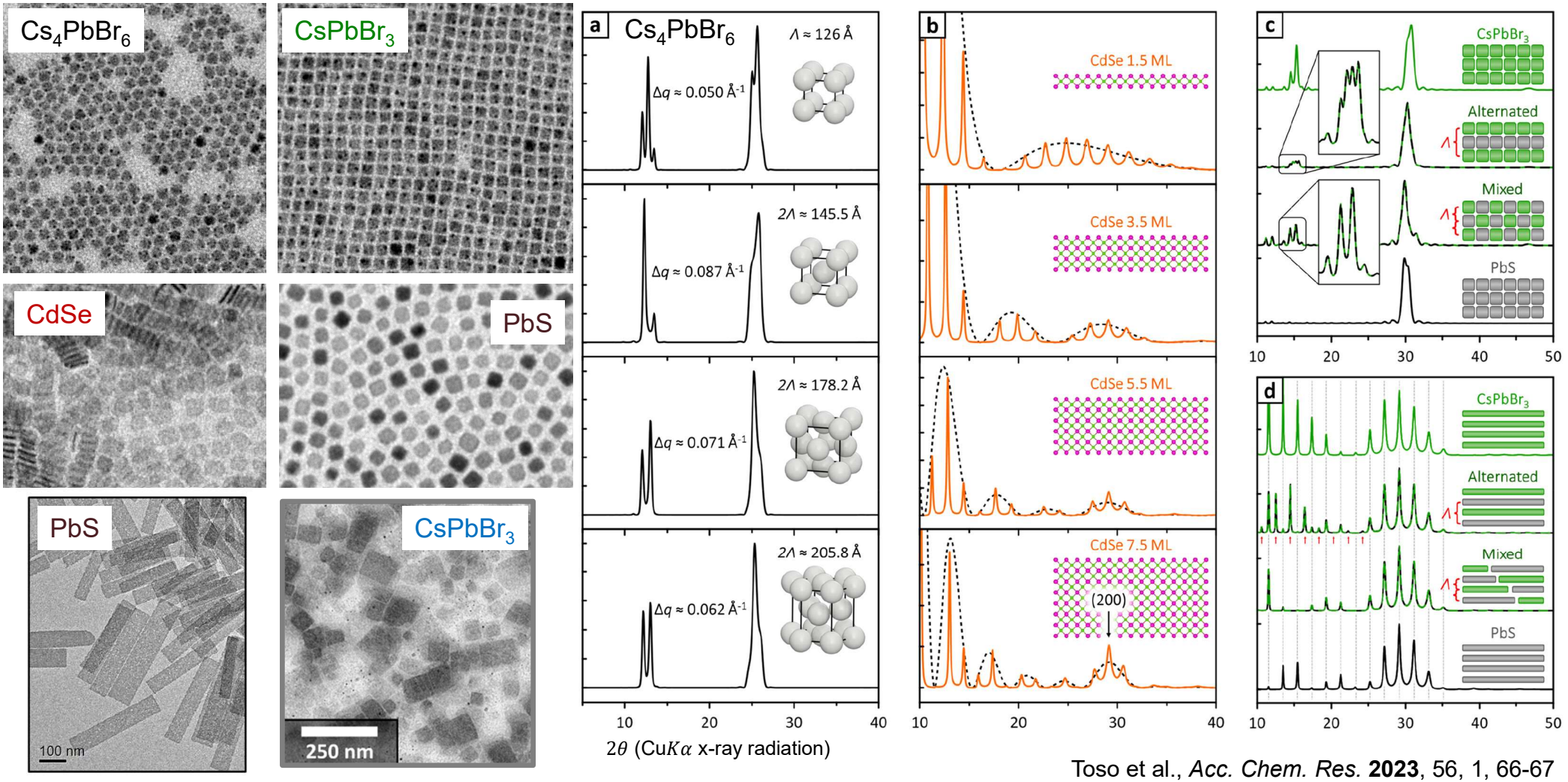
Predicting Diffraction Patterns



Toso et al., *Acc. Chem. Res.* **2023**, 56, 1, 66-67

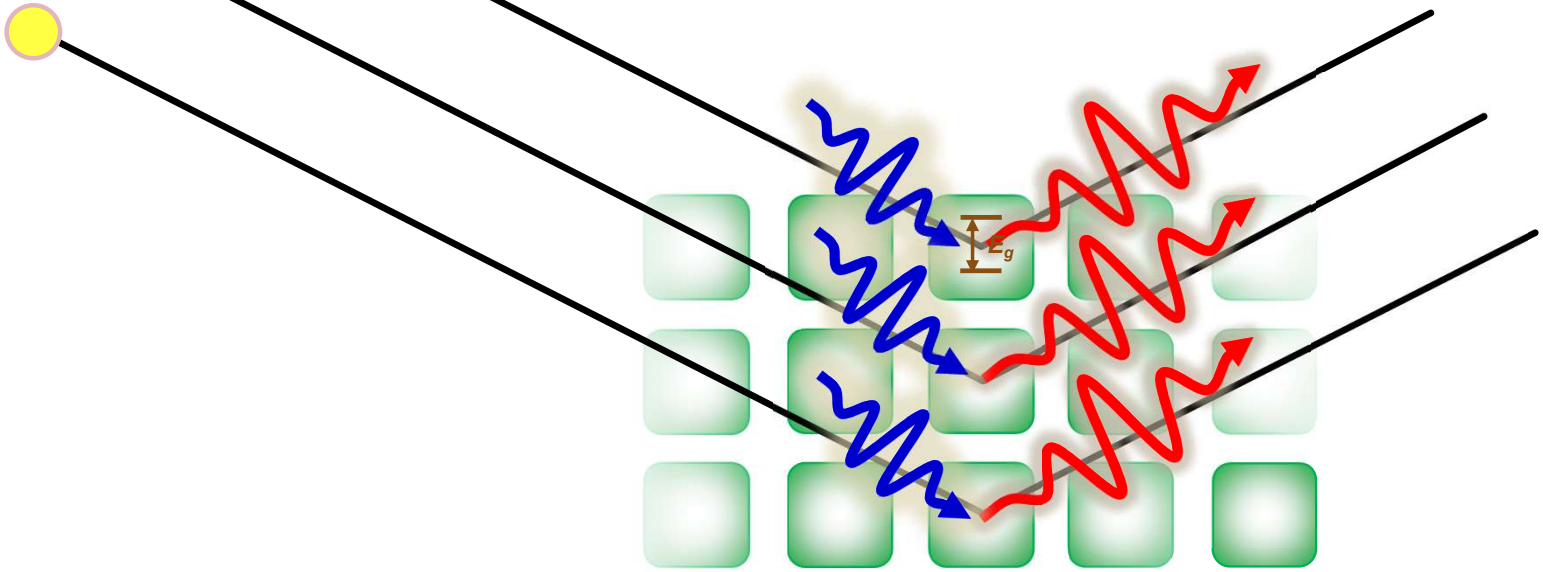
Diffraction and Interference

$$R_1 = A_1 \cos(\omega_1 t + \phi_1)$$
$$R_2 = A_2 \cos(\omega_2 t + \phi_2)$$
$$\dots$$
$$R_n = A_n \cos(\omega_n t + \phi_n)$$

$$\omega_1 = \omega_2 = \omega_n = \omega$$
$$A_1 = A_2 = A_n = A$$
$$\phi_1 = \phi_2 = \phi_n = 0$$

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

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



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Experiments on Superfluorescence/-radiance in Perovskites

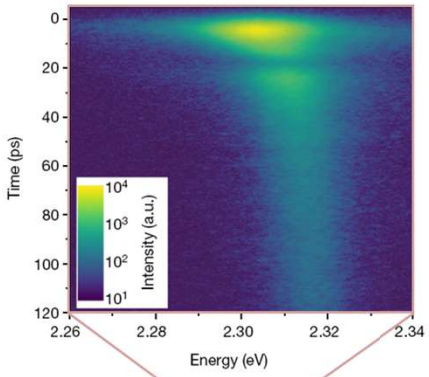
2018, Raino et al.
Nature, v563p671
OLAC/OLAM $CsPbBr_3$,
$CsPbBr_2Cl$ NC SLs,
Red-shifted SF, 4K

