ETH
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Swiss Federal Institute of Technology Zurich

Empa
Materials Science and Technology

Perovskite Nanocrystals as Non-Classical Light Sources: From Single Photon Emission to Superfluorescence

Gabriele Rainò (rainog@ethz.ch)

ETH Zürich - Department of Chemistry and Applied Biosciences
Empa - Swiss Federal Laboratories for Materials Science and Technology

Functional Inorganic Materials Group (KovalenkoLab)

Content

$CsPbX_3$ Nanocrystals:

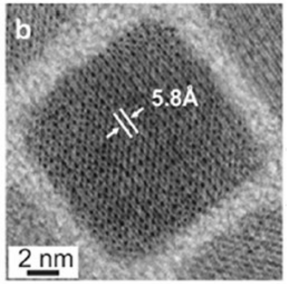
- Beyond classical light sources:
  - ✓ narrow emission linewidths
  - ✓ photon anti-bunching
  - ✓ **ultrafast radiative decay**
  - ✓ **bright triplet excitons**

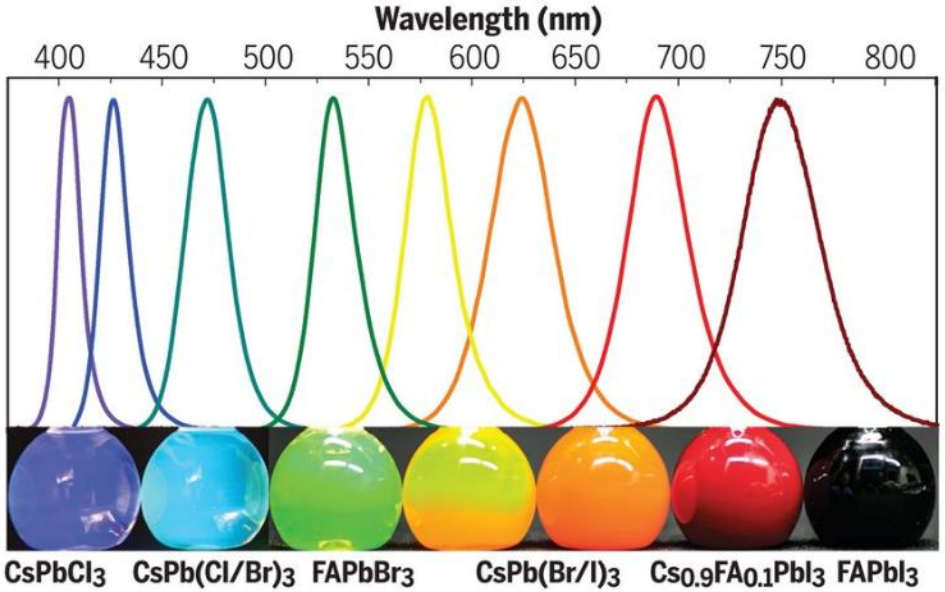
SF in QD supercrystals:

- Redshifted PL with accelerated decay time
- **Photon Bunching**
- Burnham-Chiao ringing at high excitation density
- Control on SF in binary SLs

$CsPbX_3$ quantum dots

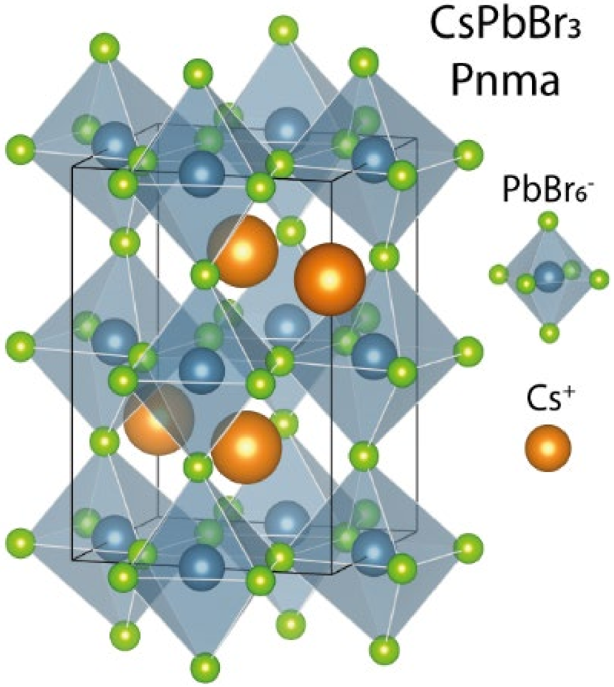
Low cost synthesis of highly-monodispersed NCs; PLQY>90%





Protesescu *et al.,* Nano Letters, 15, 3692 (2015)
Kovalenko *et al.,* Science, 358, 745-750 (2017)

Crystal structure



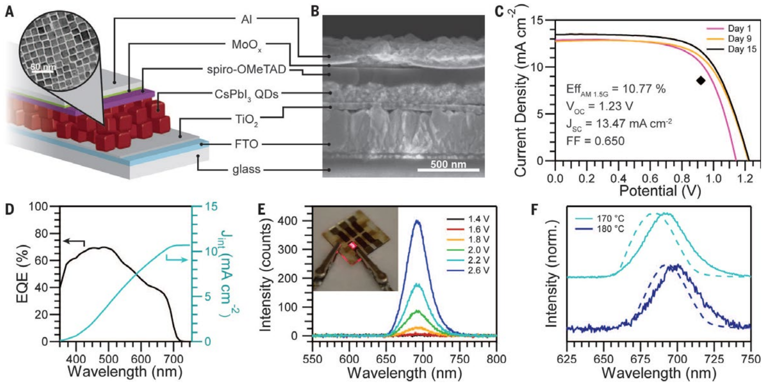
Advantages

- **Tunability** (visible - infrared)
- **Low cost** (wet chemistry approaches)
- **Easy processability** (spin coating, roll-to-roll inkjet printing)

Perovskite nanocrystals for optoelectronics

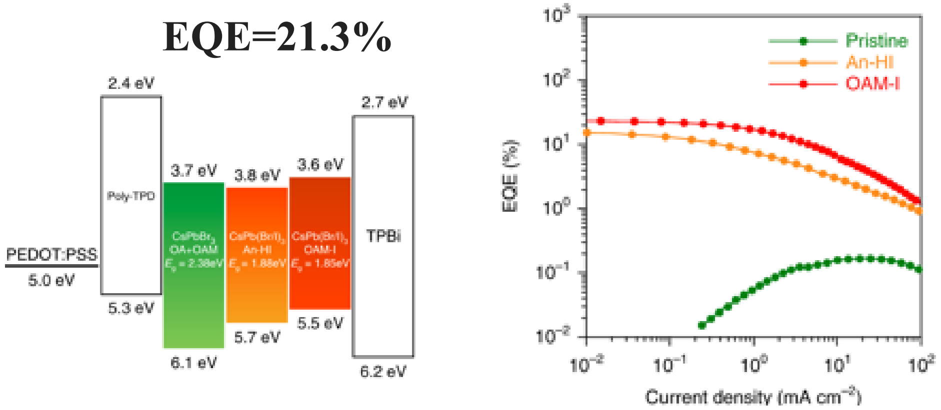
PV solar cells

E= 10.77%



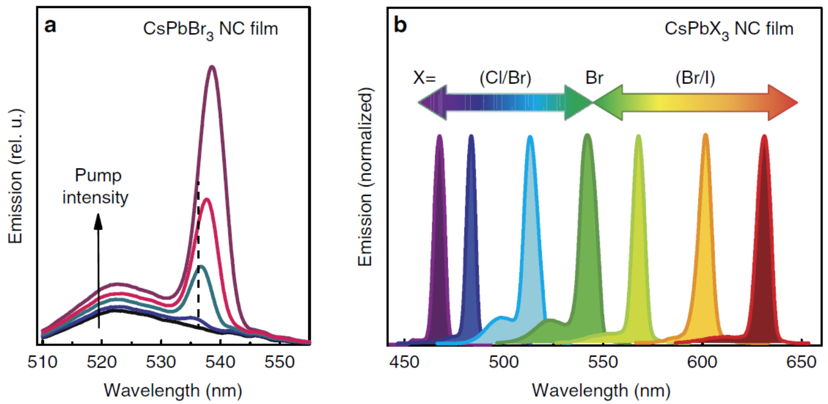
Swarnkar *et al.*, Science 354, 92 – 95 (2016)

Highly-efficient LEDs



Chiba *et al.*, Nature Photonics 12, 681–687 (2018)

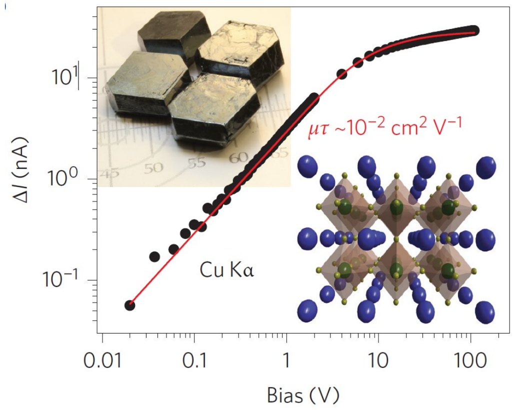
Wide-range tunable ASE

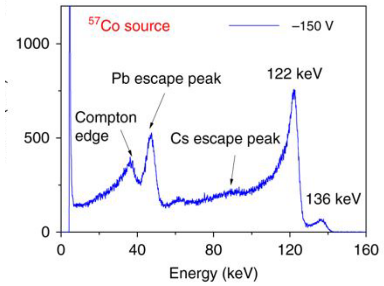


Yakunin *et al.*, Nat. Comm., doi:10.1038/ncomms9056

Gamma-ray detectors

Nat. Commun. **9**, 1609 (2018)



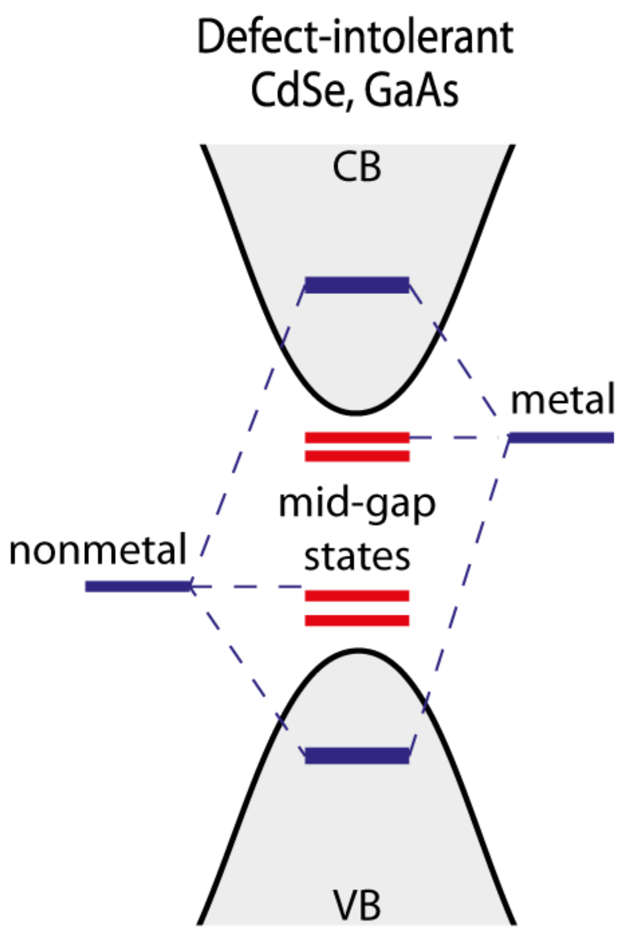


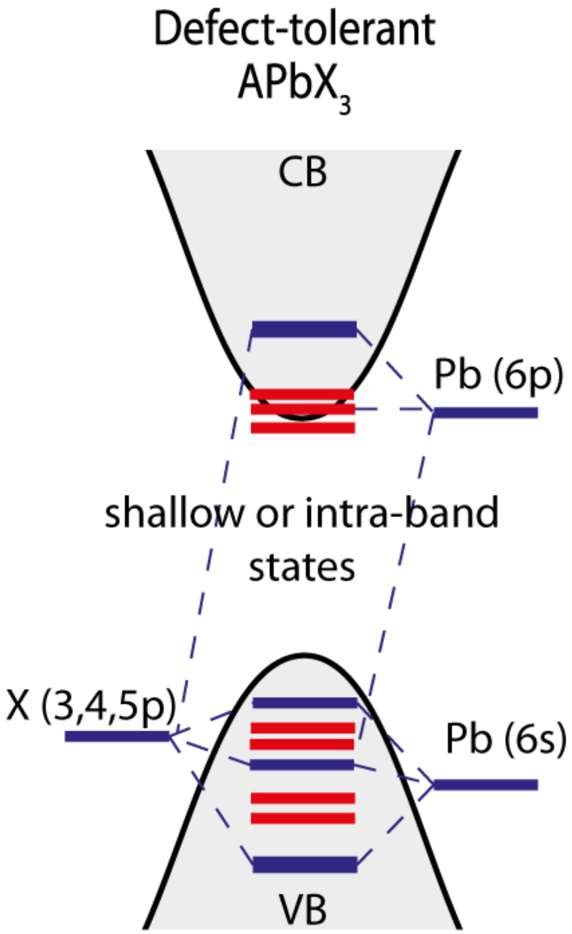
Yakunin *et al.*, Nat. Photonics 10, 585−590 (2016)

Can we harness the exceptional optoelectronic properties of perovskite materials to built nanoscale **non-classical light sources**?

