

# Trends in Lead Degradation of $\text{CsPbBr}_3$ versus $\text{CsPbCl}_3$ Nanocrystals

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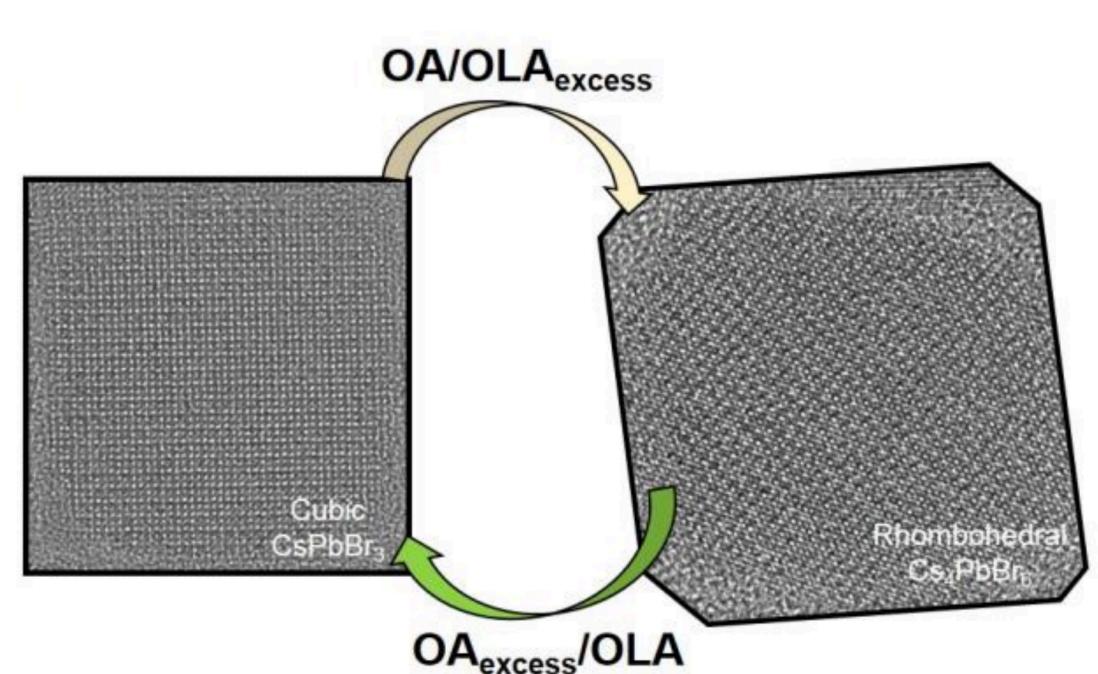


## Abstract

Perovskite nanocrystals are an emerging field of study due to the low barriers for synthesis, efficient electronic properties, and photoluminescent abilities. The cesium lead halide  $\text{Cs}_n\text{PbX}_m$  shows promising opportunities to improve its stability for usage in electronic and light-harnessing devices such as solar panel cells, but uncertainties about its thermal and chemical stability must be researched in order to create long-lasting, efficient devices. The  $\text{CsPbCl}_3$  nanocrystal has been shown to change to  $\text{Cs}_4\text{PbCl}_6$  after lead depletion in oleylamine solution. This new phase shows higher photocurrents with more defined emission peaks than the I-I-III phase, making the IV-I-VI phase more ideal for use in electronic properties. Through analysis of the  $\text{CsPbCl}_3$  nanocrystal spectra in oleylamine solution over time, we find that similar lead degradation in both crystal types cause a blue-shift in emission spectra. Similarities imply possible future interest in chloride crystals as bromide substitutes for photoelectronic usage.

