Supporting Information

Transient Sub-bandgap States in Halide Perovskite Thin Films

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Film Characterization: Hybrid $CH_3NH_3PbI_3$ thin films were fabricated by spin coating a 0.3 M stock solution prepared by dissolving $CH_3NH_3PbI_3$ powders in anhydrous dimethylformamide (DMF) with an aqueous HI solution (6% v/v) on a glass coverslip at 100 °C.[1] For characterization, a perovskite film fabricated by spin coating a 0.88 M stock solution with 6% HI additives was used to measure powder x-ray diffraction (XRD) on a RigakuMiniFlex600 X-ray diffractometer as shown in Fig. S1A. The XRD patterns of the perovskite film on a reference indium-tin-oxide (ITO) substrate (red solid line) fit well to the simulated tetragonal phase (black solid line).

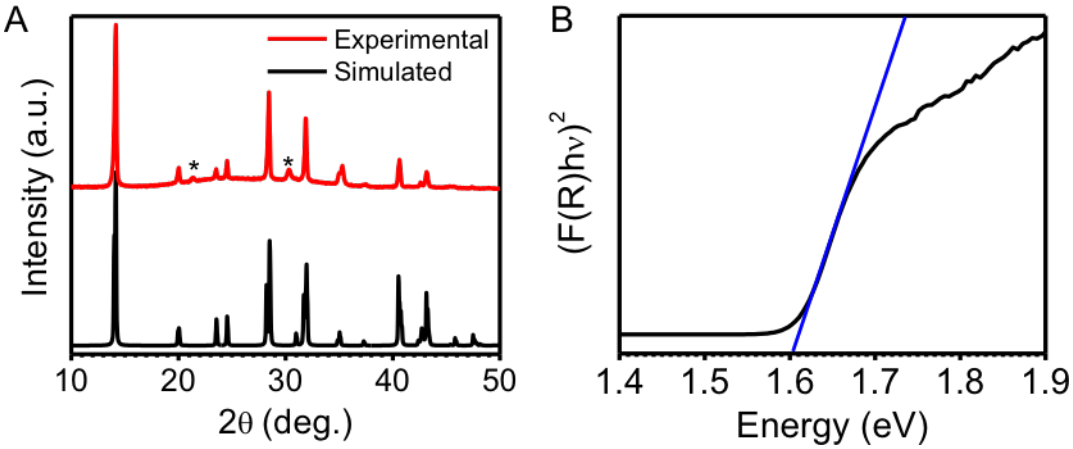

Figure. S1. (a) A typical powder XRD pattern of the $CH_3NH_3PbI_3$ film deposited on an Indium-Tin Oxide (ITO) substrate. ITO serves as an internal standard for correcting the instrumental shift. (b) A typical absorption spectrum of the same perovskite film obtained through diffuse reflectance and converted to absorbance using the Kubelka-Munk function.

Single-Particle Ultrafast Micro-Spectroscopy: The output of a Yb:KGW amplifier system (Light conversion, Pharos, 200 KHz, 190 fs, 1030 nm) is split by a beamsplitter and directed into a pump and probe arm. One portion of the beam is focused on a beta barium borate (BBO) crystal generating a pump beam centered at 2.40 eV. The other portion of the beam is focused on a yttrium aluminium garnet (YAG) crystal generating a white light continuum probe beam (1.6 – 2.0 eV). The pulse dispersion of the probe beam was compensated with two chirp mirrors. The pump pulse was measured at <130 fs, while the probe was slightly chirped but remained below 30 fs. The pump pulses were delayed relative to the probe pulses with a high-resolution motorized translation stage. Collinearly propagating pump and probe beams were sent through a dichroic mirror and focused onto the sample using a 74× reflective aluminum objective (NA 0.65) to reduce chromatic aberration and avoid additional dispersion. Transmitted signals were then collected through a 100× objective (NA 0.7), spatially filtered by a pinhole, and then sent to a high-resolution spectrometer (Horiba, IHR 320). Spectrally dispersed signals were detected by a high-speed electron multiplying charge coupled camera (EMCCD, Andor, IXon Ultra 897). The pump beam was modulated at 2.5 KHz using a Pockels cell (Eksma), and the EMCCD camera was triggered at 5 KHz. To avoid photo-damage, the samples were kept at 6 °C using a home-built cooling stage. In addition, the measurements were paused every 25 min and resumed after 7 min to minimize the sample degradation under the continuous beam exposure.

