6. Quantum nanostructures

6.3 Doped QDs

Topics of this lecture

- Doping of colloidal QDs
- New optical properties induced by doping
- Case study: the presence of copper in Cu^+:CdSe and $CuInS_2$

Doping

- 1940s: Intentional insertion of impurity atoms into a crystal - basis for the widespread application of SCs in electronic and electro-optic components
- Doping of quantum dots: additional tuning parameters on top of size effects
- But…From the synthesis side, the introduction of a few impurity atoms into a nanocrystal that contains only a few hundred atoms may lead to their expulsion to the surface or compromise the crystal structure!

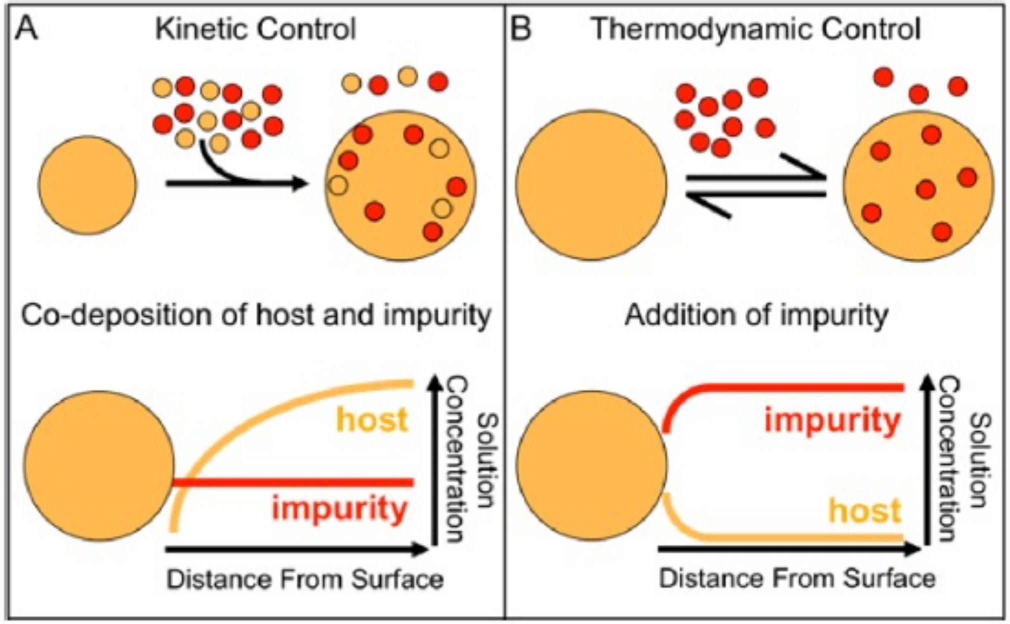
Possible strategies:

1) Remote doping, through the use of binding ligands on the nanoparticle surface (which can donate carriers)

2) The introduction of dopant precursors at specific stages of nanoparticle growth

Doping in QDs

Vlaskin et al., *JACS* **2013**, *135*, 14380−14389



Addition during growth

- Dopants must compete with host cations for available surface binding sites and nanocrystal surfaces must compete against surfactant ligands for impurity binding

- These surface competition reactions typically disfavor doping

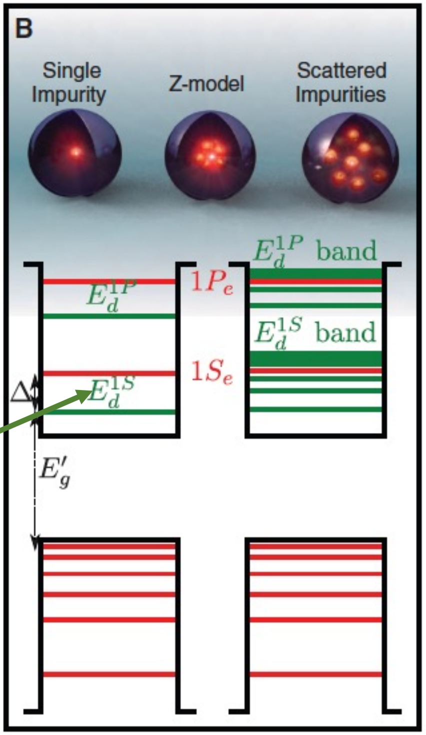
Post-synthetic cation exchange

- Optimize the concentrations of dopants to host atoms (not in growth conditions anymore!)

- Dopants are internalized via diffusion through the crystal ions

Doping in QDs

- Adding a single impurity atom to a QD with a diameter of 4 nm (~ 1000 atoms) leads to a nominal doping level of 7 x 10^{19} cm^{-3}
- In a bulk SC this is already well within the heavily doped limit, where metallic (“degenerate”) behaviour is expected
- The impurities interact with each other and an impurity sub-band emerges near the edge of the respective band
- Often, tail states (Urbach tails) also develop as a result of distortions in the crystal structure and E_g is narrowed



E’$_g$ = gap in the doped QD

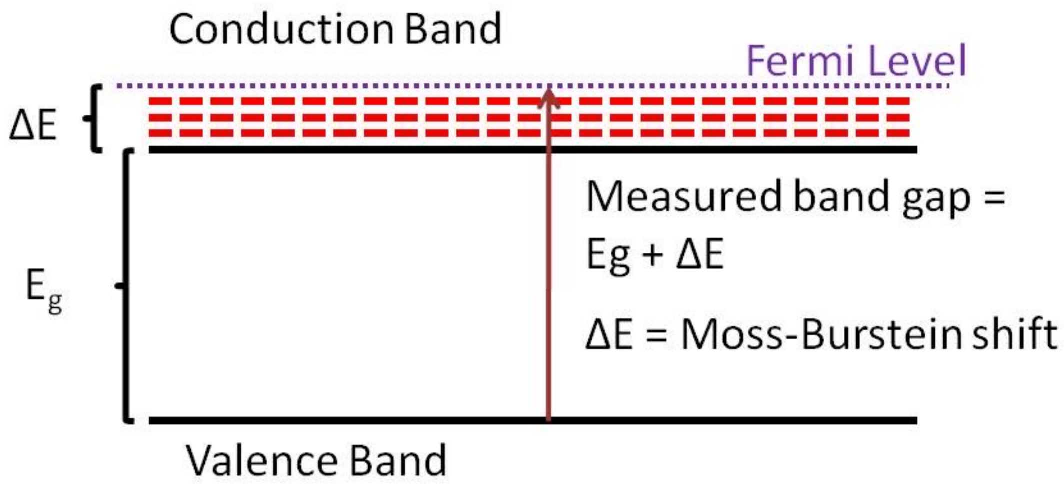
Impurity levels

Impurity levels develop into impurity bands as the number of impurities increases