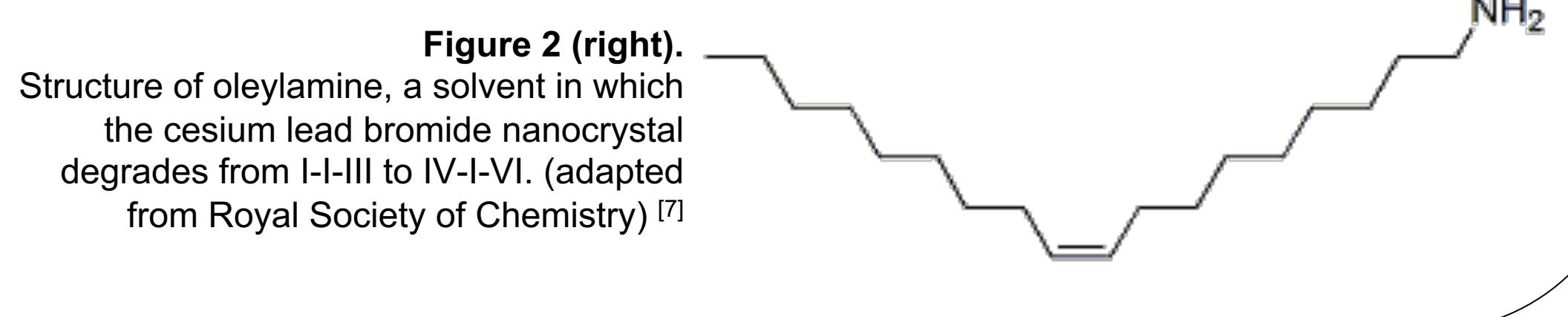
## Introduction

With the movement towards alternative sustainable energy, perovskite nanocrystals with the general structure  $\text{Cs}_n\text{PbX}_m$ , (cesium lead halide) have been of interest due to their stability in extreme conditions and their optoelectronic properties. Compared to organic halide perovskite crystals,  $\text{Cs}_n\text{PbX}_m$  have higher melting points and high thermal stability, offering greater prospective for use in solar photovoltaic cells.<sup>[1]</sup> Halide perovskite crystals have been demonstrated as effective but chemically unstable semiconductors that can achieve high open-circuit voltages.<sup>[2]</sup>



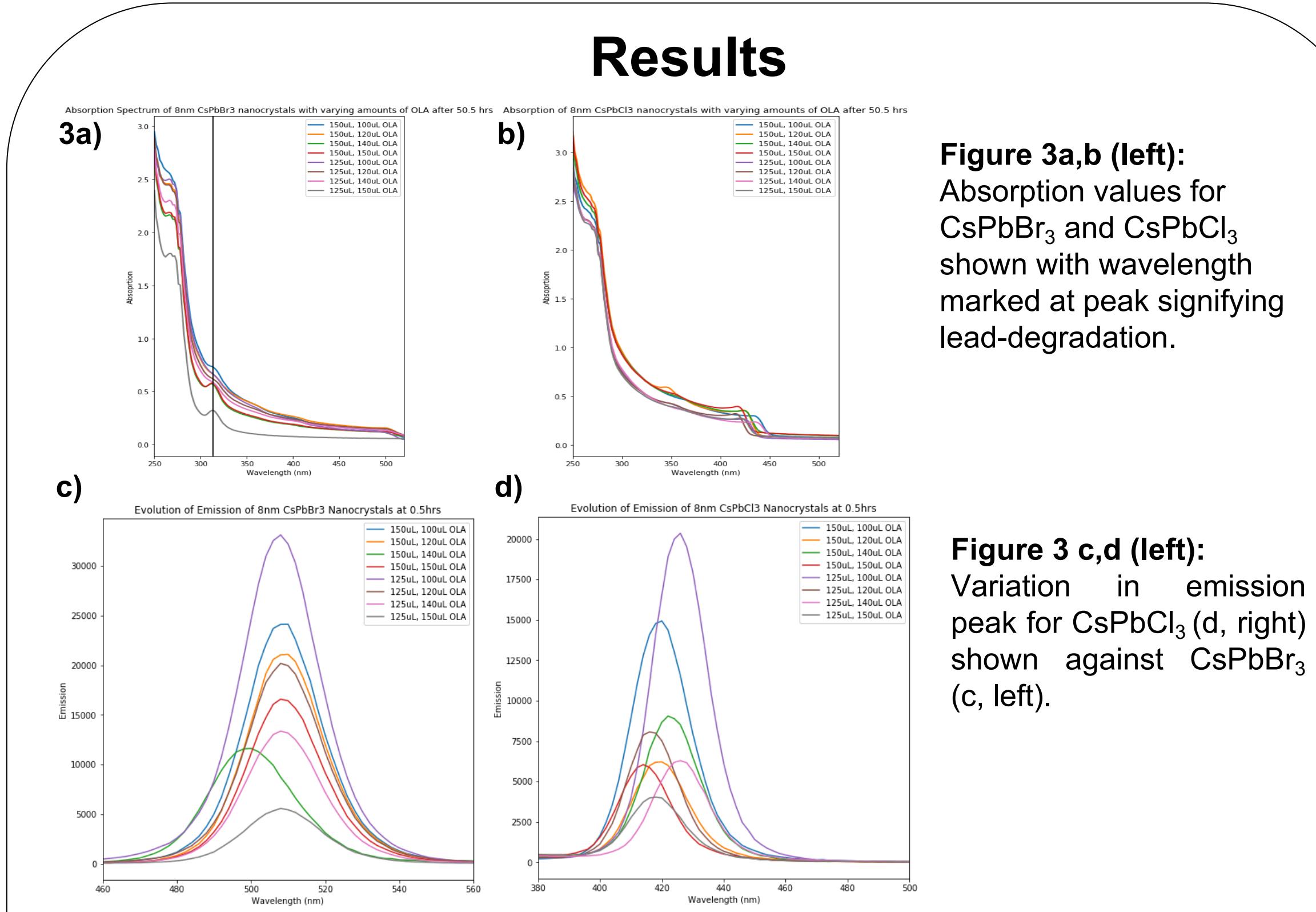
**Figure 1 (above).**  
Phase transformation of  $\text{CsPbBr}_3$  (left) into  $\text{Cs}_4\text{PbBr}_6$  (right) in excess oleylamine solution. (adapted from Jing, et.al 2019)<sup>[6]</sup>