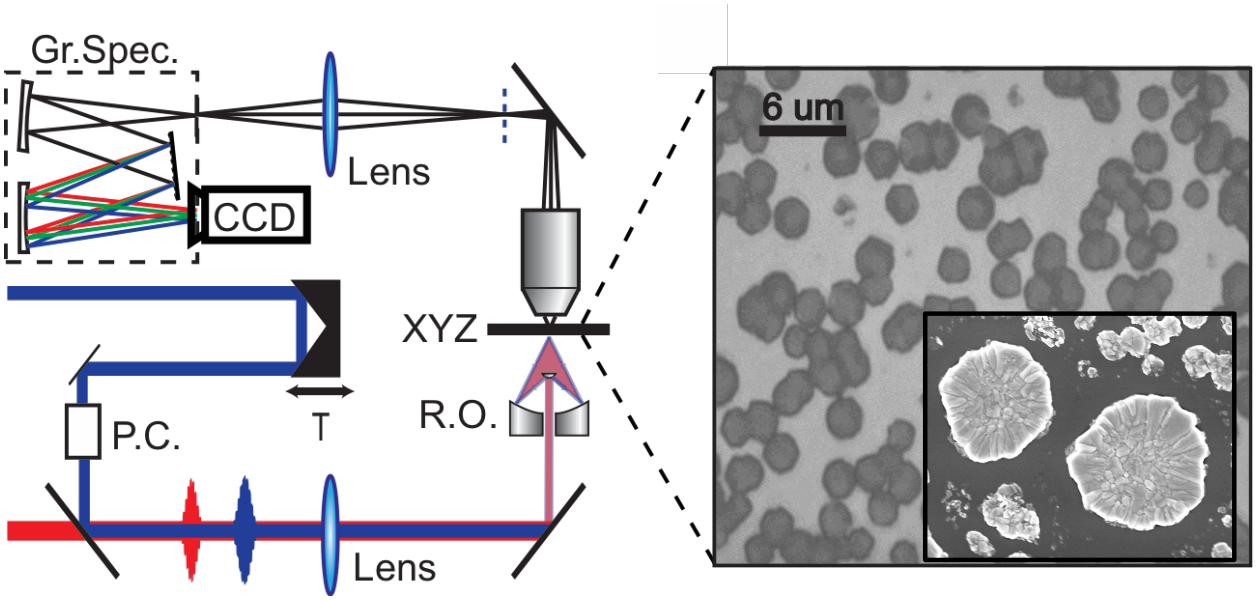

Figure S2. **Left:** Schematic of the TA microscope in confocal geometry. **Right:** Typical optical micrograph of perovskite thin film sample. Inset: Representative scanning electron micrograph of polycrystalline particles.

Transient Absorption Data.