- Wide emission tunability
- Room temperature operation
- Easy processability
- **Defect tolerant**

Role of defects

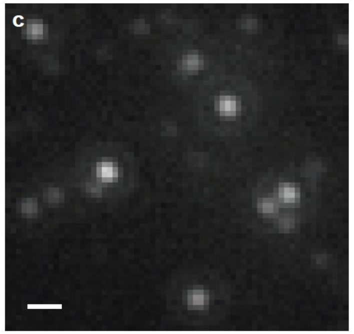




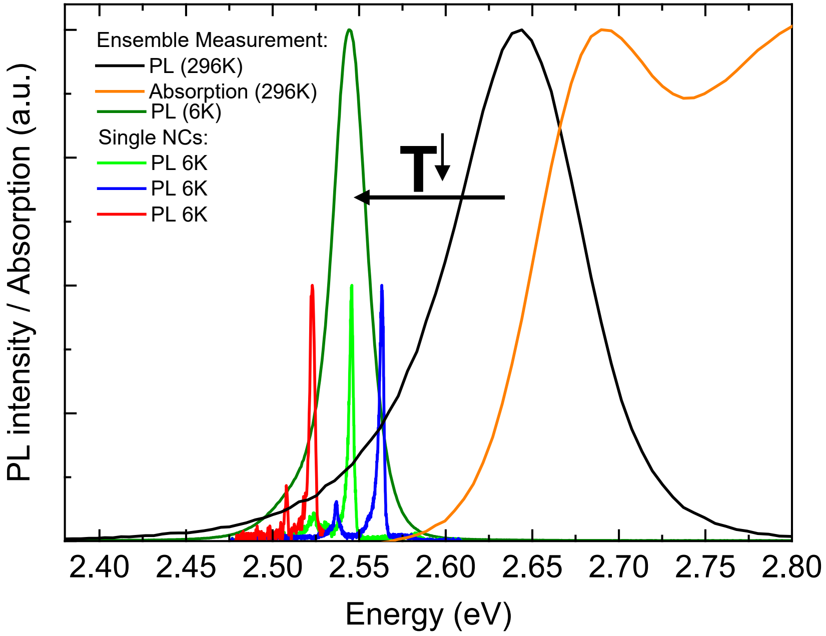
ultra-high vacuum epitaxy

poor's man semiconductor

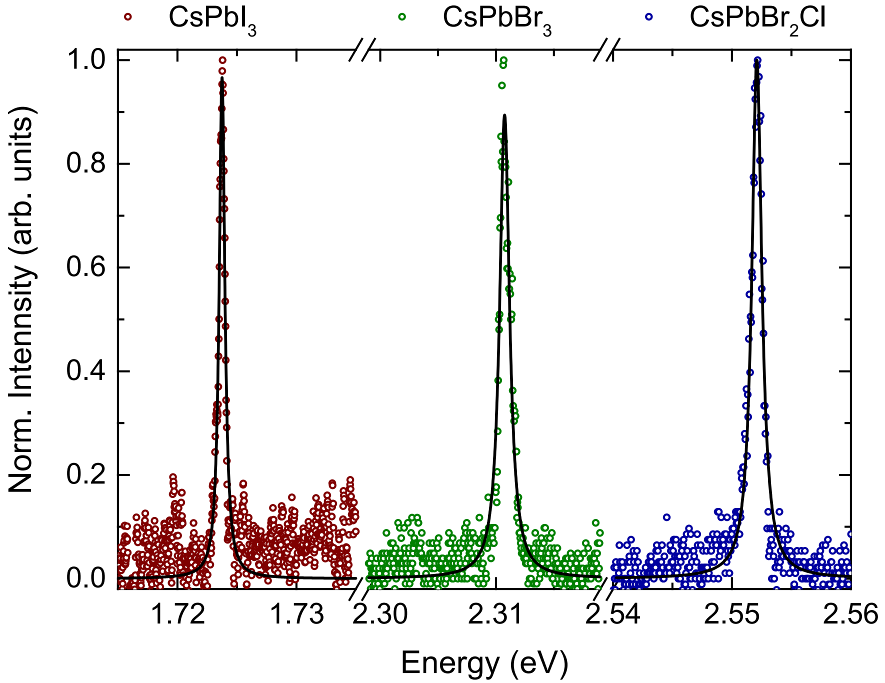
Composition dependent single $CsPbX_3$ NCs PL



Ensemble vs. Single NCs

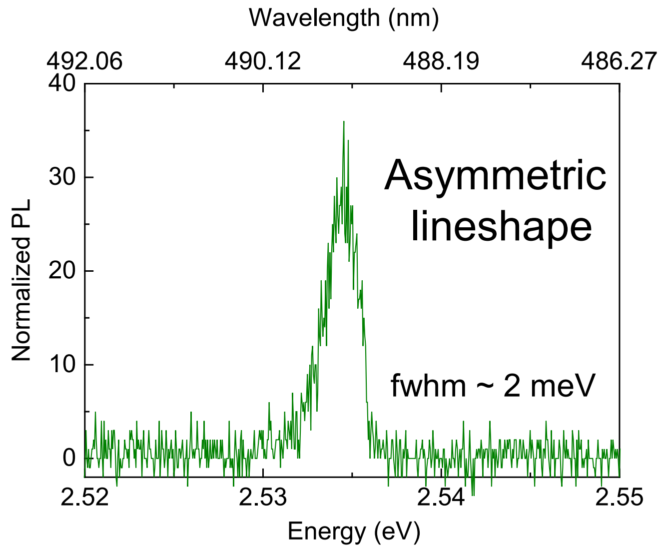


Rainò *et al.*, ACS Nano 10, 2485 (2016)

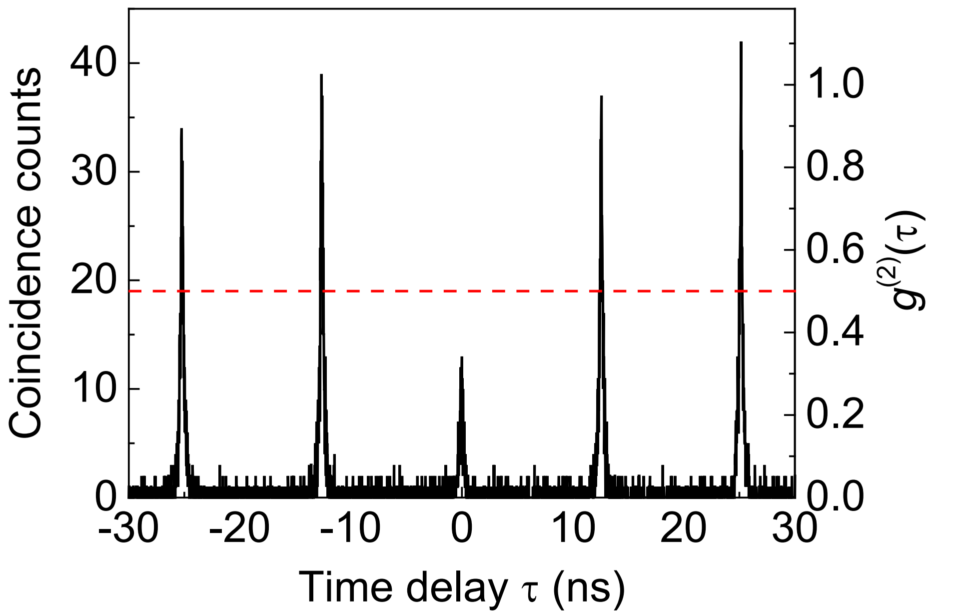


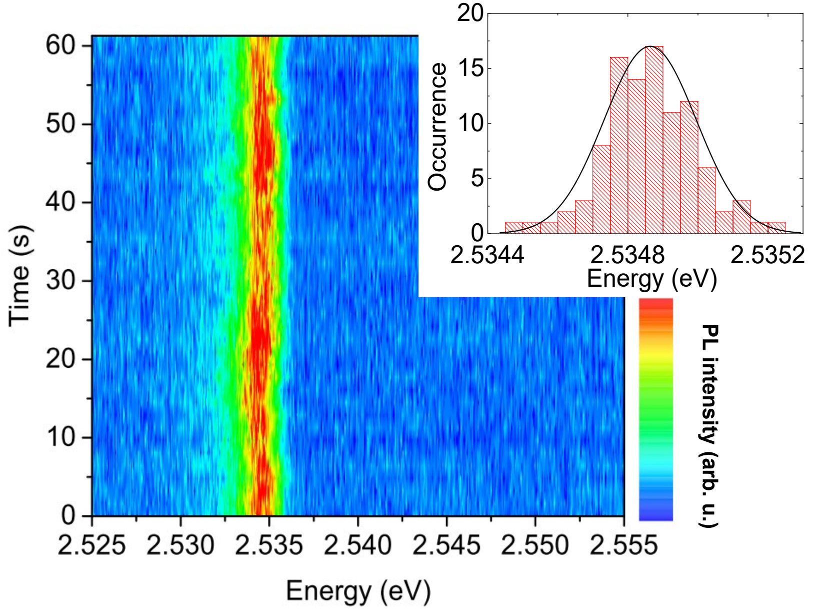
→ Narrow-band emission (FWHM < 2 meV)

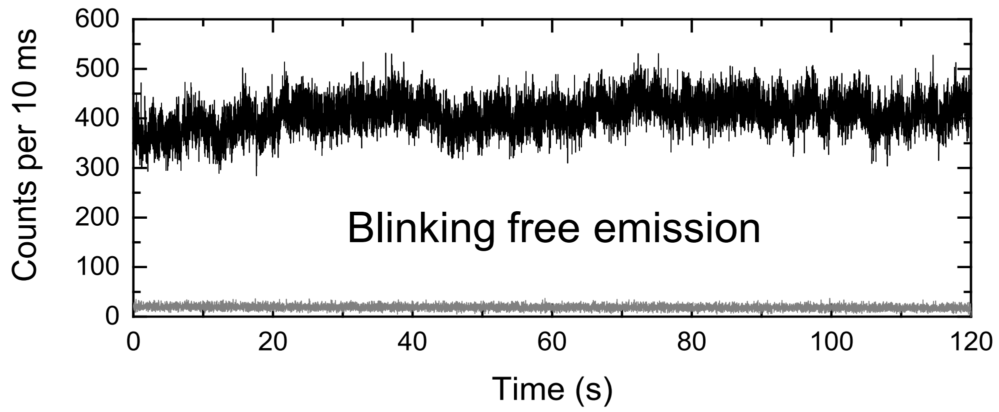
Stable single photon PL of $CsPb(Br/Cl)_3$ NCs



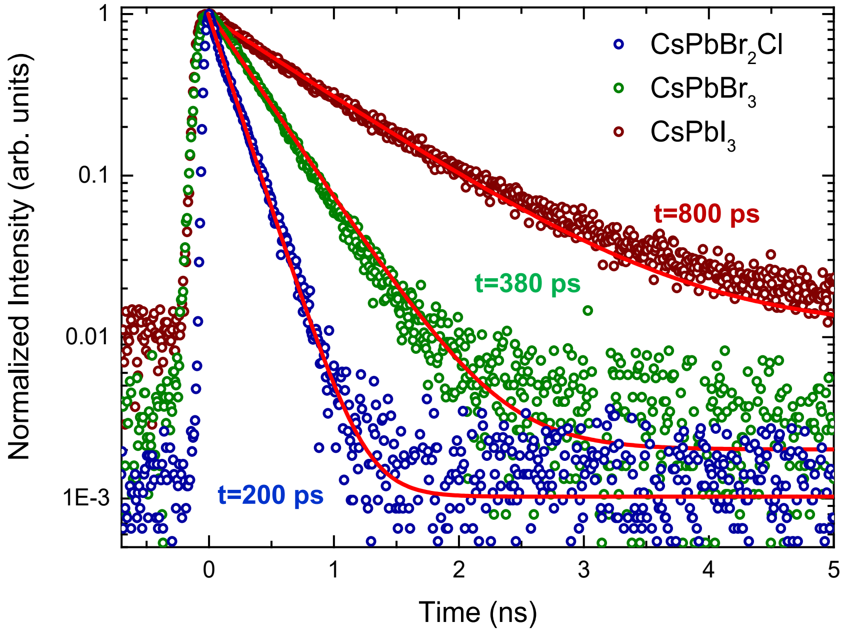
Rainò *et al.*, ACS Nano 10, 2485 (2016)







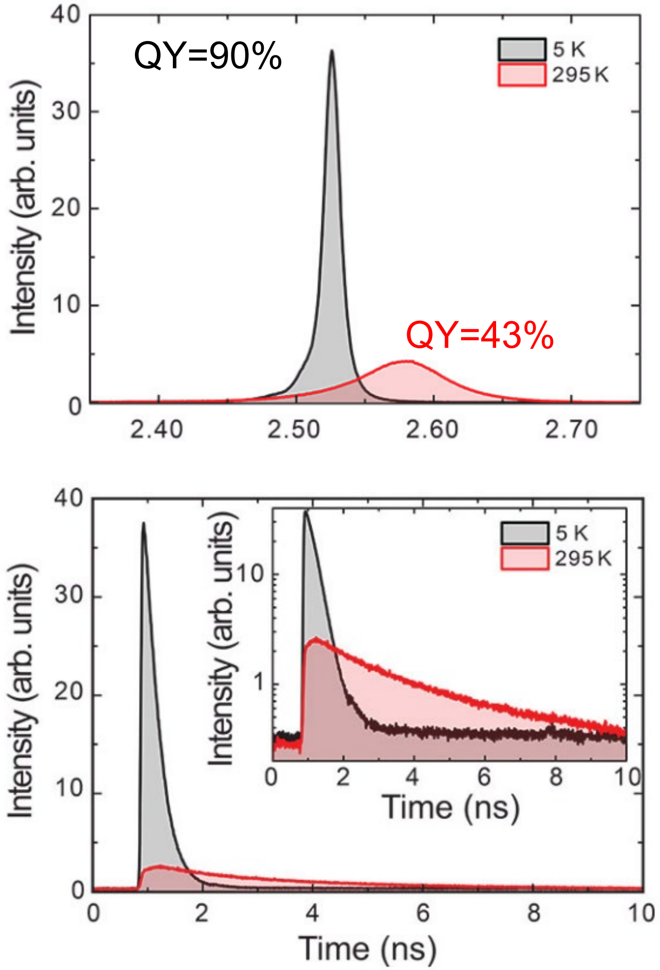
Characterization of fast radiative lifetimes in $CsPbX_3$ nanocrystals



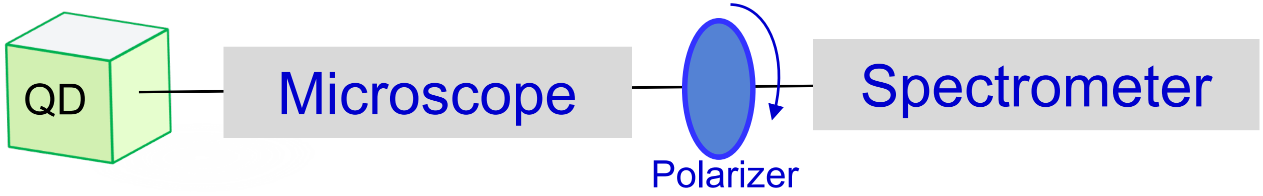
→ Ultrafast (sub-ns), composition dependent radiative decay

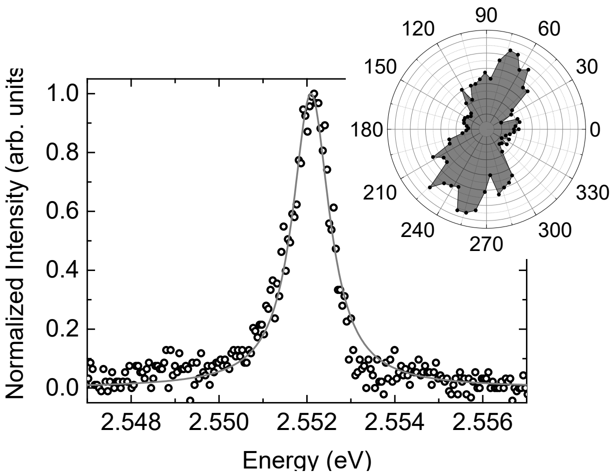
Becker *et al*., Nature, 553, 189 (2018)

