## Supporting Information

# Inverse size-dependent Stokes-shift in strongly quantum confined

## CsPbBr<sub>3</sub> perovskite nanoplates

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## Spectroscopic measurements and data analysis

The "as-measured" emission and absorption spectra were fitted to Gaussian functions using automatic curve algorithms to extract the corresponding Stokes Shift. The automated dataset was not "manually cleaned" and therefore composed of several emission and absorption peaks. However, only the first excitonic band edge of the absorption and associated emission peaks were considered. Examples of samples with multiple emission and absorption peaks are demonstrated in **Fig. S1**.

All our spectroscopic studies presented in this paper were conducted at room temperature. Thus, the spectroscopic data is influenced by vibrational phonon coupling. For the majority of crystal structures, broad optical bands are indicative of strong phonon coupling, while sharper bands (like we measure for quantum-confined perovskite) are indicative of weak coupling (i.e the phononic coupling is small). Moreover, at room temperature, higher energy phonon levels are populated, leading to broader absorption and emission bands.<sup>1</sup> Thus, our measured data is inherently broadened.

To take this thermalization effect into account one usually refers to a Huang-Rhys parameter. A connection between the Stokes shift and the Huang-Rhys parameter is presented in the following,

$$E_{\text{stokes}} = h\omega ((2S - \frac{1}{2}) \pm \frac{1}{2})$$

Where  $\omega$  is the longitudinal-optical phonon mode of the lattice vibrations and S is the Huang-Rhys parameter, which describes the microscopic details of the vibrational coupling, first purposed by Henderson and Imbusch (1989).<sup>2</sup> From the above relation, we now evaluate the Huang-Rhys parameter for our experiment. The LO phonon mode of the Pb-Br lattice vibration was taken as ~20 meV, in agreement with published results.<sup>3</sup> When taking into account the statistical spread of measured data demonstrated by the shaded red area in Fig 2, we thus calculated a Huang-Rhys parameter, S, with lower/upper bound values of 0.5-1 and 1.5-2, respectively.

Scaling of emission and absorption spectra for Huang-Rhys factor determination:

We are aware of a scaling process described in previous work of de Jong et al.<sup>4</sup> that is suggested for more accurate Huang-Rhys parameters extraction. However, the Huang-Rhys factor is not the main point of this paper. Rather the anomalous absorption and emission trends that appear when nanoplates and nanocubes of CsPbBr<sub>3</sub> are compared, which is best done when examining the stokes-shift at room temperature, and therefore phonon contribution is comparable between the systems.

An example of scaled and unscaled data is presented in **Fig. S1** (as measured). We further conducted a step-by-step analysis on the three exemplary datasets from **Fig. S2**. The scaled absorption and emission spectra were fitted for finding the Stokes Shift. A comparison of the as-measured data and suggested scaled data<sup>4</sup> is now presented in **Fig. S2**.



**Figure S1. Examples of as measured emission and absorption spectra of 80 different experiments out of more than 2000.** Panels *a-b and c-d are the "as measured" and "scaled" according to the scaling suggested in the work of de Jong et al.*<sup>4</sup> This and the fitted data presented in the next figure, demonstrate the similarities between the presented as measured data and that with the scaling.



**Figure S2.** Examples of emission and absorption spectra with their fitting to the different phases. The Stokes shift values were extracted from the emission peak correlated to the excitonic band edge absorption peak; PL spectra are shown with their gaussian fitting in red. Panels a-c and d-f are the "as measured" and "scaled" fitted data sets as discussed above.

### Scattering samples

It is important to note that usually, absorption spectra is superimposed by background and Rayleigh scattering of the NPLs inhomogeneities. However, In our data, after taking into account the Rayleigh scattering backgrounds (**Fig. S3 a-c**), as was done in the work of Achtstein et al.<sup>5</sup> and is represented by:  $D(\lambda) = A/\lambda^4 + B$ , the calculated values of the spectral shifts are: 1.3, 2 and 0.7 meV (**Fig. S3 a-c**, correspondingly, <<K<sub>B</sub>T at RT ). These values ensure that our data will not be affected by the background and scattering effect.



*Figure S3. Examples of absorption spectra with its fitting to background contribution. The calculated values of the spectral shifts are: 1.3, 2 and 0.7 meV for a-c, correspondingly.* 

In addition, among the typical sample with a Stokes shift of 0 to 100 meV, we noticed samples with extremely high stokes shift that were statistically excluded from this work; these cases include samples with non-physical negative Stokes shift and emission peaks that were out of the spectrum range. In addition, in the automated dataset, we identified a large cluster of data points with high Stokes shift (higher than 140 meV) and an emission wavelength that is not typical of any NPLs. Another issue was in "out of range" emission examples, in which the emission peak of around 400 nm (typical to 1 ML) wasn't captured in the limited range of the emission reading of the spectrophotometer (400-550 nm). We inferred that the absorption and emission peaks do not necessarily belong to one specific phase in all the cases described here. Due to the mixture of multiple phases in the automated dataset, superposition of absorption peaks, negligible peaks, and reabsorption effects create variability in the Stokes shift (**Fig. S4**, **S5 a**, **b**).

