

Supporting Information for

Hot-Carrier Dynamics in Perovskite Nanocrystal Solids: Role of the Cold Carriers, Nanoconfinement and the Surface

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Sample preparation details

1. Substrate preparation

Before deposition of the materials, CaF_2 substrates (12 mm diameter, 1 mm thickness, EKSMA Optics) were treated with O_2 plasma to improve wetting.

2. Chemicals

Cs_2CO_3 (99.9%), lead (II) acetate trihydrate (99.99%), bromine (99.9%), 1-octadecene (ODE, 90%), 3-(N,N-dimethyloctadecylammonio)propanesulfonate (ZI, >99%), oleic acid (OA, 90%), HBr (48% in water), formamidinium acetate (99%) and dimethyl sulfoxide (DMSO, 99.9%) were obtained from Sigma Aldrich/Merck. PbBr_2 (99.9%) and CsBr (99.9%) were obtained from Alfa Aesar. Trioctylphosphine (TOP, >97%) and oleylamine (OLA, >95%) were obtained from STREM. Methyl acetate was obtained from ABCR. Toluene (for synthesis), ethanol (95.9%), diethylether (99.8% not stabilized) and ethylacetate (>99.7%) were obtained from Fischer. All chemicals were used as purchased, without further purification.

3. Preparation of perovskite NC samples

3.1. ZI-capped CsPbBr_3 NCs

3.1.1. Precursor synthesis

3.1.1.1. Cs-oleate 0.4 M in ODE. Cs_2CO_3 (1.628 g, 10 mmol), OAc (5 mL, 16 mmol) and ODE (20 mL) were evacuated at 25-120 °C until the gas evolution ended.

3.1.1.2. Pb-oleate 0.5 M in ODE. Lead (II) acetate trihydrate (4.6066 g, 12

mmol), OAc (7.6 mL, 24 mmol) and ODE (16.4 mL) were mixed in a three-necked flask and evacuated at 25-120 °C until the evaporation of acetic acid and water was complete.

3.1.1.3. TOP-Br₂ 0.5 M in toluene. TOP (6 mL, 13 mmol) and bromine (0.6 mL, 11.5 mmol) were mixed under inert atmosphere. Once the reaction was complete and cooled back to room temperature, the TOP-Br₂ was dissolved in toluene (18.7 mL).

3.1.1.4. Oleylammonium bromide (OLAmBr). OLAmBr was synthesized by mixing 62.5 mL OLAm (0.19 mol, 1 eq.) and 21.5 mL HBr (0.127 mol, 0.67 eq.) in 500 mL ethanol at 0°C. The solvent was evaporated in vacuo and OLAmBr was isolated by recrystallization with diethylether.

3.1.2. ~8 nm diameter CsPbBr₃ NCs. CsPbBr₃ NCs were synthesised according to a previously published method.¹ 1 mL lead-oleate (0.5 M in ODE), 0.8 mL Cs-oleate (0.4 M in ODE), 0.0445 g of ZI and 10 mL ODE were added to a 25 mL three-neck flask and heated to 130 °C under vacuum. As soon as the reaction temperature was reached, the atmosphere was changed to nitrogen and 0.42 g of OLAmBr (dissolved in 3 mL of toluene) was injected. The reaction mixture was immediately cooled to room temperature by means of an ice bath. The crude solution was centrifuged at 29500 g for 10 min. The precipitate was discarded and ethylacetate (30 mL) was added to the supernatant (ca. 15 mL). The mixture was centrifuged at 29500 g for 10 min and the precipitate was dispersed in toluene (3 mL). This solution was subjected

to three additional rounds of precipitation with ethylacetate (6 mL) and centrifugation at 29500 g for 1 min and subsequent redispersion in toluene (3 mL).

3.1.3. ~13 nm diameter CsPbBr₃ NCs. These NCs were prepared according to the same method as for the smaller NCs above.¹ 5 mL (lead-oleate 0.5 M in ODE), 4 mL Cs-oleate (0.4 M in ODE), 0.2145 g of ZI and 50 mL ODE were added to a 100 mL three-neck flask and heated to 120 °C under vacuum, where the atmosphere was changed to nitrogen. The mixture was subsequently heated to 180 °C. When the reaction temperature was reached, 5 mL of TOP-Br₂ (0.5 M in toluene) was injected and the reaction was immediately cooled to room temperature using an ice bath.

