

ADVANCED OPTICAL MATERIALS

Supporting Information

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Direct Observation of Shallow Trap States in Thermal
Equilibrium with Band-Edge Excitons in Strongly Confined
CsPbBr₃ Perovskite Nanoplatelets

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S1. Methods

Chemicals and Materials. All chemicals were used as received without further purification. Cesium carbonate (Cs₂CO₃, 99.9%) (Lot #MKBS7779V), lead bromide (PbBr₂, 99.999%) (Lot # MKCH7695), oleic acid (OA, 90%) (Lot # MKCF0988), dodecane (≥ 99%) (Lot # WXBC8792V), and oleylamine (OAm, 70%) (Lot # STBF4991V) were purchased from Sigma-Aldrich. Methyl acetate (99+%, extra dry) (1683170) and 1-octadecene (90%) (Lot # AO355864) were purchased from Across Organics. Zinc bromide (ZnBr₂, anhydrous 98%) (Lot # 1410751) was purchased from ABCR, and n-hexane (≥99%) (Lot # 1880693) was purchased from Fisher Chemical.

Synthesis of CsPbBr₃ NPLs. The synthesis has already been described in the literature.^[1] First, a solution of cesium oleate was prepared by adding Cs₂CO₃ (2.0 mmol), OA (2.5 mL) and octadecene (17.5 mL) together in a 50 mL three-necked flask. The mixture was warmed to 120 °C and dried on a Schlenk line for 60 min. The temperature was then increased to 150 °C under an argon atmosphere for 30 min to complete the reaction between Cs₂CO₃ and OA. The as-synthesized cesium oleate solution is stable for months but should be heated up to 110 °C before utilization due to the precipitation of cesium oleate in octadecene at room temperature.

The precursor solution of Pb and Br for CsPbBr₃ was prepared by mixing PbBr₂ (0.20 mmol) with ZnBr₂ (0.13 mmol), OA (1 mL) and OAm (1 mL) in dodecane (5 mL) in a 50 mL three-necked flask. ZnBr₂ salt was used to bring an excess of bromide to stabilize the NPLs. The solution was dried on a Schlenk line for 30 min. To ensure complete solubilization of PbBr₂, the mixture was heated to 150 °C under an argon atmosphere before being cooled to room temperature. Finally, the Cs oleate precursor (0.2 mL) was injected under vigorous stirring. After 20 min, 5 mL of methyl acetate was added, and the solution was centrifuged at 5000 rpm for 5 min. The unreacted lead and the large particles precipitated and were removed. Ten milliliters of methyl acetate was added to the supernatant, and the solution was centrifuged at 5000 rpm for 15 min to remove excess ligands. Finally, the purified NPLs were dissolved in dodecane (2 mL) and kept at 4 °C.

Characterization. The NPLs were diluted and placed in a 1 mm optical path quartz cuvette (Type 61, FireflySci) for characterization, and ultraviolet-visible absorption spectra were acquired on a Perkin Elmer Lambda 950 UV/Vis/NIR spectrometer. Steady-state and TCSPC measurements were carried out on a Horiba Jobin Yvon Fluorolog-3 instrument. The excitation source for TCSPC was a nanoLED N-390 with a repetition rate of 1 MHz, a pulse duration of 1.3 ns and an excitation wavelength of 390 nm. The PL was detected at 90° relative to the excitation source with a photomultiplier tube.

Broadband fluorescence up-conversion. Time-resolved emission measurements were achieved using a CPA Ti:sapphire laser (Libra, Coherent) producing 45 fs pulses centered at 800 nm with a 1 kHz repetition rate and a FLUPS setup (LIOP-TEC). Seventy-five percent of the beam was transmitted to white light seeded optical parametric amplifiers (OPerA-Solo, Coherent) to generate 110 μ J gate pulses at 1300 nm. The rest of the original beam was frequency doubled to 400 nm by a type I BBO crystal and set to the magic angle (54.7°) to consider only the population dynamics. A small beam stop and a 400 nm filter were placed after the sample position to block most of the transmitted 400 nm pump light. The horizontally polarized gate beam and vertically polarized fluorescence interacted in the 100 μ m thick BBO crystal (Eksma Optics), which had an optical axis in the horizontal plane. The upconverted signal was generated by type II sum frequency generation since the two inputs had different polarizations. This configuration is suitable for obtaining a broad frequency range. The large angle between the fluorescence and the gate beam, here 21°, helped the phase matching requirement and background-free detection of the signal. The signal was focused onto a fiber by a concave mirror while the frequency doubled gate beam and the upconverted pump beam were sent away. The fiber transmitted the light to a so-called unfolded Czerny-Turner spectrograph. The incoming signal was separated by wavelength through a UV grating and sent to a CCD detector (Newton 920, Andor). The dynamics of the fluorescence signal were obtained using a computer-controlled delay stage (PI) in the pump path. The time correction for the instrument response function (IRF) was calculated to be 190 fs using the cross correlation between the pump and the probe. The NPLs solution used for FLUPS had an optical density of 0.5 in a 1 mm optical path quartz cuvette at 400 nm and was stirred by a tiny argon flow to avoid bleaching.

