ADVANCED OPTICAL MATERIALS

Supporting Information

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Aging Effects on the Exciton Relaxation and Diffusion Processes in $CsPbBr_3$ Nanocrystals

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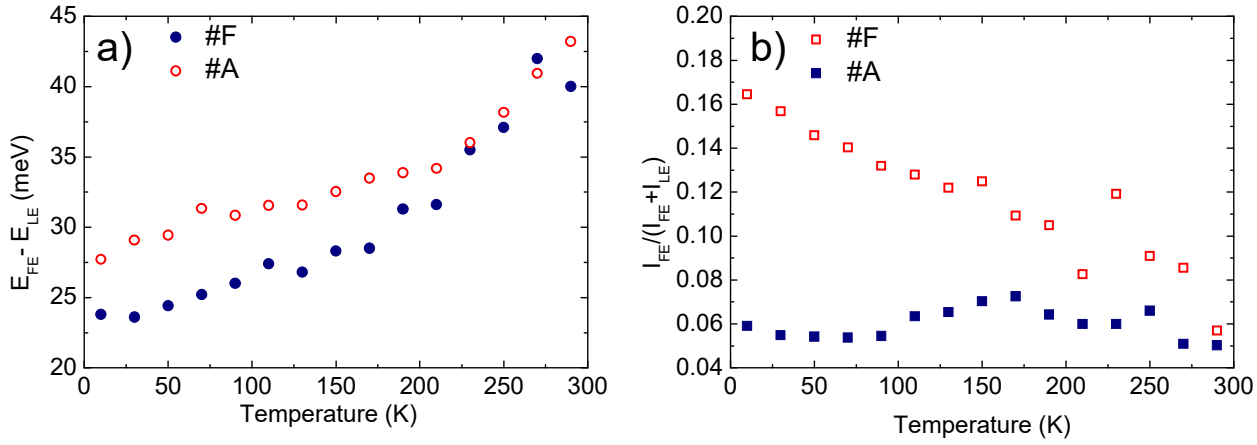

Figure S1: a) Energy difference between FE and LE bands as a function of temperature for sample # F (close-blue dots) and sample #A (open-red dots). b) Relative contribution of FE band integrated area for sample # F (close-blue squares) and sample #A (open-red squares).

PL peak energy temperature dependence

The linear increase of the peak energy is typically related to a lattice thermal expansion effect, dominating on the electron–phonons coupling contribution (that instead leads to a peak energy decrease as the temperature increases).

In order to analyse our data we performed a best fit with the following equation [S1,S2]:

$$E_g(T) = E_g(0) + A_{TE}T - S\langle E_{LO}\rangle[coth(\langle E_{LO}\rangle/2kT) - 1] \text{ (eq. SI1)}$$

where $E_g(0)$ is the band gap at 0K, A_{TE} is the thermal expansion coefficient, S is the Huang-Ring parameter (electron-phonon coupling) and $\langle E_{LO}\rangle$ is the average LO phonon energy.

The best fit curves, for the FE peaks of both samples, are reported in Figure 1 c and have been obtained for the best fit values reported in Table SI1.

Sample	Peak	E_0 (eV)	A_{TE} (meV/K)	S	$\langle E_{LO}\rangle$ (meV)
#F	FE	2.35158±0.00030	0.1244±0.0030	0	---
#A	FE	2.35471±0.00029	0.0752±0.0022	0	---

Tab SI1: Fit parameters for the temperature dependence for LE and FE bands energy, returned by eq.SI1

The best fit is obtained, for both samples, for S=0, thus evidencing the lack of contribution of LO phonons and, as a consequence, the fit doesn't allow to determine the best fit value of the average phonon energy.

