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Supplementary Information for

Multi-phase architecture for efficient amplified spontaneous emission in lead halide perovskites

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1. Results

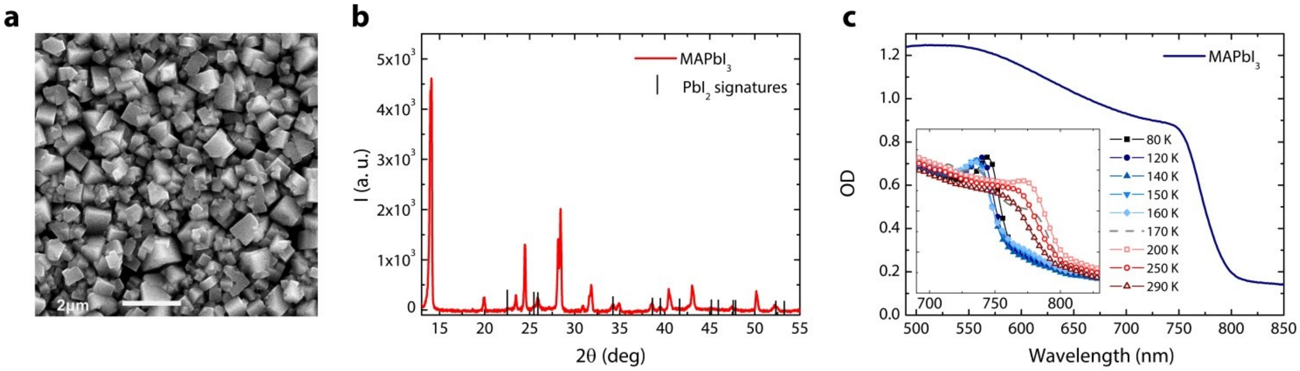

Fig. S1 (a) SEM picture of the investigated sample morphology. The scale bar is 2 µm. **(b)** XRD measurement of the sample at room temperature. **(c)** Absorption spectrum at room temperature taken with an Perkin-Elmer UV-VIS spectrophotometer with integrating sphere. The inset shows the full set of temperature dependent absorption measurements.

