

## Supporting Information

### **Accelerated Polaron Formation in Perovskite Quantum Dots Monitored Via Picosecond Infrared Spectroscopy**

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## Sample Preparation

### Chemicals:

Formamidinium bromide (FABr,  $\geq 98\%$ ), cesium bromide (CsBr, 99.9%), lead (II) bromide (PbBr<sub>2</sub>, 98%), oleyamine (OLA, technical grade 70%), N,N-Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), toluene (99.8%), and chlorobenzene (99.8%) were purchased from Sigma-Aldrich. Octadecene (ODE, technical grade 90%) and oleic acid (OA, technical grade 90%) were purchased from Alfa Aesar.

### Cs<sub>0.2</sub>FA<sub>0.8</sub>PbBr<sub>3</sub> quantum dot film:

0.008g of CsBr, 0.2g of FABr, and 0.7 of PbBr<sub>2</sub> were stirred and dissolved in 5 mL of DMF. Upon complete dissolution, 100  $\mu$ L of OA and 50  $\mu$ L of OLA were added into the solution. 200  $\mu$ L of the solution was then extracted and added into 5 mL of toluene. The solution was left to stir for a day. The solution was subsequently drop casted onto a calcium fluoride substrate. All synthesis were conducted at room temperature.

### Cs<sub>0.2</sub>FA<sub>0.8</sub>PbBr<sub>3</sub> bulk film:

0.08g of CsBr, 0.2g of FABr, and 0.7g of PbBr<sub>2</sub> were stirred and dissolved into 1.67 mL of DMSO till complete dissolution. Chlorobenzene was first spin-coated (4000 rpm) onto a calcium fluoride substrate and the solution was subsequently spin-coated on top of the sample. The resulting film was baked at 100°C for an hour. All synthesis was conducted under nitrogen environment.

Transmission electron microscopy (TEM) was conducted on a JEM-1400 flash electron microscope operating at 100 kV. The TEM samples were prepared by drop-casting the quantum dot solution onto a TEM grid consisting of a carbon supporting film and copper grids.

## UV/VIS, PL and Infrared Spectroscopy

Steady-state UV/VIS spectra were recorded on a Shimadzu 1900i spectrometer. Infrared spectra were obtained using a Bruker Vertex 80v FTIR spectrometer. To reduce water vapor absorption effects, the entire spectrometer was evacuated. PL spectra were recorded with a home-made set-up consisting of an iO matchbox wavelength combiner, suitable filters and an Avantes avaspec 3648 fiber spectrometer.

## Time-Resolved Infrared Spectroscopy

The time-resolved infrared spectroscopy set-up is based on a Ti:Sapphire CPA-amplifier (Coherent Libra, 100 fs, 1 kHz, 800 nm). The samples were excited close to the band edge at 525 nm employing a two-stage non-collinear optical parametric amplifier (NOPA, Ag Riedle). The pump pulse is polarized parallel to the probe pulse using a lambda/2 plate and a polarizer. After passing a linear delay stage, the pump beam is focused to a diameter of about 100  $\mu\text{m}$ . The probe beams are generated using the signal and idler output of two-stage NIR optical parametric amplifier in a difference frequency generation stage with a AgGaS<sub>2</sub> crystal. The probe beam is split into two and is focused onto the sample. One of the probe beams acts as a reference to improve s/n-ratio passing the sample in an unpumped spot. Both probe beams are detected on 2x64 pixel HgCdTe detector (Infrared Associates). The absorbance change  $\Delta OD$  is calculated as  $\Delta OD = -\log_{10} T/T_0$  with T being the transmission measured for the pumped sample and T<sub>0</sub> being the reference signal with the pump pulse being blocked by a chopper wheel.

