Supporting Information

Single Crystal of Two-Dimensional Mixed-Halide Copper-based Perovskites with Reversible Thermochromism

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\textbf{Fig. S1} Crystal growth of 2D-centimeter-sized Cu-based perovskites at (water/air) interface: C4 (a) BB (b). Bulk crystals of mixed-halides Cu-perovskites (c).
Fig. S2  2D-Cu perovskite crystals after grinding with mortar where (CC: yellow, C6.5: orange, C5: red, C4: dark red, C3: reddish-brown, C2: dark brown, C0.5 and BB: dark green)

Fig. S3  Scanning electron microscope (SEM) images show the two-dimensional structures of Cu-perovskites. Elemental mapping of halides though perovskite crystals where blue and green spots for Br- and Cl-distributions respectively.
Fig. S4  Crystal structures of (CH$_3$NH$_3$)$_2$CuCl$_4$ \(^1\) (a), (CH$_3$NH$_3$)$_2$CuCl$_2$Br$_2$ \(^2\) (b). Green Cu, blue N, gray C, red Cl, brown Br and pink H.
Fig. S5  (a) Powder XRD of Cu-perovskite crystals after grinding with mortar. (b) Expansion of XRD-first peak.
Fig. S6  (a) Thermogravimetric analysis (TGA) of Cu-perovskites. (b) Decomposition temperature values of Cu-perovskites extracted from TGA analysis.
Fig. S7  Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated C6.5 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm\(^{-1}\) and 2500-3000cm\(^{-1}\), respectively.
Fig. S8  Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated C5 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000 cm⁻¹, respectively.
Fig. S9 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated C4 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000 cm⁻¹, respectively.
Fig. S10 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated C3 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000cm⁻¹, respectively.
Fig. S11  Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated C2 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000 cm⁻¹, respectively.
Fig. S12 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated Co.5 flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000 cm⁻¹, respectively.
Fig. S13  Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated BB flakes, scale bar (10 μm). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm⁻¹ and 2500-3000cm⁻¹, respectively.
Fig. S14 Temperature-induced XRD of CC for one heating/cooling cycle.
Fig. S15  (a) and (b) Temperature-induced color change of C6.5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C6.5: (c) Expansion of 2Θ = 42.6° reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.
Fig. S16 Temperature-induced XRD of C6.5 for one heating/cooling cycle.
Fig. S17  (a) and (b) Temperature-induced color change of the C5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C5: (c) Expansion of $2\Theta = 49.7^\circ$ reflection at different temperatures. (d) d-spacing calculated from the $2\Theta$ values extracted from the XRD patterns at different temperatures.
Fig. S18 Temperature-induced XRD of C5 for one heating/cooling cycle.
Fig. S19 (a) and (b) Temperature-induced color change of the C4 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C4: (c) Expansion of $2\theta = 49.7^\circ$ reflection at different temperatures. (d) d-spacing calculated from the $2\theta$ values extracted from the XRD patterns at different temperatures.
Fig. S20 Temperature-induced XRD of C4 for one heating/cooling cycle.
Fig. S21 (a) and (b) Temperature-induced color change of the C3 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C3: (c) Expansion of 2θ = 28.5° reflection at different temperatures. (d) d-spacing calculated from the 2 θ values extracted from the XRD patterns at different temperatures.
Fig. S22 Temperature-induced XRD of C3 for one heating/cooling cycle.
Fig. S23 (a) and (b) Temperature-induced color change of the C2 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C2: (c) Expansion of $2\theta = 42.6^\circ$ reflection at different temperatures. (d) d-spacing calculated from the $2\theta$ values extracted from the XRD patterns at different temperatures.
Fig. S24 Temperature-induced XRD of C2 for one heating/cooling cycle.
Fig. S25 (a) and (b) Temperature-induced color changes of the C0.5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C0.5: (c) Expansion of $2\theta = 73.4^\circ$ reflection at different temperatures. (d) d-spacing calculated from the 2 $\theta$ values extracted from the XRD patterns at different temperatures.
Fig. S26 Temperature-induced XRD of C0.5 for one heating/cooling cycle.
Fig. S27 (a) and (b) Temperature-induced color change of the BB crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of BB: (c) Expansion of $2\theta = 36.9^\circ$ reflection at different temperatures. (d) d-spacing calculated from the $2\theta$ values extracted from the XRD patterns at different temperatures.
Fig. S28 Temperature-induced XRD of BB for one heating/cooling cycle.
Fig. S29  Differential scanning calorimetry (DSC) of CC (a), C6.5 (b), C5 (c), and C4 (d) with scan rate of 10 K/min.
Fig. S30  Differential scanning calorimetry (DSC) of C3 (e), C2(f), C0.5 (g), and BB (h) with scan rate of 10 K/min.
Fig. S31 Temperature dependence of transmittance spectra of CC and C6.5 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.
Fig. S32 Temperature dependence of transmittance spectra of C5 and C4 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.
Fig. S33 Temperature dependence of transmittance spectra of C3 and C2 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.
Fig. S34 Temperature dependence of transmittance spectra of C0.5 and BB samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.
**Supplementary note:**

Comparison between d-space and transmittance hysteresis loops

Consider

The transmittance of the sample at 30 °C before heating and after cooling are T30H and T30C, respectively.

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Two probabilities are observed:

1. T30H > T30C

According to this behavior, the sample color, after cooling, is darker than its color before heating. Thus, d30H < d30C and the crystal lattice is still in its expanded form. This means that the sample just requires more time to return-back to its normal color. This behavior was observed for CC, C6.5, C5, C3, C0.5 and BB samples.

2. T30H < T30C

According to this behavior, the sample color after cooling is lighter than its color before heating. Thus, d30H > d30C. This means that the sample has lighter color than its initial color after heating/cooling cycle, i.e. the crystal lattice is more compressed than its initial one. This behavior was observed for C2 and C4 samples.

**References**