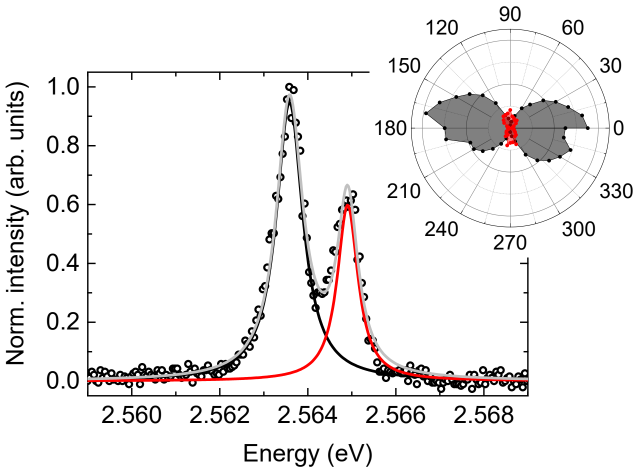
Temperature dependent PL and TRPL

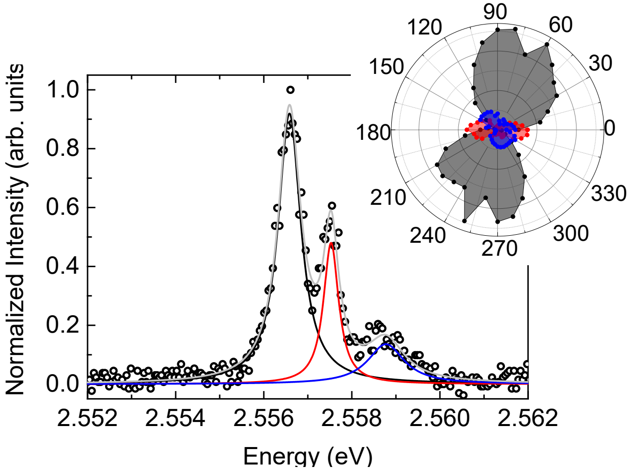


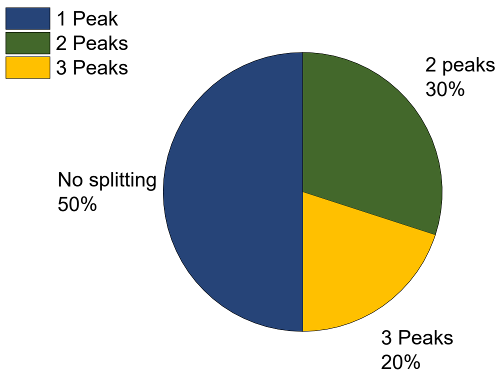
Polarization dependent PL measurements



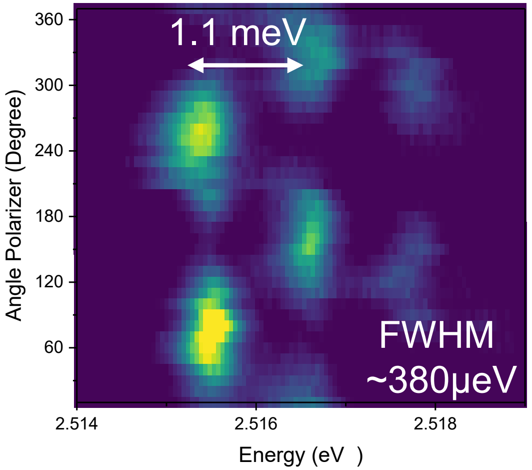








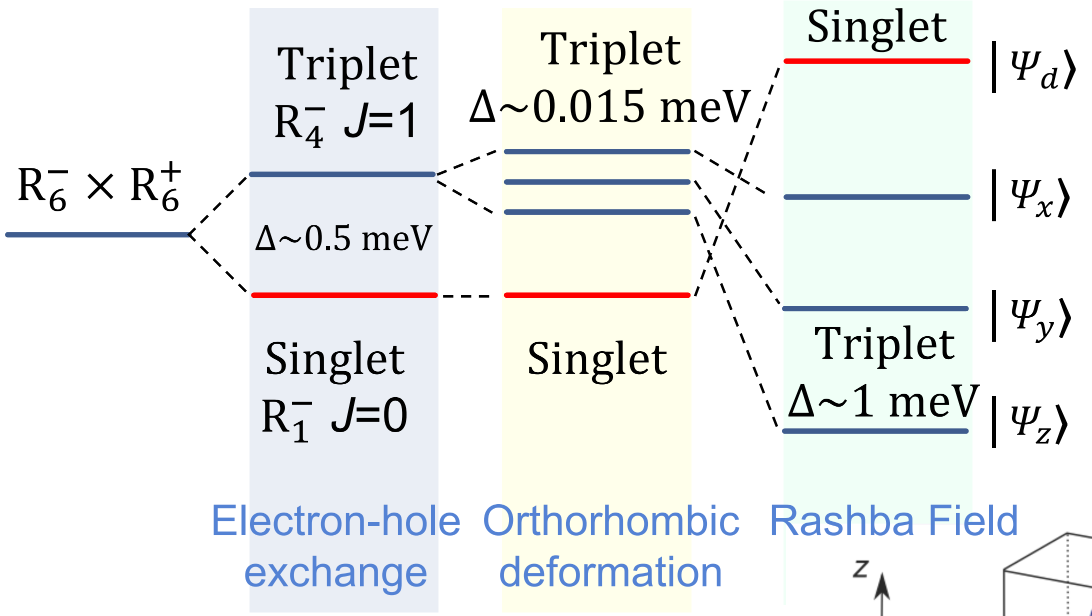
Are these emitting states associated to the FSS?

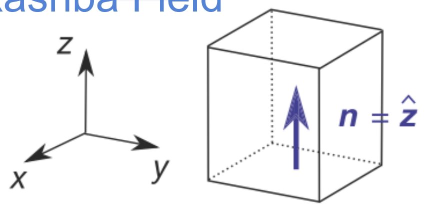


Exciton fine structure splitting (FSS)

Electron-hole exchange interaction

$$H_{exc} \sim -\alpha_{exc}\Omega_0(\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_h)\delta(\boldsymbol{r}_e - \boldsymbol{r}_h)$$



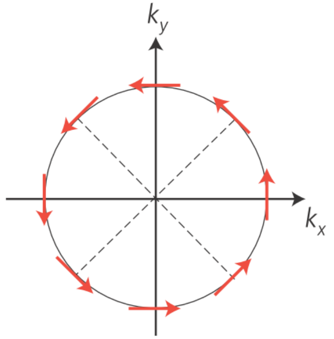


Rashba Effect (in orthorhombic symmetry)

→ Strong spin-orbit coupling & inversion symmetry breaking

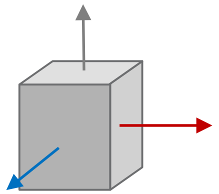
ISB → electric field $E = E_z n$

$$H_{Rashba} \sim \alpha_R^{e,h} \underbrace{(\boldsymbol{n} \times \boldsymbol{p})}_{\boldsymbol{B_R}} \cdot \boldsymbol{\sigma}_{e,h}$$



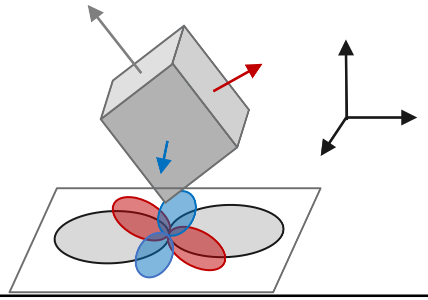
$$\boxed{\alpha_R^{e,h} = 0.38 \text{ eVÅ}}$$

Manchon *et al.*, Nat. Mat. 14, 871 (2015)



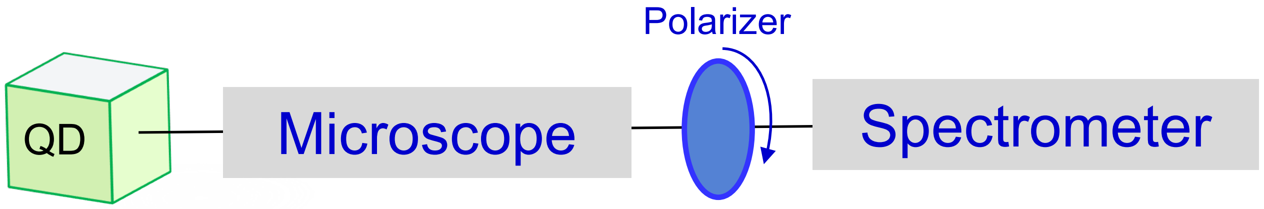
Assumptions:
- Three orthogonal dipoles

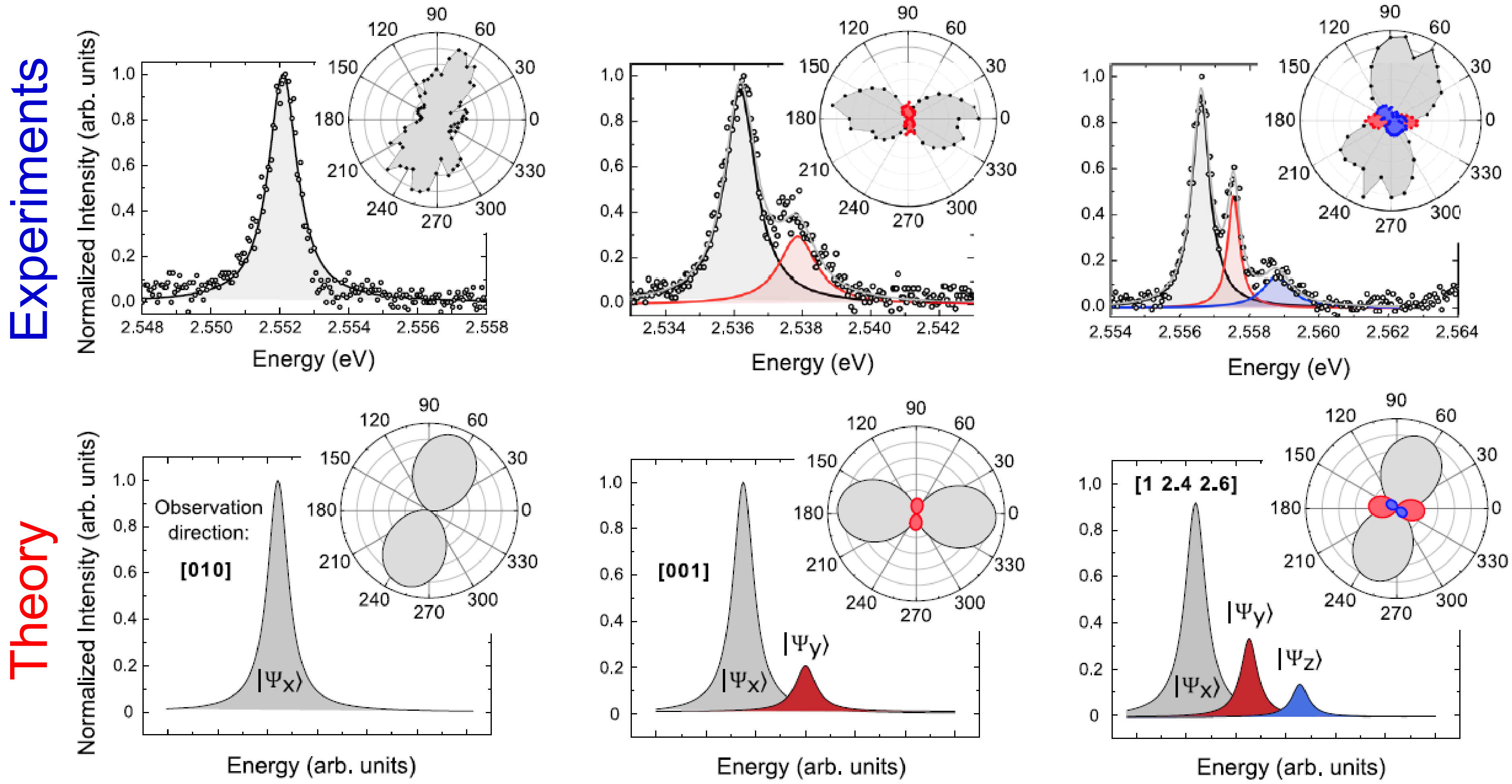
Calculate:
- NC Orientation
- Boltzmann distribution



Bright Triplet Excitons

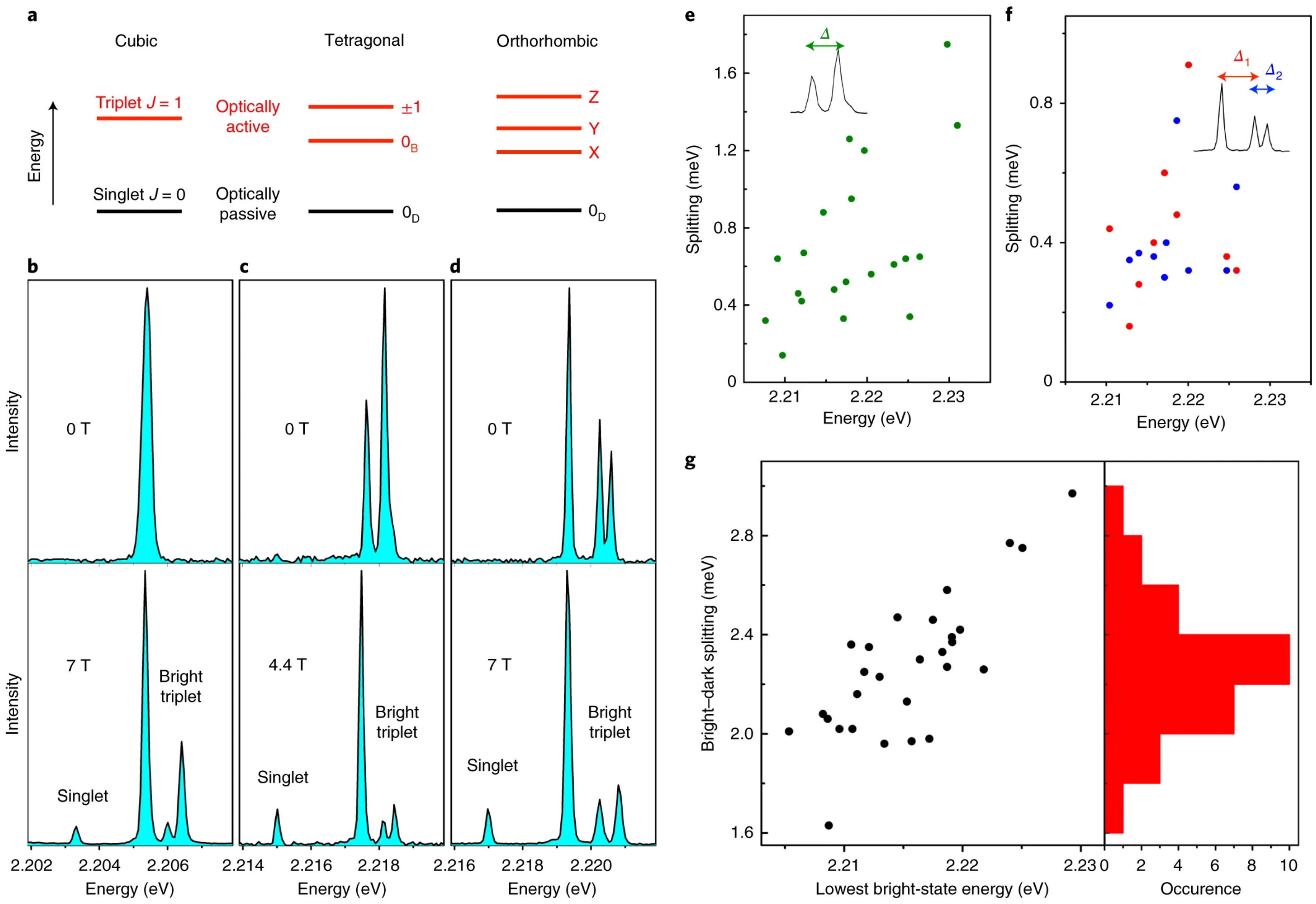
Becker *et al.*, Nature, 553, 189 (2018)