## Stokes shift vs. wavelength



*Figure S4. Automated dataset before filtering.* Solid lines refer to the emission and absorption wavelength of 1ML, 2ML, 3ML, 4ML from <sup>6,7</sup>. Stokes shift versus absorbrion wavelength (a) and emission wavelength (b).



*Figure S5. Stokes Shift Results vs. emission wavelength.* Solid lines refer to the emission and absorption wavelength of 1ML, 2ML, 3ML, 4ML. Stokes shift versus the emission wavelength in the automated dataset (a). The size of the datapoint is the maximal fraction of the phase in the sample. Stokes shift versus the emission wavelength in the manual dataset (b). The color of the datapoint refers to ligand type. The ligand type creates a blue/red shift of both emission and absorption peaks, but it shows no effect on the value of stokes shift.

## Assigning statistical weights to morphology.

To determine the relative concentration of the individual morphologies produced by our automated synthesis while varying compositions of (Cs-Pb-Br). We used the fact that each of these morphologies has slightly different absorption spectra. Alas, some of the spectral features of the 9 different morphologies overlap. In previous work, Dahl et al<sup>8</sup> developed an automated method for determining the relative product amount. Essentially, the absorption spectrum of each sample was treated as a linear combination of reference spectra of the individual morphologies. Then, a spectral deconvolution using the algorithm of LASSO (Least Absolute Shrinkage and Selection Operator) was allowed to extract the statistical weight of the individual morphologies produced by the automated synthesis. We thus assign these statistical weights to the relative concentration of the individual morphologies.

## **Stokes shift Error Estimation**



Figure S6. Error estimation of Stokes shift

The Stokes shift with the extrinsic error due to errors in measuring the wavelengths, will be noted as:

 $SS \pm \delta SS$ . In **Fig. S6** we plot the error is Stokes Shift  $\delta SS$  against an error of E in emission wavelength. We take the stringent case in which both emission and absorption wavelengths have an offset of E.

$$\delta SS = SS_{True} - SS_{E offset} = hc \frac{-E(\lambda_a^2 + \lambda_e^2 + E(\lambda_e - \lambda_a))}{\lambda_a \lambda_e (\lambda_a - E)(\lambda_e + E)} \quad (S1)$$

From the plotted results, we can see that the error of the Stokes shift increases when: (i) the error of wavelegths increases, (ii) the wavelengths are smaller, or (iii) the wavelength difference increases.

Since the resolution of the spectrophotometer samples is in 1 nm, we will take this value of half of the unit (E = 0.5 nm) as an error for both wavelengths and according to the plot this brings a range of:

9 < δSS < 16 [meV]

Additional method for Stokes shift error estimation is the statistical, more conservative one, using the formula:

$$\delta SS_{mean} = \sqrt{\left(\frac{\partial SS}{\partial \lambda_a}E\right)^2 + \left(\frac{\partial SS}{\partial \lambda_e}E\right)^2} \qquad (S2)$$

Substituting E = 0.5 nm and the cases ( $\lambda_e = 401 nm$ ,  $\lambda_a = 396 nm$ ) and ( $\lambda_e = 522 nm$ ,  $\lambda_a = 520 nm$ ), we get:

$$3.2 < \delta SS_{mean} < 5.5 \ [meV]$$

## **Cluster shape analysis**

We create artificial datasets of emission and absorption values to analyze the characteristics of a single cluster in the stokes shift figures (**Fig. 2**).

In **Fig. S7**, we show that the standard deviation of the absorption wavelength and the emission wavelength directly affects the size of the cluster.



Figure S7. Effect of standard deviation of the data on the cluster size. Stokes Shift plotted against emission wavelength, with  $\lambda_{ab}=430[nm]$  and  $\lambda_{em}=435\pm std[nm]$  (a). Stokes Shift plotted against absorption wavelength, with  $\lambda_{ab}=430\pm std$  [nm] and  $\lambda_{em}=435$  [nm] (b).

In order to explain the slope of the datapoints in **Fig. 2** and in **Fig. S7**, we write a Taylor expansion of the stokes shift (**eq. 3**):

$$\Delta E_s = \frac{hc}{\lambda_{ab}} - \frac{hc}{\lambda_{em}} \quad (S3)$$

is done separately for  $\Delta E_s(\lambda_{ab})$  and  $\Delta E_s(\lambda_{em})$  around the points  $\lambda_{ab} = 430$  and  $\lambda_{em} = 435[nm]$  respectively. This results in:

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$$\Delta E_{s}|_{\lambda_{em}} = 435 = \frac{124}{3741} + \frac{248(\lambda_{em} - 435)}{37845} + O((\lambda_{em} - 435)^{2}) \sim 6.553 \lambda_{em} - 2817.4 \quad (S4)$$
$$\Delta E_{s}|_{\lambda_{ab}} = 430 \approx \frac{124}{3741} - \frac{62(\lambda_{ab} - 430)}{9245} + O((\lambda_{ab} - 430)^{2}) \sim 6.706 \lambda_{em} + 2916.9 \quad (S5)$$

The artificial datasets in **Fig. S7** show a good agreement to the calculations in eq. (S4) and (S5). This confirms that the slopes obtained in **Fig. 2** are due to mathematical values and not due to intrinsic physical phenomenon.