TA measurement. Ultrafast TA spectra of CsPbBr₃ NPLs were obtained using a CPA Ti:sapphire laser (Clark-MXR, CPA-2001) to produce 120 fs pulses centered at 778 nm with a 1 kHz repetition rate. A part of the beam was focused into a CaF₂ crystal, which yielded a white light continuum from 400 to 780 nm. The rest of the pump beam was frequency doubled to 389 nm by a 0.5 mm BBO crystal and chopped at 500 Hz. The probe light was smaller and weaker than the pump beam to obtain a homogeneously probed area. The probe beam was split before the sample into a reference and a signal, the latter went through the sample, and both were sent separately into a spectrograph (Princeton Instruments, Spectra Pro 2150i) and detected shot-to-shot by CCD cameras (Hamamatsu S07030-0906). The dynamics of the photoinduced spectra were acquired using a digitally controlled delay stage (PI) in the pump path. The time resolution of the experiment was calculated to be 250 fs.

S2. Data treatment

Data treatment for FLUPS. Data extraction and correction were achieved with a MATLAB routine. The numbers of counts depending on the time and pixel number (p) of the CCD camera were stored as 2D matrices. First, pixels were converted into wavelengths corresponding to the recorded upconverted signal, λ_U , using a calibration curve recorded with a standard mercury lamp. Then, the gate wavelength was precisely calculated by subtracting the energy of the upconverted pump beam by the scattering of the unconverted pump beam. The gate energy was subsequently subtracted from λ_U to obtain the wavelength of visible fluorescence light, λ_F . Moreover, the intensity of the signal was also corrected for each wavelength since the pixels of the CCD camera had different energy widths: a pixel in the UV part corresponds to a wider photon energy range than a pixel in the visible part. Hence, the number of counts was multiplied by λ_U^2/λ_F^2 to obtain the “true” signal as a function of both time and wavelength. The time correction for the IRF was calculated using the cross correlation between the pump and the probe. This peak was fitted with a 2D Gaussian function, and the full width at half maximum (FWHM) and the center of the Gaussian function (t_0) were extracted. Each time was then subtracted by t_0 . The group delay of light pulses over a given distance in fused silica was calculated and adjusted to match the experimental data. Then, the shifted time delays were interpolated to give the time-corrected signal.

Fitting of the model. Before fitting the data to the model using *Wolfram Mathematica* software, 10 kinetics traces around the peak position of each sample were averaged and normalized. The data before 0.5 ps were cut to ensure that the hot carriers relaxed to the lowest excited state. The differential equations (**Equation 2-4**) with the starting conditions shown in **Equation S1** were analytically solved using *Mathematica* for a 0.5-1200 ps interval, covering the data.

$$N_{X_1}(0) = 1 - a ; N_{X_S}(0) = 0 ; N_{X_1'}(t) = a \quad (\text{S1})$$

where N_{X_1} , N_{X_S} and $N_{X_1'}$ correspond to the populations of the excitons that cannot be trapped into deep trap states, excitons trapped into shallow states and excitons that can be trapped into deep trap states, respectively. k_1 , k_{-1} , k_2 , and k_3 are the rate constants for trapping into the shallow trap states (S), detrapping from the shallow trap states, trapping into the deep trap states (D) and radiative recombination, respectively, and a is the proportion of particles with deep trap states (D). Since we consider the trapping into the shallow trap states to be reversible, the population distribution between the lowest excitonic state (1) and the shallow trap states (S) follows a Maxwell-Boltzmann distribution. Therefore, k_1 and k_{-1} are related to each other by **Equation 1**. The FLUPS signal and GSB intensity are then simulated using **Equation 5-6**.

A global analysis of the data recorded for the sample with an excess of bromide was carried out to extract the proportion of particles with deep trap states. We applied the analytical solution found by solving differential Equations 2-4, and fitted at the same time all the traces with k_1 , k_2 , k_3 , ΔE and a . The first four parameters should not be affected by sample ageing and were linked together while the proportion of particles with deep trap state was let free. The

fits are shown in **Figure S4** and **S6**, while the extracted values for k_1 , k_2 , k_3 , ΔE and a are displayed in **Table S1** and **S2**.