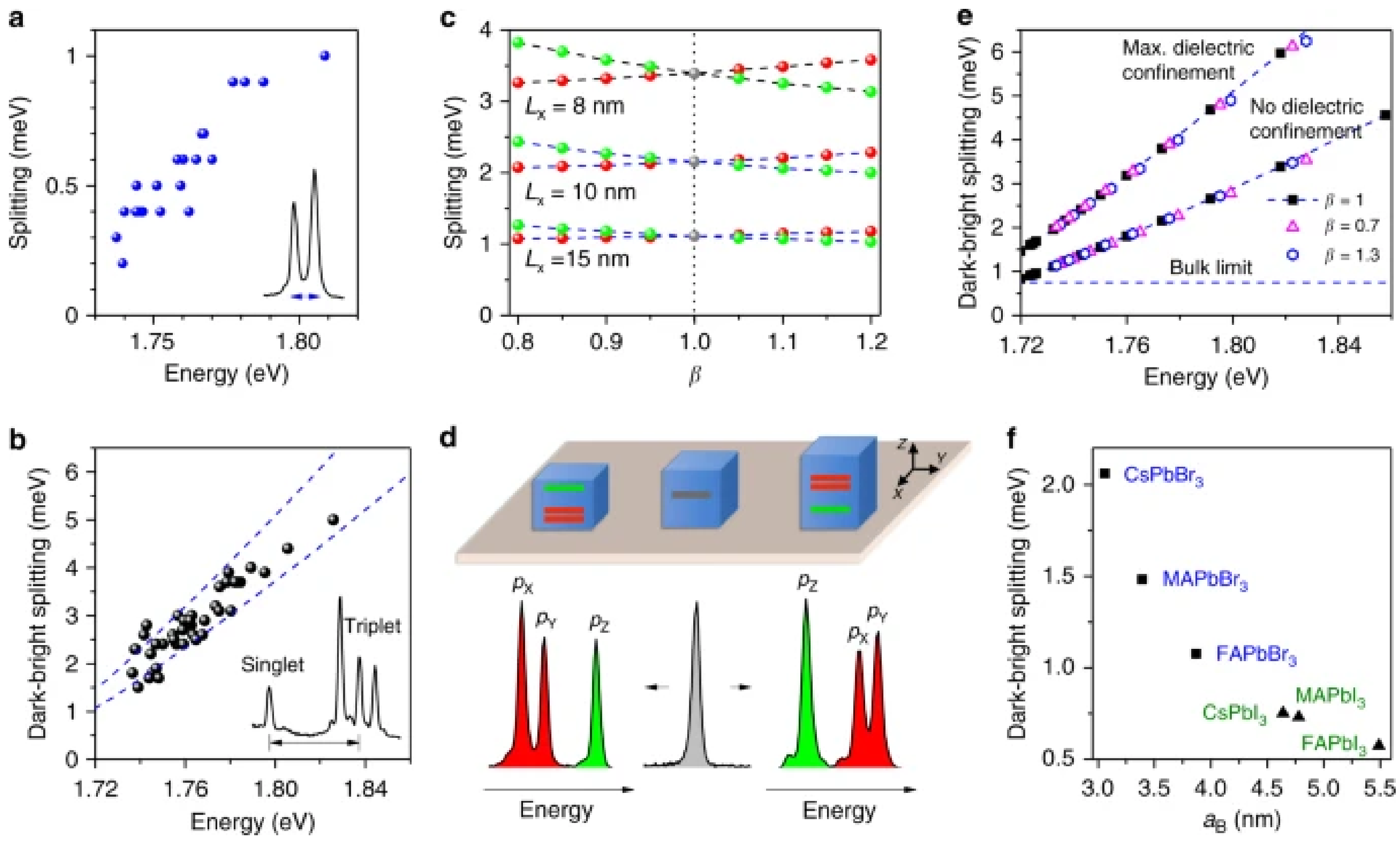
Dark singlet exciton in $FAPbBr_3$ NCs

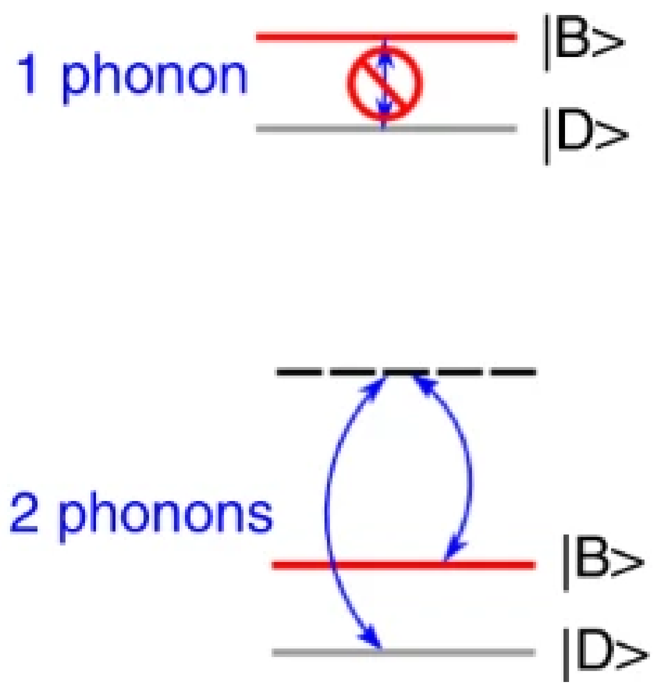
Tamarat *et al.*, Nat. Mater, 18, 717 (2019)



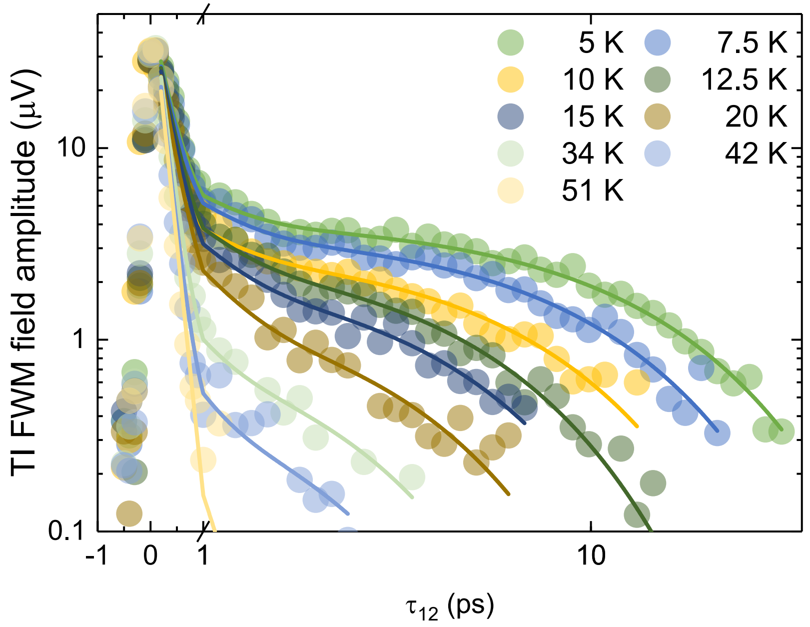
Dark exciton ground state in $CsPbI_3$

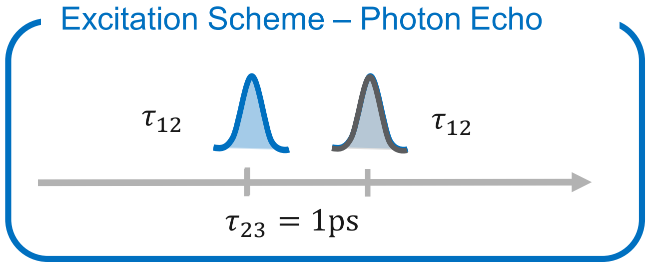
Tamarat *et al.*, Nature Communications 11, Article number: 6001 (2020)





Exciton Dephasing Time (FWM – Photon-Echo)

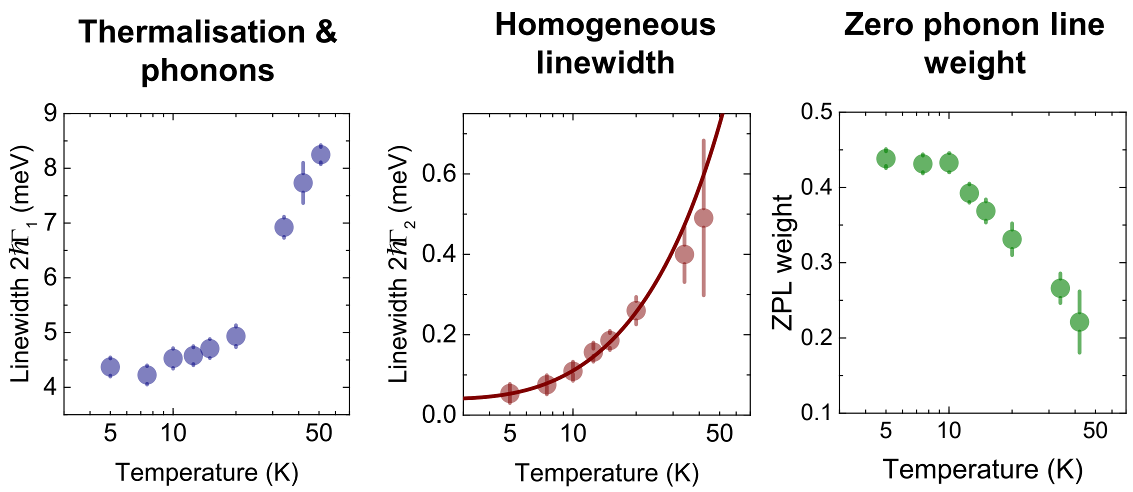




Exciton Dephasing

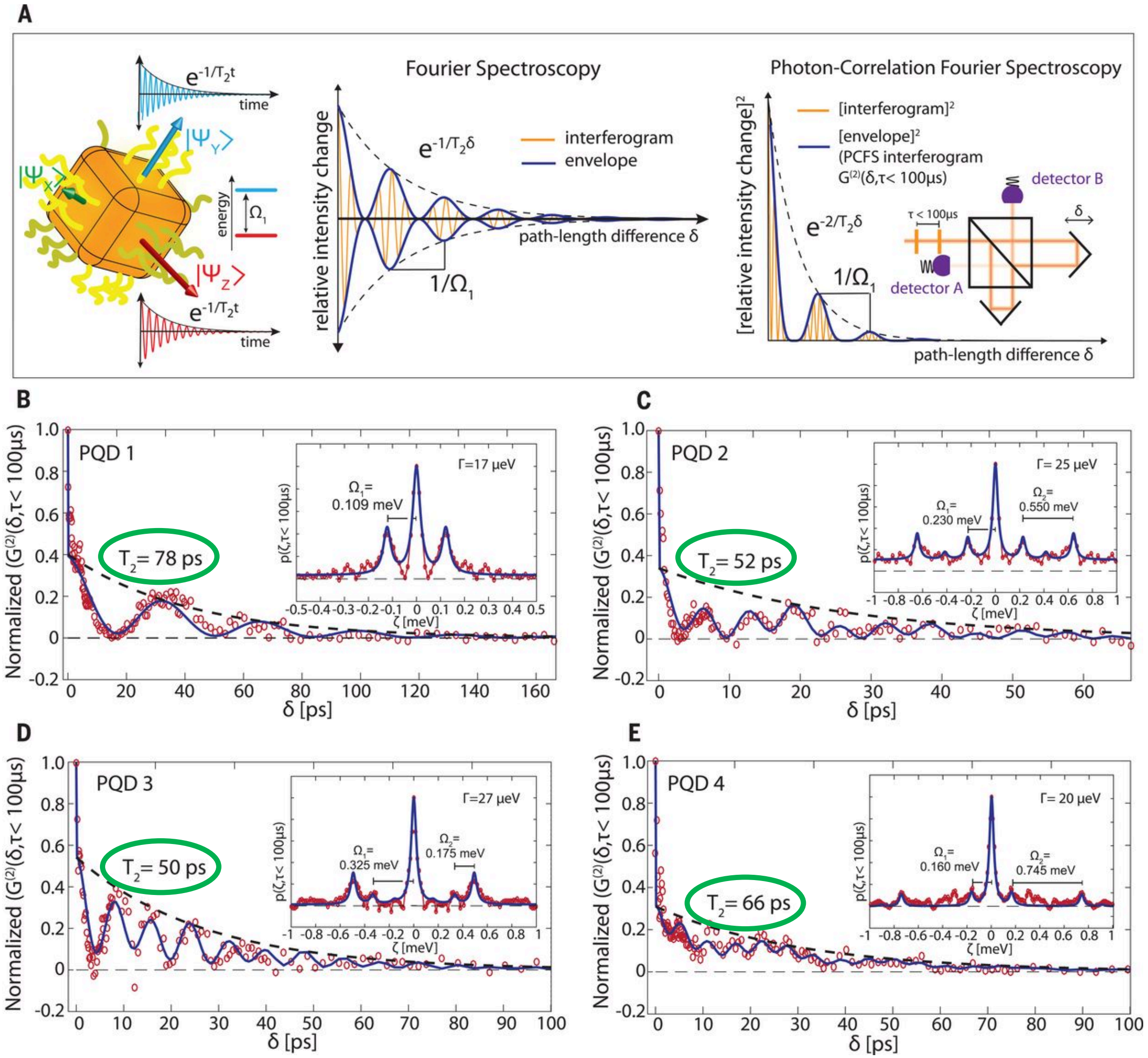
- Initial decay: Phonon assisted thermalisation between FSS
- Long decay: **Homogeneous Linewidth $\sim 55\mu\text{eV}$ ($T_2 \sim 25$ ps)**
    - Activation energy $\Delta = 1.23 \pm 0.35$ meV

→ Scattering into fine structure states ($\Delta_{FSS} = 1.15 \pm 0.26$ meV)



Becker *et al.*, Nano Letters 18, 7546–7551 (2018).

