Challenge to the Donor-Acceptor-Pair Photoluminescence Mechanism in Alloyed Ag-In-Zn-S Quantum Dots

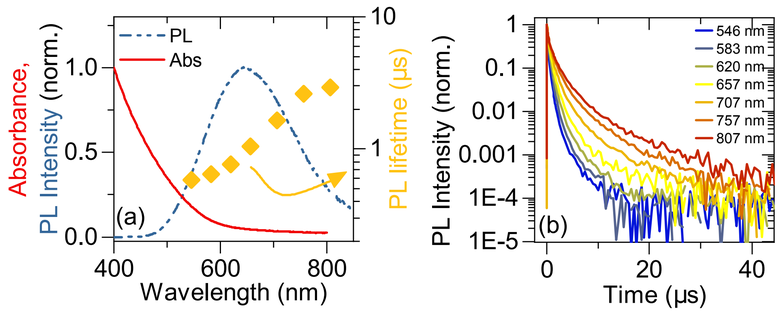
Adam Ćwilich[1], Daria Larowska-Zarych[2], Patrycja Kowalik[3], Kamil Polok[2], Piotr Bujak[3], Magdalena Duda[1], Tomasz Kazimierczuk[4] Adam Proń[3], Wojciech Gadomski[2], and Łukasz Kłopotowski[1]

[1]Institute of Physics, Polish Academy of Sciences, Poland
[2]Faculty of Chemistry, University of Warsaw, Poland
[3]Faculty of Chemistry, Warsaw University of Technology, Poland
[4]Faculty of Physics, University of Warsaw, Poland

Photoluminescence (PL)

▶ Solution-phase PL

- ▹ Featureless absorption spectra
- ▹ Large PL linewidths (~ 0.6 eV)
- ▹ Large Stokes shifts (~ 0.5 eV)
- ▹ Long decay times (~ 500 ns)
- ▹ Wavelength-dependent PL dynamics



- ▹ these properties are commonly attributed to a donor-acceptor-pair (DAP) transition

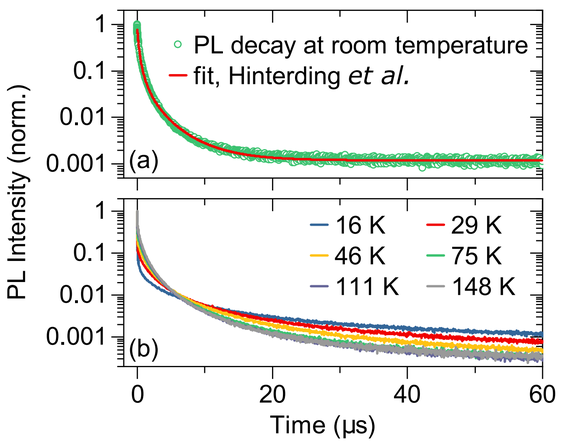
Moodelly et al. J. Mat. Chem., C 2019, 7 11665.

▶ Samples

Kowalik et al. Chem. Mater., 2022, 34 809..

Sample	Shape	Size	Structure	PL QY	Image
$Ag_{1.0}In_{1.5}Zn_{1.9}S_{3.6}$	Spherical	D = 3.7 nm	Orthorhombic	40%	
$Ag_{1.0}In_{1.5}Zn_{4.4}S_{6.8}$	Rod-like	D = 3.9 nm L = 9.0 nm	Orthorhombic	18%	

▶ Temperature-dependent PL dynamics

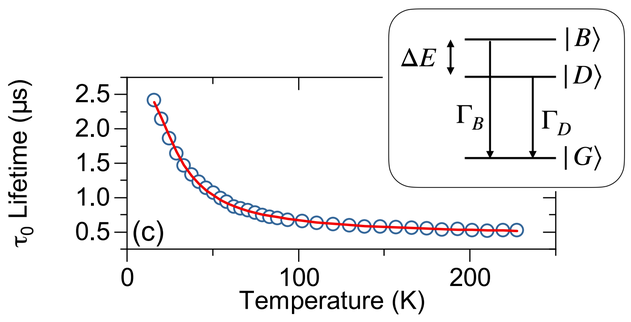


- ▹ non-exponential PL decays can be modeled by assuming electron transitions to holes at localization sites randomly distributed inside the QD volume

$$I(t) = A\int_0^{r_{\max}} \frac{\exp(-t/\tau(r_{\rm loc}))}{\tau(r_{\rm loc})} dr_{\rm loc} + I_0$$

$$\tau(r_{\rm loc}) = \tau_0 \frac{\pi^2 r_{\rm loc}^2}{a^2 \sin^2(\pi r_{\rm loc}/a)}$$

Hinterding et al. Nano Lett., 2021, 21 658.