We will note that the stokes shift slope is different for different wavelength ranges (red vs blue), and for different wavelength spectra (emission vs absorption), due to different Taylor expansion that is obtained around the investigated area.



Figure S8. Stokes shift dependence on solvent concentration. Emission spectra of 2ML phase of  $CsPbBr_3$ , for concentrations of 1 to 1/64 of Hexane (a) and ODE (b). Stokes shift of 2ML phase of  $CsPbBr_3$ , for concentrations of 1 to 1/64, for two different solvents: ODE and Hexane (c). A significant change in stokes shift (20-30 meV) occurs in both solvents.



Difference of Stokes shift between automated and manual synthesis

*Figure S9. Stokes shift dependence on the phase fraction.* The figures show no significant effect as the stokes shift values for full fraction samples are in the average value of the stokes shift of the mixed fraction samples.

## **The studied Parameters**

Parameter	Meaning	Value	Source
$\varepsilon_b$	Dielectric constant of Oleylamine ligands	2.13 <sup><i>ɛ</i>0</sup>	9
$\varepsilon_{QD}$	Dielectric constant of quantum dot	$4.96^{arepsilon_0}$	10
L <sub>b</sub>	Organic spacing between QDs	3.4 [nm]	Unpublished work
$m_e$ in cubes	Exciton electron mass in cubes	$0.14m_0$	10
$m_h$ in cubes	Exciton hole mass in cubes	0.15m <sub>0</sub>	
B <sub>x</sub>	Exciton Binding energy	40 [meV]	$B_x = \left(\frac{\mu}{m_0}\right) \frac{R_H}{\varepsilon_{QD}^2}$
a <sub>x</sub>	3D exciton radius	3.6 [nm]	$a_x = \varepsilon_{QD} \frac{m_0}{\mu} a_H$
$m_e$ in NPLs	Exciton electron mass in NPLs	$0.215m_0$	11
$m_h$ in NPLs	Exciton hole mass in NPLs	0.211m <sub>0</sub>	
a <sub>b</sub> '	2D exciton radius in NPLs	1.23 [nm]	$a_b = \frac{a_x}{2}$
Eg	Bulk band gap	2360 [meV]	12

### Table S1. Constants and parameters used in the paper

## Where:

 $m_0$  = Free electron mass,  $\varepsilon_0$  = Vacuum permittivity,  $a_H$  = Bohr radius of Hydrogen,  $R_H$  = Rydberg constant.



## Estimation of nanocrystal edge length from the central wavelength

Figure S10. Transformation of absorption and emission wavelengths to the edge length of CsPbBr3 in cubic phase, based on <sup>13</sup>.

## Additional less successful theoretical models for nanoplates

The first model <sup>14</sup> is the most general model (**eq. 5**).

The second model <sup>15</sup> consider the ligand type (**eq. S6**).

$$E_{x} = E_{g} + \frac{\hbar^{2}\pi^{2}}{2\mu L^{2}} + E_{b}^{x} \quad (S6)$$
Where:
$$E_{b}^{x} = -\frac{e^{2}}{\varepsilon_{QW}L} \left( ln \left( 8 \frac{\varepsilon_{QW}L_{b}}{\varepsilon_{b}a_{b}'} \right) - 2C + 2\gamma_{0} \right) \qquad L \ll a_{x} \quad strong \ confinement$$

where  $\varepsilon_{QW}$ ,  $\varepsilon_{b}$  are dielectric constants for the quantum well and barrier respectively,  $L_{b}$  is the width of the ligand barrier, C is Euler's constant,  $a_{b'}$  is the effective exciton radius, and  $\gamma$  is an eigenvalue which does not depend on the parameters of the problem. See **Table S1** for the parameters used.

The third model <sup>16</sup> considers the dielectric effect, using DFT.

The fourth model <sup>11</sup> considers SOC (spin-orbit coupling) effect, together with DFT analysis.

The last model <sup>17</sup> considers both quantum confinement and dielectric confinement effect in a single lawscale formula (**eq. 6**).



Figure S11. Comparison to theoretical models for NPLs.



## Stokes Shift Vs. initial conditions of the reaction

*Fig S12:* Correlation plots of Stokes Shift vs. initial conditions of the reaction. The spread of the points shows that there is no specific single factor which is responsible for the size of Stokes Shift.

## PLE and Absorption characterization

PLE characterization for nanoplates of the thickness of two monolayers and three monolayers. The data is presented together with the relevant absorption data.

These samples are purer than 0.82 and indeed the excitation characterization reflects this in the overlap of peaks in abs and PLE.



Fig S13: PLE and Absorption spectra for 2ML and 3ML nanoplates thickness.

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