3.1.4. Didodecyldimethylammonium bromide (DDAB) capped CsPbBr₃ NCs

3.1.4.1. Preparation of cesium oleate. 815 mg Cs₂CO₃ (99.9%), 40 mL ODE (90%) and 2.5 mL OAc (90%) were loaded into 100 mL three-neck flask, dried for 1h at 100 °C, and then heated under N₂ to 120-130 °C until all Cs₂CO₃ reacted with OAc. Before injection, Cs-oleate was pre-heated to ca. 100 °C.

3.1.4.2. Synthesis of CsPbBr₃ NCs. 69 mg PbBr₂ (0.188 mmol) was suspended in 5 mL ODE and dried at 100 °C for 30 min. 0.5 mL OAc (vacuum-dried and stored in glovebox) and 0.5 mL OLAm (vacuum-dried and stored in glovebox) were injected into the flask at 120 °C. The reaction mixture was heated up to 180 °C and 0.4 mL pre-heated caesium oleate in ODE was injected. The reaction mixture was cooled for 10 s with an ice bath to room temperature.

3.1.5. Purification and size-selection of CsPbBr₃ NCs. The crude solution was centrifuged (Eppendorf 5804) at 12.1 krpm for 5 min. The supernatant was discarded and the precipitate was dissolved in 300 µL hexane. The hexane solution was

centrifuged again at 10 krpm for 3 min and the precipitate was discarded. The supernatant was diluted two times and used for further DDAB/PbBr₂ treatment.

3.1.6. DDAB/PbBr₂ treatment of CsPbBr₃ NCs. DDAB/PbBr₂ solution was prepared by dissolving 36.7 mg PbBr₂ (0.1 mmol) and 92 mg DDAB (0.2 mmol) in 3 mL toluene. 0.6 mL toluene and 150 μ L of the DDAB/PbBr₂ solution were added to the colloidal solution of CsPbBr₃ NCs. The mixture was stirred for 1 h, followed by the precipitation with 1.8 mL of ethyl acetate and centrifuged at 12.1 krpm for 3 min. The precipitate was redispersed in 0.5 mL toluene.

3.2. DDAB-capped FAPbBr₃ NCs

3.2.1. Preparation of oleylammonium bromide (OLAmBr). 12.5 mL OLAm and 100 mL ethanol were mixed in a 250 mL flask. The reaction mixture was cooled in an ice/water bath and 8.56 mL HBr (48% aqueous solution) was added. The reaction mixture was left to react overnight under nitrogen flow. Then the solution was dried in a rotary evaporator and the obtained precipitate was washed multiple times with diethyl ether. The resultant white powder was dried under vacuum at room temperature for several hours. OLAmBr was stored in the glovebox.

3.2.2. Synthesis of FAPbBr₃ NCs. 76 mg lead (II) acetate trihydrate (0.2 mmol) and 78 mg formamidinium acetate (0.75 mmol) were suspended in 8 mL ODE and 2 mL OAc heated to 50 °C, then dried under vacuum for 30 min. Then the reaction mixture was heated to 130 °C and a mixture of 266 mg OLAmBr (0.8 mmol) in 2 mL anhydrous toluene was injected into the reaction flask. To dissolve the OLAmBr

in toluene, the mixture was heated to 40-50 °C. After another 30 s, the reaction mixture was cooled by an ice/water bath.

3.2.3. Purification of NCs. 16 mL of methyl acetate was added to the crude solution followed by the centrifugation at 12.1 krpm for 5 min and the supernatant was discarded. The precipitate was dissolved in toluene (5 mL) and the solution was centrifuged again at 3 krpm for 2 min. The supernatant was retained for the DDAB-treatment, while the precipitated NCs were discarded.

3.2.4. DDAB-treatment of FAPbBr₃ NCs. 5 mL toluene was added to FAPbBr₃ colloidal solution prepared as described above. Then 0.1 mL of OAc and 0.54 mL of DDAB (0.05 M in toluene) were added to 10 mL colloidal solution of FAPbBr₃ NCs. The mixture was stirred for 1 h, followed by the precipitation with 16 mL ethyl acetate and centrifuged at 12.1 krpm for 3 min. The precipitate was redispersed in 2.5 mL toluene and this solution was additionally filtered through a 0.45 µm PTFE filter.

