Electronic Supplementary Information (ESI)

Influence of Hidden Halogen Mobility on Local Structure of CsSn(Cl_{1-x}Br_x)_3 Mixed-Halide Perovskites by Solid-State NMR

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EXPERIMENTAL

Materials

Starting materials were purchased from the following commercial sources and were used without further modification: CsCl (Terochem Laboratories Ltd. 99.7%), CsBr (Sigma, 99.99%), SnCl₂ (Alfa Aesar, >99%), SnBr₂ (Alfa Aesar, 99.2%), SnBr₄ (Sigma, 99%), HBr (Anachemia, 48%), and H₃PO₄ (Sigma, 50 wt.% in H₂O).

High-Temperature Synthesis of CsSn(Cl₁–ₓBrₓ)₃ (0 ≤ x ≤ 1): Various members of the solid solution CsSn(Cl₁–ₓBrₓ)₃ were prepared by reactions at high temperature. CsX and SnX₂ (X = Cl, Br) were combined in stoichiometric ratios on a 0.5-g scale, finely ground using an agate mortar and pestle, pressed into pellets, and loaded into fused-silica tubes which were evacuated under a pressure of 10⁻³ mbar and sealed. The tubes were heated at 1.5 K/min to either 673 or 723 K (depending on composition), held at that temperature for 15 h, and then cooled to room temperature at 5 K/min. The samples were stored in glass vials and further characterized under ambient conditions.

Cubic CsSnCl₃ was obtained as a metastable phase at room temperature as follows: a sample of CsSnCl₃ prepared as described above was heated to 673 K, kept at this temperature for 15 h, cooled to 573 K at 5 K/min, and then quenched in an ice-water bath.

Mechanochemical Synthesis of CsSnBr₃: A mixture of 1.5 mmol each of CsBr and SnBr₂ was ground using an agate mortar and pestle for 10 min. Within an argon-filled glove box, the mixture was transferred to a 50-mL zirconia grinding vessel (containing ca. 50 g of zirconia balls with 3–8 mm diameter), which was sealed with parafilm to minimize exposure to air. The sample was ground in a Changsha Deco DECO-PBM-V-0.4L electric planetary ball mill at a rotation frequency of 550 rpm for 0.5 h. The vessel was opened to scratch its inner wall by using a clean spatula and sealed again under an inert atmosphere (Ar glove box). This process was repeated four times for a total of 2.5 h of grinding time.

Solvent Synthesis of CsSnBr₃: A mixture of 1 mmol each of CsBr and SnBr₂ was placed in a 40-mL glass vial to which 4.5 mL of concentrated HBr and 0.5 mL of H₃PO₄ were added. The mixture was heated under a nitrogen atmosphere to 120 °C on a hot plate, with continuous stirring by a magnetic stir bar. A black precipitate formed immediately. After the mixture was heated for 0.5 h, it was cooled over 1 h to room temperature. The precipitate was filtered under reduced pressure, washed with isopropyl alcohol, dried for 0.5 h, and quickly packed into a 4-mm o.d. ZrO₂ rotor for the solid-state NMR experiments.

Solvent Synthesis of Cs₂SnBr₆: A mixture of CsBr (2 mmol) and SnBr₄ (1 mmol) was placed in a 10-mL glass vial to which 5 mL of concentrated HBr was added. The mixture was heated to 120 °C on a hot plate, with continuous stirring by a magnetic stir bar. A white precipitate formed immediately. After the mixture was heated for 1 h, it was cooled over 1 h to room temperature. The precipitate was filtered using a Buchner funnel, washed with 95% ethanol, dried overnight, and stored in a vial under ambient conditions.
**Powder X-ray Diffraction:** Powder XRD patterns were collected on a Rigaku Ultima IV diffractometer equipped with a Co Kα radiation source (Kα1, 1.78900 Å; Kα2, 1.79283 Å) operated at 38 kV and 38 mA, and a D/Tex Ultra detector with a Fe filter to eliminate Kβ radiation (1.62083 Å). The samples were placed on zero background plates. Data were collected in continuous scan mode between 5 and 90° in 2θ with a step size of 0.0200°. Profile fitting was performed using the FullProf suite of software and unit cell parameters were refined.

**Energy-dispersive X-ray Spectroscopy and Field Emission Scanning Electron Microscopy:** Samples were examined on Zeiss Sigma 300 VP field emission scanning electron microscope equipped with dual silicon drift detectors for energy-dispersive X-ray spectroscopy to determine chemical compositions.

