Synthesis of (n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ single crystals

(n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ SCs were synthesized and purified by moderate liquid method based on previous report. The materials used in the experiments were purchased from Sigma-Aldrich and used without further processing.

PbO powder (2.232 g), 57 % w/w HI (water solution, 10 mL) and 50 % w/w H$_3$PO$_2$ in water (1.7 mL) were mixed, and kept heating under constant stirring until PbO was completely dissolved. 5 mL HI was also added dropwise into 924 μL n-Butylamine in an ice bath to make a n-C$_4$H$_9$NH$_3$I solution. Then, the n-C$_4$H$_9$NH$_3$I solution was dropped into the hot mixture under magnetic stirring. The combined solution was cooled to room temperature, allowing layered orange crystals to grow. The crystals were rinsed with anhydrous ether and extracted by suction filtration, before dried at 60 °C for 24 h under reduced pressure.

High-quality single crystals were formed through a recrystallized process from the orange raw crystals: 8.5 mL H$_3$PO$_2$ and 5 mL HI were mixed under stirring. The
well-dried flake crystals were dissolved in the HI/H₃PO₂ solution, and then the mixture was saturated by vaporizing the solvent at a fixed temperature of 70 °C. The grown crystals were again washed by anhydrous ether, filtered out, and dried at 60 °C for 24 h under reduced pressure.

**Photoluminescence (PL)-scanned imaging microscope experiment**

We used a home-built photoluminescence (PL)-scanned imaging microscope coupled with a time-correlated single photon counting (TCSPC) module to map the PL kinetics on an individual crystal. The excitation beam is a picosecond pulse diode laser with 405 nm output wavelength (20 MHz or 0.5 MHz repetition rate). For wide-field illumination, the laser beam is defocused before a 100× air objective lens (NA = 0.95) to form an excitation spot of ~ 60 μm in diameter, which ensures the single crystal is excited homogeneously. A lateral scan of PL on the sample was achieved by rotating a galvanometer mirror before the detector. Each scanning image contains 256 × 256 pixels, The PL signal was collected using a high-speed detector (HPM-100-50, Hamamatsu, Japan) with a 550 nm long pass filter, 480 ± 10 nm band pass filter, 525 ± 20 nm band pass filter or 510 nm long pass filter and 540 nm short pass filter.

**Ultrafast transient absorption (TA) Measurement**

The femtosecond TA setup is based on a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ pulse⁻¹, and 1 kHz repetition rate), nonlinear frequency mixing techniques and the Femto-TA100 spectrometer.
Briefly, the 800 nm output pulse from the regenerative amplifier was split into two beams by a 50% beam splitter. The transmitted part was used to pump a $\beta$-BaB$_2$O$_4$ crystal (BBO) to generate a 400 nm output, which is selected as pump beam due to its higher power stability than TOPAS OPA output. The reflected 800 nm beam was split again into two parts. One part with less than 10% was attenuated with an OD filter and focused into a 2 mm thick sapphire window to generate a white light continuum (WLC) from 400 nm to 800 nm used as probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 1 kHz. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked).

**Structure characterization**

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were obtained on JEM-2100 microscope. X-ray diffraction (XRD) patterns were obtained on a X'pert Pro X-Ray Diffractometer (PANalytical, Netherlands) using Cu Kα radiation.

**Definition of the degree of phase transition in 2D perovskite crystals**

Normally, the degree of phase transition (here denoted as $x$) from the RT phase
to the LT phase in 2D perovskite single crystals can be described by the ratio of the amounts between LT phase at low temperatures and RT phase at 293 K as follows.

\[ x = \frac{n_{LT}}{n_{RT}} \]  
(S1)

where \( n_{LT} \) and \( n_{RT} \) represent the amount of LT phase at low temperatures and RT phase at 293 K respectively. For 2D perovskites, the PL lifetime is mainly determined by nonradiative process due to the existence of lots of defects; therefore, their PL intensity should be proportional to the product of their amount and PL lifetime as:

\[ I_{LT} \propto n_{LT} \tau_{LT} \]  
(S2)

\[ I_{RT} \propto n_{RT} \tau_{RT} \]  
(S3)

where \( I_{LT} \) and \( I_{RT} \) are the PL intensity of the LT phase and the RT phase respectively, and \( \tau_{LT} \) and \( \tau_{RT} \) represent the PL lifetime of LT phase and RT phase. Therefore, the degree of phase transition (\( x \)) can be derived according to Eq. (S1) as follows:

\[ x \propto \frac{I_{LT}}{I_{RT}} \frac{1}{\frac{\tau_{LT}}{\tau_{RT}}} \propto \frac{I_{LT}/RT}{\tau_{LT}/RT} \]  
(S4)

where \( I_{LT/RT} \) (\( \tau_{LT/RT} \)) represent the ratio of the intensity (lifetime) between LT-phase PL at 83 K and RT-phase PL at 293 K.