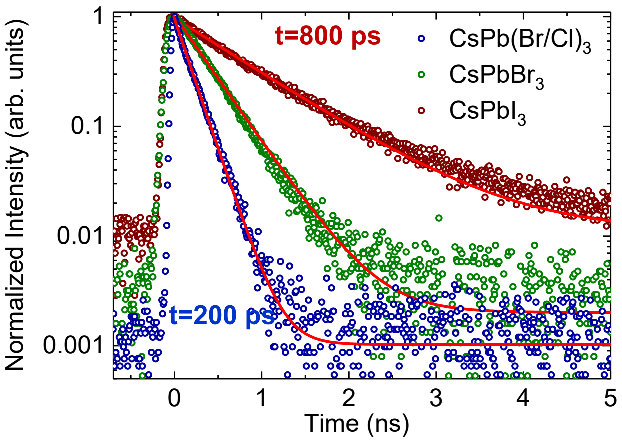
Highly-coherent single-photon emission



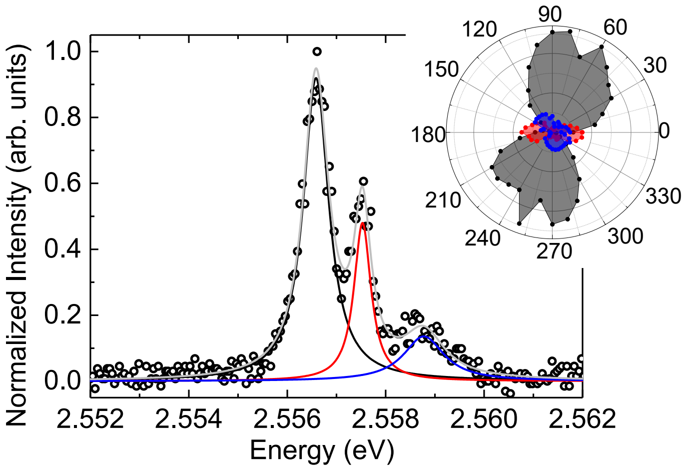
Utzat *et al.,* Science 363, 1068-1072 (2019).

Perovskite NCs as single photon sources

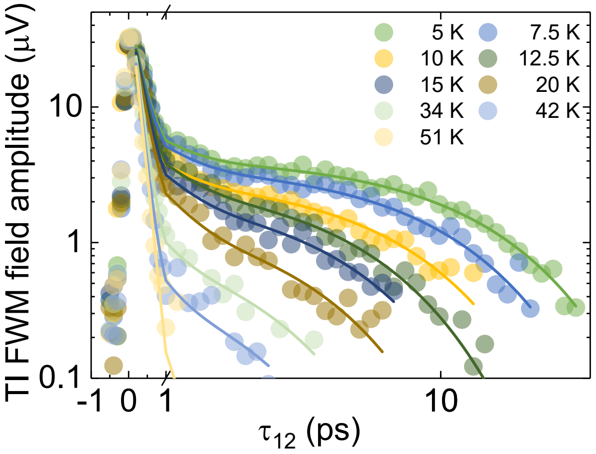
Ultrafast radiative decay



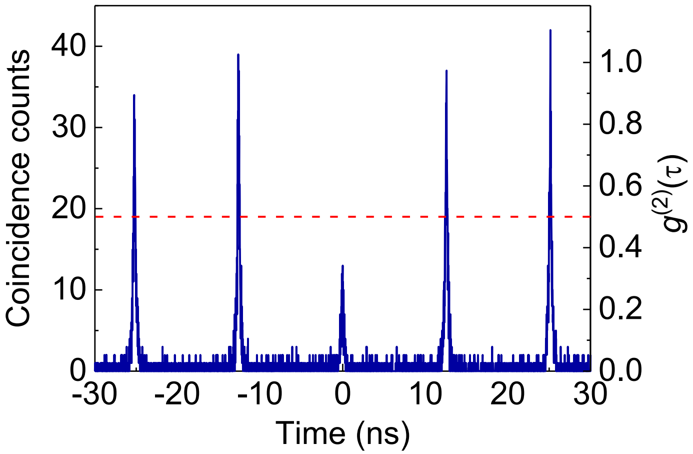
Bright triplet excitons



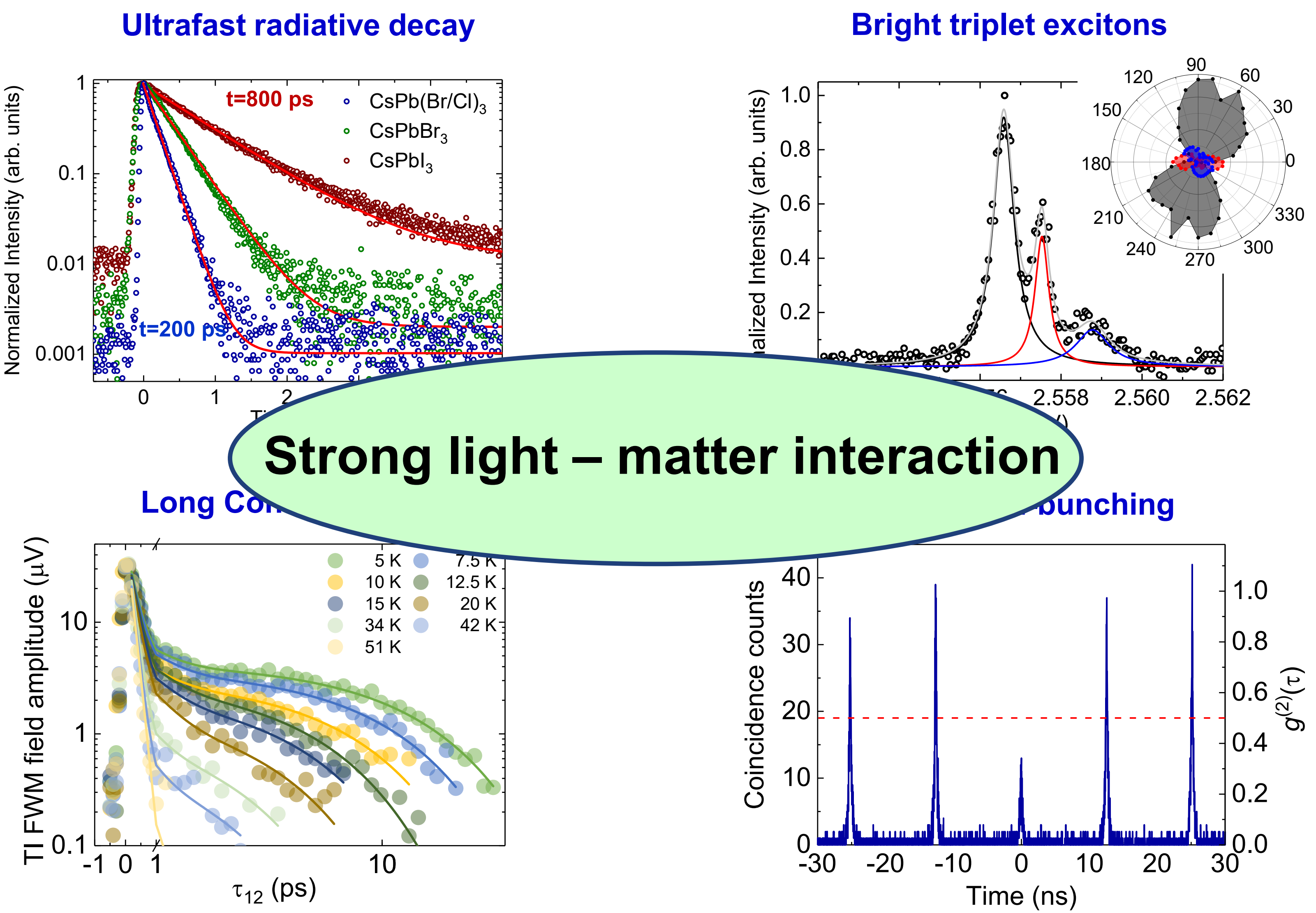
Long Coherence Time



Photon anti-bunching

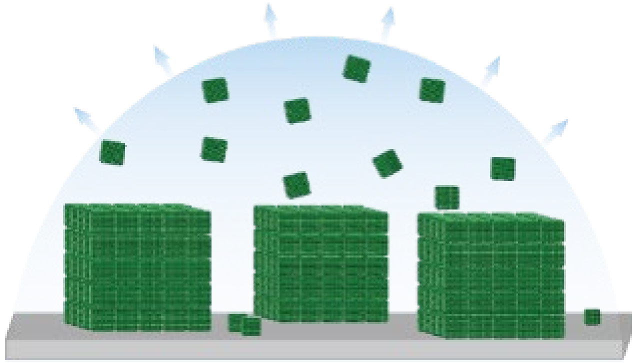


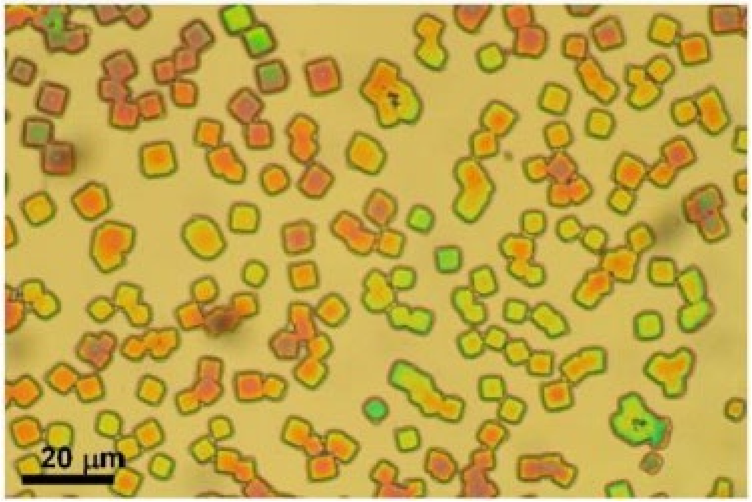
Perovskite NCs as single photon sources

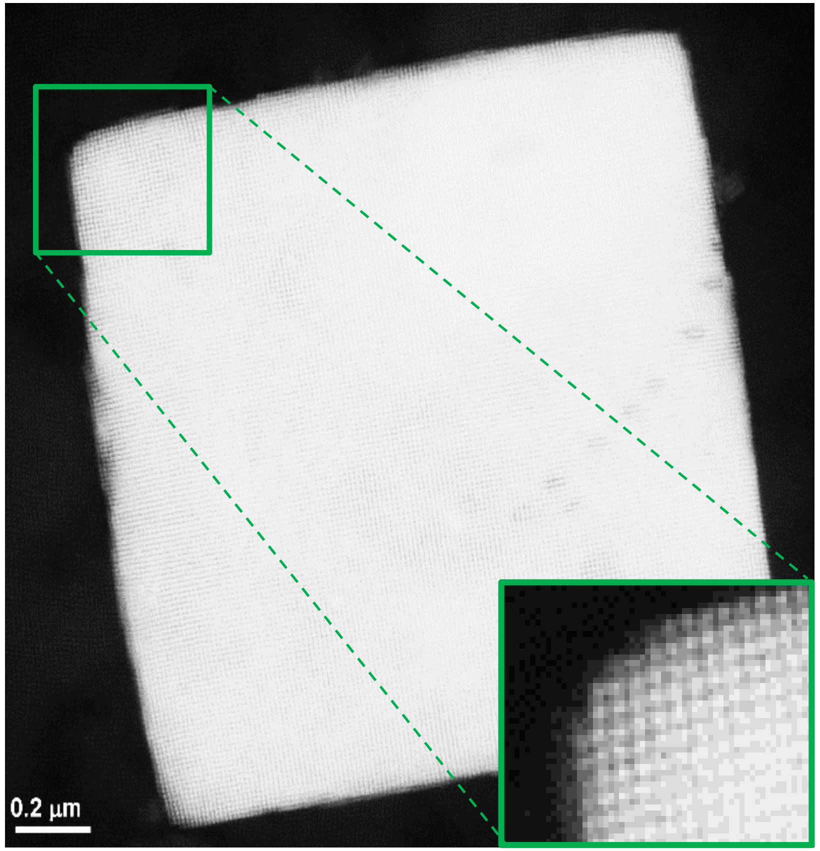


$CsPbX_3$ Perovskite QD superlattices

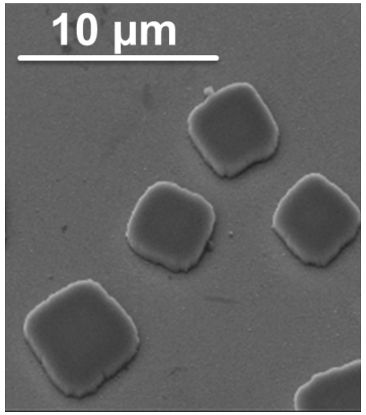
drying-mediated self-assembly







Tilted-view SEM image

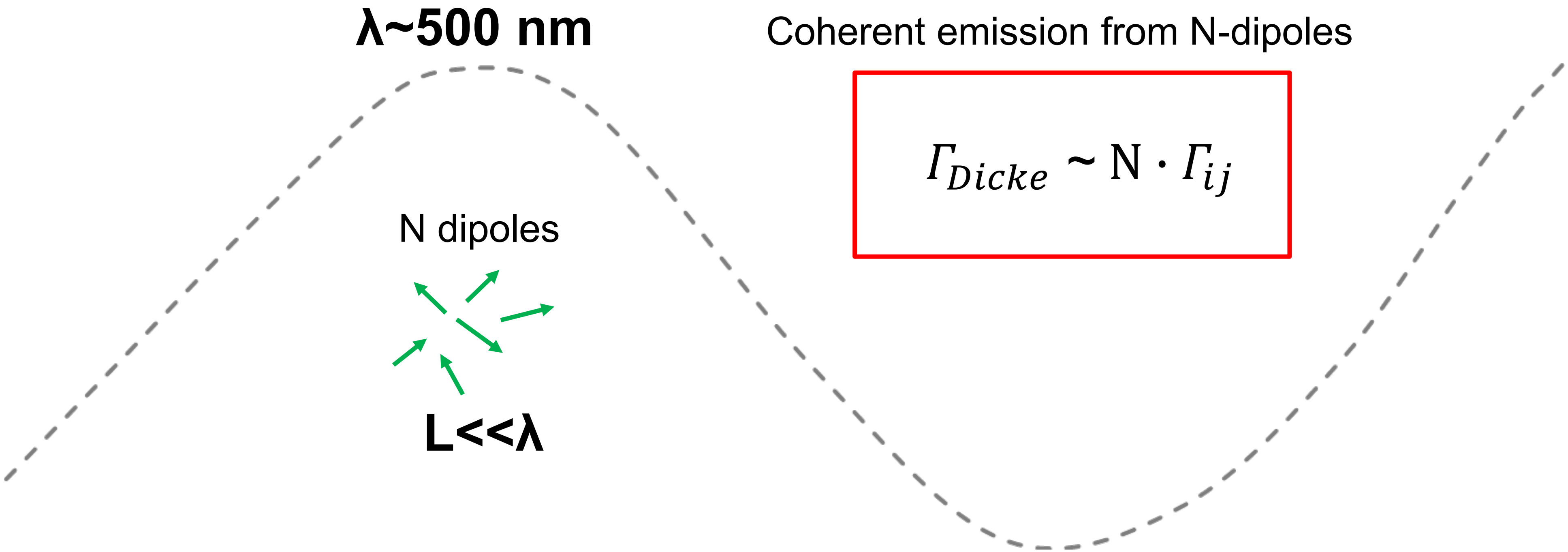


NC superlattices as an excellent experimental platform to explore
collective phenomena in NC solids

Dicke superradiance

"For want of a better term, a gas which is radiating <u>strongly</u> because of <u>coherence</u> will be called 'superradiant'."