The  $\text{CsPbBr}_3$  (I-I-III) structure and its lead depleted derivative  $\text{Cs}_4\text{PbBr}_6$  (IV-I-VI), induced from ligand addition in polar solvents like oleylamine,<sup>[5]</sup> have been compared in conductance of photocurrent.  $\text{Cs}_4\text{PbBr}_6$  exhibited high photocurrents with defined emission peaks than the I-I-III structure<sup>[5]</sup>, making it more ideal for usage in photoelectronic devices. This study aims to determine if similar conditions will cause degradation in the I-I-III  $\text{CsPbCl}_3$ .

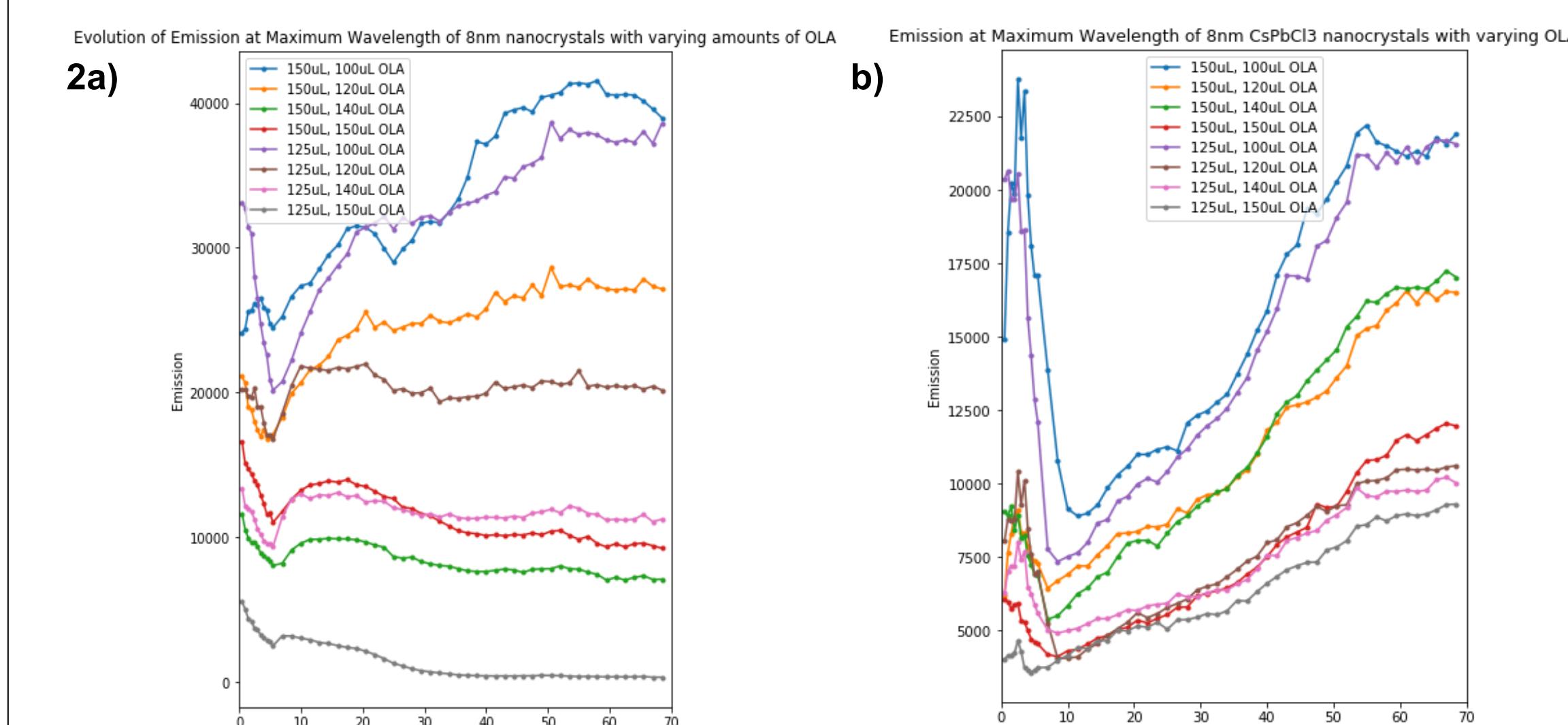


## Methods

8nm-edge length cubic  $\text{CsPbBr}_3$  nanocrystals were synthesized and dissolved in dodecane. Varying amounts of oleylamine were added as additives in a 1mm cuvette. The absorbance and emission of the nanocrystal solutions were measured over hourly intervals at room temperature and ambient conditions. Data analysis was performed through Python JupiterNotebook.