- ▹ temperature-dependent PL dynamics probes the nature of the luminescent state
- ▹ average PL lifetime increases with decreasing temperature — increased population of a lower energy, dark state

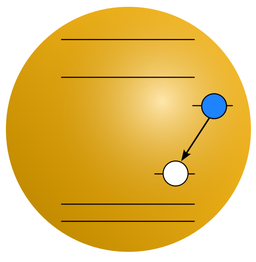
Discussion & Conclusions

- ▹ within DAP mechanism: carrier localization, strong electron-phonon coupling, and a correlation between PL energy and donor-acceptor distance explain the solution-phase PL properties

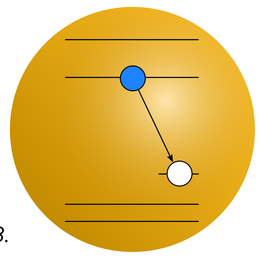
$$E_{\rm DAP} = E_g + E_e + E_h - E_{e,loc} - E_{h,loc} + \frac{e^2}{4\pi\epsilon_0\epsilon r_{DA}}$$

- ▹ however, presence of long-lived delocalized carriers and lack of ns PL rise time, show that DAP is not the luminescent state
- ▹ our results are consistent with the PL ocurring as a result of a free-to-bound transition — recombination of a delocalized electron and localized hole, similar to the case of $CuInS_2$ QDs.

Donor-Acceptor Pair



Free-to-bound



- ▹ electron-hole exchange induces a splitting of the luminescent state and a strong temperature dependence of the PL lifetimes

Knowles et al. JACS, 2015, 137 13138.
Szymura et al. J. Phys. Chem. C, 2023, 127, 6768.

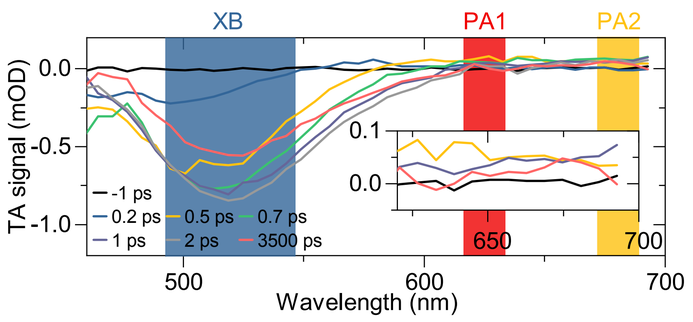
- ▹ assuming thermal equilibrium within the fine structure and pure-spin states:

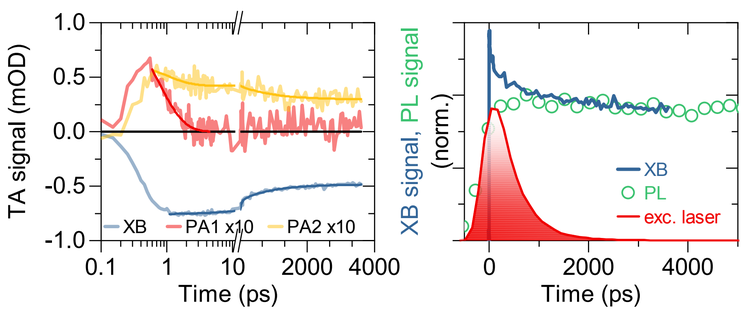
$$\tau_0(T) = \frac{1 + 3\exp\left(\frac{\Delta E}{k_B T}\right)}{\Gamma_A + \Gamma_F 3\exp\left(\frac{\Delta E}{k_B T}\right)}$$

- ▹ allows to retrieve the splitting at the bright state radiative lifetime for the centrally localized hole: ΔE= 6.3 meV, τ_{0B} = 120 ns

Transient absorption (TA)