— R. H. Dicke (1954)

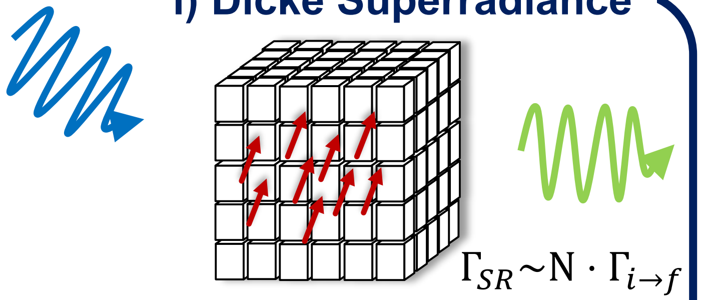


Coherent emission from N-dipoles

$$\boxed{\Gamma_{Dicke} \sim \mathrm{N} \cdot \Gamma_{ij}}$$

Coherent emission from ensembles of emitters

i) Dicke Superradiance



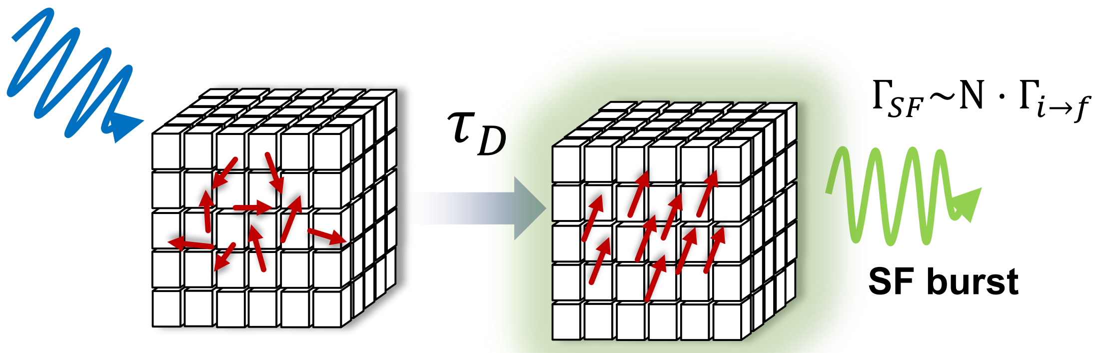
Superfluorescence

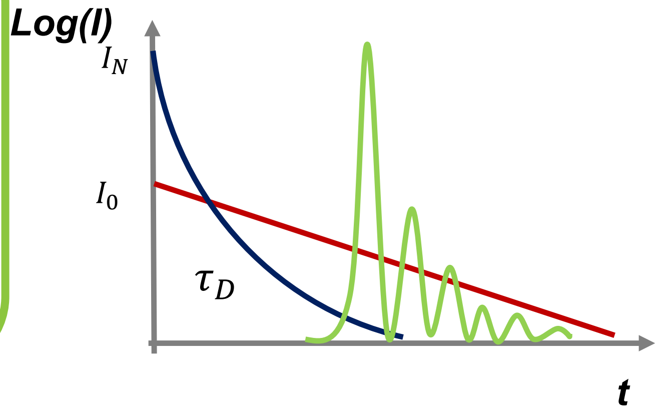
Superradiance

- **Shortening of radiative decay** $\tau_{SR/SF} \sim \tau_R / N$
- **Superlinear increase of intensity** $I \sim N^2$

- **Built-up time** $\tau_D \sim \dfrac{\ln(N)}{N}$
- **Coherent Rabi-type oscillations**

ii) Superfluorescence

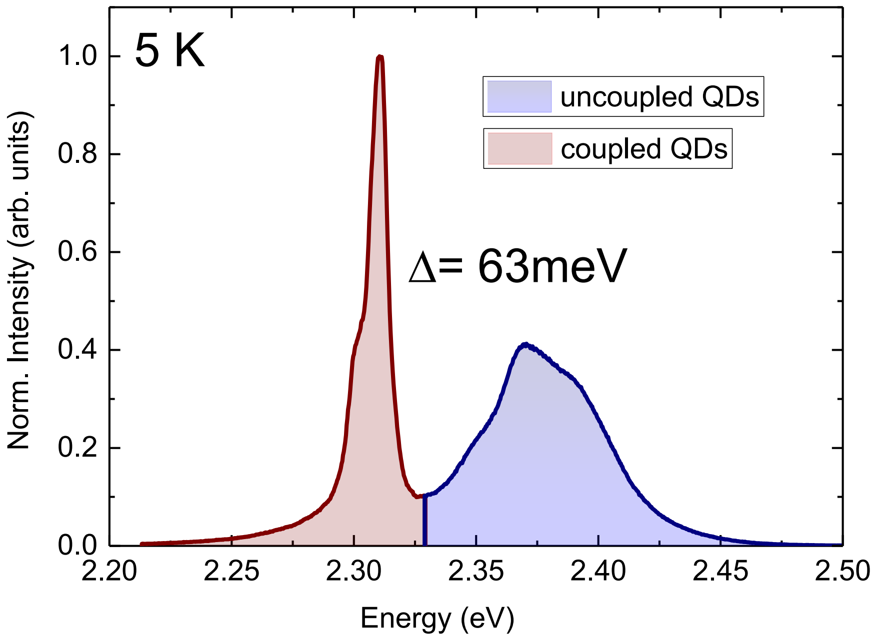




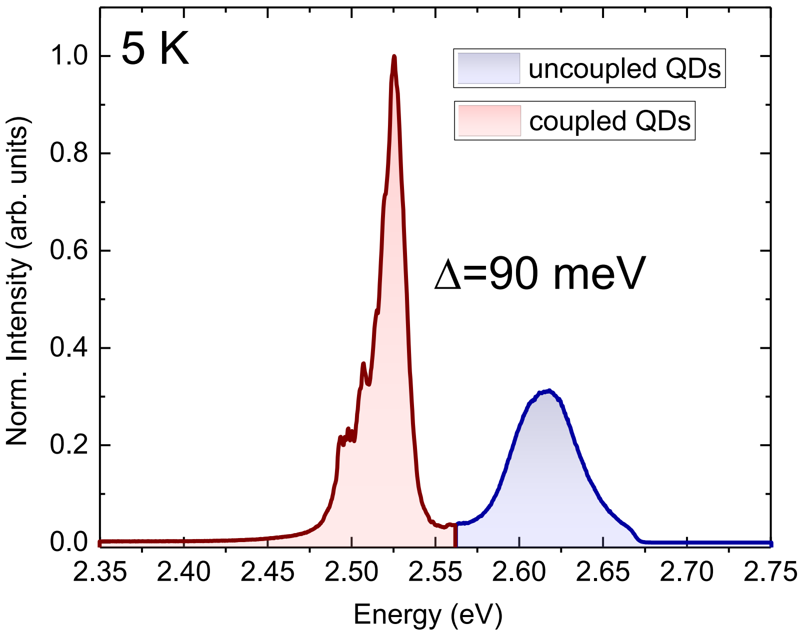
Optical properties of $CsPbX_3$ QD superlattices

μ-photoluminescence experiments

Single $CsPbBr_3$ superlattice PL



Single $CsPb(Br/Cl)_3$ superlattice PL

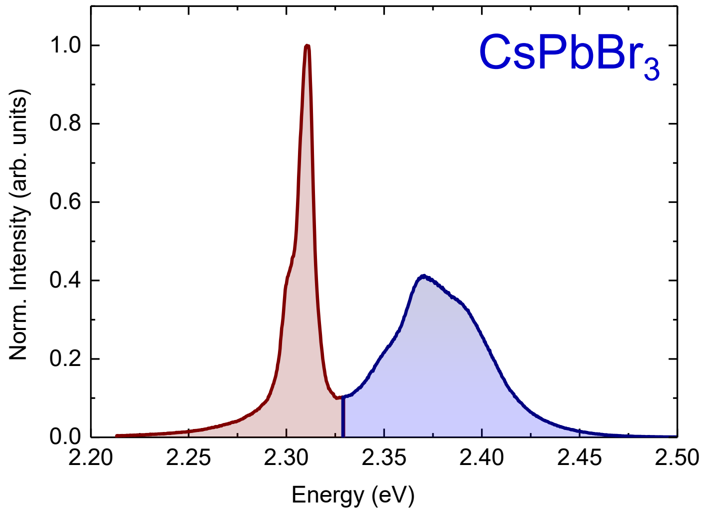


- Redshifted band assigned to coupled QDs (different SF domains)
- Redshift more pronounced in $CsPb(Br/Cl)_3$ QDs, probably due to the enhanced oscillator strength

Rainò *et al.*, Nature 563, 671–675 (2018)

Optical properties of $CsPbX_3$ QD superlattices

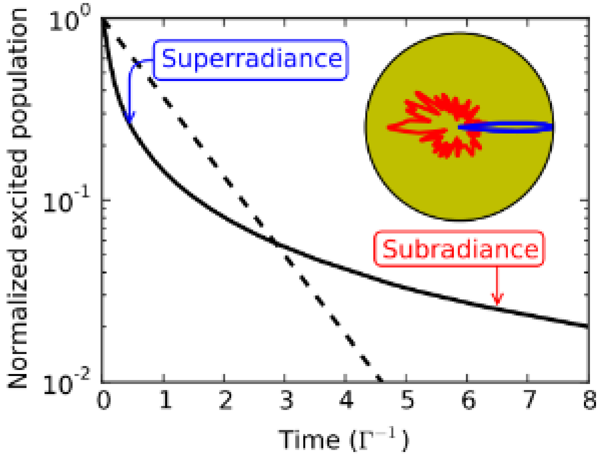
Enhanced radiative rate

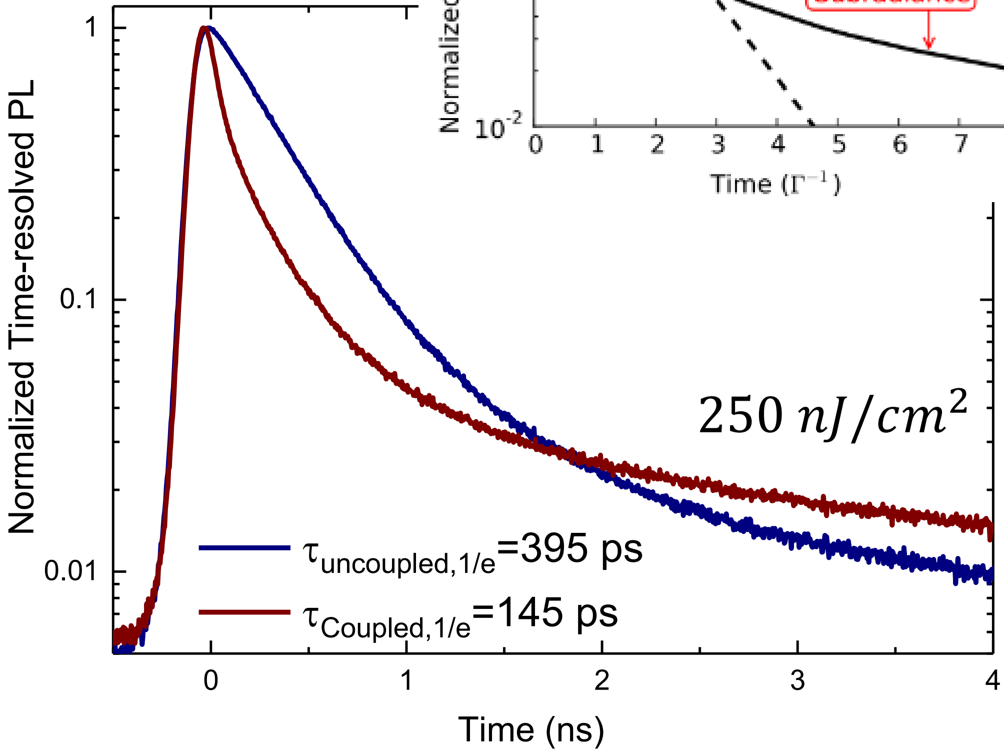


SF decay:
- Highly non-exponential
- Strongly power-dependent

Rainò *et al.*, Nature 563, 671–675 (2018)

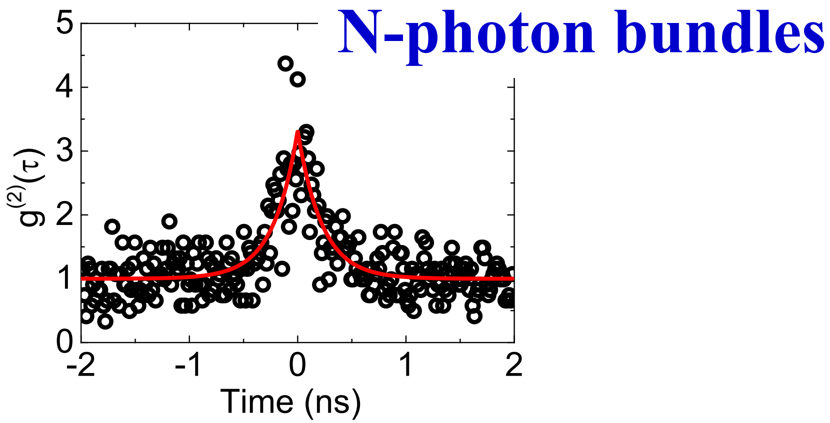
Bienaimé *et al.*, PRL **2012**, 108, 123602