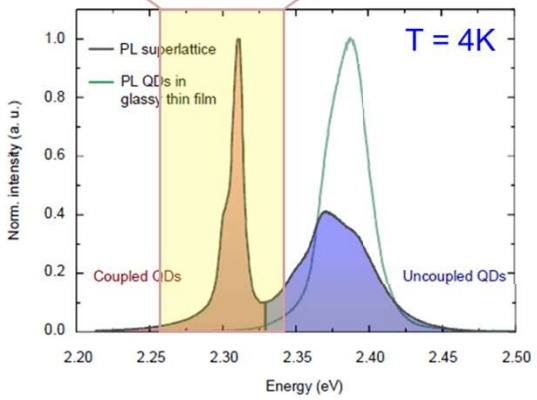
2020, Krieg et al.
ACS Central Sci., v7p135
SF in $CsPbBr_3$@Sulfobetaine
NC SLs, red-shifted SF, 4K

2021, Cherniukh et al.
Nature, v593p535
BNSLs $CsPbBr_3$ NC
Blue/red-shifted SF, 4K

2022, Cherniukh et al.
ACS Nano, v16p7210
BNSLs $CsPbBr_3$ NC
Collective states

2023, Boehme et al.
ACS Nano, v17p2089
Rhomb SLs $CsPbBr_3$
no SF, 4K





2020, Zhou et al.
Nat. Commun., v11p329
Cavity-enh SF,
aged $CsPbBr_3$ NC SLs

2020, Findik et al.
Nat. Photon., v15p676
MAPI thin film, **77K**

2021, Cherniukh et al.
ACS Nano, v15p16488
BNSLs $CsPbBr_3/LaF_3$ disks
Blue/red-shifted SF, 6K

2021, Wang et al.
Adv. Opt. Mater., v9p2100879
Single $CsPbBr_3$ NC,
superbunching

2021, Baranov et al.
ACS Nano, v15p650
Fresh $CsPbBr_3$ NC SLs no SF,
Aged – maybe, bulk effect?

2022, Zhong et al.
Adv. Opt. Mater., v10p2102290
Cavity-enh SF,
aged $CsPbBr_3$ NC SLs

2022, Biliroglu et al.
Nat. Photon., v16p324
PEA:$CsPbBr_3$ thin film, **300K**

2022, Blach et al.
Nano Lett., v22p7811
$CsPbBr_3$ NC SLs, SR

2023, Be'er et al.
arXiv, 2301.01608
SF by CL, $CsPbBr_3$ NCs, 4K

2023, Miloch et al.
arXiv, 2303.08791
Maybe collective state,
Aged $CsPbBr_3$ NC SLs, 17K

2023, He et al.
JPC Lett, v14p2627
$CsPbBr_3$/NaCsYYbErF, 4K
Magnetic field

2023, Chen et al.
Adv. Sci., 2301589
Blue Cavity-enh SF,
$CsPbBr_2Cl$ NC SLs

- What is this effect?
- How to achieve it?