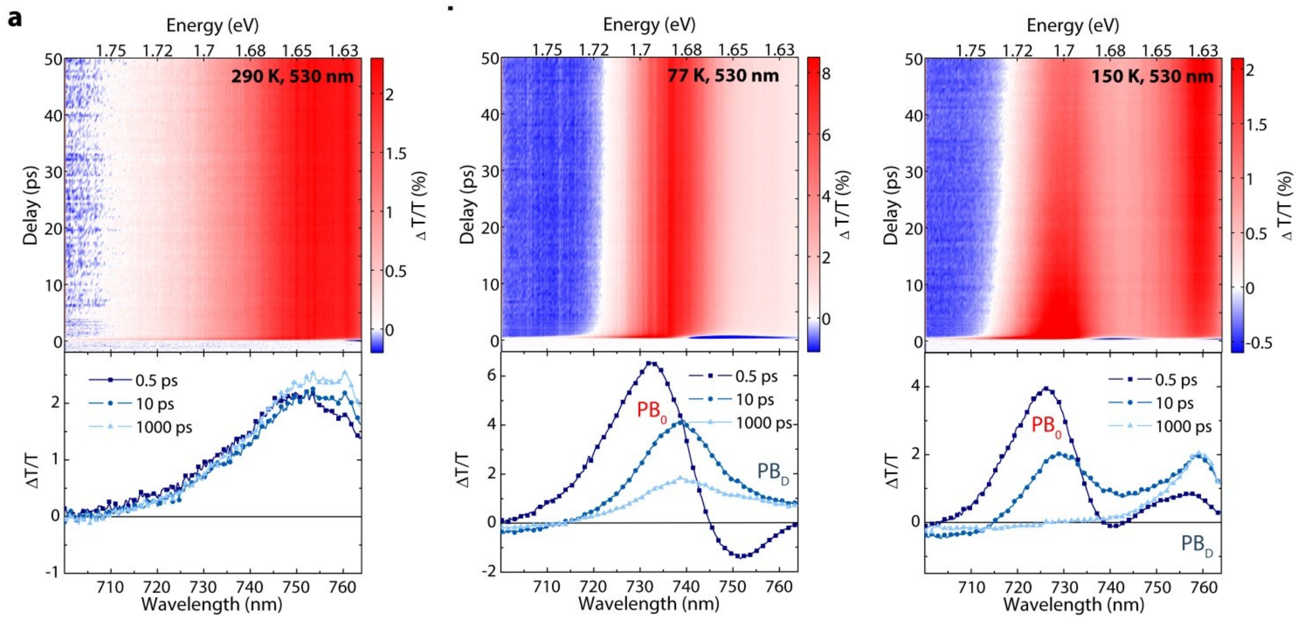

Fig. S2 Spectral evolution of the TA signal within a 50 ps time window for 290 K **(a)** 77 K **(b)** 150 K **(c)**. The PB$_D$ is visible as a red shoulder even at 77 K.