**UV-Visible Diffuse Reflectance Spectroscopy:** Diffuse reflectance spectra were collected on a Cary 5000 UV-vis-NIR spectrophotometer between 200 and 800 nm and calibrated with a Spectralon (>99%) reflectance standard. The diffuse reflectance spectra were converted to absorption spectra using the Kubelka-Munk function, \( \alpha/S = (1-R)^2/2R \), where \( \alpha \) is the Kubelka-Munk absorption coefficient, \( S \) is the scattering coefficient, and \( R \) is the reflectance. Direct bandgaps were extrapolated from the intercepts in Tauc plots of \( (\alpha hv)^2 \) vs \( E \) (eV).

**Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy:**

*I. Cesium-133 NMR Spectroscopy:* Solid-state \(^{133}\)Cs NMR measurements were performed at 11.75 T (1H, 500 MHz) on a Bruker Avance NEO 500 spectrometer, under magic angle spinning (MAS) conditions using a 4 mm H/X MAS Bruker probe with \( \omega_c/2\pi(^{133}\text{Cs}) = 65.6 \text{ MHz} \). All samples were packed into 4 mm o.d. ZrO\(_2\) rotors and NMR data were acquired using a Bloch decay pulse sequence using a short tip angle pulse of 1.38 µs \( (\pi/2 \text{ pulse} = 5.5 \mu s) \), solution \( \gamma_B/2\pi = 45.5 \text{ kHz} \) with an acquisition time of 100 ms and an optimized recycle delay of 10 to 1800 s. The nuclear spin-lattice relaxation time \( (T_1) \) values of \(^{133}\)Cs nuclei for all samples were measured using an inversion recovery pulse sequence. The \( T_1 \) values were calculated by fitting the peak intensity values using a three-parameter exponential decay function: \( I(t) = I(\infty) + A e^{-t/T_1} \), where \( I(0) \) and \( I(\infty) \) are the NMR signal intensities measured at time \( t \) and at \( t \) infinity, respectively, and \( T_1 \) are \( A \) the spin-lattice relaxation time and pre-exponential constant, respectively. All \(^{133}\)Cs NMR spectra discussed here were referenced by setting a 0.1 M CsNO\(_3\) (aq.) solution at \((^{133}\text{Cs}) = 0.00 \text{ ppm} \).

*I. Tin-119 NMR Spectroscopy:* Solid-state \(^{119}\)Sn NMR measurements were performed at 11.75 T (1H, 500 MHz) on a Bruker Avance NEO 500 spectrometer under both MAS and non-spinning conditions using a 4 mm H/X MAS Bruker probe with \( \omega_c/2\pi(^{119}\text{Sn}) = 186.5 \text{ MHz} \). All samples were packed into 4 mm o.d. ZrO\(_2\) rotors and NMR data were acquired using a 4.0 µs \( \pi/2 \) \( (\gamma_B/2\pi = 62.5 \text{ kHz}) \) either with a Hahn-echo pulse sequence \((\pi/2)_k - t_1 - (\pi)_y - t_2 - ACQ \), where \( t \) represents the interpulse and refocusing delays) or with a Bloch pulse sequence with an acquisition time of 4-5 ms and an optimized recycle delay of 0.01-200 s.
Variable temperature (VT) $^{119}$Sn NMR spectra were acquired between 230 and 418 K with the same instrument under non-spinning conditions using a Bruker VT unit and calibrated using the $^{207}$Pb chemical shifts of MAPbCl$_3$. Dry N$_2$(g) was used as the VT gas and gas flow rates were adjusted to reach the target temperatures. The $^{119}$Sn $T_1$ values were measured using an inversion recovery pulse sequence as discussed in the $^{133}$Cs NMR experimental section. All $^{119}$Sn NMR spectra were referenced by setting the $^{119}$Sn signal of a tetracyclohexyl-tin(IV) powder to $\delta(^{119}\text{Sn}) = -97.35$ ppm, a secondary reference with respect to Sn(CH$_3$)$_4$ at $\delta(^{119}\text{Sn}) = 0.00$ ppm.