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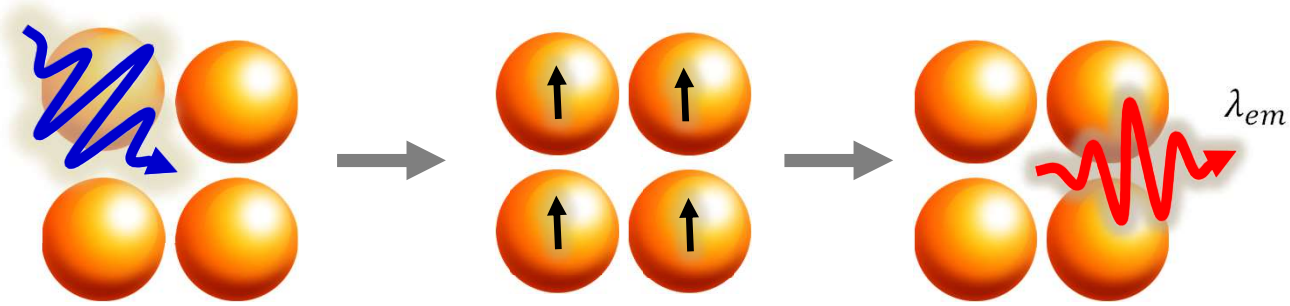
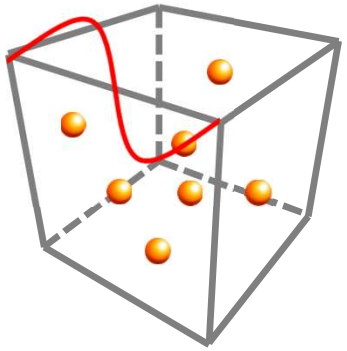
Dicke Superradiance, 1954



$V = \lambda_{em}^3$



$Peak\ I_{SR} \propto N^2$