REFERENCES

(1) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G., Ruddlesden–Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. Chem. Mater. 2016, 28, 2852-2867.
Figure S1. (a) TEM image and selected area electron diffraction (SAED) image (inset) of (n-C₄H₉NH₃)₂PbI₄ crystal; (b) The visible image of a bunch of (n-C₄H₉NH₃)₂PbI₄ crystals at 293 K.

Figure S2. Temperature-dependent XRD patterns of single crystals above 273 K (a) and below 243 K (b).
Figure S3. (a) TA spectra of \((n-C_4H_9NH_3)_2\)PbI\(_4\) SCs at delay of 2 ps under the excitation at 400 nm with indicated intensities. (b) The plot of the peak intensity of TA spectra \((-\Delta A\) recorded at 517 nm as a function of excitation intensity, indicating that the transient absorption response is linear for the pump intensity less than 3.5 \(\mu J/cm^2\).
Figure S4. TA spectra of (n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ SCs at indicated delays with 400 nm excitation probed respectively at (a) $T = 293$ K, (b) $T = 83$ K and (c) $T = 263$ K; (d) The comparison of TA spectra of (n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ SCs at fixed delay ($\sim 2$ ps) measured at different temperatures.
Figure S5. Normalized TA bleach kinetics respectively from (a) RT-phase (probed at 517 nm) and (b) LT-phase (probed at 489 nm) excitons in \((n-C_4H_9NH_3)_2PbI_4\) SCs at different temperatures.

Figure S6. (a) The visible image of \((n-C_4H_9NH_3)_2PbI_4\) SC (crystal #1) used in the main text at 293 K; (b) The PL spectra of \((n-C_4H_9NH_3)_2PbI_4\) SC (crystal #1) from 83 K to 293 K.
Figure S7. Temperature-dependent PL spectra from (a) Crystal #2, (b) Crystal #3 and (c) Crystal #4 collected under various temperatures from 83 K to 293 K. The upper panels are their optical images at 293 K.
Figure S8. The measured PL spectra and kinetics of broadband emission from crystal #2 (a, b) and crystal #5 (c, d) at 83 K. The insets in panel b and d are their optical images at 293 K.
**Figure S9.** The PL intensity images from RT phase (a) and LT phase (b) in an individual (n-C₄H₉NH₃)₂PbI₄ SC (i.e., crystal #1 used in the main text) measured at other low temperatures.
Figure S10. The PL intensity images from RT phase recorded at 293 K (a - c) and at 83 K (d - f) respectively, as well as from LT phase at 83 K (g - i) in three different \((n-C_4H_9NH_3)_2PbI_4\) SCs. Similar to the crystal in main text, the PL images from two different phases at 83 K in these SCs also show inhomogeneous but roughly complementary distribution trend.
Figure S11. (a) The comparison of the PL spectra from the \((n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4\) SC (crystal \#1) at 83K under 405 nm excitation with different cooling rates, implying that the slower cooling rate leads to the higher degree of phase transition. (b) The map of the normalized degree of phase transition at 83 K under a slower cooling rate of 5 K/min, which also exhibits an inhomogeneous distribution with a slightly higher degree of phase transition and less phase inhomogeneity, compared to those under the faster cooling rate of 40 K/min (see Figure 3b in main text).
**Figure S12.** (a) The RT-phase PL lifetime image measured in an individual (n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ SC at 293 K. (b) The distribution map of the relative completion degree of phase transition at 83 K calculated according to Eq.(S4), showing a rough inverse correlation relative to the RT-phase PL lifetime image shown in panel a. (c) The comparison of the RT-phase PL lifetimes and the degrees of phase transition from panel b at various positions (denoted by red points) as shown in panel a.
Figure S13. (a) The RT-phase PL lifetime image measured in an individual (n-C₄H₉NH₃)₂PbI₄ SC at 293 K. (b) The distribution map of the relative completion degree of phase transition at 83 K calculated according to Eq.(S4), showing a rough inverse correlation relative to the RT-phase PL lifetime image shown in panel a. (c) The comparison of the RT-phase PL lifetimes and the degrees of phase transition from panel b at various positions (denoted by red points) as shown in panel a.
Figure S14. (a) The RT-phase PL lifetime image measured in an individual (n-C$_4$H$_9$NH$_3$)$_2$PbI$_4$ SC at 293 K. (b) The distribution map of the relative completion degree of phase transition at 83 K calculated according to Eq.(S4), showing a rough inverse correlation relative to the RT-phase PL lifetime image shown in panel a. (c) The comparison of the RT-phase PL lifetimes and the degrees of phase transition from panel b at various positions (denoted by red points) as shown in panel a.