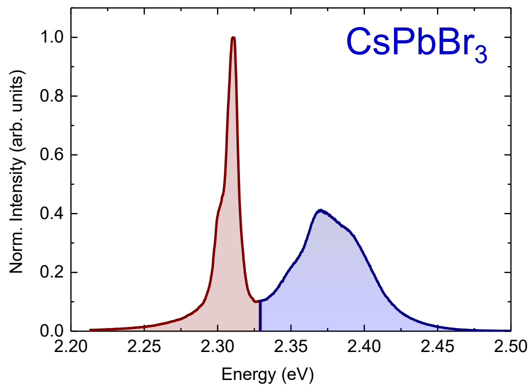




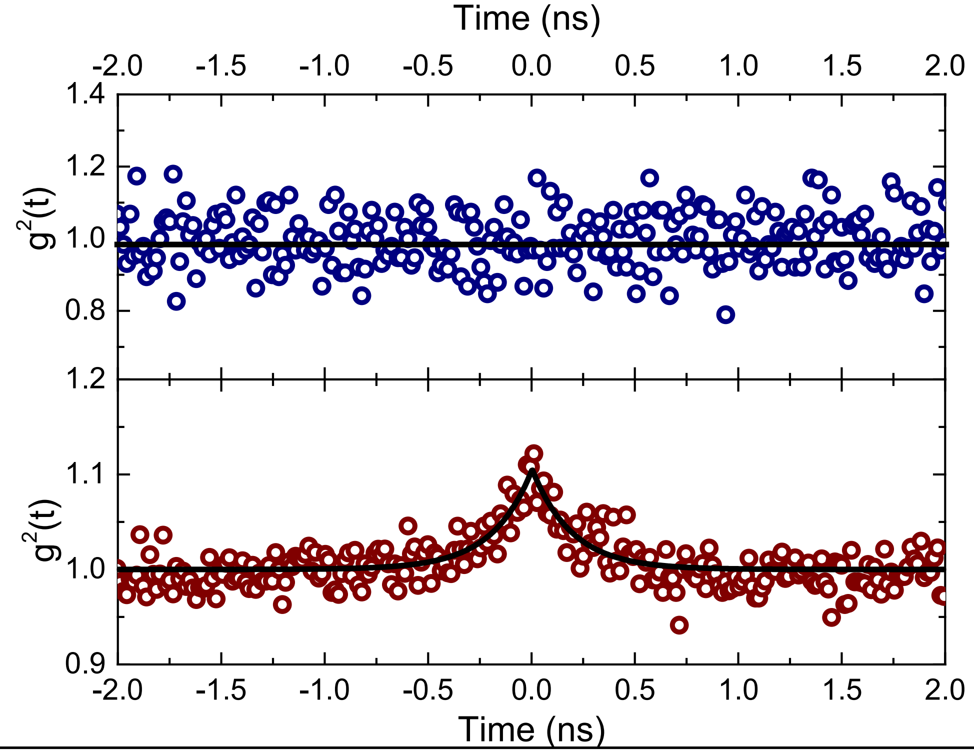
Coherence properties

Second-order coherence measurements



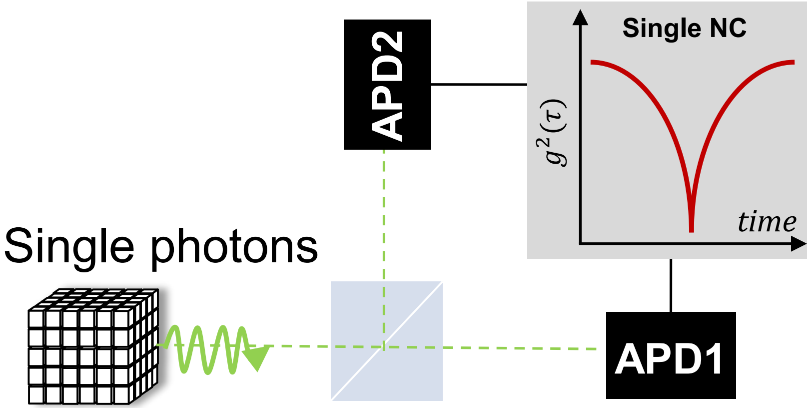


Photon bunching



Hanbury-Brown Twiss setup

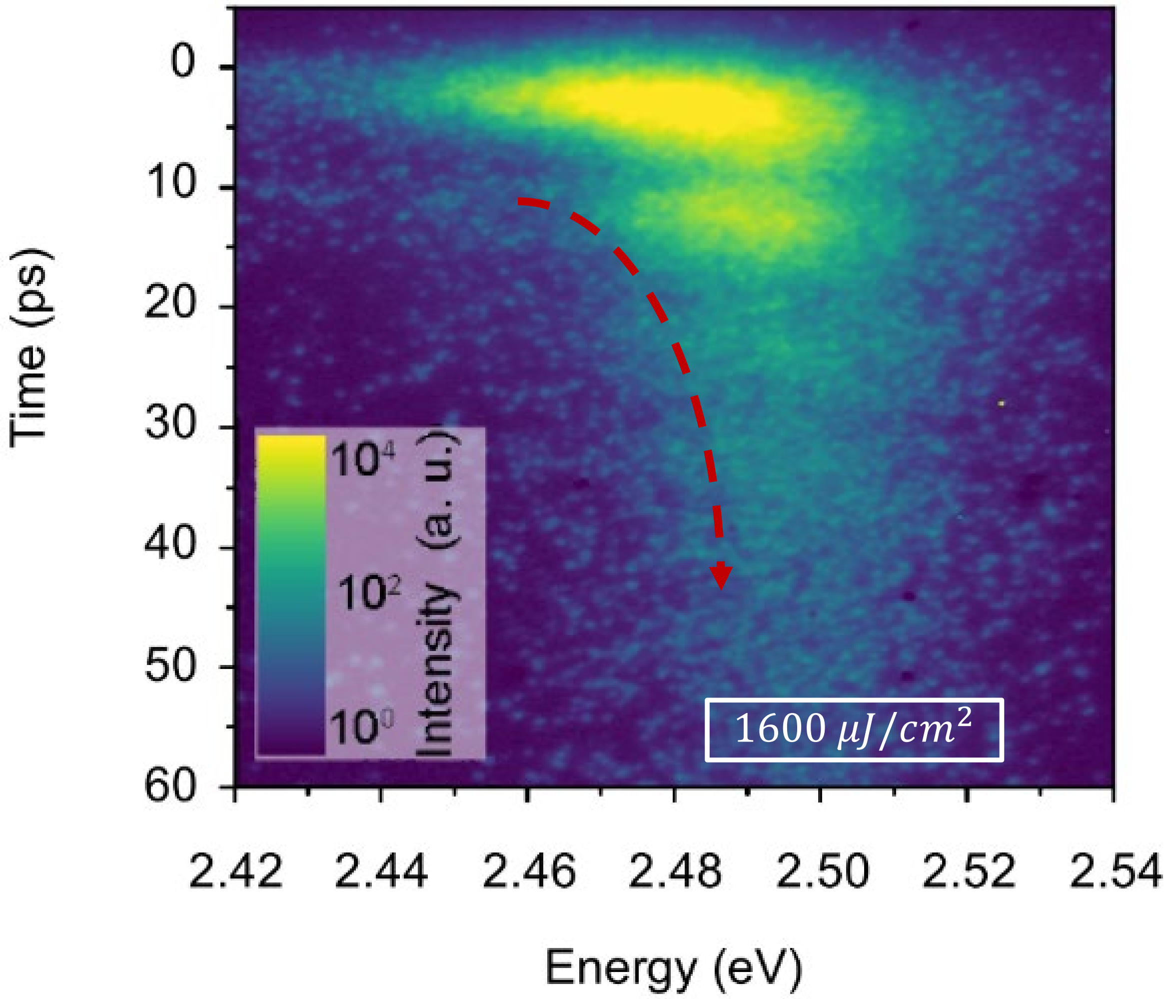
Single photons



Rainò *et al.*, Nature 563, 671–675 (2018)

Time and energy- resolved PL measurements

Streak camera image (time res. 2 ps)



Excitation:
400 nm; 1 KHz

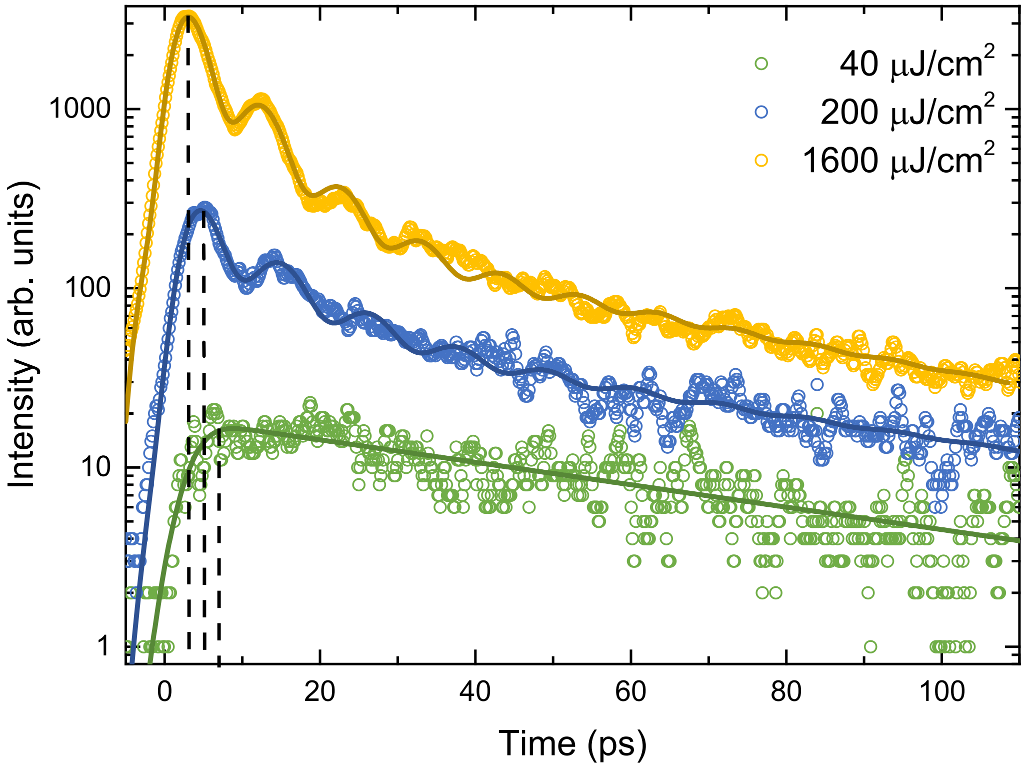
I) Dynamical energy shift during decay

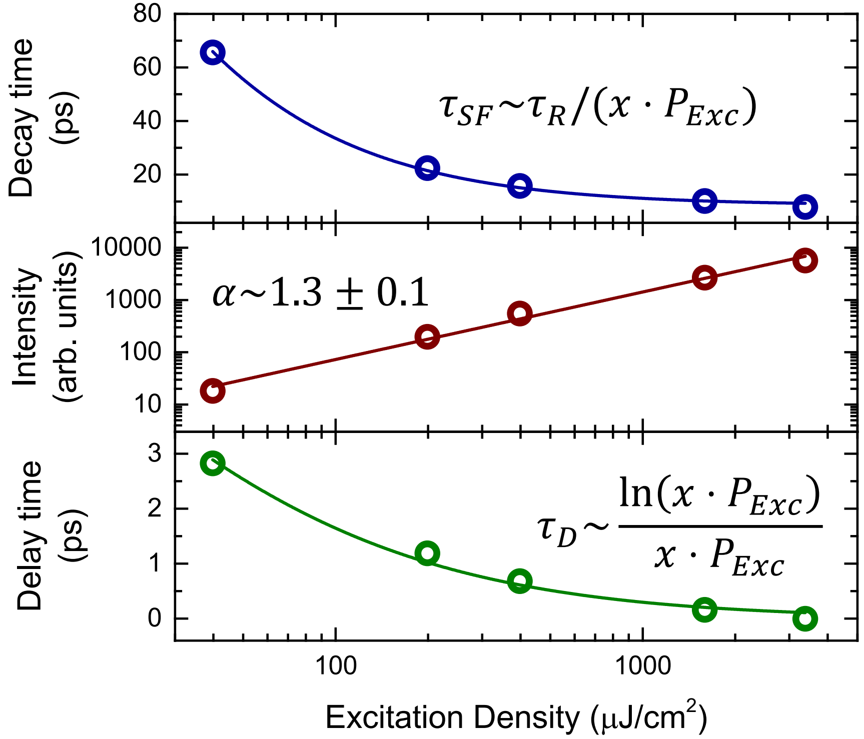
II) Pronounced oscillations in time domain

Rainò *et al.*, Nature 563, 671–675 (2018)

Burnham-Chiao ringing

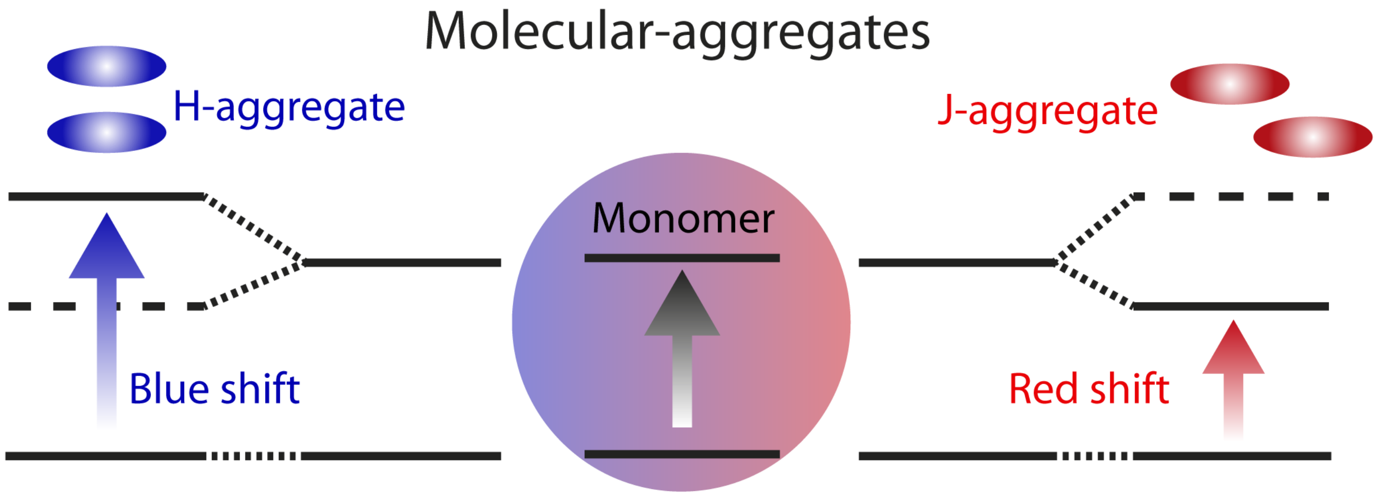
Fit model:
- exponential decay functions
- damped oscillations