**Table S1.** Elemental analysis of CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials measured by EDS.

| Sample (Nominal composition) | Elemental atomic % | %Cl : %Br |
|------------------------------|--------------------|------------|
| CsSnCl$_3$                  | Cs 19.3, Sn 19.4, Cl 61.3, Br - | 100 : 0 |
| CsSn(Cl$_{0.90}$Br$_{0.10}$)$_3$ | Cs 18.9, Sn 19.5, Cl 54.6, Br 7.0 | 89 : 11 |
| CsSn(Cl$_{0.67}$Br$_{0.33}$)$_3$ | Cs 18.8, Sn 19.4, Cl 39.6, Br 22.2 | 64 : 36 |
| CsSn(Cl$_{0.50}$Br$_{0.50}$)$_3$ | Cs 18.8, Sn 18.6, Cl 29.4, Br 33.2 | 47 : 53 |
| CsSn(Cl$_{0.33}$Br$_{0.67}$)$_3$ | Cs 18.3, Sn 19.1, Cl 19.0, Br 43.6 | 30 : 70 |
| CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$ | Cs 19.4, Sn 18.7, Cl 6.0, Br 55.9 | 10 : 90 |
| CsSnBr$_3$                  | Cs 17.3, Sn 18.0, Br - | 64.7 |

**Table S2.** Unit cell constants (a) and direct bandgap values for CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials.

| Sample                  | Unit cell constant, a (Å) | Direct bandgap (eV) |
|-------------------------|---------------------------|---------------------|
| CsSnCl$_3$ (cubic)      | 5.5894(5)                 | 2.83                |
| CsSn(Cl$_{0.90}$Br$_{0.10}$)$_3$ | 5.6108(3)                 | 2.71                |
| CsSn(Cl$_{0.67}$Br$_{0.33}$)$_3$ | 5.6642(3)                 | 2.42                |
| CsSn(Cl$_{0.50}$Br$_{0.50}$)$_3$ | 5.6991(6)                 | 2.26                |
| CsSn(Cl$_{0.33}$Br$_{0.67}$)$_3$ | 5.7353(7)                 | 2.10                |
| CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$ | 5.7830(2)                 | 1.87                |
| CsSnBr$_3$              | 5.8031(3)                 | 1.79                |
**Table S3.** Room temperature solid-state $^{133}$Cs NMR experimental parameters, chemical shifts, fwhm and spin-lattice relaxation ($T_1$) values for CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials. The $^{133}$Cs NMR spectra were acquired at 11.75 T using a Bloch pulse sequence.

| Sample                  | $\nu_{\text{rot}}$ (kHz) | Recycle delay (s) | $^{133}$Cs fwhm (Hz $\pm 5$) | $\delta$ ($^{133}$Cs) (ppm $\pm 0.1$) | $T_1$ ($^{133}$Cs) (s) |
|-------------------------|---------------------------|-------------------|-----------------------------|--------------------------------------|------------------------|
| CsSnCl$_3$ (cubic)      |                           |                   |                             |                                      |                        |
| CsSn(Cl$_{0.90}$Br$_{0.10}$)$_3$ |                           |                   |                             |                                      |                        |
| CsSn(Cl$_{0.67}$Br$_{0.33}$)$_3$ |                           |                   |                             |                                      |                        |
| CsSn(Cl$_{0.50}$Br$_{0.50}$)$_3$ |                           |                   |                             |                                      |                        |
| CsSn(Cl$_{0.33}$Br$_{0.67}$)$_3$ |                           |                   |                             |                                      |                        |
| CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$ |                           |                   |                             |                                      |                        |
| CsSnBr$_3$              |                           |                   |                             |                                      |                        |

**Table S4.** Room temperature solid-state $^{119}$Sn NMR experimental parameters, chemical shifts, fwhm and spin-lattice relaxation ($T_1$) values for CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials. The $^{119}$Sn NMR spectra were acquired at 11.75 T using a Hahn-echo ($\nu_{rf} = 62.5$ kHz).