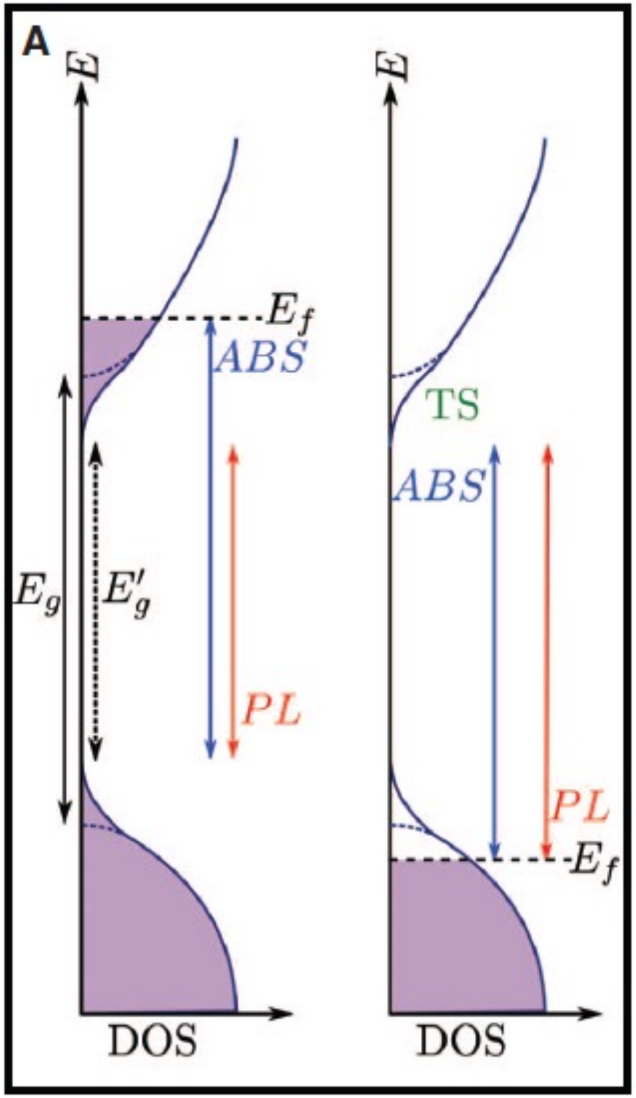
Mocatta et al., *Science*, **2011**, *332*, 77-81

The Moss-Burstein shift

Mocatta et al., *Science*, **2011**, *332*, 77-81



https://commons.wikimedia.org/w/index.php?curid=17883460



n-type:

- The absorption is blue-shifted as a result of conduction band-filling by donated e-

- The emission emanating from the bottom of the CB is red-shifted

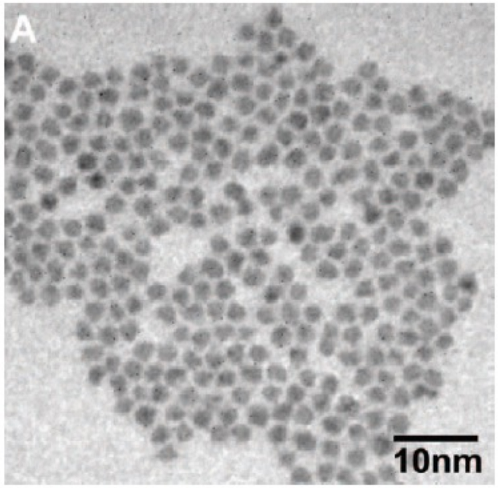
p-type:

- Red shift of both abs and PL

Example: Doped InAs QDs

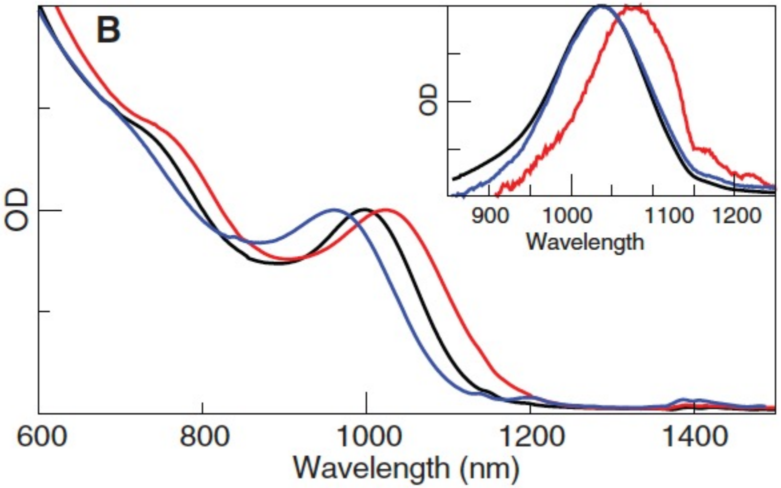
For low amount of dopant atoms, no metal regions are detectable by TEM

→ The impurity atoms are dispersed



Cu doping **Ag doping**

Au doping: No shift observed



Mocatta et al., *Science*, **2011**, *332*, 77-81

The three impurities lead to qualitatively different effects on the optical spectra and hence on the electronic properties of the doped NCs

Case study:

Copper-containing nanocrystals

Copper phosphors (bulk SC)

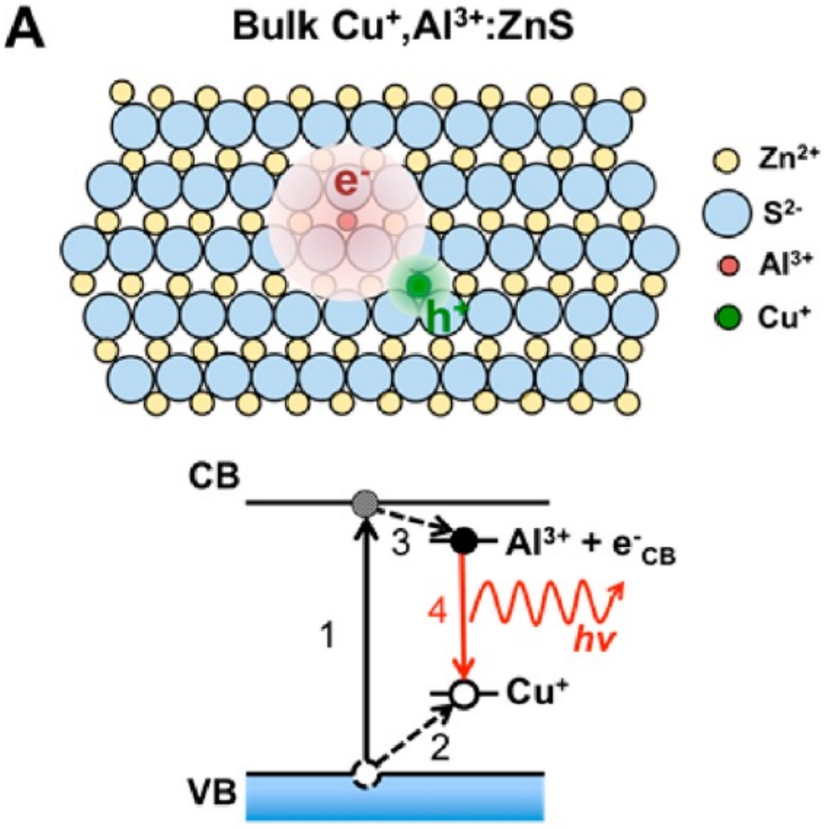
http://www.johngineer.com/blog/?p=648

Luminophore $\longrightarrow$ **ZnS doped with Cu, Al**

Copper phosphors (bulk SC)

Knowles et al., *Chem. Rev*. **2016**, *116*, 10820-10851

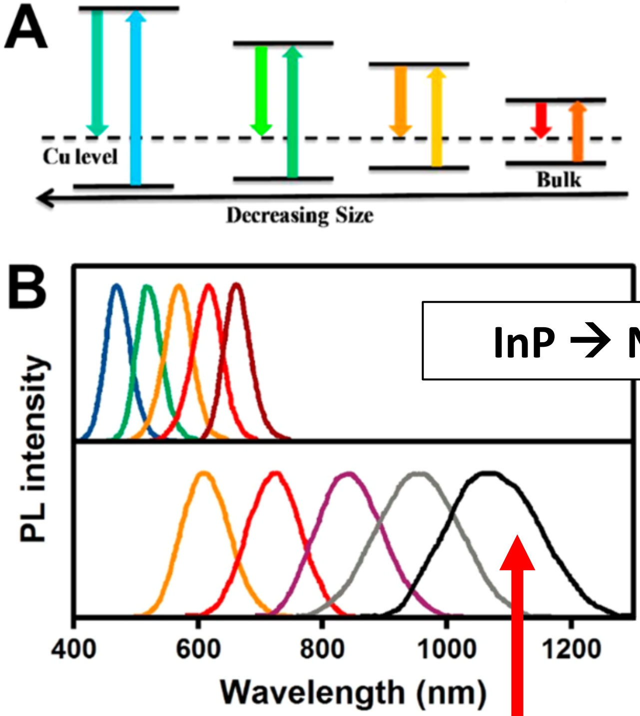
- The specific luminescence feature that is observed depends primarily on the ratio of **activator (Cu^+)** to charge-compensating **coactivator (e.g., Al^{3+})** ions
- Both are randomly distributed over substitutional lattice sites
- Strong **electron–phonon coupling** makes the PL much broader than the host's band-edge emission
- In addition, **different intrapair distances** or donor-electron binding energies causes further inhomogeneity in both the luminescence bandshape and the luminescence decay time



PL can exceed minutes in bulk and is responsible for the characteristic afterglow!