## Computational Methods

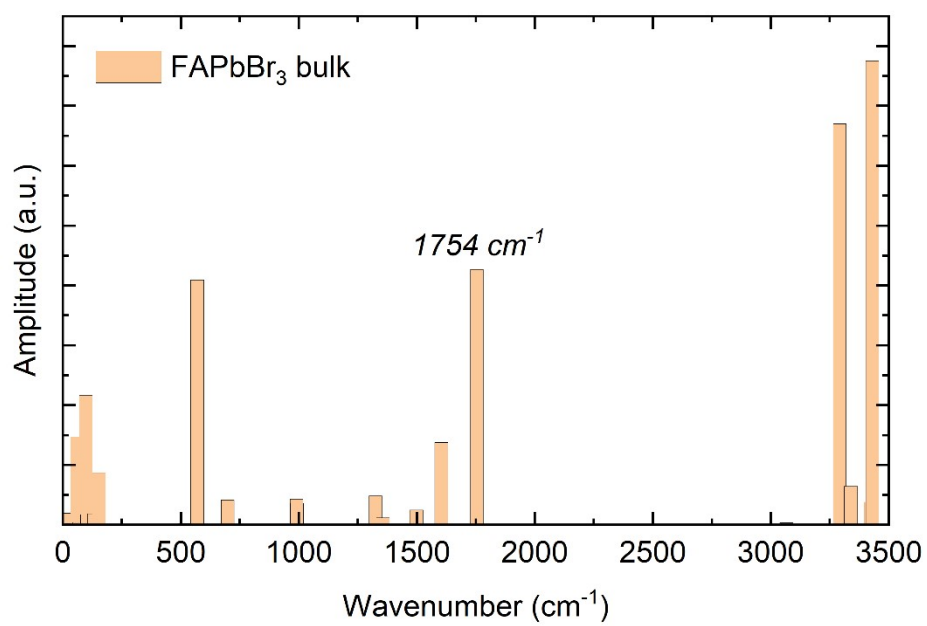
The density functional theory (DFT) calculations were performed using the PWSCF code as implemented in Quantum ESPRESSO (QE) package.<sup>1</sup> The crystal structure of cubic-phase FAPbBr<sub>3</sub> was optimized by local density approximation (LDA) exchange-correlation functional and norm-conserving pseudopotentials with electrons from H (1s<sup>1</sup>), C (2s<sup>2</sup>, 2p<sup>2</sup>), N (2s<sup>2</sup>, 2p<sup>3</sup>), Br (4s<sup>2</sup>, 4p<sup>5</sup>), and Pb (6s<sup>2</sup>, 6p<sup>2</sup>). The plane-wave basis set cutoff for the wave functions was 50 Ry and for the charge density was 400 Ry, and a uniform grid of 6x6x6 *k*-mesh was used. The crystal structure was fully relaxed until the total force on each atom was less than 0.01 eV/Å. The resulting crystal parameters of ground state for FAPbBr<sub>3</sub> are  $a = 5.96 \text{ \AA}$ ,  $b = 5.77 \text{ \AA}$ ,  $c = 5.90 \text{ \AA}$ . The infrared vibrational mode positions and intensities (at the  $\Gamma$  point of the first Brillouin zone) for FAPbBr<sub>3</sub> were calculated with the Phonon code as implemented in the QE package. The uniform grids of 8x8x8 Monkhorst-Pack scheme were used for the *k*-point sampling together with self-consistency threshold of 10<sup>-14</sup> Ry.