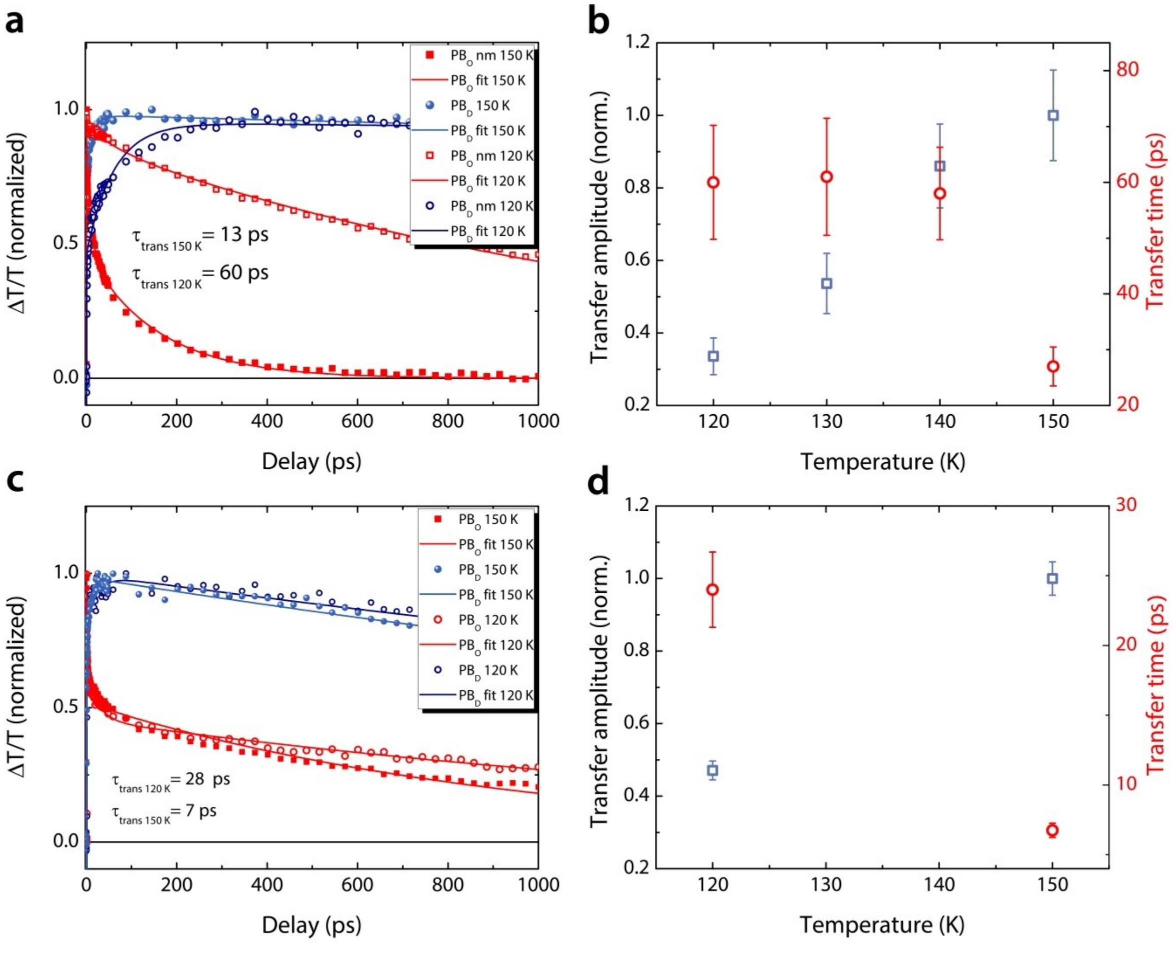

Fig. S3 Dynamics of PB$_O$ and PB$_D$ and exponential fits for 120 and 150 K for **(a)** large crystallites (1 µm) and **(c)** small crystallites (< 200 nm). Amplitude of the transfer component and transfer time within the exponential model as a function of temperature for large crystallites **(b)** and small crystallites **(d)**. **(b)** was taken from a different sample with respect to **(a)**, fabricated following the same procedure and shows the reproducibility of the investigated process.

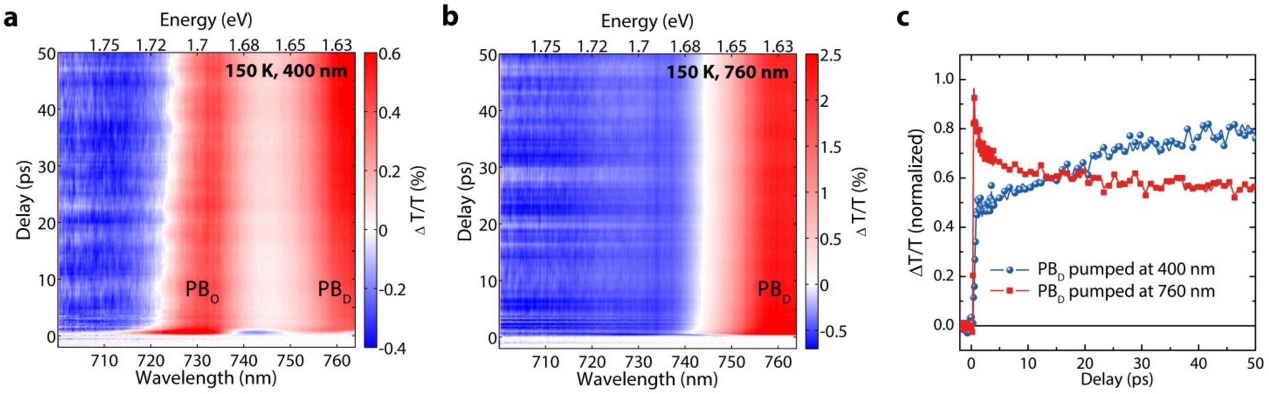

Fig. S4 Spectral evolution of the TA signal when exciting both phases at 400 nm **(a)** and only the low energy phase at 760 nm **(b)**. **(c)** Time evolution of PB$_D$ for λ_{ex}=400 nm and λ_{ex}=760 nm. No transfer takes place when exciting only the low energy phase, the signal shows merely the recombination dynamics.