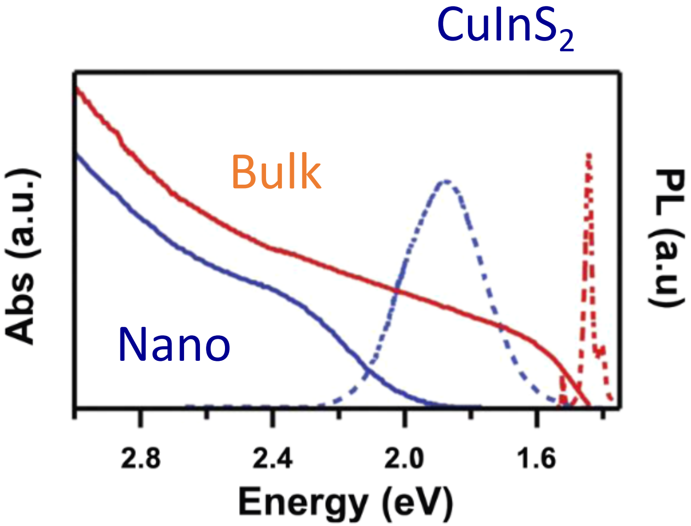
What happens when we move to the nanoscale?

Copper-containing nanocrystals



InP → Narrow

Cu^+:InP
→ Very broad PL

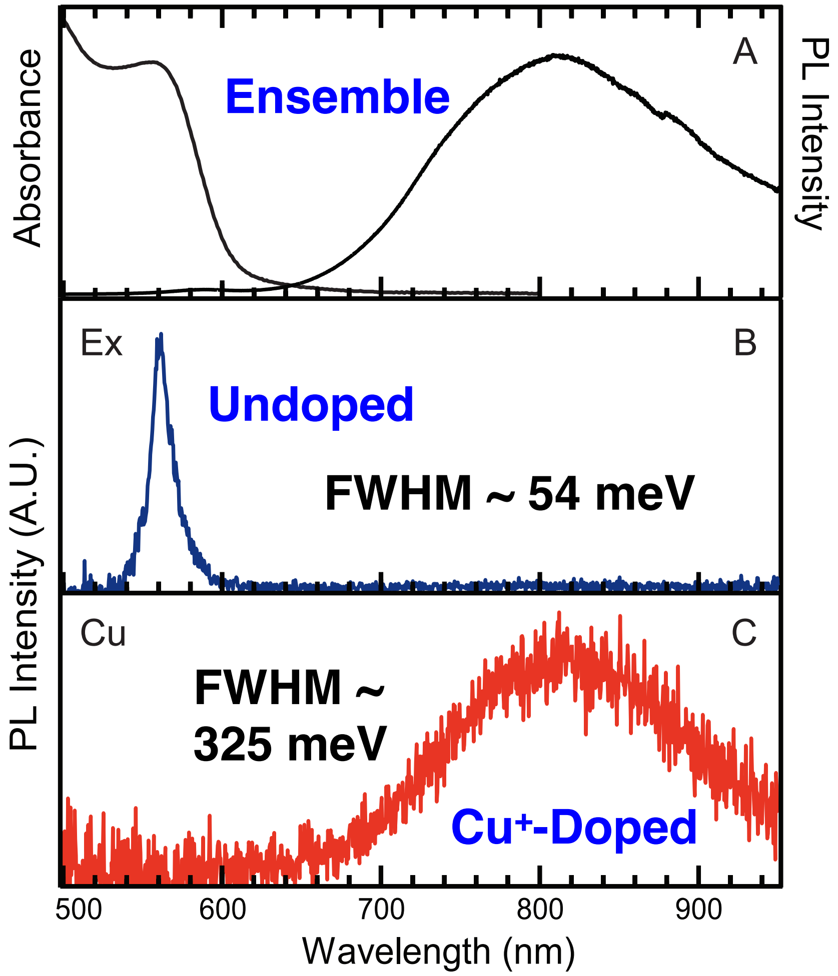


- Large shift between absorption edge and PL: **Stokes shift**
- Reabsorption of PL in the material is minimized: Good for lasers and luminescent solar concentrators

Knowles et al., Chem. Rev. 2016, 116, 10820-10851
Knowles et al., J. Am. Chem. Soc. 2015, 137, 13138-13147.

Single-particle photoluminescence

Cu^+:CdSe



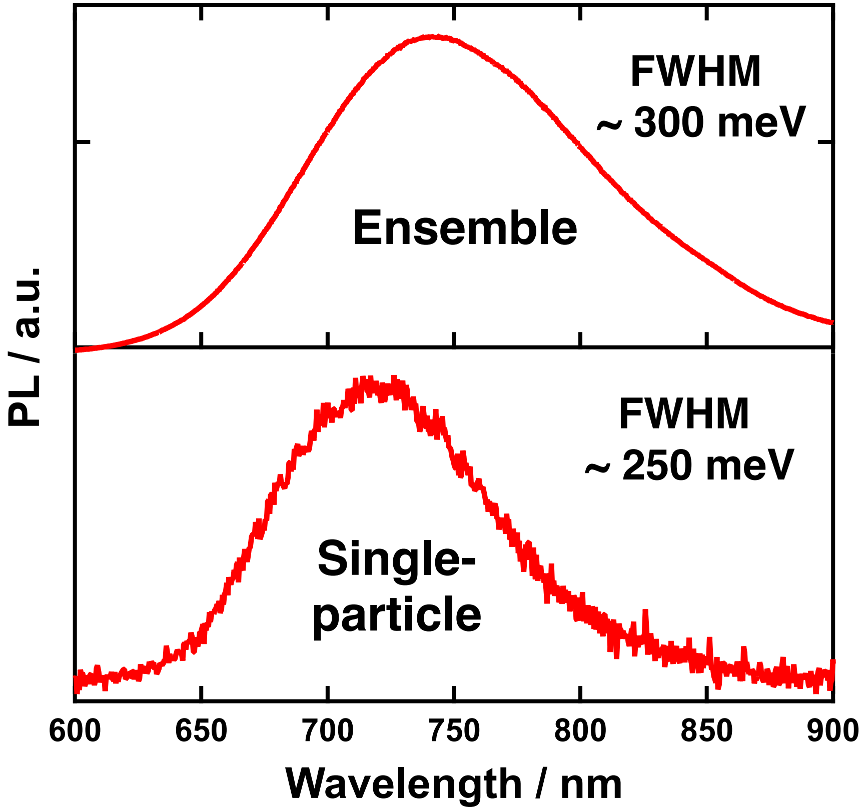
- The broad PL is an **intrinsic property** of such systems and is not due to a large size distribution!
- At 0.6% Cu^+, the average number of Cu^+/NC is about two
- A Poissonian distribution of Cu^+ among the ensemble of nanocrystals results in ~14% of the NCs possessing no copper
- Distribution of energies of Cu^+ levels due to differences in local environments, especially at the interface **+** distortion around Cu^+ (Jahn-Teller effect, mechanism of symmetry breaking)