3.3. Dropcasting of NCs. The concentrated NC inks were dropcast from solution onto the cleaned substrates in a N₂ atmosphere. The thickness of the thin films were determined to be ~300 nm by UV-vis ellipsometry.

4. Preparation of bulk CsPbBr₃ films

The bulk CsPbBr₃ films were prepared by dissolving a 1:1 mole ratio of PbBr₂ and CsBr in DMSO with concentration of 0.4 M and stirring at 50 °C overnight. Afterwards, ~35 µL of the as-prepared solution was dropped onto the substrate and spin-coated at 3000 rpm for 2 min. The solvent extraction method was then applied by using 300 µL chloroform after 1 min

spinning.^{2,3} The as-formed thin films were then thermally annealed on a hot plate at 100 °C for 10 min inside the glovebox. The thin film layer thicknesses were determined by UV-vis ellipsometry to be ~300 nm.

Optical characterization. UV-Vis absorption spectra were obtained for the perovskite films on CaF₂ using a Shimadzu 2600 spectrometer equipped with an ISR-2600Plus integrating sphere attachment. The slit width was 5 nm and the sampling interval was 1 nm. Steady-state PL spectra were obtained using a Fluorolog-3 spectrofluorometer (Jobin Yvon, HORIBA). The excitation was set to 350 nm, and spectra were collected between 400 and 600 nm with a 0.2 s integration time, and 10 nm slit width. Films were measured in the front-facing geometry.

Electron microscopy. The edge length of all NC samples was determined by scanning transmission electron microscopy (STEM). A TEM grid was mounted on a cooling holder, and measurements were performed using an aberration-corrected, dedicated STEM microscope (HD-2700CS, Hitachi) at an acceleration potential of 200 kV (cold field emitter). A probe corrector (CEOS) in the microscope column between the condenser lens and the probe-forming objective lens provides a resolution below 0.1 nm. Images were recorded with a high-angle annular dark field (HAADF) detector. In HAADF-STEM (Figure 1(b)), the image is generated with incoherently scattered electrons, resulting in an intensity (Z-contrast) which strongly increases with the atomic number. The images (1024×1024 pixels) were recorded with frame times between 10 and 20 s. The sample was cooled to 77 K with liquid nitrogen.

Ultrafast optical spectroscopy. A 4 kHz Ti:sapphire regenerative amplifier (Astrella, Coherent) provided seed pulses (800 nm, ~35 fs) to two optical parametric amplifiers (TOPAS-Prime, Coherent). The pump energy was selected by tuning the signal output of “TOPAS 1” and the articulation of a β -barium borate crystal as appropriate. The NIR idler output (2073 nm) of “TOPAS 2” was split into two paths; ~90% of the intensity was used as the push, and the remaining ~10% was used as the probe. The pump was modulated at 2 kHz by an optical chopper, and the time delays of the pump and probe were controlled using mechanical delay stages. The pump and probe adopted a collinear geometry, with the push beam travelling on a separate optical path. The pump and probe beams were directed to a ~200 μm diameter spot on the sample using a 10 cm concave mirror. The push was slightly defocused to facilitate beam overlap and prevent photodegradation of the sample, and blocked completely for pump-probe measurements. For each material system, at least three spots on two separate films were measured. The sample was housed in a N_2 -purged quartz cuvette during measurements. Changes to the transmission of the probe were detected by an amplified PbSe photodetector (PDA20H-EC, ThorLabs), coupled to a lock-in amplifier (SR830, Stanford Research Systems).