| Sample                  | $\nu_{\text{rot}}$ (kHz) | Recycle delay (s) | $\delta$ ($^{119}$Sn) (ppm) | $^{119}$Sn fwhm (kHz $\pm 0.1$) | $T_1$ ($^{119}$Sn) (s) |
|-------------------------|---------------------------|-------------------|-------------------------------|--------------------------------|------------------------|
| CsSnCl$_3$ (cubic)      |                           |                   |                              |                                  |                        |
| CsSn(Cl$_{0.90}$Br$_{0.10}$)$_3$ |                           |                   |                              |                                  |                        |
| CsSn(Cl$_{0.67}$Br$_{0.33}$)$_3$ |                           |                   |                              |                                  |                        |
| CsSn(Cl$_{0.50}$Br$_{0.50}$)$_3$ |                           |                   |                              |                                  |                        |
| CsSn(Cl$_{0.33}$Br$_{0.67}$)$_3$ |                           |                   |                              |                                  |                        |
| CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$ |                           |                   |                              |                                  |                        |
| CsSnBr$_3$              |                           |                   |                              |                                  |                        |
Table S5. Room temperature solid-state $^{119}$Sn NMR experimental parameters, chemical shifts, fwhm and spin-lattice relaxation ($T_1$) for CsSnBr$_3$ materials prepared by the solvent synthesis (SS), high temperature (HT) and mechanochemical synthesis (MCS) methods. The $^{119}$Sn NMR spectra were acquired at 11.75 T using a Hahn-echo ($\nu_{rf} = 62.5$ kHz).

| Sample           | $v_{rot}$ (kHz) | Recycle delay (s) | $\delta^{(119)Sn}$ (ppm) | $^{119}$Sn fwhm (kHz) | $T_1^{(119)Sn}$ (s) |
|------------------|-----------------|-------------------|---------------------------|----------------------|---------------------|
| CsSnBr$_3$ (SS)  | 0.0             | 0.05              | $-386 \pm 2$              | 7.5 ± 0.2            | 0.025 ± 0.001       |
| CsSnBr$_3$ (HT)  | 0.2             | 2.84              | $-284 \pm 5$              | 21.0 ± 0.5           | 0.007 ± 0.001       |
| CsSnBr$_3$ (MCS) | 0.2             | 295 ± 10          | 34.0 ± 1.0                | 0.003 ± 0.001        |

Table S6. Variable-temperature $^{119}$Sn NMR parameters for CsSnBr$_3$ (SS) acquired under non-spinning sample conditions at 11.75 T using a 4.0 µs $\pi/2$ Bloch pulse sequence.

| T(set) (K) | T(calibrated) (±2) (K) | $\delta_{iso}$ $^{119}$Sn (ppm) | $\Omega$ (ppm) | $\kappa$ † | $^{119}$Sn fwhm (kHz) ± 0.1 | $^{119}$Sn $T_2^*$ (ms) | $^{119}$Sn $T_1$ (ms) |
|------------|------------------------|---------------------------------|----------------|-----------|-----------------------------|------------------------|------------------------|
| 233        | 229.5                  | −393                            | 85             | −0.1      | 14.7                        | 0.068                  | 635(200)               |
| 253        | 250.9                  | −393                            | 75             | −0.1      | 13.6                        | 0.074                  | 390(85)                |
| 273        | 273.6                  | −390                            | 75             | −0.25     | 10.6                        | 0.094                  | 123(12)                |
| 292.4      | 295.4                  | −386                            | 35             | −1.0      | 7.2                         | 0.139                  | 25(1)                  |
| 313        | 318.7                  | −371                            | 0              | NA        | 6.5                         | 0.154                  | 14(1)                  |
| 333        | 341.5                  | −364                            | 0              | NA        | 6.1                         | 0.164                  | 8.8(5)                 |
| 353        | 366.4                  | −350                            | 0              | NA        | 5.7                         | 0.175                  | 4.12(15)               |
| 373        | 385.5                  | −334                            | 0              | NA        | 6.0                         | 0.167                  | 2.16(9)                |
| 393        | 407.6                  | −319.6                          | 0              | NA        | 5.4                         | 0.185                  | 1.14(5)                |
| 403        | 417.9                  | −317.7                          | 0              | NA        | 4.5                         | 0.222                  | 0.92(2)                |

NA – not applicable; † - $\delta_{iso}$, $\Omega$ and $\kappa$ are isotropic chemical shift, span and skew, respectively, where $\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}$, $\Omega = (\delta_{11} - \delta_{33})$ and $\kappa = 3\left(\frac{\delta_{22} - \delta_{iso}}{\Omega}\right)$

Supplementary note 1:

The variable temperature $^{119}$Sn spin-lattice relaxation time ($T_1$) is related to the absolute temperature values for CsSnBr$_3$ (SS) as shown in Table S6. $\log_{10}[T_1/s]$ linearly depends on [1000/T(K)] (i.e., an Arrhenius relationship) within the temperature range of 230 to 418 K. The slope of the Arrhenius fit is related to the activation energy as $E_a = (2303 \cdot R)$ (slope), where $R = 8.314$ J/(mol·K). A slope value of $1.51 \pm 0.06$ K was obtained from the least-squares Arrhenius fit; hence $E_a = 28.9 \pm 1.2$ kJ/mol or $0.30 \pm 0.01$ eV
Table S7. Solid-state $^{133}$Cs NMR acquisition parameters and experimental conditions used for the CsSnBr$_3$ areal degradation study (see Figure 9b in the manuscript). The $^{133}$Cs NMR spectra were acquired at 11.75 T using a Bloch pulse sequence.

| Material          | $T_1$ (s) | $\nu_{\text{rot}}$ (kHz) | Recycle delay (s) | # of scans | Acquisition time (min) |
|-------------------|-----------|---------------------------|-------------------|------------|------------------------|
| CsSnBr$_3$ (degraded) | -         | 5 kHz                     | 1800              | 4          | 120                    |
| CsSnBr$_3$        | 34.9      |                           |                   |            | 4                      |
| Cs$_2$SnBr$_6$    | 170       |                           |                   | 4          | 33                     |
| CsBr              | 631       |                           |                   | 4          | 20                     |

Table S8. Solid-state $^{119}$Sn NMR acquisition parameters and experimental conditions used for the CsSnBr$_3$ areal degradation study (see Figure 9c in the manuscript). The $^{119}$Sn NMR spectra were acquired at 11.75 T using a Hahn-echo ($\nu_{\text{rf}} = 62.5$ kHz).

| Material          | $T_1$ (s) | $\nu_{\text{rot}}$ (kHz) | Recycle delay (s) | # of scans | Acquisition time (min) |
|-------------------|-----------|---------------------------|-------------------|------------|------------------------|
| CsSnBr$_3$ (degraded) | region-1  | -                         | 0                 | 512        | 1.7                    |
|                   | region-1  | 10                        | 0.2               | 512        | 1.7                    |
|                   | region-2  | -                         | 10                | 512        | 853                    |
|                   | region-3  | -                         | 10                | 512        | 853                    |
|                   | region-4  | -                         | 12                | 2,000,000  | 736                    |
| CsSnBr$_3$        | 0.006     | 10                        | 0.2               | 1024       | 3.4                    |
| Cs$_2$SnBr$_6$    | 12.3      | 10                        | 100               | 32         | 53                     |
| SnO$_2$           | 3.1$^{\text{ref.3}}$ | 10                        | 30               | 32         | 15                     |
| SnBr$_4$          | 1.95$^{\text{ref.4}}$ | 0                         | 3                | 512        | 25.6                   |
| SnBr$_2$          | 1.12$^{\text{ref.4}}$ | 13                        | 1.5              | 512        | 12.8                   |
| (trace metal grade) | $\beta$-Sn region | 0.00012$^{\text{ref.4}}$ | 12               | 2,000,000  | 537                   |
Figure S1. Room temperature solid-state $^{133}$Cs NMR spectra of CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials at 11.75 T with a magic angle spinning frequency of 13 kHz. Expansion shows the corresponding spinning side band.

Figure S2. Room temperature PXRD (a) and $^{133}$Cs NMR spectra (b) of CsSnCl$_3$ materials prepared by the high-temperature sealed-tube method followed by slow-cooling (5 K/min). PXRD patterns were collected within 24 h of synthesis and $^{133}$Cs NMR spectra were acquired at 11.75 T after six days of synthesis. The asterisks (*) in (b) indicate spinning sidebands for monoclinic CsSnCl$_3$. Plot of $^{133}$Cs NMR peak area for the cubic CsSnCl$_3$ phase as a function of time (up to 72 days) showing mono-exponential like decay kinetics for the cubic to monoclinic phase transition in CsSnCl$_3$ (c). The data points between 10 to 72 days are missing because of the sudden institutional lockdown (~ 60 days) during the first wave of COVID-19 pandemic in early 2020.
| Material                        | Cs | Sn | Cl   | Br   |
|--------------------------------|----|----|------|------|
| CsSnCl$_3$                     |    |    |      |      |
| CsSn(Cl$_{0.90}$Br$_{0.10}$)$_3$|    |    |      |      |
| CsSn(Cl$_{0.67}$Br$_{0.33}$)$_3$|    |    |      |      |
| CsSn(Cl$_{0.33}$Br$_{0.67}$)$_3$|    |    |      |      |
| CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$|    |    |      |      |
| CsSnBr$_3$                     |    |    |      |      |