Whitham et al., *Nano Lett.* **2015** *15* (6), 4045-4051

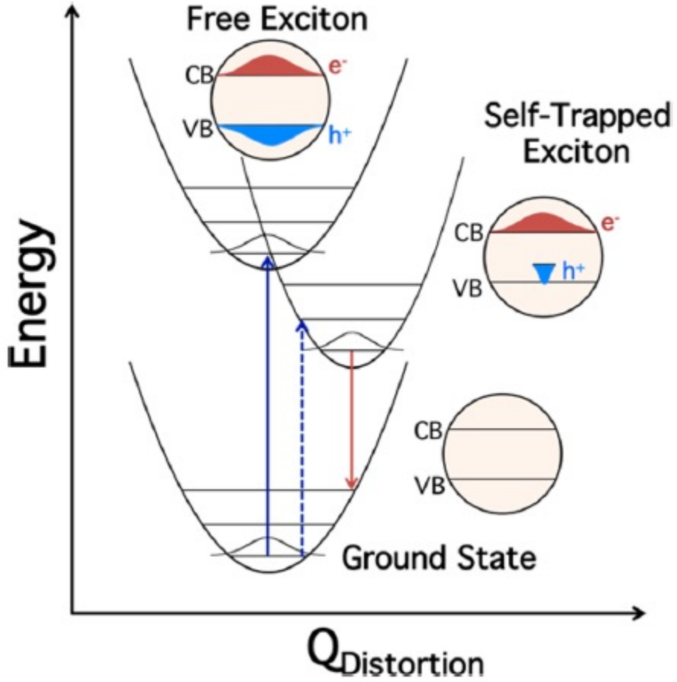
Single-particle photoluminescence

$CuInS_2/CdS$

Data: Courtesy of P. Whitham



Knowles et al., *JACS,* **2015**, 137, 13138–13147

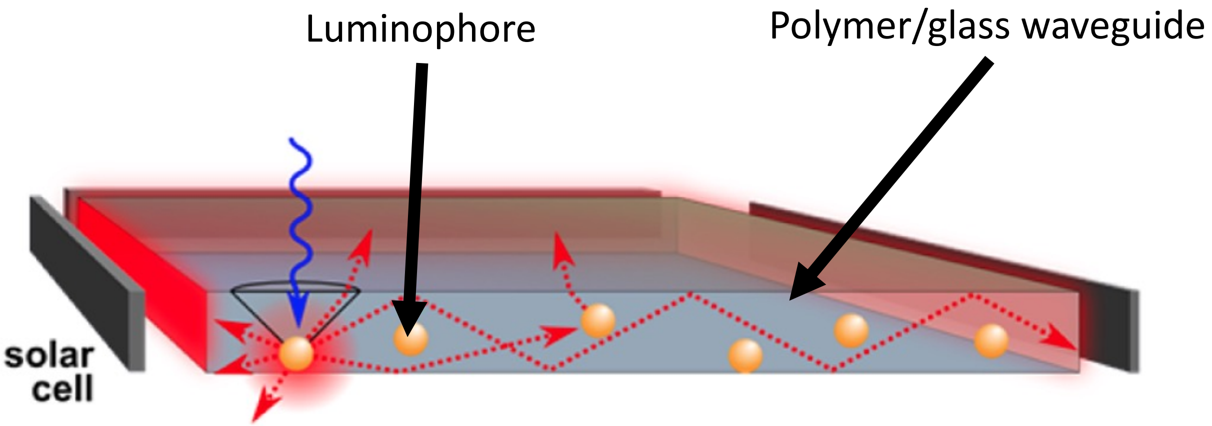


- Self-trapping is due to the h^+ being stabilized by a local lattice distortion
- Likely involves Jahn−Teller effect, which is particularly strong for Cu^{2+}

- The broad PL is an intrinsic property of such systems and is not due to a large size distribution!

Why is a broad PL interesting?

Luminescent Solar Concentrators

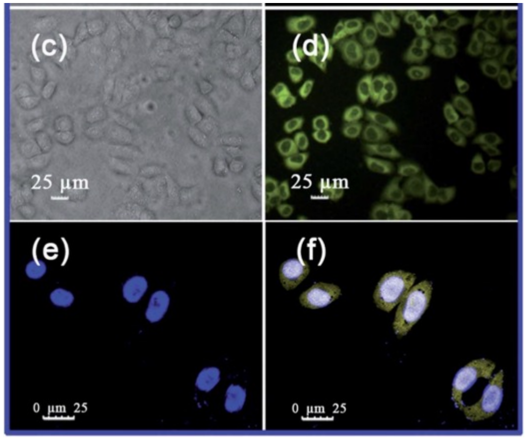


Bradshaw, Knowles, McDowall, Gamelin, Nano Lett. 2015, 15, 1315-1323

- Strong, broad absorption throughout the solar spectrum
- High quantum yield, photostable
- $E_{PL} > E_g$
- No reabsorption (minimum overlap between absorption and PL spectra)

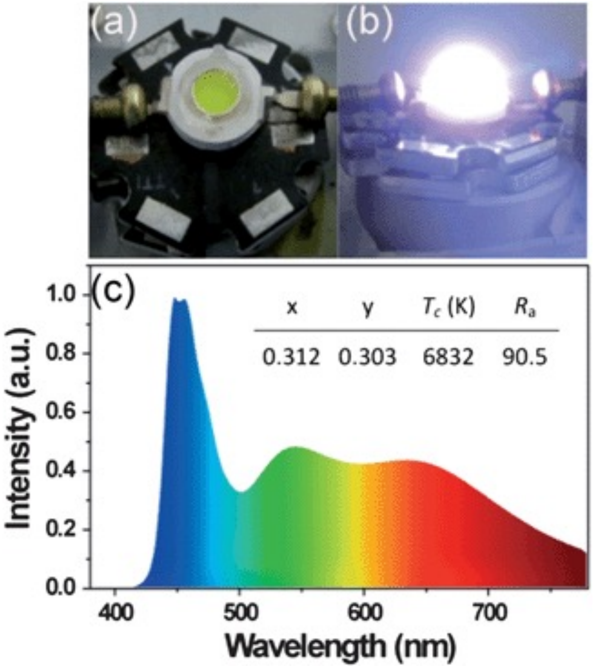
Why is a broad PL interesting?