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

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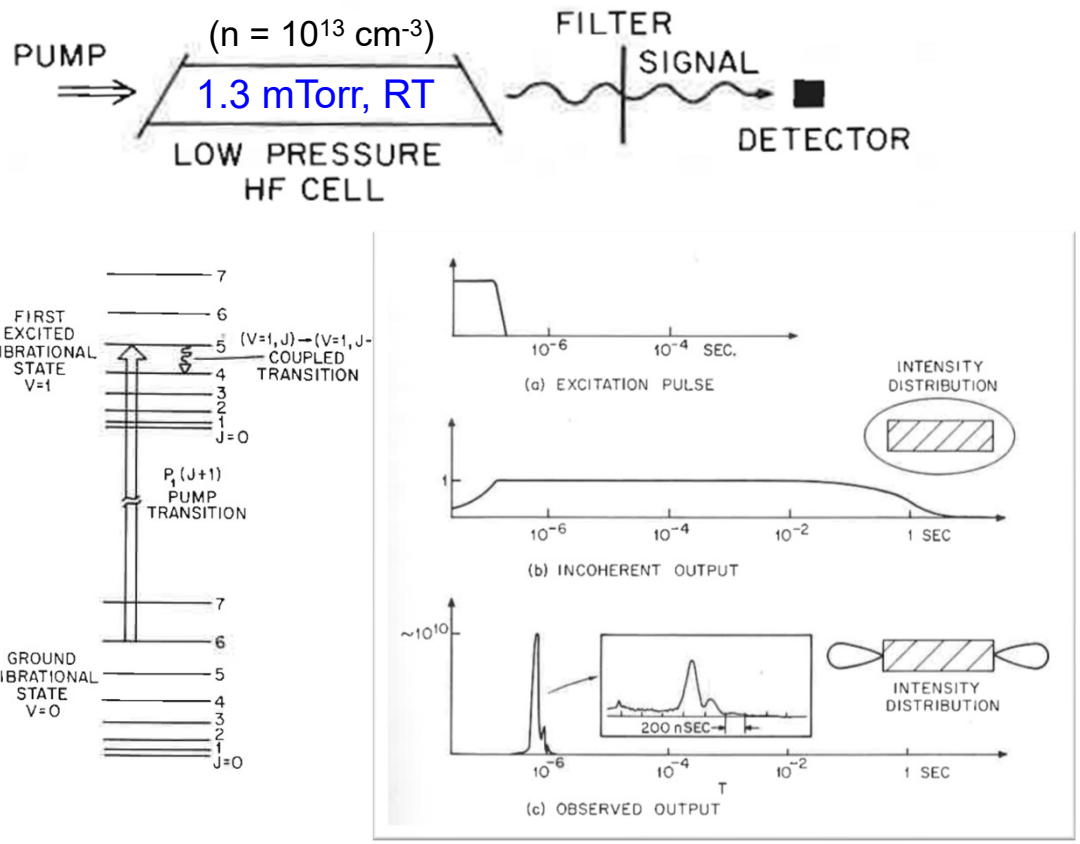
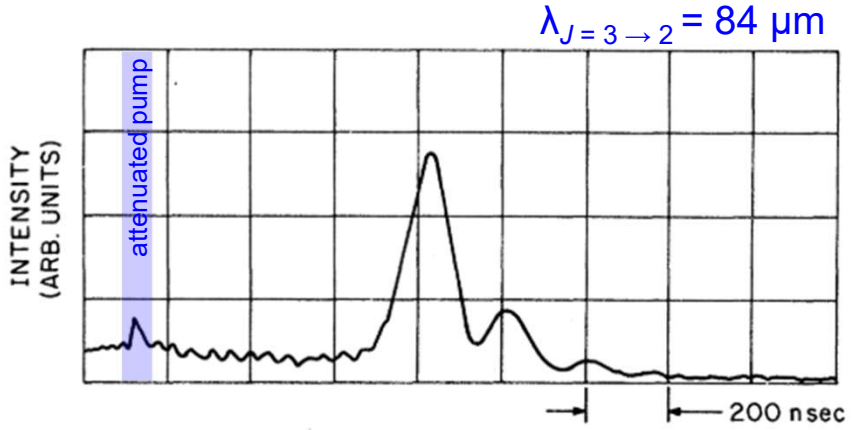
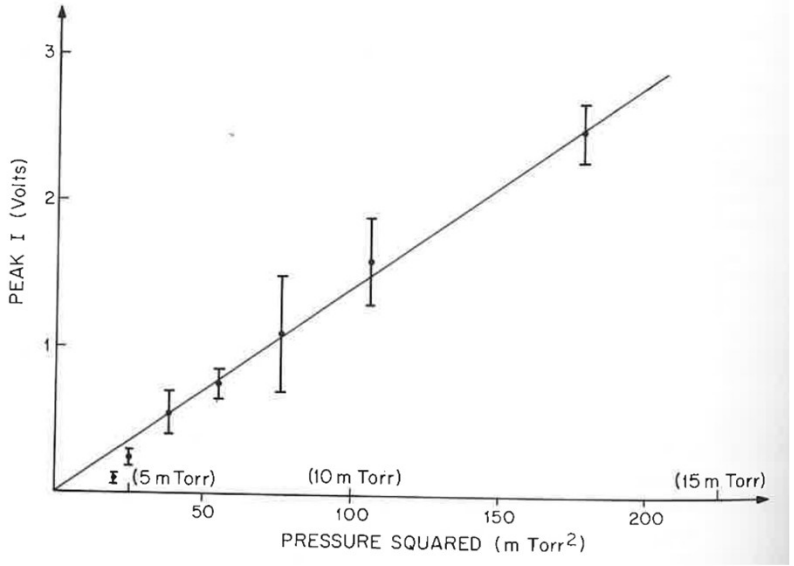
Experiment with HF gas, 1972