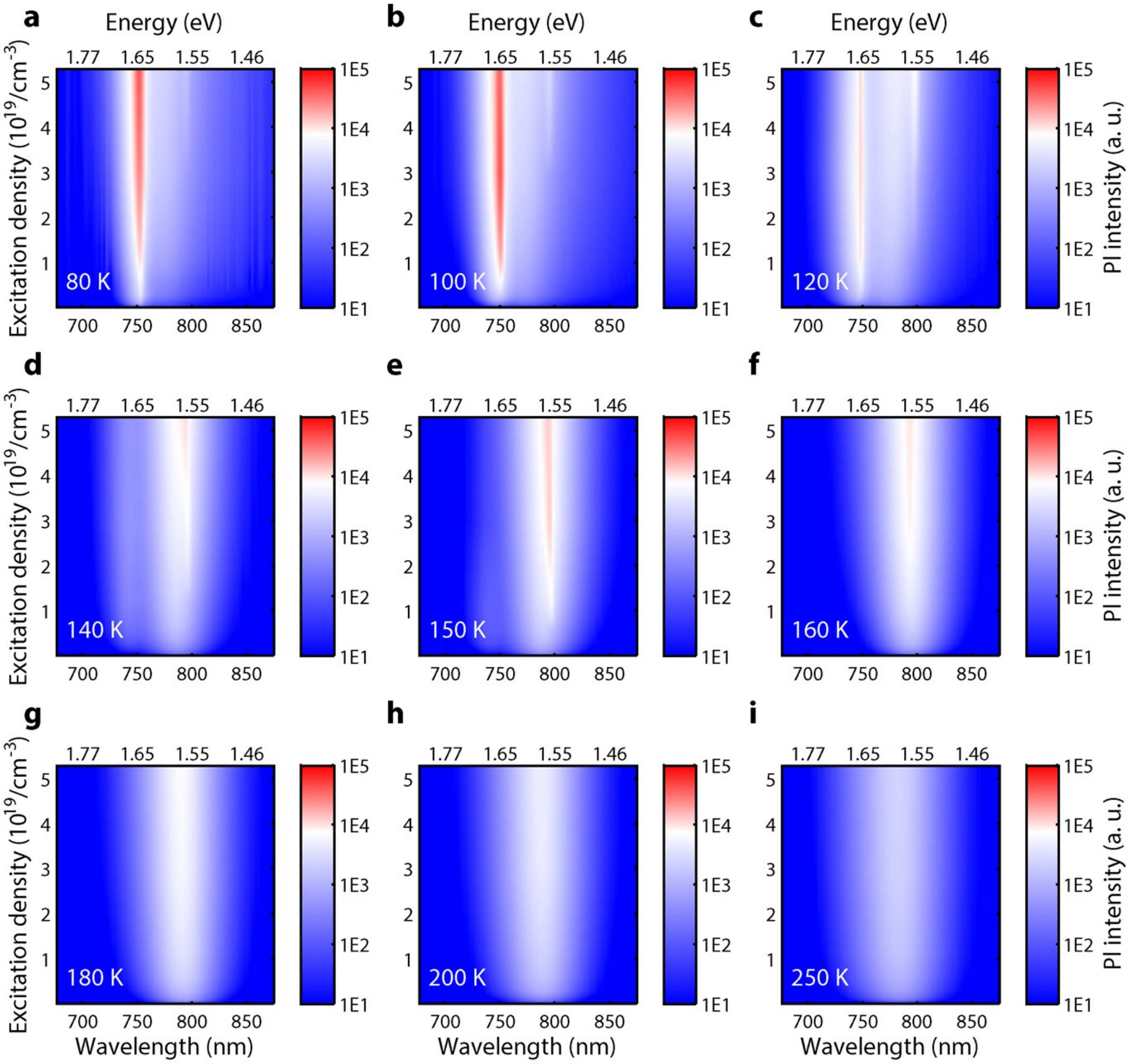

Fig. S5 Intensity dependent PL measurements for 80 K **(a),** 100 K **(b),** 120 K **(c),** 140 K **(d),** 150 K **(e),** 160 K **(f),** 180 K **(g),** 200 K **(h),** 250 K **(i)**.

2. Experimental details

Temperature dependent optical absorption: measurements were carried out in a cw photo-induced absorption setup, using a continuous flow static exchange gas cryostat (Oxford Instruments Optistat CF), illuminated by a 30 W tungsten-halogen lamp through parabolic mirror optics. The transmitted light was modulated by a mechanical chopper, thereupon dispersed by a SP DK240 1/4 Meter monochromator and detected with a silicon photodiode coupled to a Stanford Instruments lock-in amplifier SR830, tuned to the chopper frequency. All spectra were corrected by the transmission through the bare substrate. For the cw photoluminescence measurements, the same sample spot was excited with a green cw laser with 0.5 W/cm^2 at 560 nm central wavelength. The same detection system was used, phasing the lock-in to the modulation frequency of the pump beam. For all measurements, the temperature was varied between 77 K and room temperature, using liquid nitrogen as coolant. For all measurements, the sample was first cooled down to 77 K and then heated up in steps to prevent ambiguous data due to hysteresis effects in the heating up and cooling-down procedure[1].