In Vivo Imaging



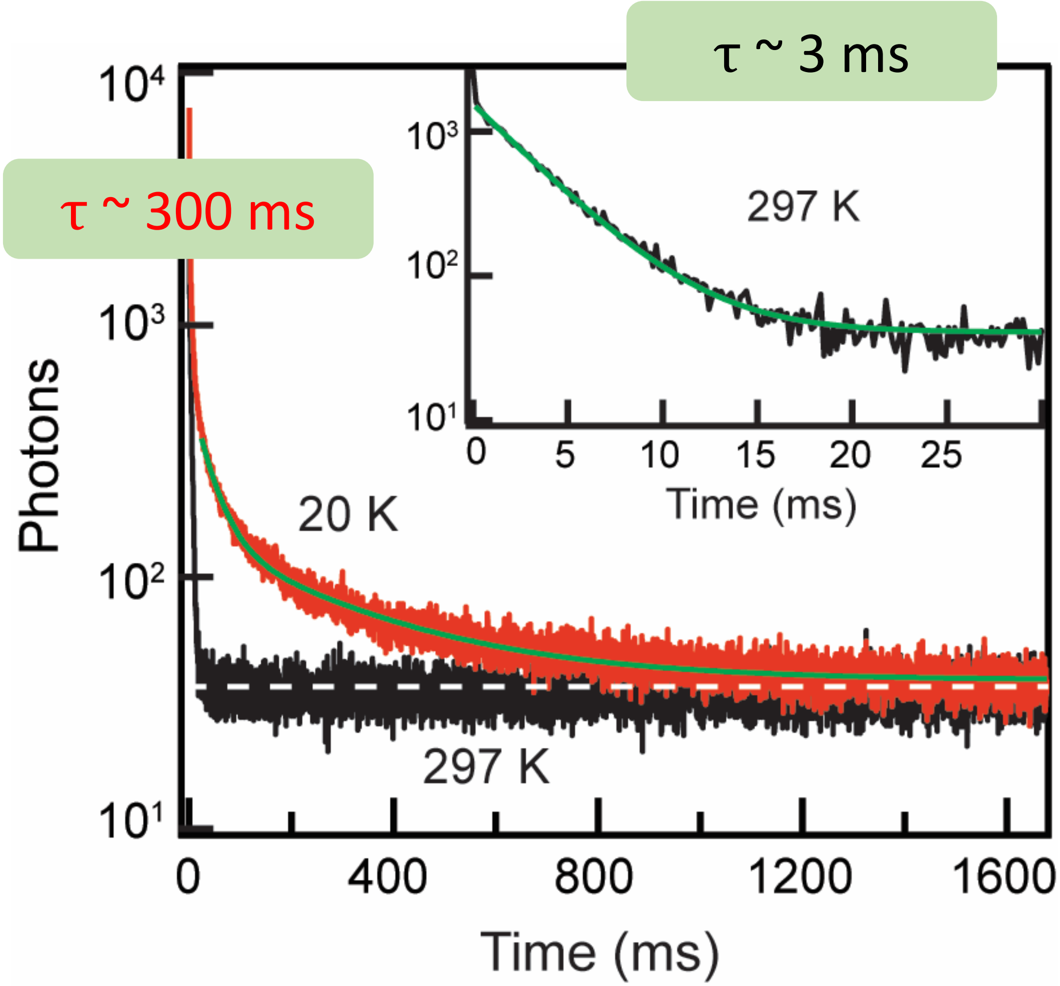
Chen, Zhong, Wang, Liu, Zou, Nanoscale 2013, 5, 3514-3519.

White LEDs



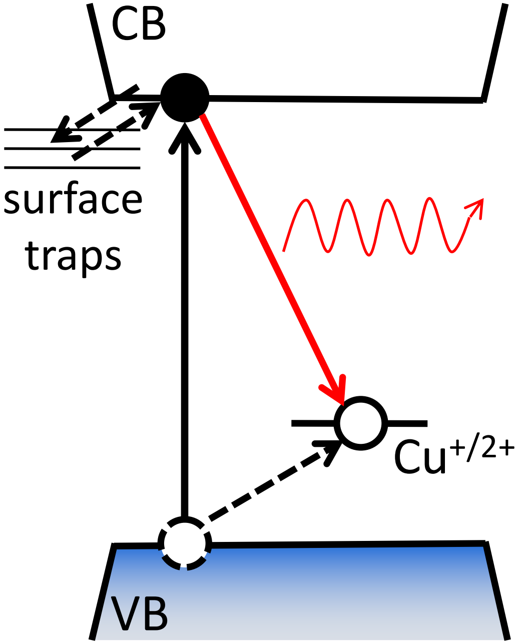
Jiang, Song, Wang, Ye, Wang, Zhang, Yang, Xia, Zhu, Xu, Mater. Chem. B 2015, 3, 2402.

Delayed luminescence in Cu^+:CdSe



τ ~ 300 ms

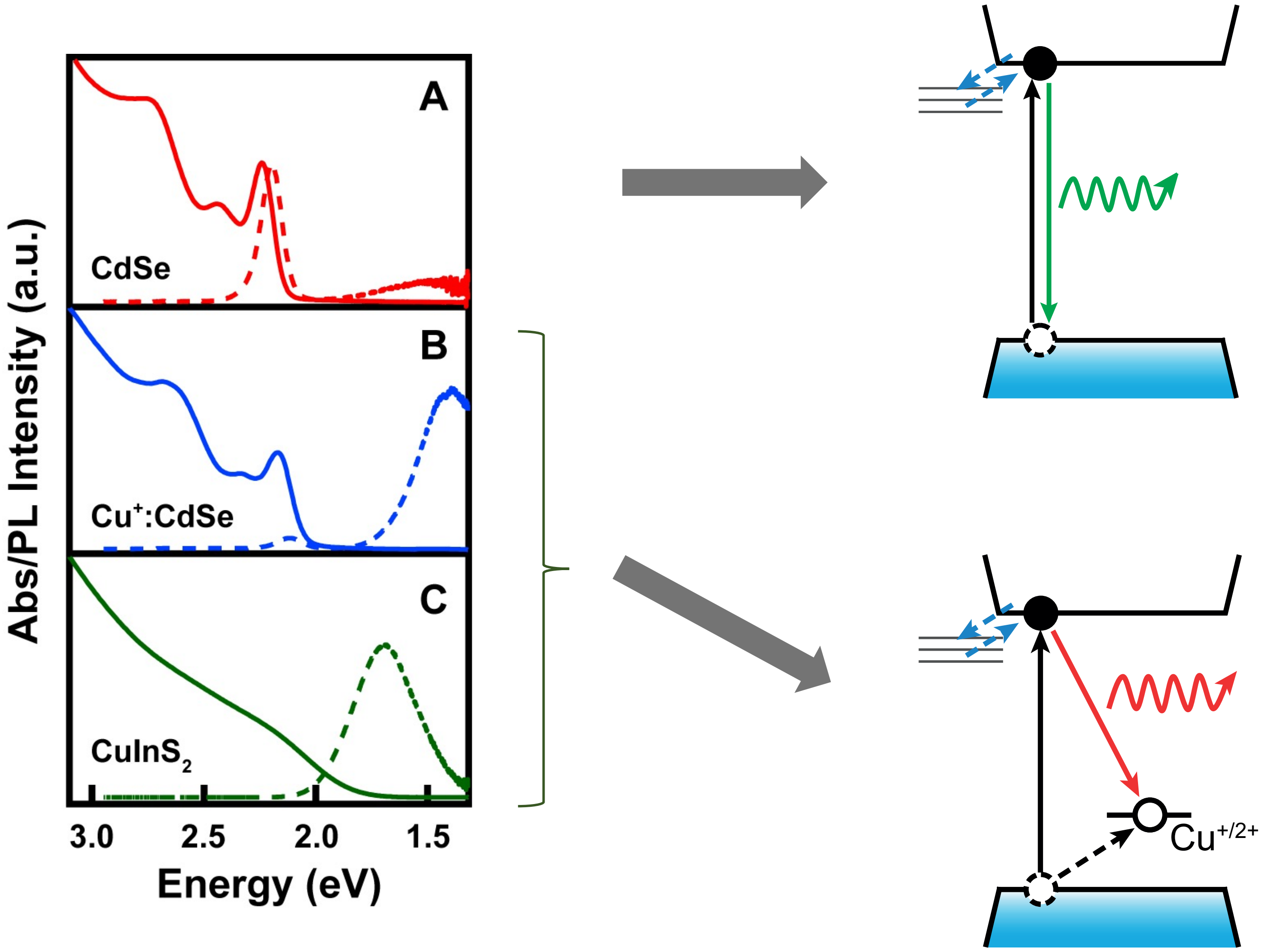
τ ~ 3 ms



Hypothesis:
Surface traps reversibly intercept $e\text{-}_{CB}$
Long-lived metastable charge-separated state