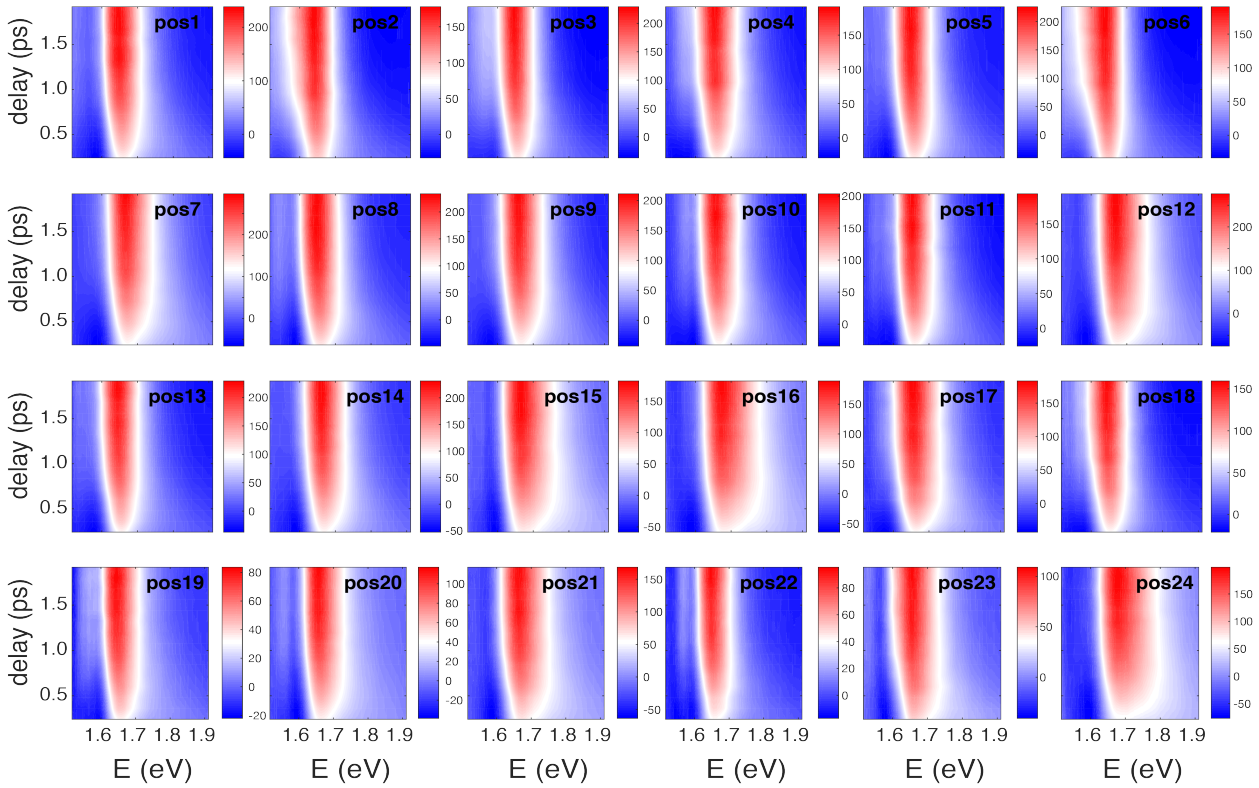

Figure S3. TA surface plots for all 24 positions measured at intermediate pump fluence.