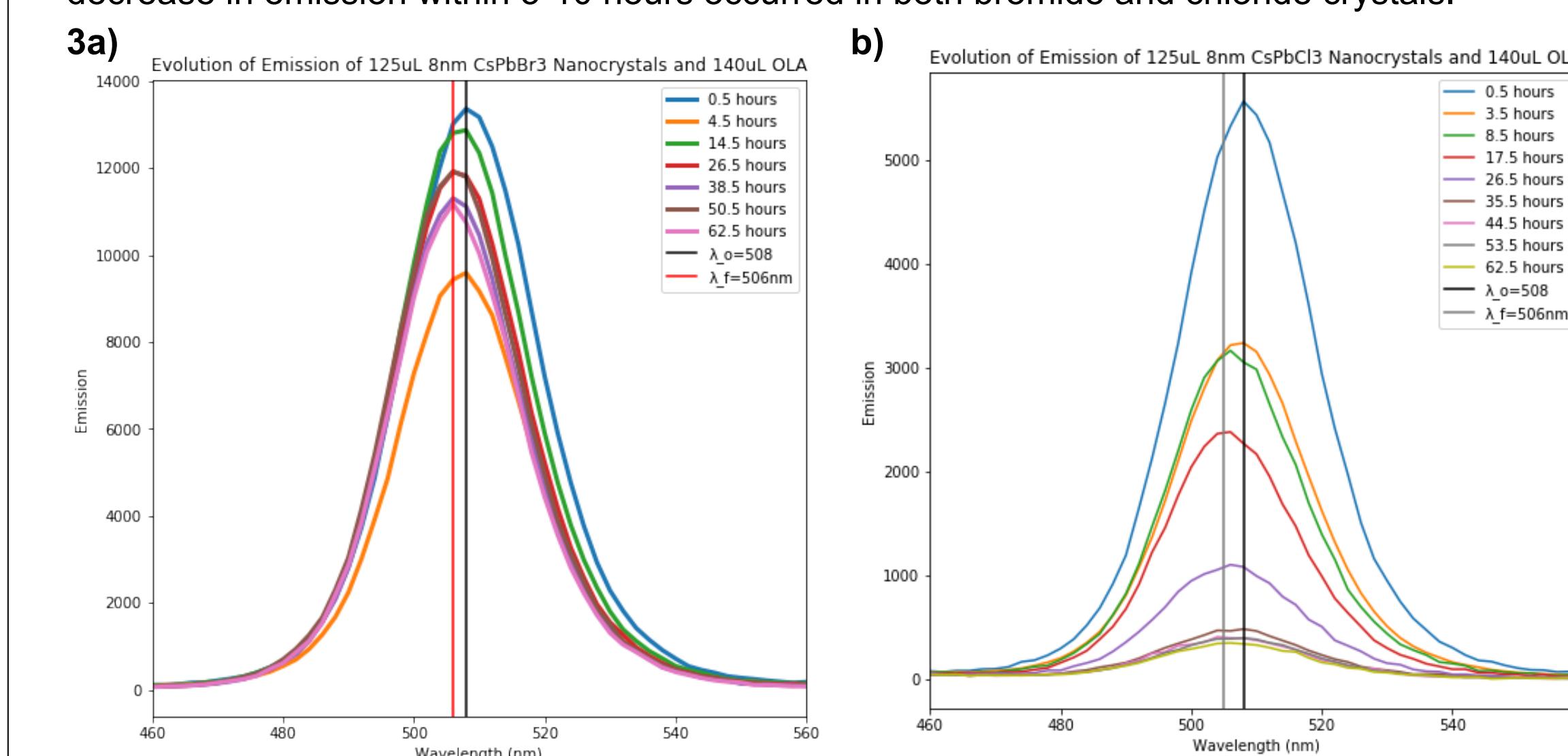


**Figure 3a,b (left):**  
Absorption values for  $\text{CsPbBr}_3$  and  $\text{CsPbCl}_3$  shown with wavelength marked at peak signifying lead-degradation.



**Figure 3 c,d (left):**  
Variation in emission peak for  $\text{CsPbCl}_3$  (d, right) shown against  $\text{CsPbBr}_3$  (c, left).

**Figure 2a (left, above):** Emission in  $\text{CsPbBr}_3$  versus  $\text{CsPbCl}_3$  (right, above) for different oleylamine added. Lower four curves show lead degradation emission change. Similar decrease in emission within 5-10 hours occurred in both bromide and chloride crystals.



**Figure 3a (left, above):** Emission spectra given for  $\text{CsPbBr}_3$  showing wavelength shift in peak during lead degradation phase. **Figure 3b (right, above):**  $\text{CsPbCl}_3$  emission spectra also given showing similar wavelength shift as  $\text{CsPbBr}_3$ .

## Conclusions

The amine-induced degradation of the synthesized cubic  $\text{CsPbBr}_3$  nanocrystals to a lead-depleted phase (presumably 4-1-6, 4-2-6, or 4-3-6) is observed by the presence of the characteristic absorption peak at 313nm. A time series analysis of the emission of the  $\text{CsPbBr}_3$  nanocrystals indicate a general decrease in the emission at greater OLA/Pb ratios, although an increasing trend in the emission is shown at lower OLA/Pb ratios. The decrease in emission (at higher OLA/Pb