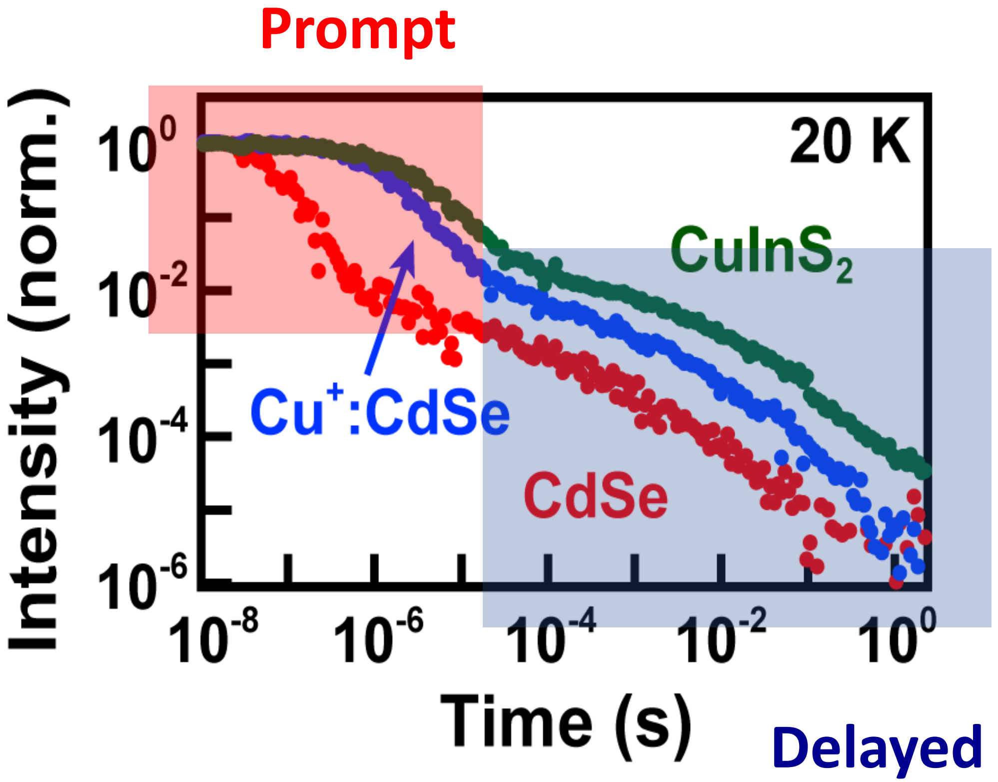
Whitham, Knowles, Reid, Gamelin, Nano Lett. 2015 15 (6), 4045-4051

What do we expect for other NCs?



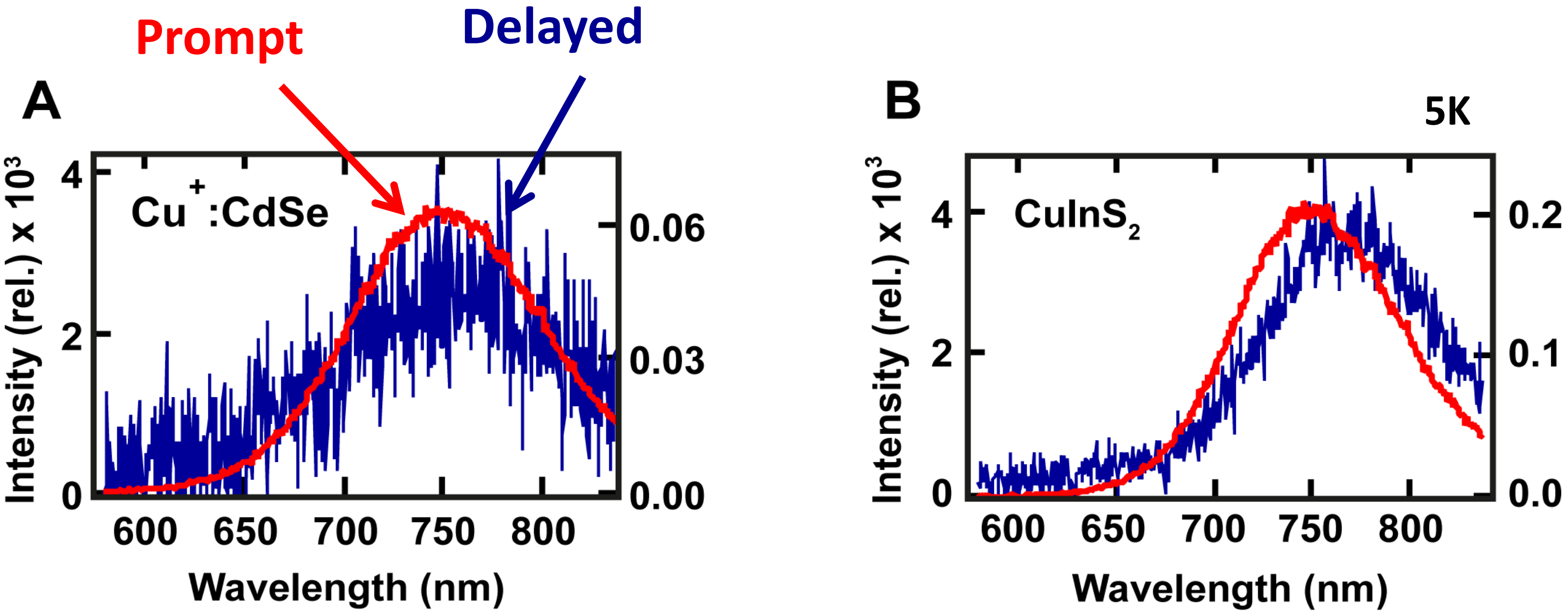
Marchioro, Whitham, Knowles, Kilburn, Reid, Gamelin, J. Phys. Chem. C, 2016, 120, 27040

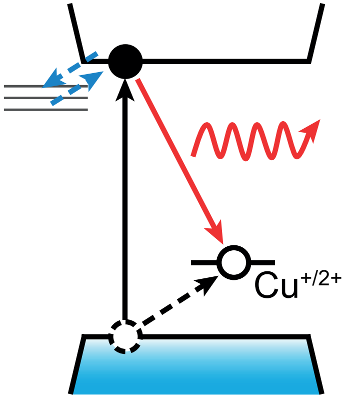
Delayed luminescence is everywhere!



- Measured by TCSPC
- Different materials show remarkably similar dynamics

Is DL due to detrapping ?





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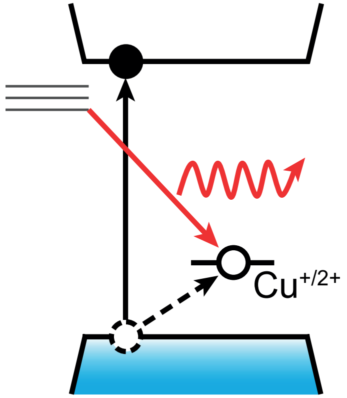