**Figure S3.** FESEM images and the corresponding EDS elemental mapping for Cs, Sn, Cl and Br for the CsSn(Cl$_{1-x}$Br$_x$)$_3$ materials (top to bottom: $x = 0.00, 0.10, 0.33, 0.67$ and $1.00$).
Figure S4. Room temperature experimental and fitted PXRD diagrams for the CsSn(Cl$_{1-x}$Br$_x$)$_3$ series. All the diffraction data are fitted assuming a cubic (Pm-3m) space group symmetry.
Figure S5. Tauc plots showing direct bandgaps of the cubic phases of CsSn(Cl\textsubscript{1−x}Br\textsubscript{x})\textsubscript{3} materials; c-CsSnCl\textsubscript{3} (a), CsSn(Cl\textsubscript{0.90}Br\textsubscript{0.10})\textsubscript{3} (b), CsSn(Cl\textsubscript{0.67}Br\textsubscript{0.33})\textsubscript{3} (c), CsSn(Cl\textsubscript{0.50}Br\textsubscript{0.50})\textsubscript{3} (d), CsSn(Cl\textsubscript{0.33}Br\textsubscript{0.67})\textsubscript{3} (e), CsSn(Cl\textsubscript{0.10}Br\textsubscript{0.90})\textsubscript{3} (f) and CsSnBr\textsubscript{3} (g).
Figure S6. Solid-state $^{119}$Sn NMR spectra of CsSnBr$_3$ at 7.05 and 11.75 T under non-spinning sample conditions. The scales are vertically normalized.

Figure S7. Solid-state $^{119}$Sn NMR spectra of c-CsSnCl$_3$ (a), CsSn(Cl$_{0.50}$Br$_{0.50}$)$_3$ (b) and CsSnBr$_3$ (c) at 11.75 T acquired with spinning frequencies of 0 and 10 kHz. The scales are vertically normalized.
Figure S8. Solid-state $^{119}\text{Sn}$ NMR spectra of CsSn(Cl$_{0.10}$Br$_{0.90}$)$_3$ at 11.75 T acquired with spinning frequencies between 0 to 13 kHz with the Hahn-echo pulse sequence and with various echo-delays as indicated. The scales are vertically normalized.

Figure S9. Solid-state $^{119}\text{Sn}$ NMR chemical shifts vs the inverse of direct bandgap values for the CsSn(Cl$_{1-x}$Br$_x$)$_3$ series.
Figure S10. Room temperature PXRD patterns for the CsSnBr$_3$ parent material synthesized by the solvent synthesis (SS), high temperature (HT) and mechanochemical synthesis (MCS) methods. The dagger (†) indicates signal from Cs$_2$SnBr$_6$.

Figure S11. UV-Vis absorption spectra (a) and Tauc plots showing direct bandgaps (b-d) for the CsSnBr$_3$ parent material synthesized by the solvent synthesis (SS), high temperature (HT) and mechanochemical synthesis (MCS) methods.
Figure S12. $^{119}\text{Sn} T_2^*$ (i.e., $\frac{1}{\text{fwhm}}$) relaxation time as a function of absolute temperature (230-418 K) for the CsSnBr$_3$ (SS) material. $^{119}\text{Sn}$ NMR spectra were acquired at 11.75 T under non-spinning sample conditions. The data were fit by a least-squares method with the following equation: $T_2^*/ms = -0.09756(0.02587) + 7.35516(0.77322) \times 10^{-4} \cdot T/K$

Figure S13. UV-Vis absorption spectra for a CsSnBr$_3$ sample that was stored under ambient laboratory conditions over 300 days (degraded CsSnBr$_3$), pristine CsSnBr$_3$ and Cs$_2$SnBr$_6$. 
Figure S14. Solid-state $^{119}\text{Sn}$ NMR spectra of the degraded CsSnBr$_3$ parent and SnBr$_2$ starting precursor at 11.75 T acquired with spinning frequencies of 12 kHz with 2,000,000 scans each.

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