Fs-transient absorption spectroscopy: the system is driven by a mode Coherent Micra Ti:Sapphire oscillator, generating 20 fs pulses at 80 MHz repetition rate and a center-wavelength of around 800 nm. The pulses are stretched and amplified in the amplification system, consisting of a grating based pulse stretcher (Coherent 9040) and Q-switched Ti:Sapphire based regenerative amplifier (RegA 9000). The output pulses of approximately 6 µJ energy, with 40 fs duration and 250 kHz repetition rate were used to generate pump and probe light. The pump was converted by a two-pass BBO-based collinear OPA (Coherent 9450), allowing spectral tuning in the wavelength range between 480 and 750 nm and resulting in a temporal broadening to 120 fs. Additionally, the SH-output of 400 nm as well as the idler in the range of 850-2400 nm can be used as pump beam. The probe light was generated by white light supercontinuum generation in a sapphire plate with the main spectral weight between 480 and1100 nm and a temporal width of around100 fs. The delay between the two pulses was controlled by a motorized delay-stage and the signal was detected using an Acton SP2300i imaging spectrograph in conjunction with a custom-built Stresing silicon based CCD array, equipped with an electronic shutter. Temperature dependent measurements were carried out with the cryostat (Oxford Instruments Optistat CF). The pump energy for all measurements was kept at 250 nJ/cm^2 , resulting in excitation densities of 6.5 x10^{16}/cm^3, 5.7 x10^{16}/cm^3 and 4.9x10^{16}/cm^3 for 530, 760 and 400 nm respectively. All measurements were done in a nitrogen atmosphere to prevent sample degradation due to oxygen or water.

Power dependent photoluminescence: for the measurements, the second harmonic output of 400 nm of the OPA (Coherent 9450, see above) was used as pump beam and focused by a 15 mm lens on the sample, resulting in a spot size of 70 µm. The emission from the sample was filtered to cut out pump scatter and collected with a multimode fiber connected to an Ocean Optics Maya2000 Pro spectrometer. During the measurement, the sample was kept in nitrogen atmosphere within the cryostat. The pump fluencies were controlled using a gradual neutral density filter. The excitation density was estimated by assuming that all the photons in each pulse are absorbed within a volume given by the spot diameter and penetration depth at the pump wavelength.

Sample preparation: all samples were prepared on glass microscope slides in controlled nitrogen atmosphere. For $CH_3NH_3PbI_3$, a two-step deposition method was used. Substrates were cleaned by two cycles of sonication in water, acetone and isopropanol for 10 minutes respectively, followed by oxygen plasma treatment for 10 minutes. A hot (70°C) solution of PbI_2 in DMF (462 mg/ml) was spin coated at 2000 rpm for 60 sec in order to obtain a layer thickness of around 300 nm. Afterwards, the sample was annealed at 70°C for 30 min to from a thin PbI_2 film. Varying the concentration and temperature of CH_3NH_3I allows to realize different crystal sizes. To obtain $CH_3NH_3PbI_3$, with crystal sizes around 1 µm, the PbI_2 coated substrate was dipped into a CH_3NH_3I solution (concentration of 0.045M in IPA) for 2 minutes at 70°C. For small crystals (< 200 nm) the concentration was changed to 0.063M and dipping was performed at room temperature. As final step, the samples were rinsed in anhydrous IPA to remove any excess of unreacted CH_3NH_3I. The data of this paper was taken from two different samples containing large crystals and two with small crystals. Absorption, PL and ASE measurements were taken on a different sample with respect to the TA measurements.

1 C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, L. M. Herz, C. Wehrenfennig, M. Liu and H. J. Snaith, *APL Mater.*, 2014, **081513**.