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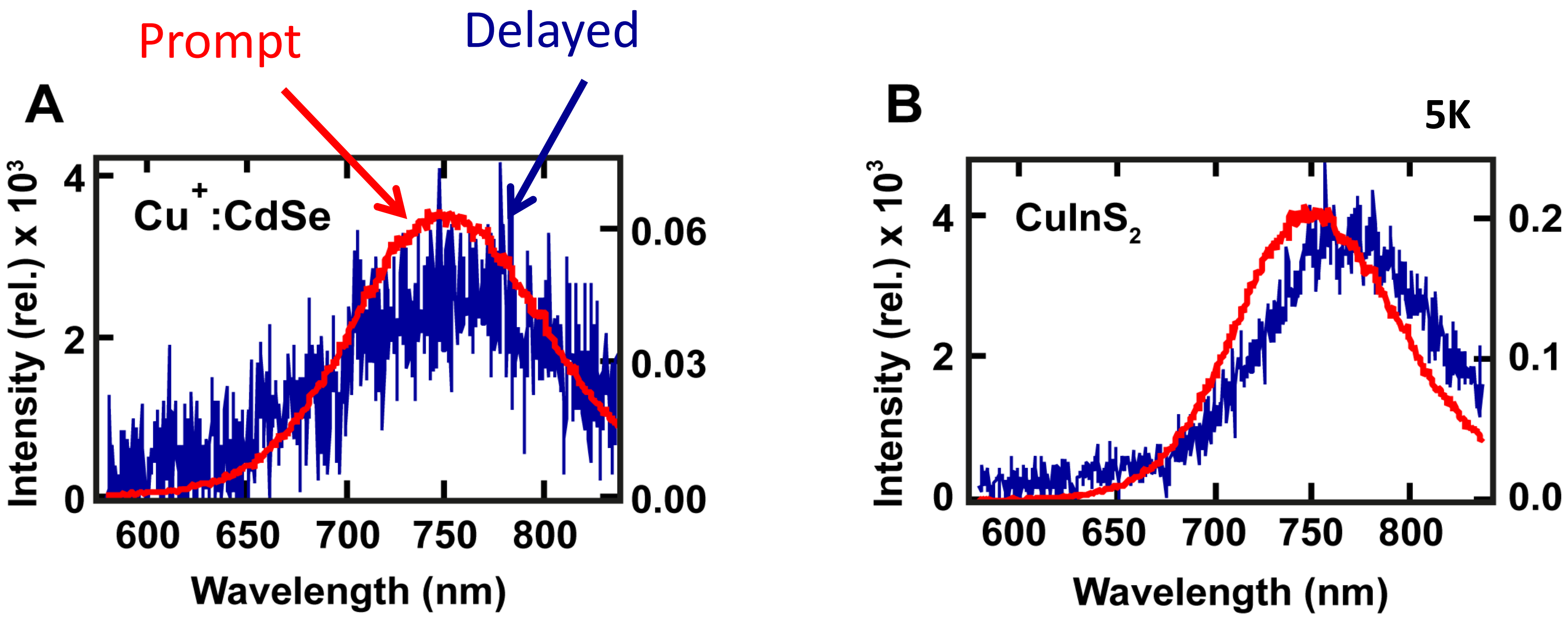
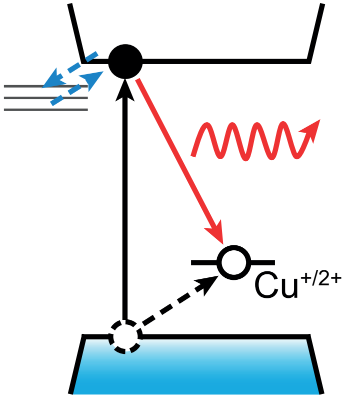
Is DL due to detrapping ?





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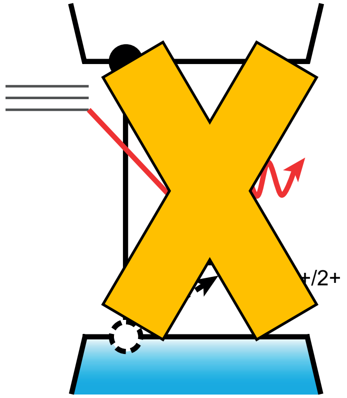

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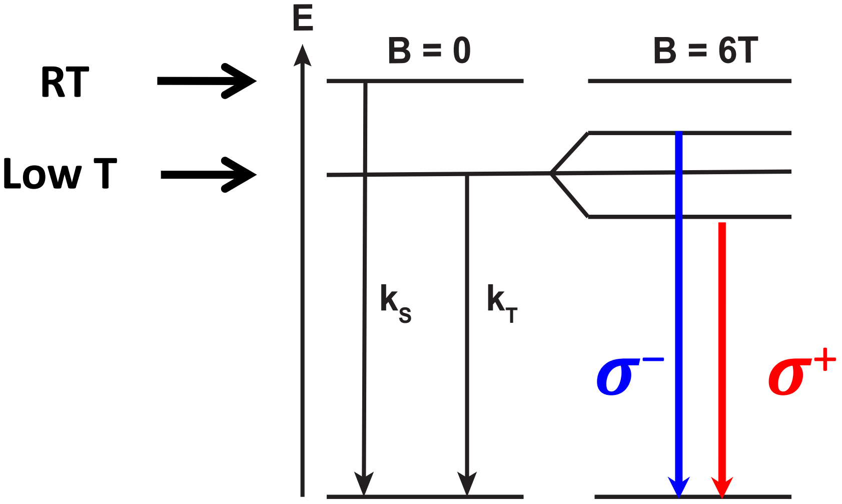
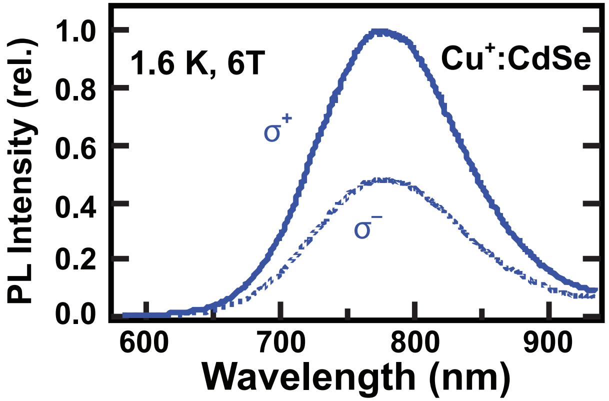
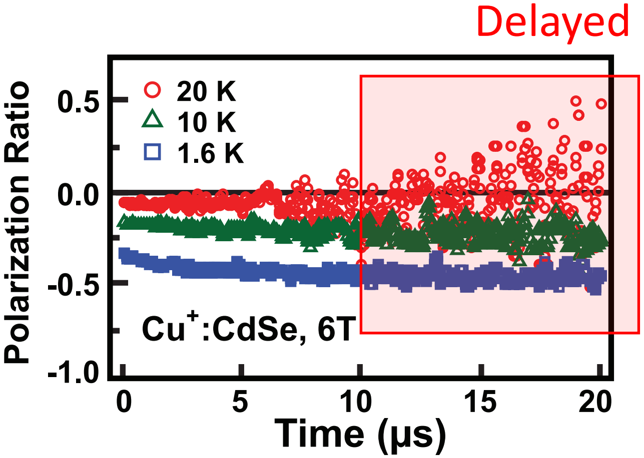
MCPL shows decay from original emissive state

Magnetic Circularly Polarized Luminescence (MCPL)







Polarization Ratio

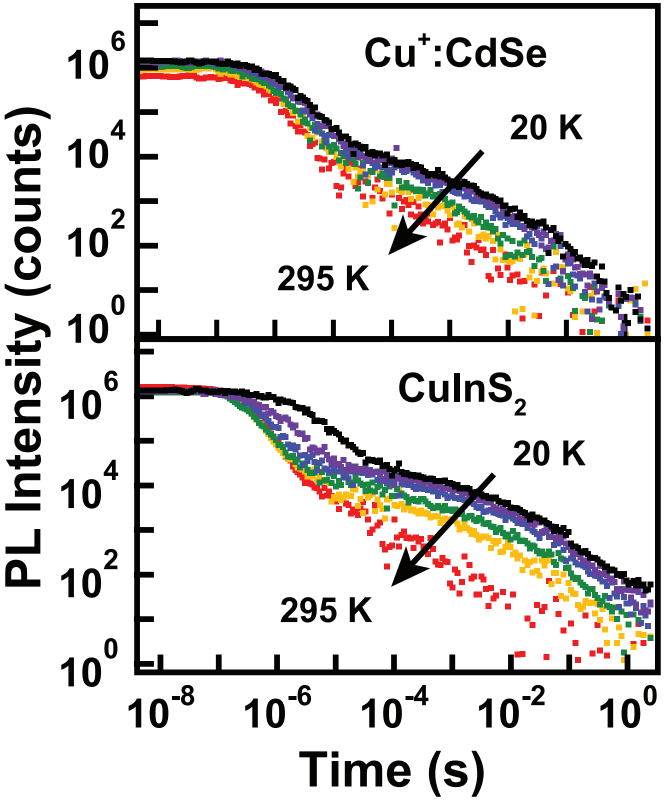
$$\frac{\sigma^- - \sigma^+}{\sigma^- + \sigma^+}$$