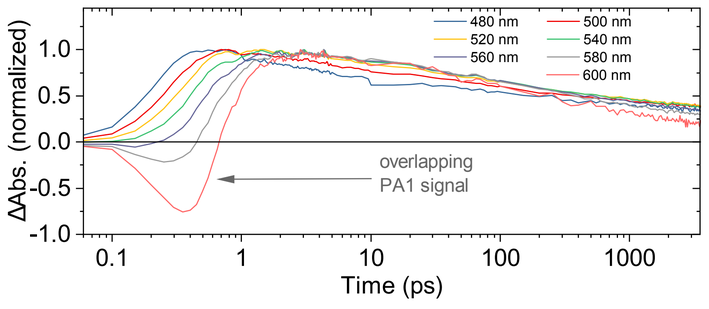
▶ Bare Ag-In-Zn-S QDs





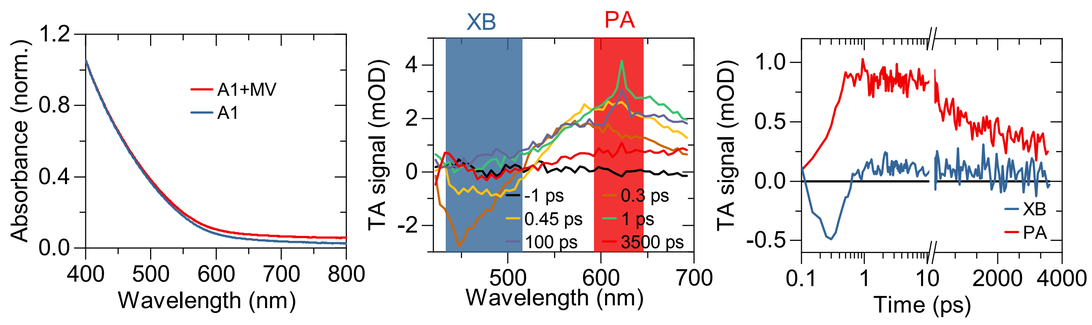
- ▹ XB — ground state bleach (delocalized carriers)
- ▹ PA1 — short-lived (~1 ps) photoinduced absorpion (hot biexcitons)
- ▹ PA2 — long-lived photo-induced absorption (mid-gap localized holes)
- ▹ XB, PA2 initial decay due to surface trapping
- ▹ long decay of on a timescale of tens of ns
- ▹ PL rise time on ps timescale
- ▹ conclusion: delocalized carriers participate in the PL

▶ Carrier cooling dynamics



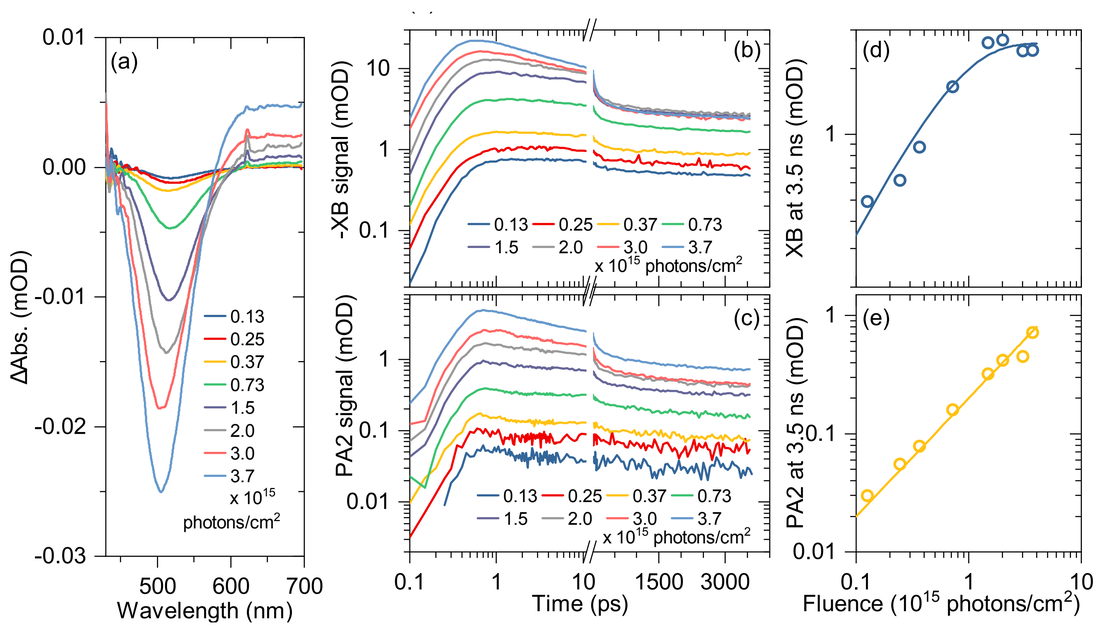
- ▹ spectral dependence of XB rise dynamics
- ▹ faster rise at shorter wavelengths (higher energies)
- ▹ carrier cooling to the ground state occurs in ~ 1 ps

▶ QDs conjugated with electron scavenger (methyl viologen)



- ▹ conjugation with MV — no change in absorption, complete quenching of the PL
- ▹ ultrafast decay of XB signal before cooling complete — hot carrier extraction
- ▹ PA2 weakly affected, indicating its origin related to localized holes

▶ Excitation power dependent TA



- ▹ at large delays, saturation of XB signal with excitation power — Auger recombination of multiexcitons
- ▹ XB(3.5 ns) = C(1-exp(-σJ)), where J is fluence and σ the absorption cross-section
- ▹ fitting yields σ = 1.42x10^{-15} cm^2, roughly 10 times smaller than for CdSe QDs
- ▹ PA2 increases linearly with power — no Auger process for localized holes

For more information:
lukasz.klopotowski@ifpan.edu.pl

Funding: 2019/35/B/ST3/04235
National Science Centre Poland