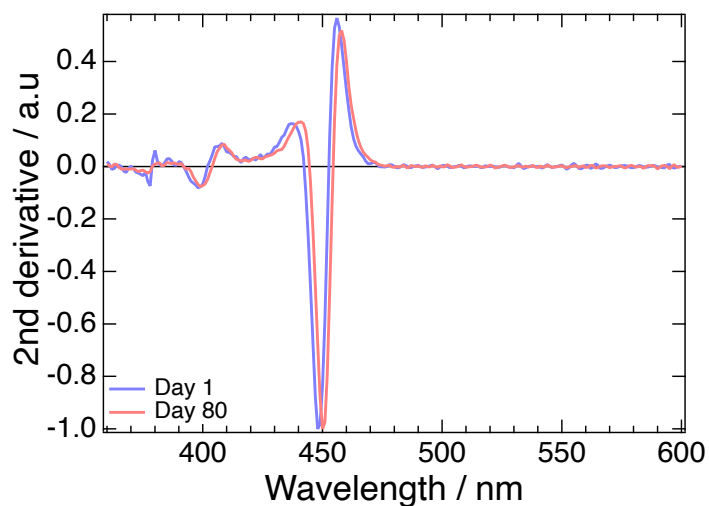


Figure S1. Second derivative of the absorption spectrum of as-synthesized CsPbBr₃ NPLs (blue line) and after 80 days (red line).

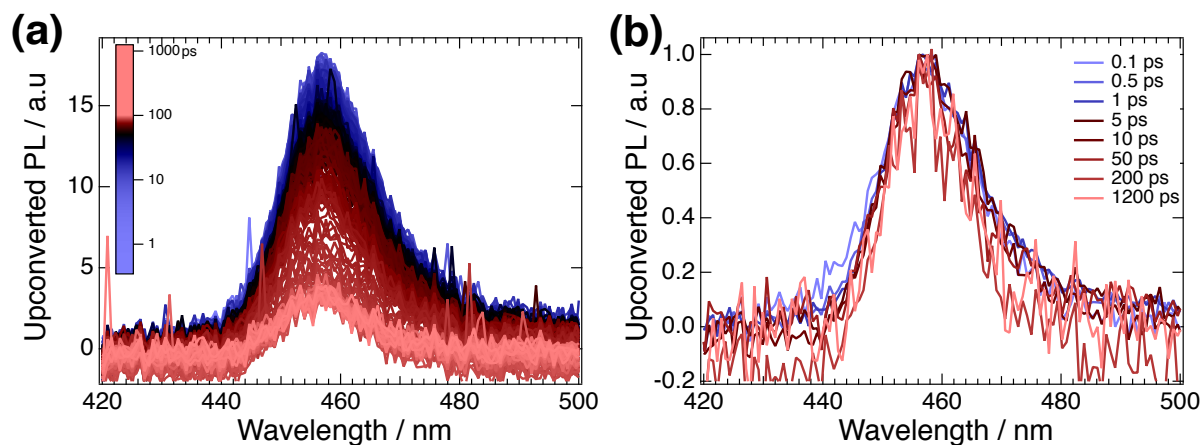


Figure S2. (a) Time-resolved emission spectral slices of CsPbBr₃ acquired by FLUPS ($\lambda_{\text{exc}} = 400$ nm) for $\langle N_{\text{exc}} \rangle = 0.2$. (b) Normalized spectral slices after given time delays.

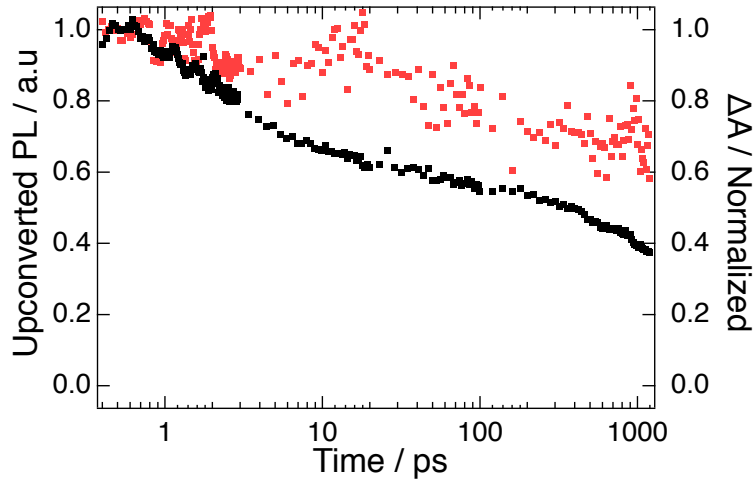


Figure S3. (a) Logarithmic plot of the time-evolution of the absorbance change (ΔA) at the exciton bleaching peak ($\lambda = 450$ nm) in the TA spectra (red dots) and of the photoluminescence intensity (PL) at peak ($\lambda = 455$ nm) in the FLUPS spectra (black dots).