## Time-Resolved PL Measurements

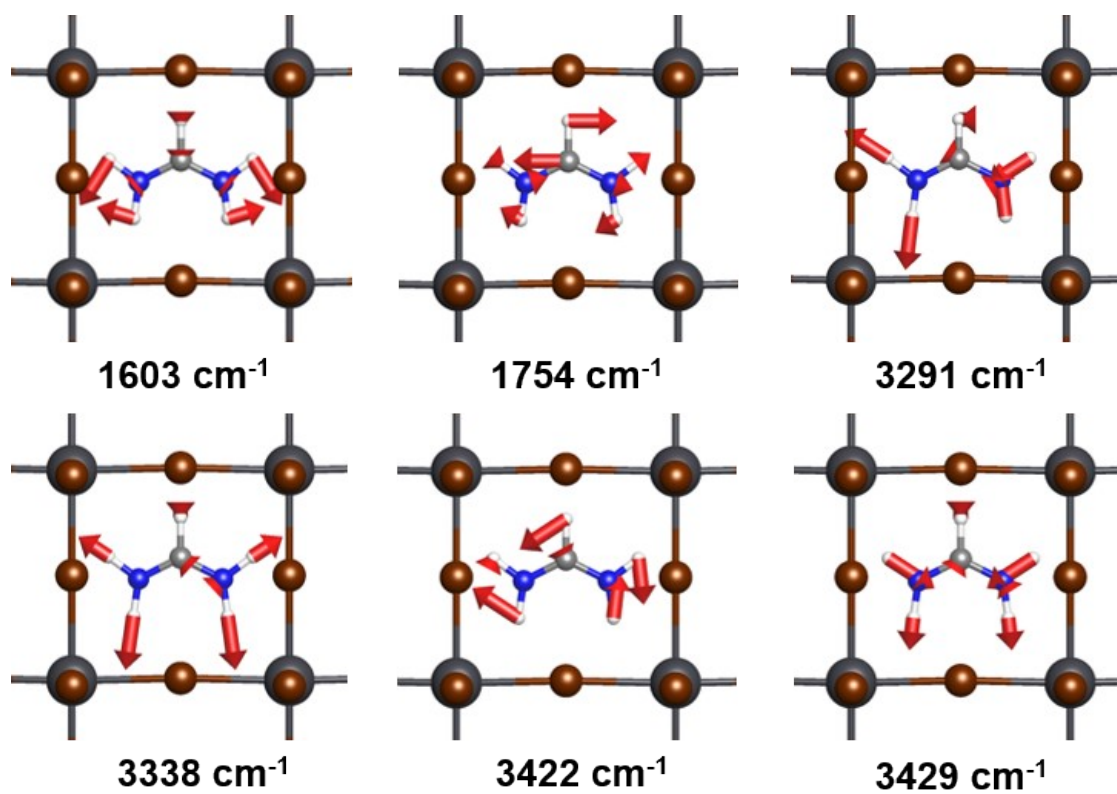
To complement the mIR-TA measurements present in the main text, we conducted time-correlated single photon counting experiments using a home-made set-up. Employing the

NOPA output (as described above) as the pump pulse (with a stretched pulse duration due to an optical fibre involved), the PL signal was recorded by a PerkinElmer SPCM-AQRH-13-FC single photon counter and a Picoquant PicoHarp 300 time tagger.

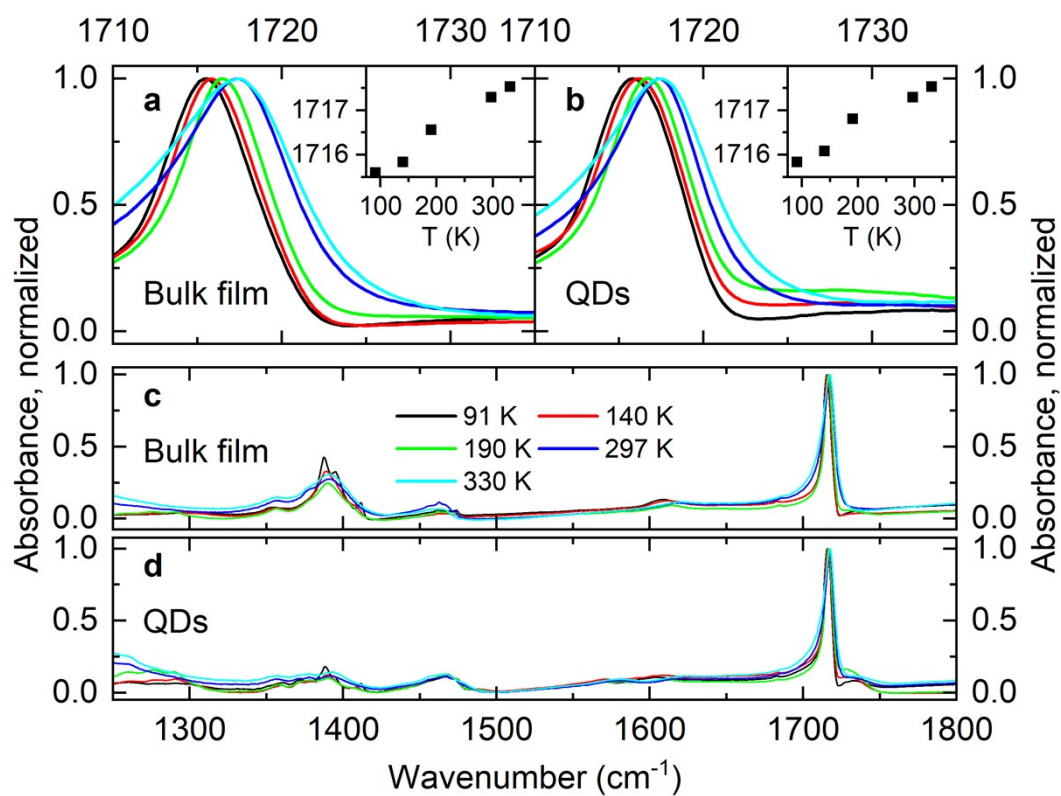
In the TCSPC measurements, shown below in Figure S4, we find a clearly bimolecular trend lasting up until the ns range.