Rainò *et al.*, Nature 563, 671–675 (2018)

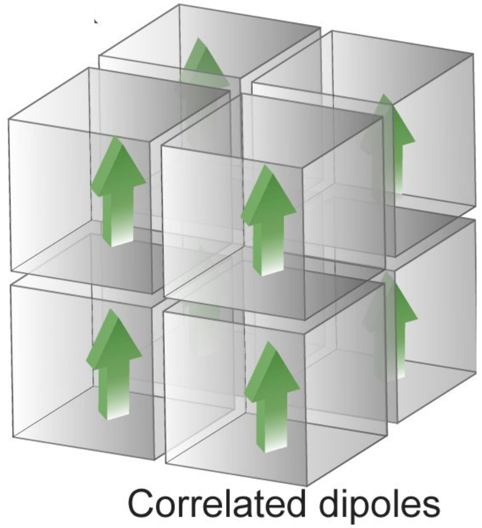
SF in binary SLs



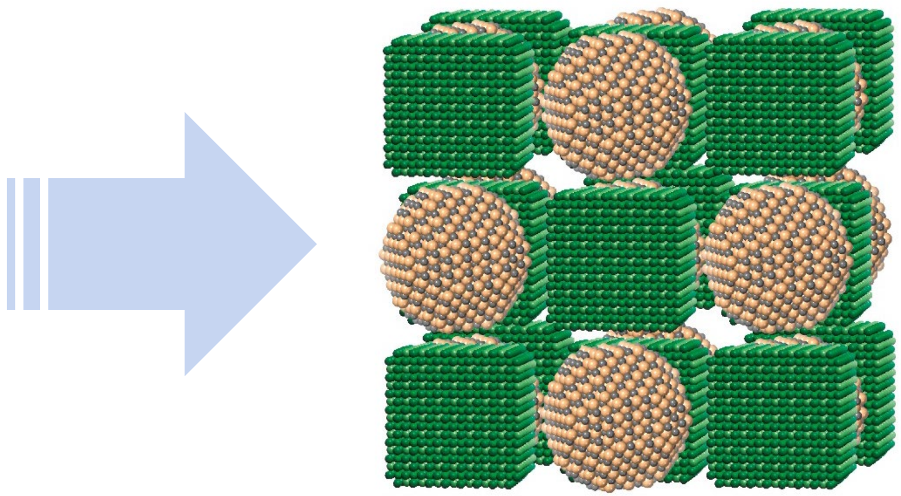
Kasha model
.. and beyond

Acc. Chem. Res. 2017, 50, 2, 341–350

Mono-component SLs



binary SLs



Control NC-to NC distance and mutual orientation

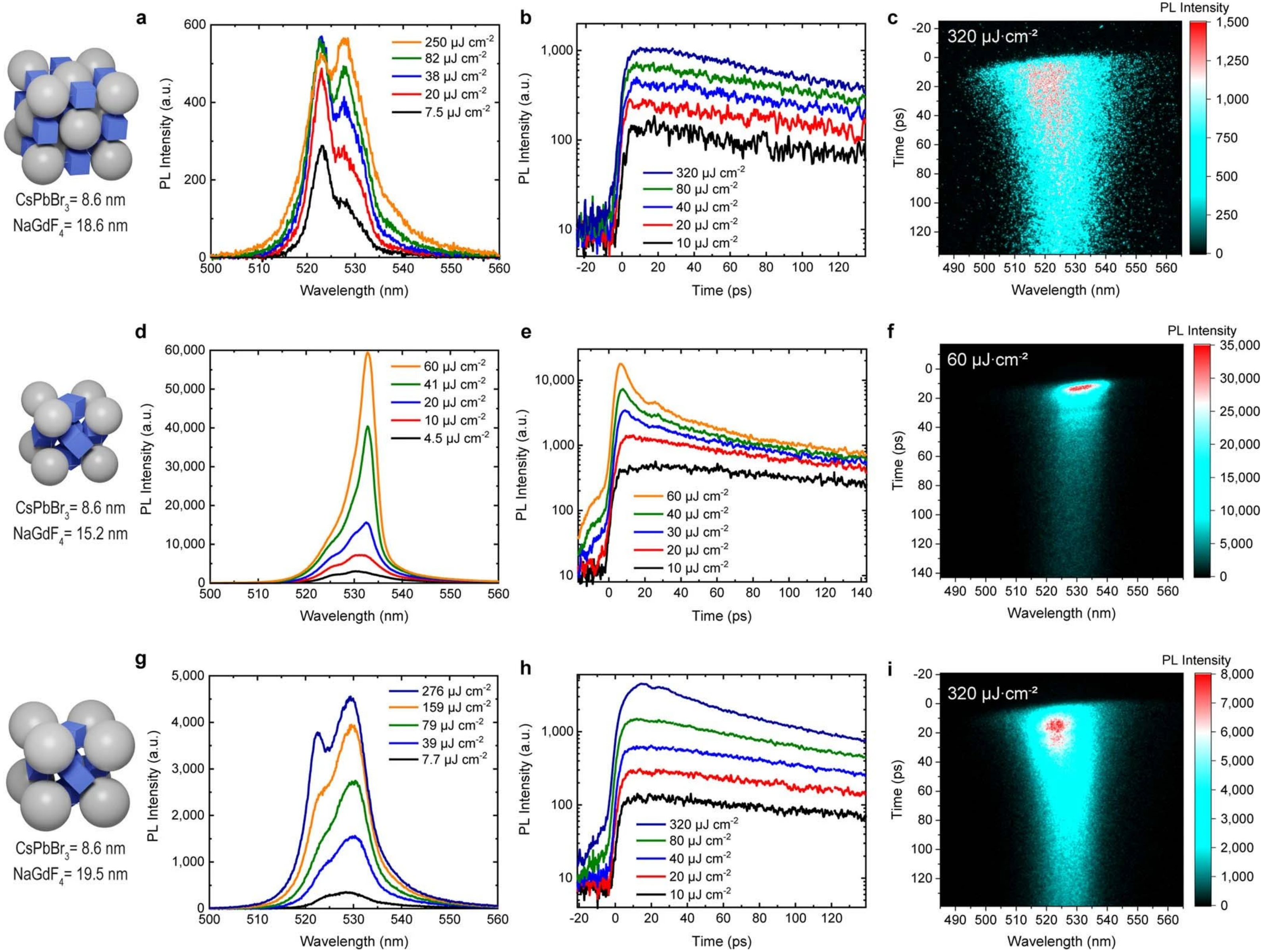
SF in binary SLs

Cherniukh *et al.*, Nature 593, 535–542 (2021)

NC volume fraction
0.0748

NC volume fraction
0.291

NC volume fraction
0.201

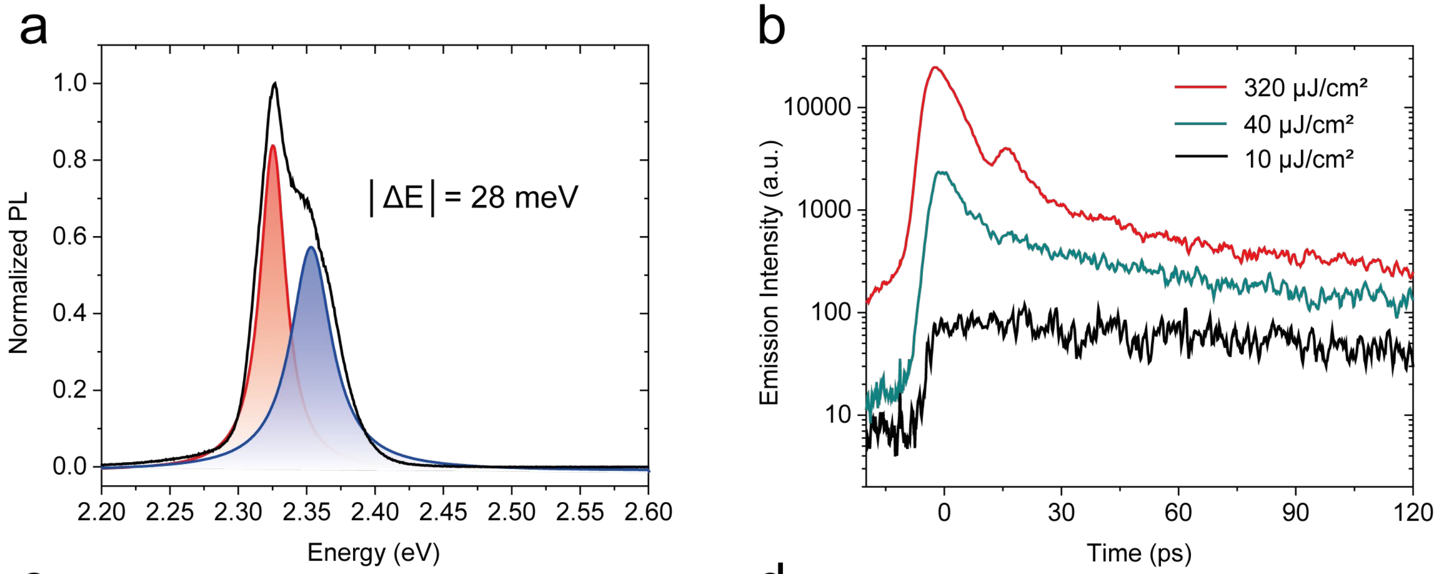


SF in binary SLs

Cherniukh *et al.*, ACS Nano 593, 535–542 (2021)

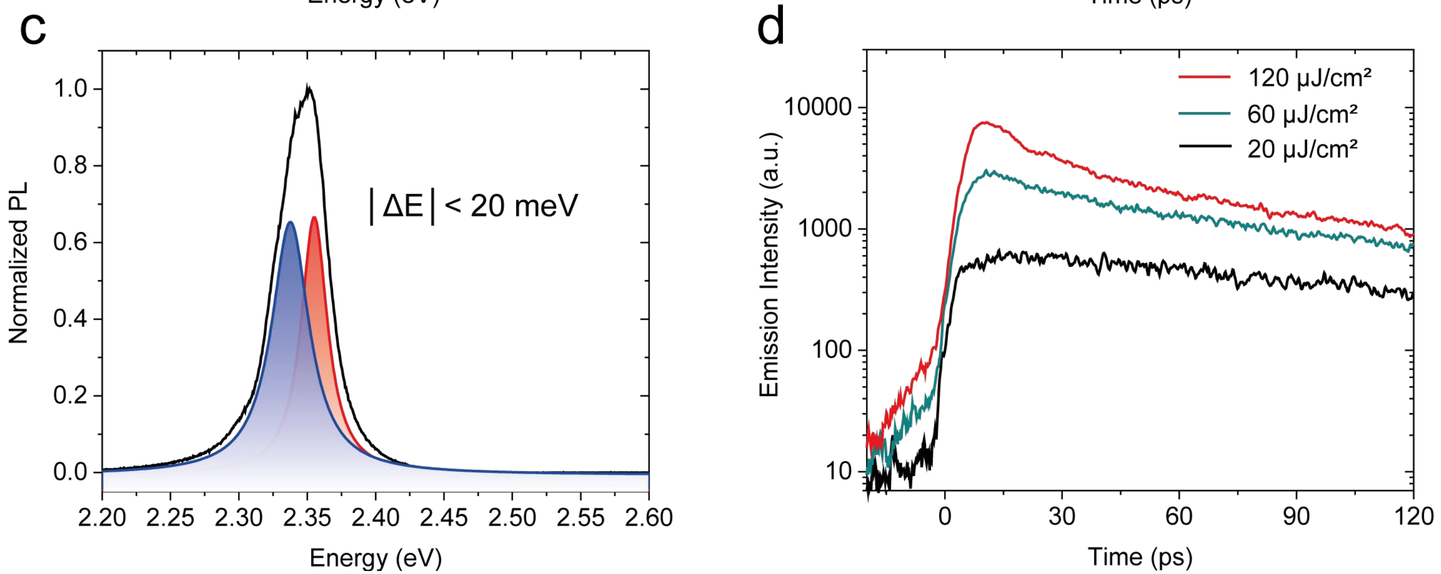
NC volume fraction
0.188

$CsPbBr_3$= 8.6 nm
LaF_3= 9 nm



NC volume fraction
0.136

$CsPbBr_3$= 8.6 nm
LaF_3= 18.5 nm

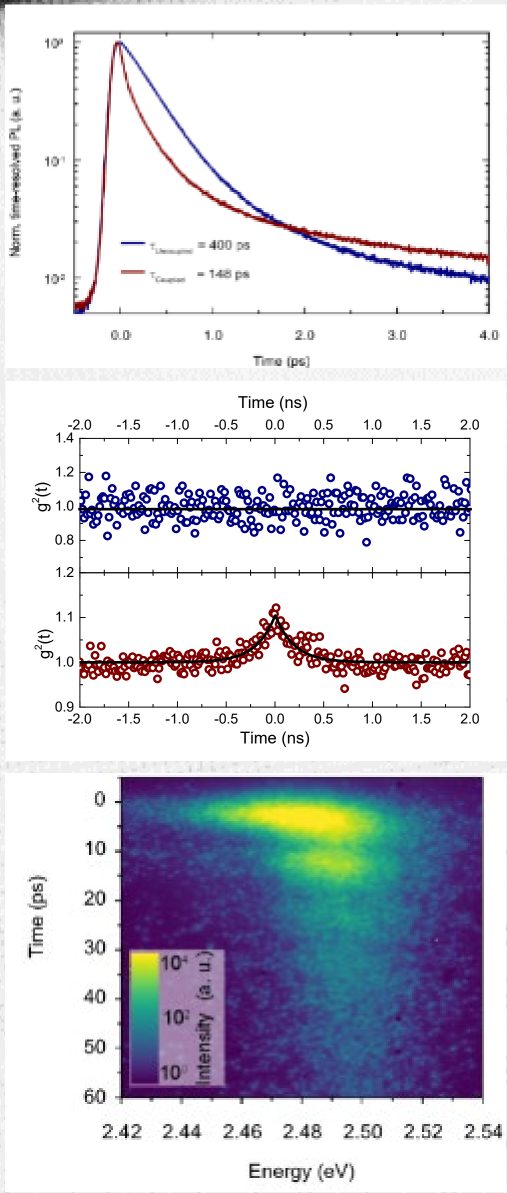


Supefluorescence in QD Supercrystals:

Accelerated Radiative Decay

Photon bunching

Burnham-Chiao ringing



enabling entangled multi-photons quantum light sources…

Conclusions

- Perovskite QDs as single photon source
  - ✓ Bright triplet excitons
  - ✓ Ultrafast decay

- Perovskite QD SLs as time-correlated photon source
  - ✓ Bunching
  - ✓ Rabi-type time oscillations

- Binary SLs as a mean to tune interactions

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Functional Inorganic Materials Group

THANK YOU!