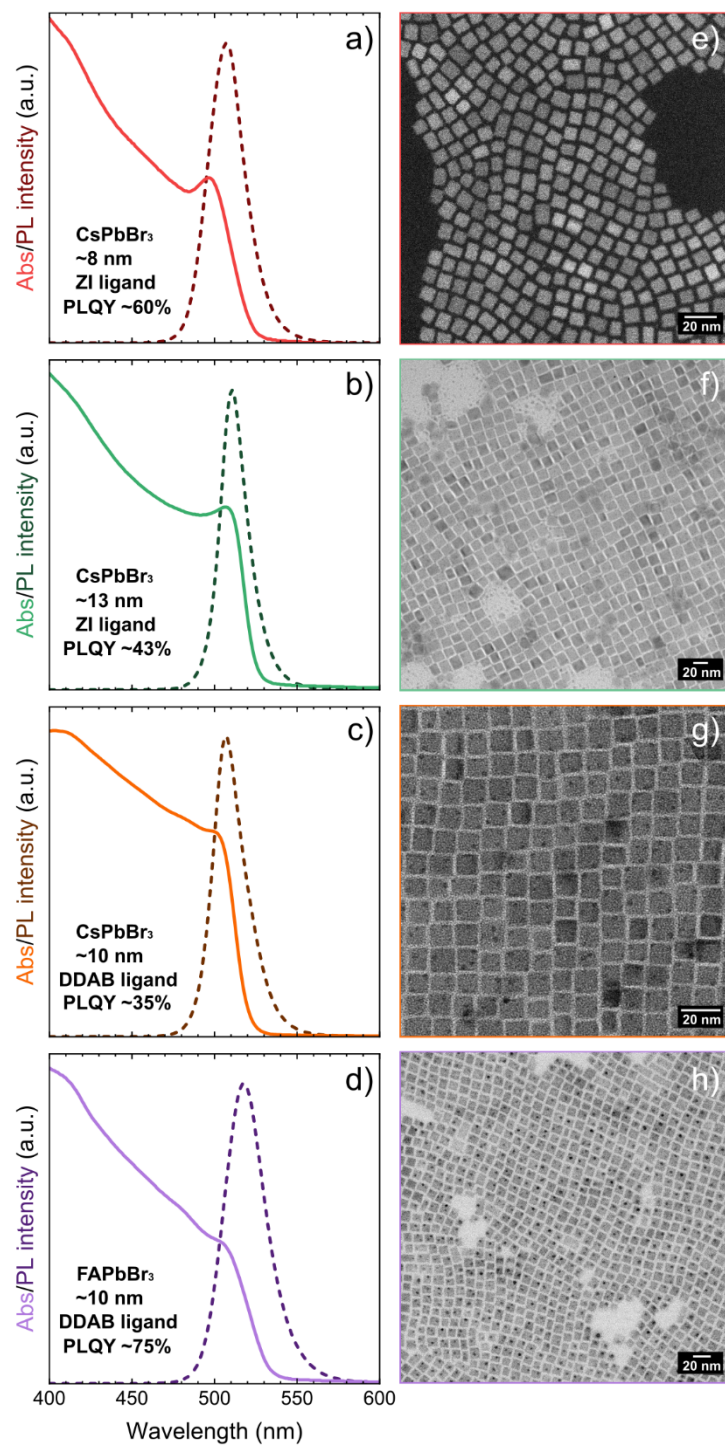


Figure S1. Steady-state absorption (solid lines) and emission data (dashed lines) for the dropcast films (a-d) alongside the electron micrographs for the corresponding NCs (e-h).

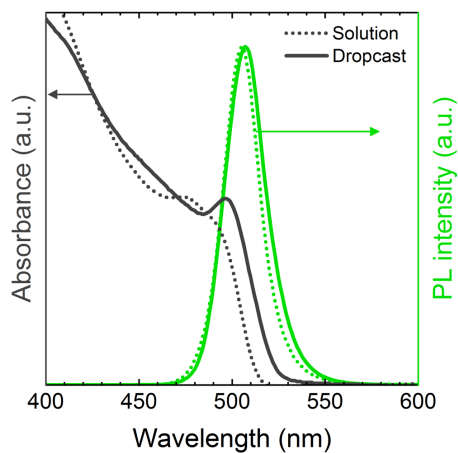


Figure S2. Steady-state absorption (black) and emission data (green) for the ZI-capped ~ 8 nm CsPbBr_3 NCs dropcast film (solid line) and solution (dotted line).