ratios) is indicative of the morphological transformation of the cubic  $\text{CsPbBr}_3$  to polygonal  $\text{Cs}_4\text{PbBr}_6$ . The emission spectra also demonstrated a shift in the wavelength of maximum emission from 508nm to 506nm for the  $\text{CsPbBr}_3$  nanocrystals, indicating a change in the size of the nanocrystal. Both the  $\text{CsPbBr}_3$  and  $\text{CsPbCl}_3$  nanocrystals exhibit a decrease in emission upon the onset of addition of OLA, followed by a subsequent increase in emission. It was observed that the addition of OLA results in a more disperse size distribution in the  $\text{CsPbCl}_3$  nanocrystals (as observed in the emission and absorption profiles) compared to the  $\text{CsPbBr}_3$  nanocrystals. The lead depletion evident in  $\text{CsPbBr}_3$  nanocrystals may be due to the difference in size of the edge length of the crystal lattice as well as the holes in the crystal structure. The larger size of the Br- ion allows for the Pb+ cation to be more easily removed from the crystal lattice, resulting in a lead depleted phase in  $\text{CsPbBr}_3$  but not in  $\text{CsPbCl}_3$ . The researchers recommend the use of XRD (X-Ray Dispersion) to accurately determine the molar composition of each element (Cs, Pb, and X=I, Cl, Br, F) to ascertain the identity of the lead-depleted product.

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## Acknowledgements