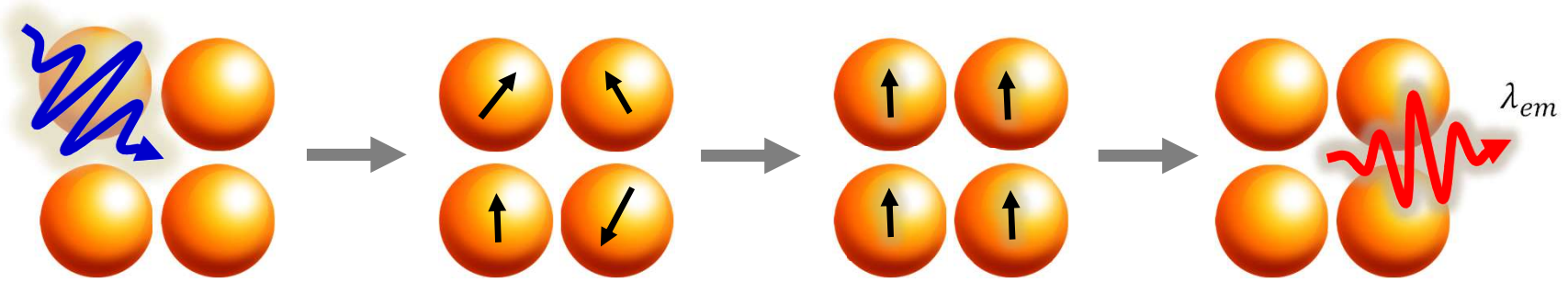






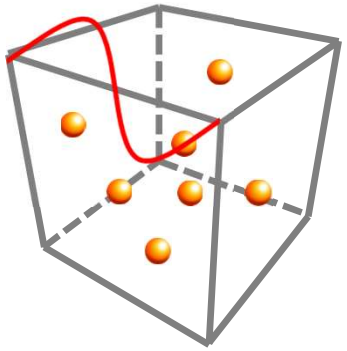
Skribanowitz et al., *Appl. Phys. Lett.* 20 (11), 428-431, **1972**
Skribanowitz et al., *PRL* 30 (8), 309-312, **1973**
Herman et al., in *Laser Spectroscopy*, 379-492, **1974**

Superfluorescence, 1975



excitation **buildup of coherence** **superfluorescence**

$V = \lambda_{em}^3$



$I_{SR} \propto N^2$

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

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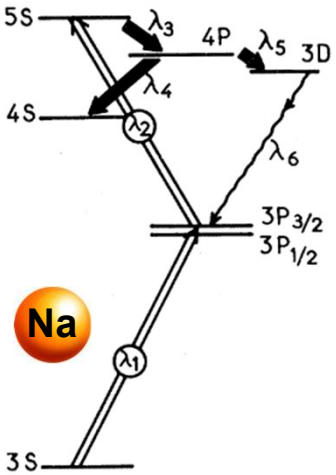
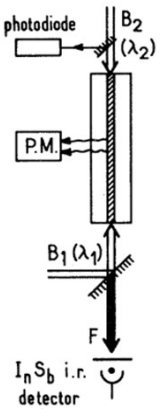
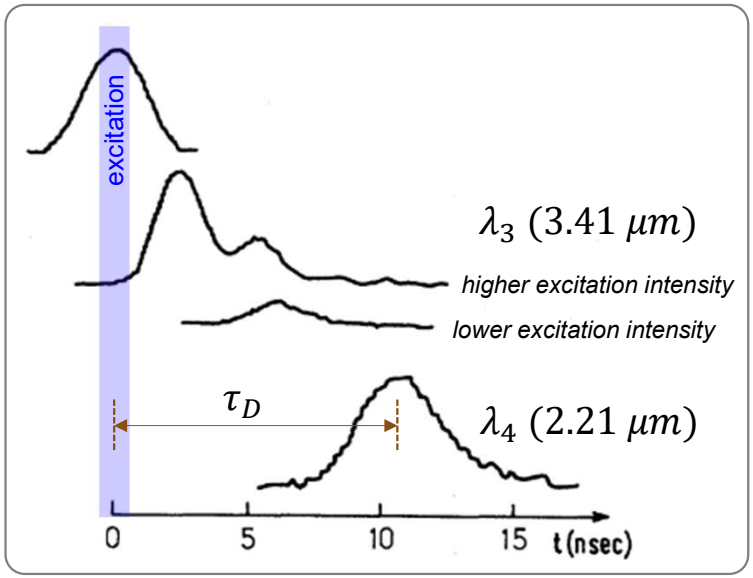
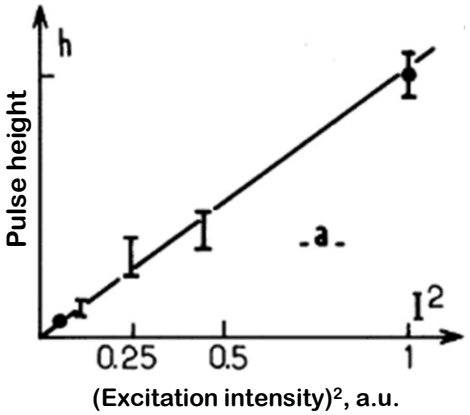
Experiment with Na vapor, 1976