Linewidth temperature dependence

The FWHM values as a function of temperature, for both FE and LE bands have been fitted in the frame of Bose-Einstein approximation:

$$\Gamma(T) = \Gamma_0 + \gamma T + \frac{\Gamma_{LO}}{e^{E_{LO}/kT}-1} \qquad \text{(eq.SI2)}$$

Where Γ_0 is the homogeneous broadening at 0K, γ is the exciton-acoustic phonons coupling constant, Γ_{LO} is the exciton-LO phonon coupling constant, and E_{LO} is the LO phonon energy. The lines through the data in Fig. 1d) represent the best-fit curves. In Tab.SI2 we report the parameter values returned by the fitting procedure.

Sample	Peak	Γ_0 (meV)	γ (meV/K)	Γ_{LO} (meV)	E_{LO} (meV)
#F	FE	30.23±0.38	0	30±21	26.3±9.0
#A	FE	28.00±0.64	0	17±12	22.1±9.1
#F	LE	70.58±0.56	0.056±0.018	40.4±4.0	17.9±2.3
#A	LE	77.11±0.33	0.0643±0.0081	51±10	32.1±4.7

Tab SI2: Fit parameters obtained for FWHM vs T analysis (eq.SI2) for #F and #A sample

We observe that in the FE bands, the fit is obtained for γ=0, demonstrating that the broadening is only due to due to optical phonon coupling and the LO phonon energy is compatible with the value expected for $CsPbBr_3$ [S3]. On the contrary, the LE band broadening can be reproduced by the fitting curve, but the best fit values of the LO phonon energy of the #A sample is clearly not consistent with the $CsPbBr_3$ LO phonon energy. This suggests that the LE broadening cannot be simply ascribed to phonon coupling.

PL relaxation dynamics

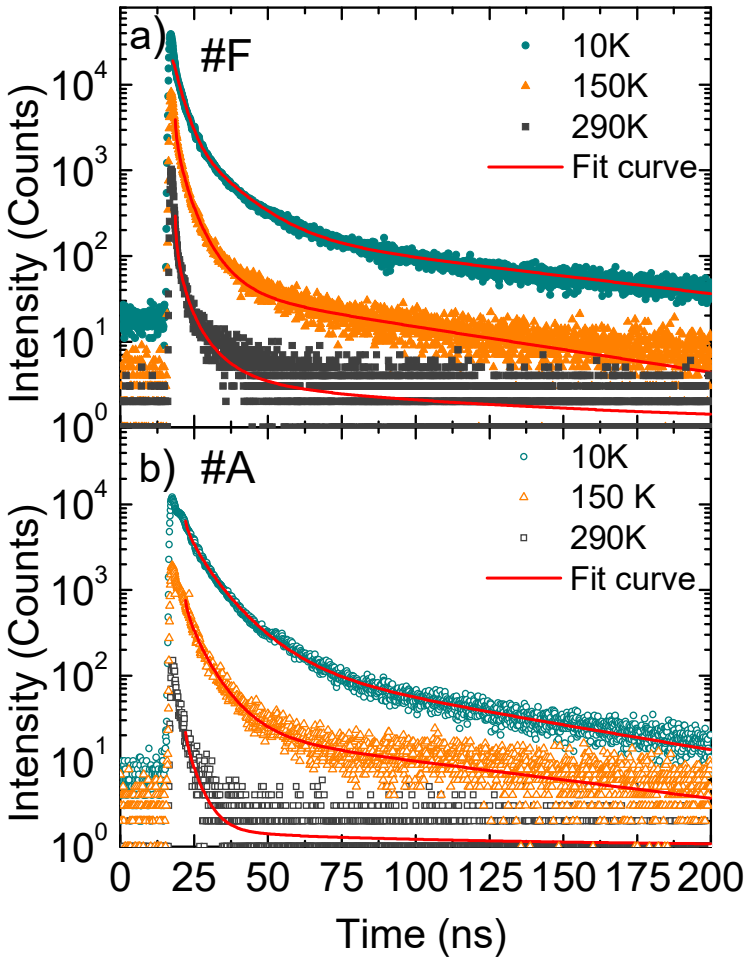

Figure S2: TRPL traces recorded at 10K, 150K and RT for sample #F (a) and sample #A (b).