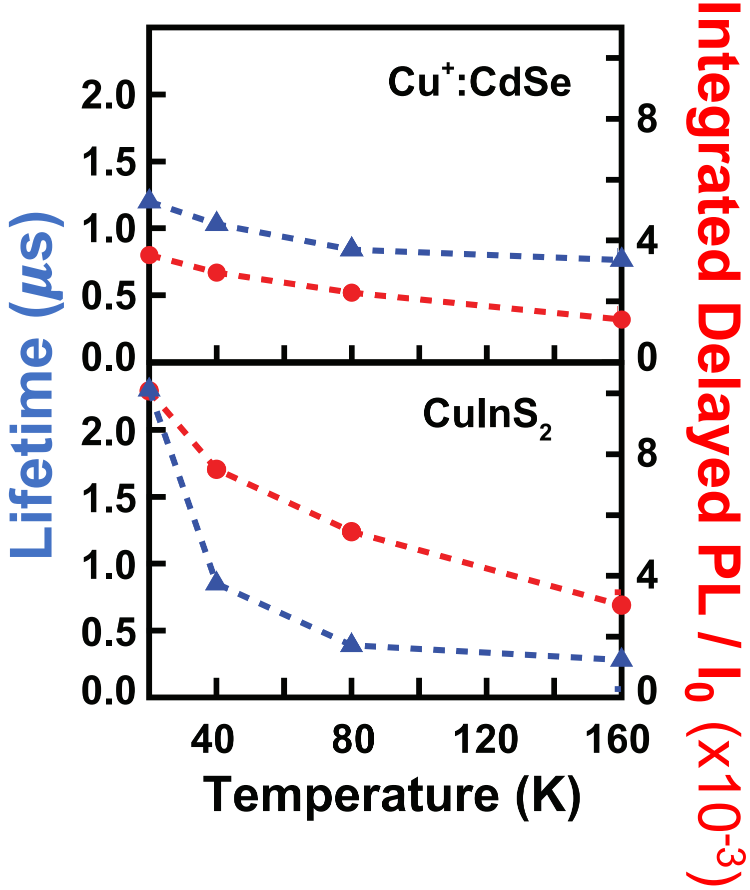
T-(in)dependence

- Broadly distributed kinetics mostly independent of T (parallel decays)

- Variation of DL lifetimes follows variations of prompt lifetimes

→ The probability of populating the DL state directly depends on the prompt lifetime





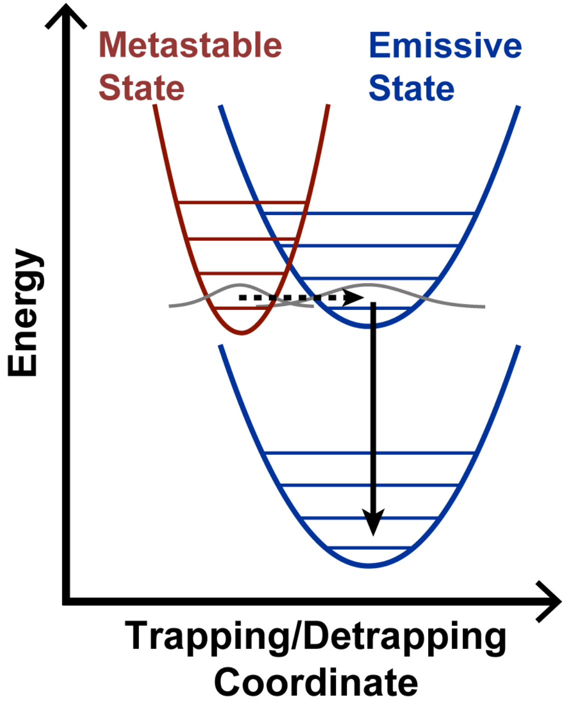
Is this a tunneling process?

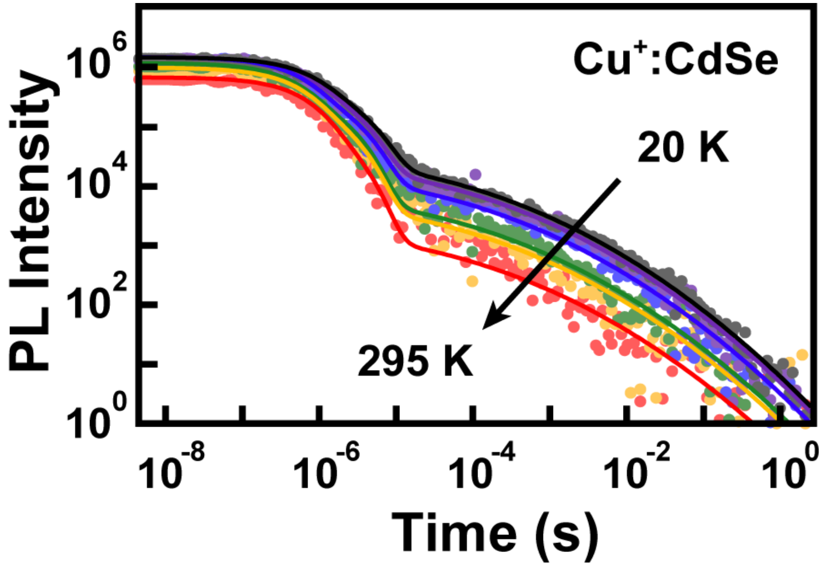
Tunneling Model

$$I(t) = A_P \overbrace{\exp(-k_{prompt} t)}^{\textbf{Prompt}} + \overbrace{A_D \int_0^\infty p(a) \cdot \exp(-k_{tunnel}(a) \cdot t)\, da}^{\textbf{Delayed}}$$

Barrier width

Gaussian distribution of tunneling barrier widths





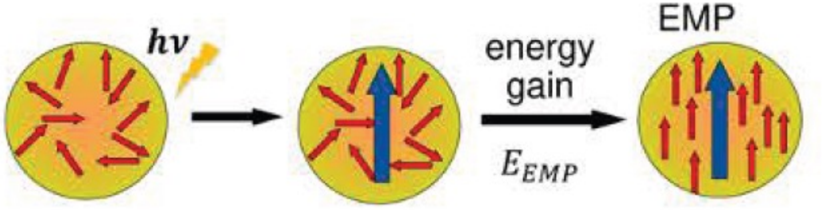
Summary

- Doping is an additional way to tune the already exceptional properties of QD!!

- Modifies the optical properties, the magnetic properties, etc…

Ex: Mn^{2+} doping and "excitonic magnetic polarons"

Exchange field between exciton and dopant:
→ Effective magnetic field experienced by the dopants
→ ***Write magnetic memories with light!***



More in: Beaulac et al., *Science* **2009**, *325*, 973-976

Delayed luminescence is the NC-equivalent of the "green afterglow" seen in toys and oscilloscopes, for example!

- Observed in many different NCs and longer in copper-doped and copper-based systems

- A **reversible** charge trapping-detrapping process where the delayed photon originates from the same state as the prompt photon

- **Temperature independent** and reflects a tunneling process