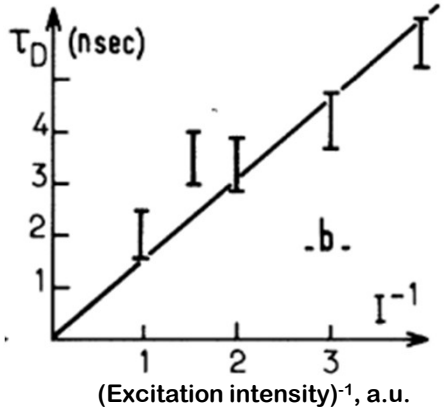




n = 10^9-10^{10} cm^{-3}







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

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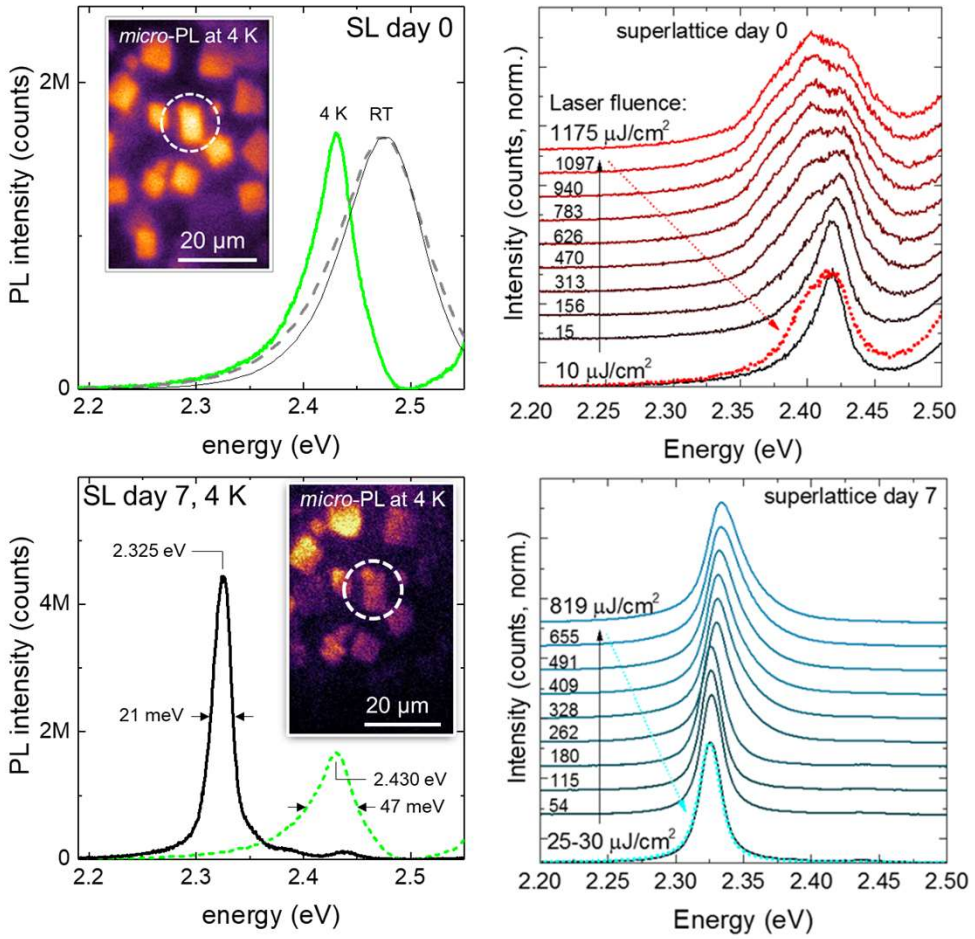
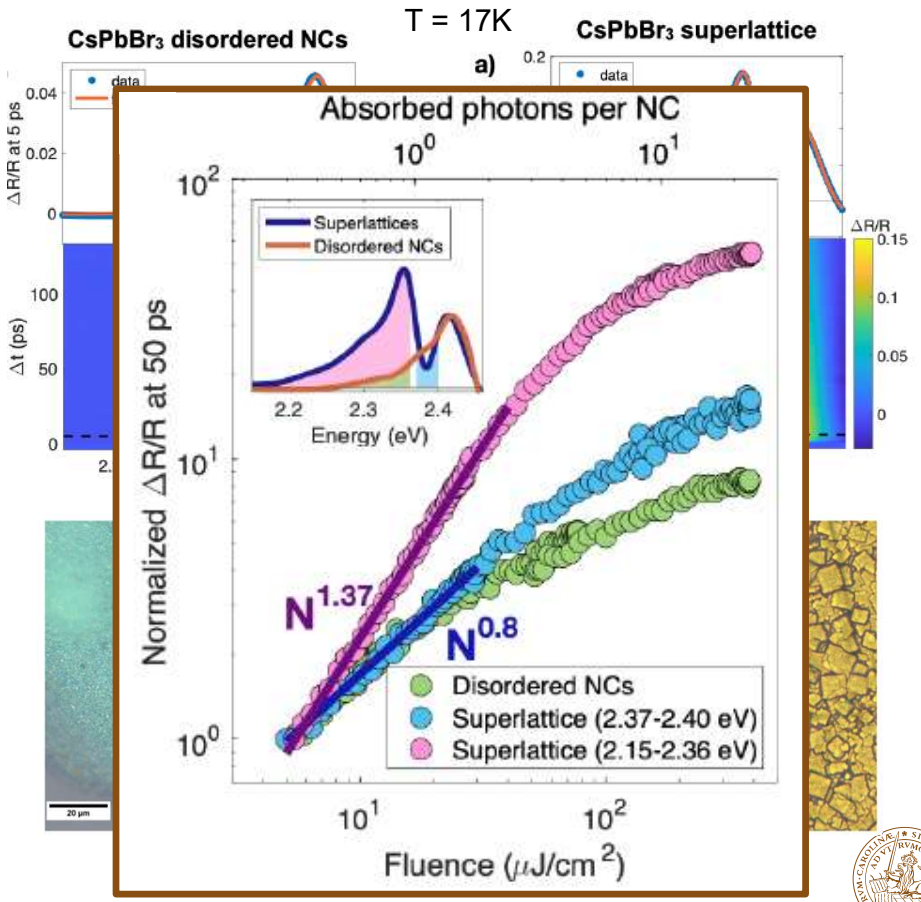
Looking for Superfluorescence