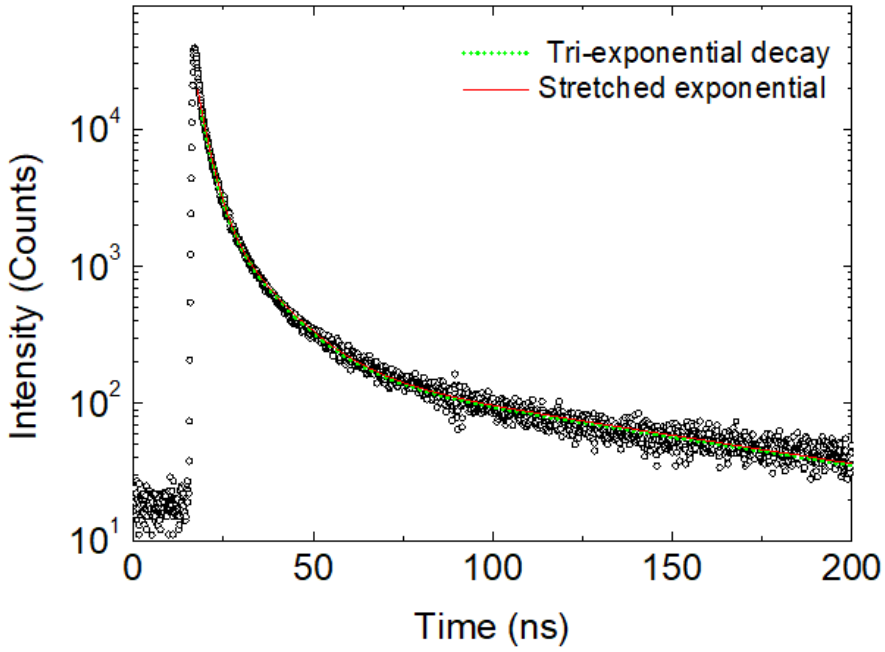

Figure S3: Experimental data of the PL decay in the #F sample at T=10 K (dots), compared with the best fit curve with a tri-exponential decay (green dotted line) and with Equation 2. It is evident that both fit-functions allow to excellently reproduce the experimental data.