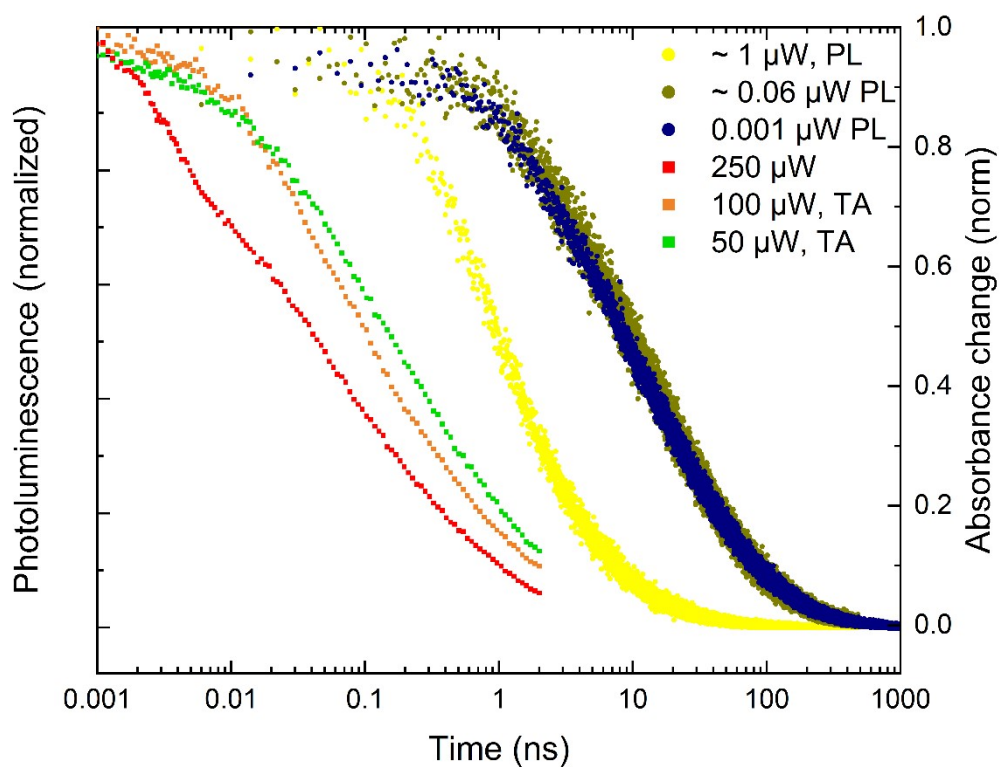
**Figure S1:** Vibrational spectrum as obtained from DFT calculations for a FAPbBr<sub>3</sub> bulk crystal.



**Figure S2:** Vibrational normal modes for bulk  $\text{FAPbBr}_3$  as obtained from DFT calculations.



**Figure S3:** Normalized (to the 1717 cm<sup>-1</sup> mode) FTIR spectra of the Cs<sub>0.2</sub>FA<sub>0.8</sub>PbBr<sub>3</sub> perovskite QDs (a, c) and Cs<sub>0.2</sub>FA<sub>0.8</sub>PbBr<sub>3</sub> bulk film (b, d) over a wide temperature range. In (a) and (c), the mode around 1717 cm<sup>-1</sup> is shown in detail with the peak position depending on the temperature shown in the insets. In (c) and (d), the overall infrared spectrum is shown.



**Figure S4:** Normalized TCSPC and mIR-TA dynamics at different excitation densities (note that the excitation power of mIR-TA experiments and TCSPC experiments cannot be compared due to different experimental conditions).

### References

(1) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.