Baranov et al., *ACS Nano*, 15 (1), 650-664, **2021**



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

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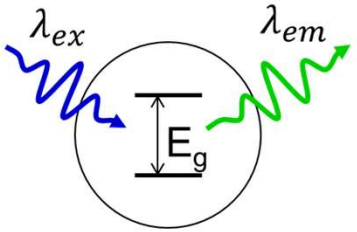
Important Open Questions

Timescales:
- Radiative vs. decoherence vs. cooperative

Disorder:
- Energy, position, and orientation

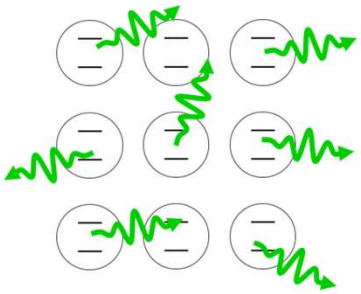
Interactions:
- Dipole-dipole, long-range

Structure:
- intrinsic or necessary superlattice



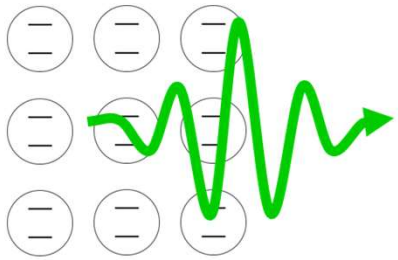
T_1, radiative decay
T_2, decoherence time
T_{SR}, characteristic time

$T_1 > T_{SR} > T_2$



$I_{max}(t) \propto N$

$T_1 > T_{SR} < T_2$



$I_{max}(t) \propto N^2$

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