TEM and XRD Measurements

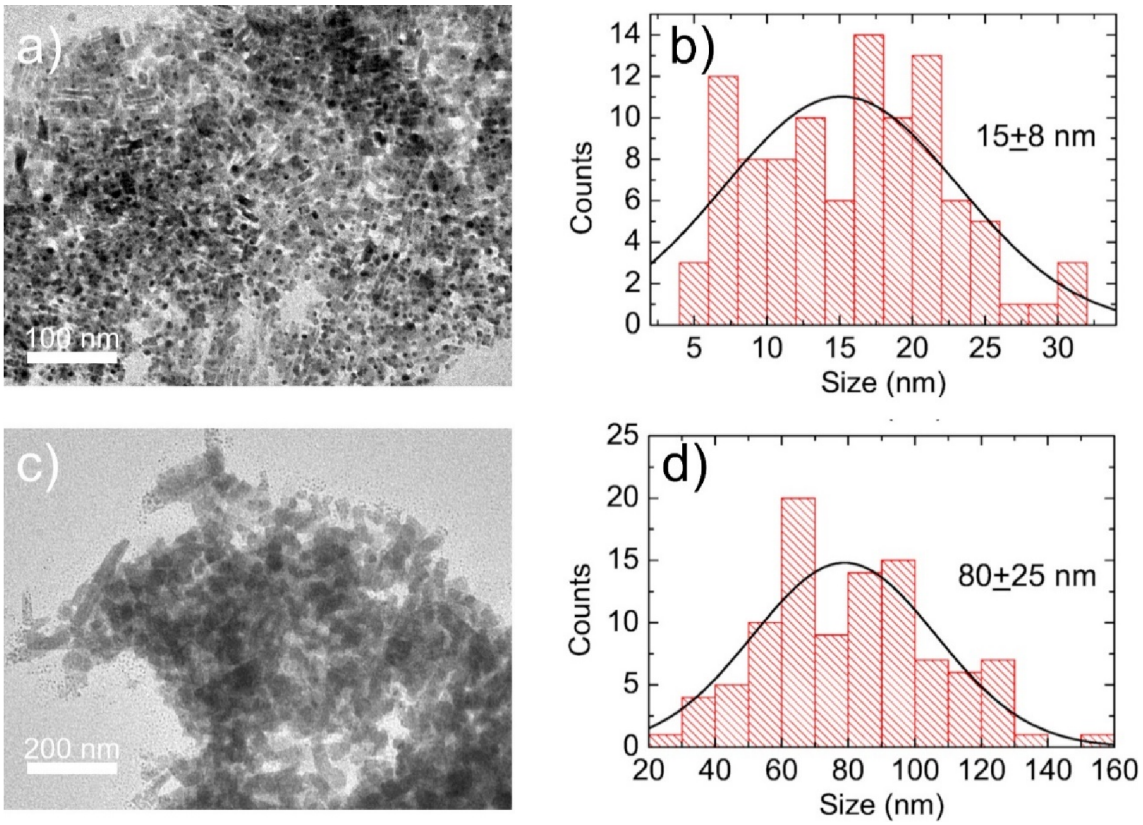

Figure S4: a) Transmission electron microscope image of the fresh NCs. b) Size distribution of the diagonal length of 100 different fresh NCs. c)Transmission electron microscope image of the aged NCs, clearly showing the size increase. d) Size distribution of the diagonal length of 100 different aged NCs.

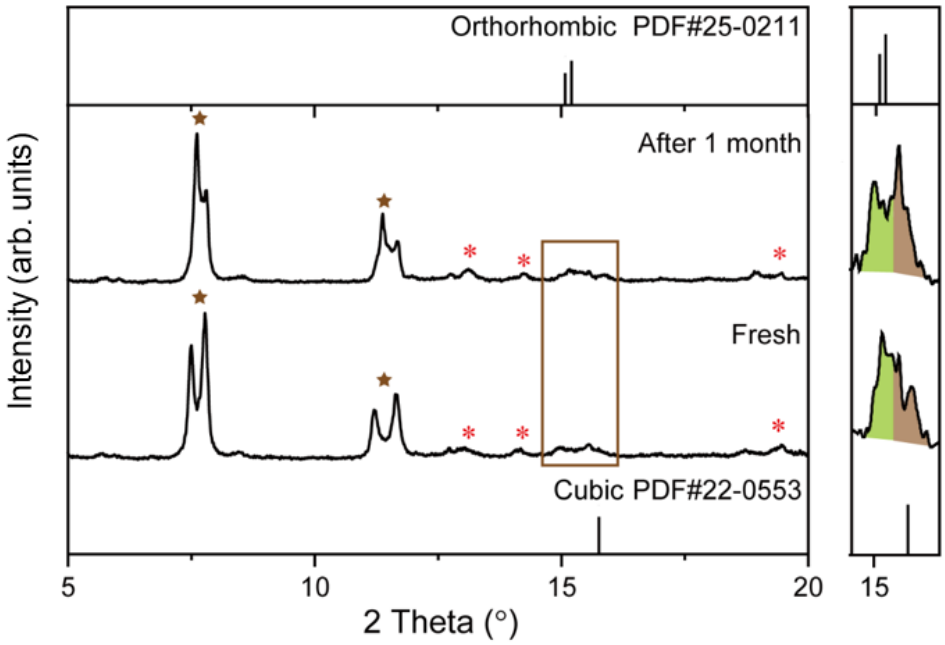

Figure S5: XRD spectra of the fresh and aged NCs, evidencing the absence of aging induced differences. The strong peaks at 7.7° and 11.5° evidenced an organized self-assembly of NC. The broad peak at 15.6° suggested a mixed phase of $CsPbBr_3$ with both cubic and orthorhombic, where the latter content decreased after one-month aging. The red astroids marked several impurity phases that were generated during synthesis.