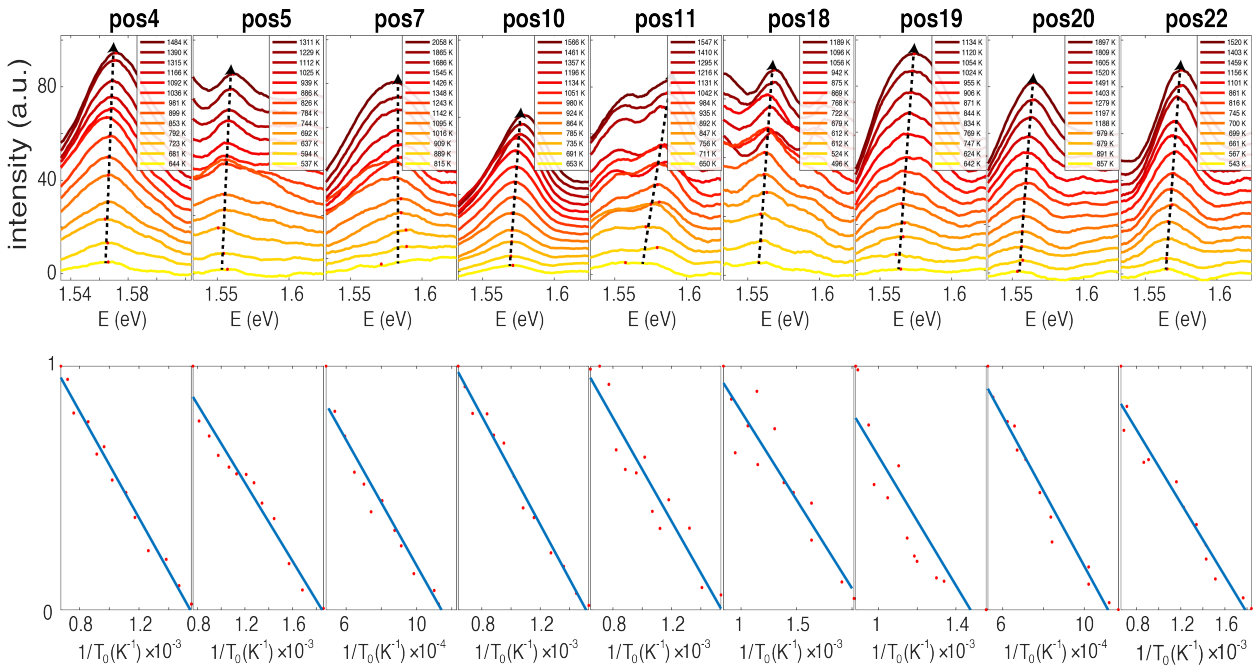

Figure S4. **Top:** Residual sub-bandgap feature, isolated by subtracting band-filling model fit from TA spectrum. Only shown for select positions where the feature is clearly visible. Note that in some positions, two peaks are resolved. Dotted line represents fit to the maximum of each peak. **Bottom:** Peak intensity as a function of inverse temperature, showing near-linear behavior.

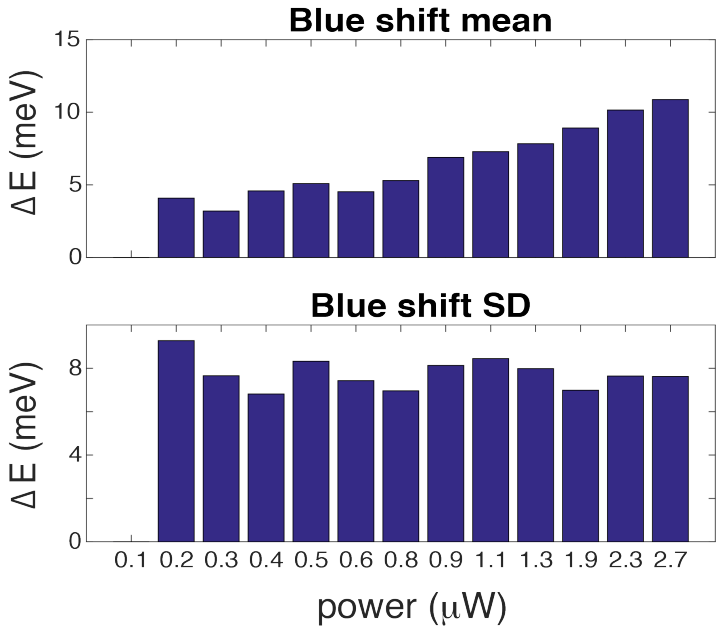

Figure S5. Blue-shift mean and standard deviation calculated by analyzing statistics from the 9 positions (4, 5, 7, 10, 11, 18, 19, 20, 22) shown in Figure S3. The blue-shift is relative to the peak position at the lowest power (0.1 μW).

Photoluminescence.