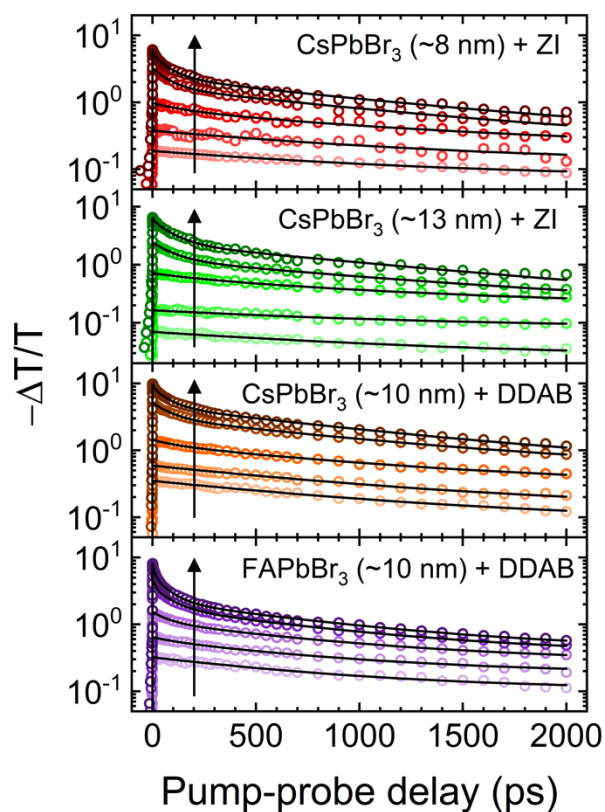


Figure S3. Fluence-dependent pump-probe kinetics for the dropcast NC films. Fluences used: 0.8, 1.6, 4.0, 16 and 32 $\mu\text{J cm}^{-2}$. Pump: 500 nm, probe: 2100 nm. Solid lines are multiexponential fits as a guide to the eye.

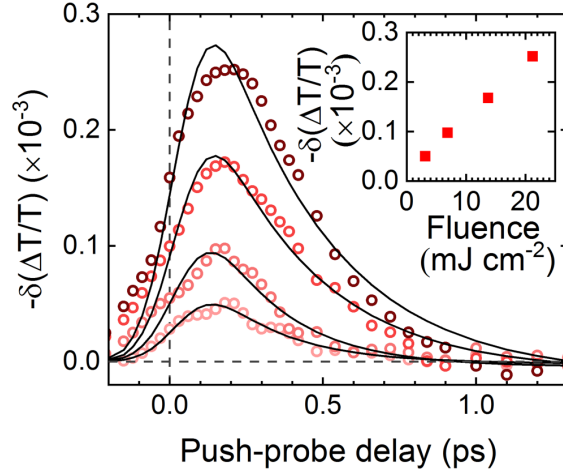


Figure S4. Push fluence dependence of the differential transmission signal for the dropcast film of ZI-capped ~ 8 nm CsPbBr₃ NCs at a fixed pump fluence ($3 \mu\text{J cm}^{-2}$). The peak amplitude of the push-induced bleach is shown as a function of the push fluence in the inset. Pump: 500 nm, push: 2100 nm, probe: 2100 nm. Solid lines are monoexponential fits convoluted with a Gaussian.

Determination of $\langle n_0^{\text{hot}} \rangle$:

The average initial hot carrier density, $\langle n_0^{\text{hot}} \rangle$, is derived from the product of the average initial cold carrier density, $\langle n_0^{\text{cold}} \rangle$ and the ratio between the amplitude of the push-induced bleach and the pump-induced absorption. $\langle n_0^{\text{cold}} \rangle$ is determined as:

$$\langle n_0^{\text{cold}} \rangle = \frac{E_{\text{inc}}(1 - 10^{-A})}{\pi R^2 d E_{\text{exc}}}$$

where E_{inc} is the incident energy per pump pulse, E_{exc} is the pump photon energy, A is the sample absorbance at the pump wavelength, R is the beam radius and d is the sample thickness.

Because this procedure directly incorporates the value of the push-induced bleach, any “saturation effect” is accounted for in the calculation of $\langle n_0^{\text{hot}} \rangle$, which is the basis of the x-axis in the main experimental results.

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- (2) Kerner, R. A.; Zhao, L.; Xiao, Z.; Rand, B. P. Ultrasooth Metal Halide Perovskite Thin Films via Sol–Gel Processing. *J. Mater. Chem. A* **2016**, 4 (21), 8308–8315.
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