Table S1. Parameters extracted from the fits displayed in Figure S4 for different ligands or passivation strategies.

Ligand / passivation	k_1 [s^{-1}]	k_2 [s^{-1}]	k_3 [s^{-1}]	ΔE [meV]	a
OA / ZnBr ₂	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.05
OA	1.4×10^{11}	4.9×10^{10}	8.3×10^8	10	0.19
TOPO	3.2×10^{11}	2.9×10^{10}	7.7×10^8	-2	0.20

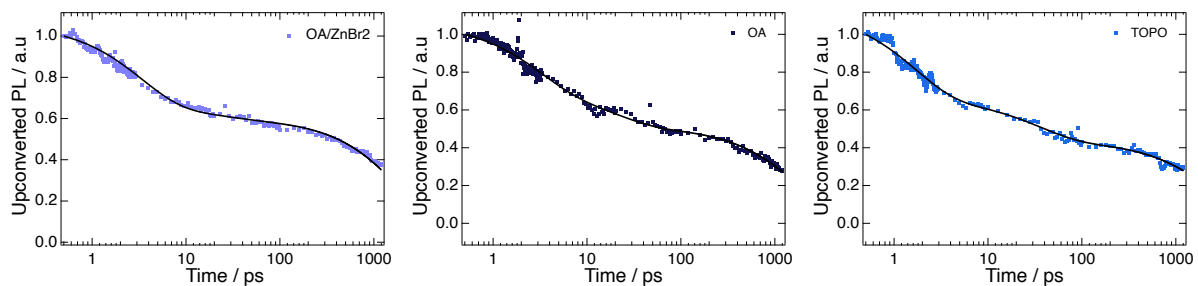


Figure S4. Normalized PL decays (dots) and best fits (lines) obtained according to the abovementioned procedure for different ligands or passivation strategies.

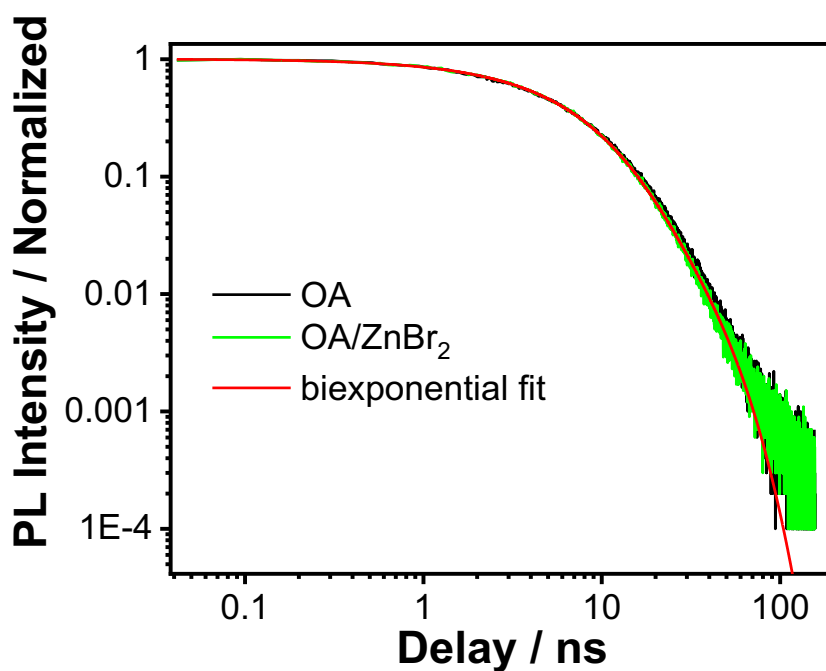


Figure S5. PL decay on longer timescales measured by TCSPC technique.



Figure S6. Normalized PL decays (dots) and best fits (lines) obtained according to the abovementioned procedure for different sample ages.

Table S2. Parameters extracted from the fits displayed in Figure S5 for different sample ages.

OA / ZnBr ₂	k_1 [s ⁻¹]	k_2 [s ⁻¹]	k_3 [s ⁻¹]	ΔE [meV]	a
Day 1	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.05
Day 10	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.22
Day 20	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.28
Day 40	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.38
Day 80	1.2×10^{11}	4.5×10^{10}	7.5×10^8	10	0.49
TA - day 1	/	4.5×10^{10}	7.5×10^8	/	0.07

Reference

- [1] B. R. C. Vale, E. Socie, A. Burgos-Caminal, J. Bettini, M. A. Schiavon, J.-E. Moser, *J. Phys. Chem. Lett.* **2020**, *11*, 387-394.