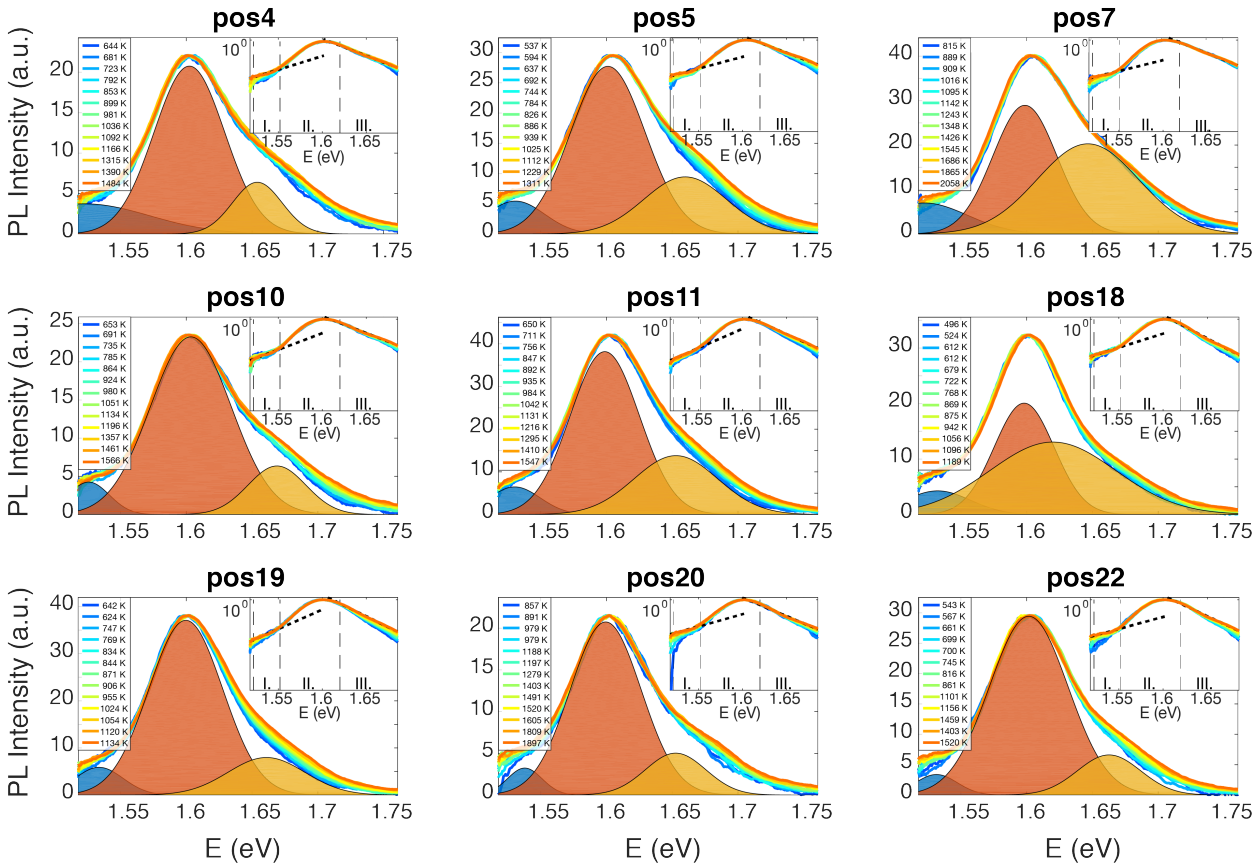

Figure S6. PL spectra at 9 positions where sub-bandgap state is observed. Colors of lines indicate the initial carrier temperature extracted from fits to the TA spectra. Inset shows the same data on a semi-logarithmic scale. Dashed lines are fit to the highest temperature data (i.e. at highest pump fluence) in regions labelled I. and III.

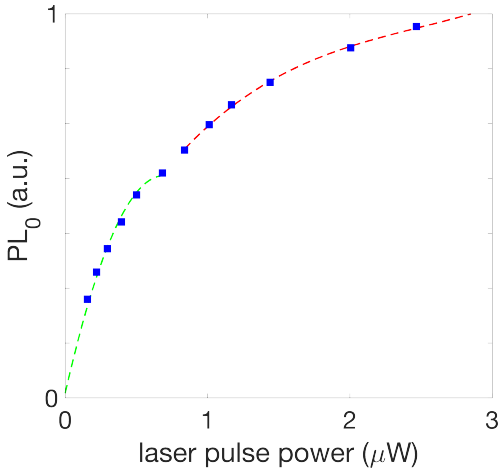

Figure S7. Integrated PL as a function of pump laser power. Dashed green line is a quadratic fit to powers less than 1 μW, corresponding to a regime dominated by bimolecular recombination (e.g. electron and hole radiative recombination). Above 1 μW, the data is fit to a third-order polynomial (red dashed line), indicating the presence of some Auger recombination or other higher-order process such as amplified spontaneous emission. Note, the PL does not saturate, indicating that the carrier density is insufficient for complete band filling.

References

1. Soe, C. M. M.; Stoumpos, C. C.; Harutyunyan, B.; Manley, E. F.; Chen, L. X.; Bedzyk, M. J.; Marks, T. J.; Kanatzidis, M. G. *Chemsuschem* **2016,** 9, (18), 2656-2665.