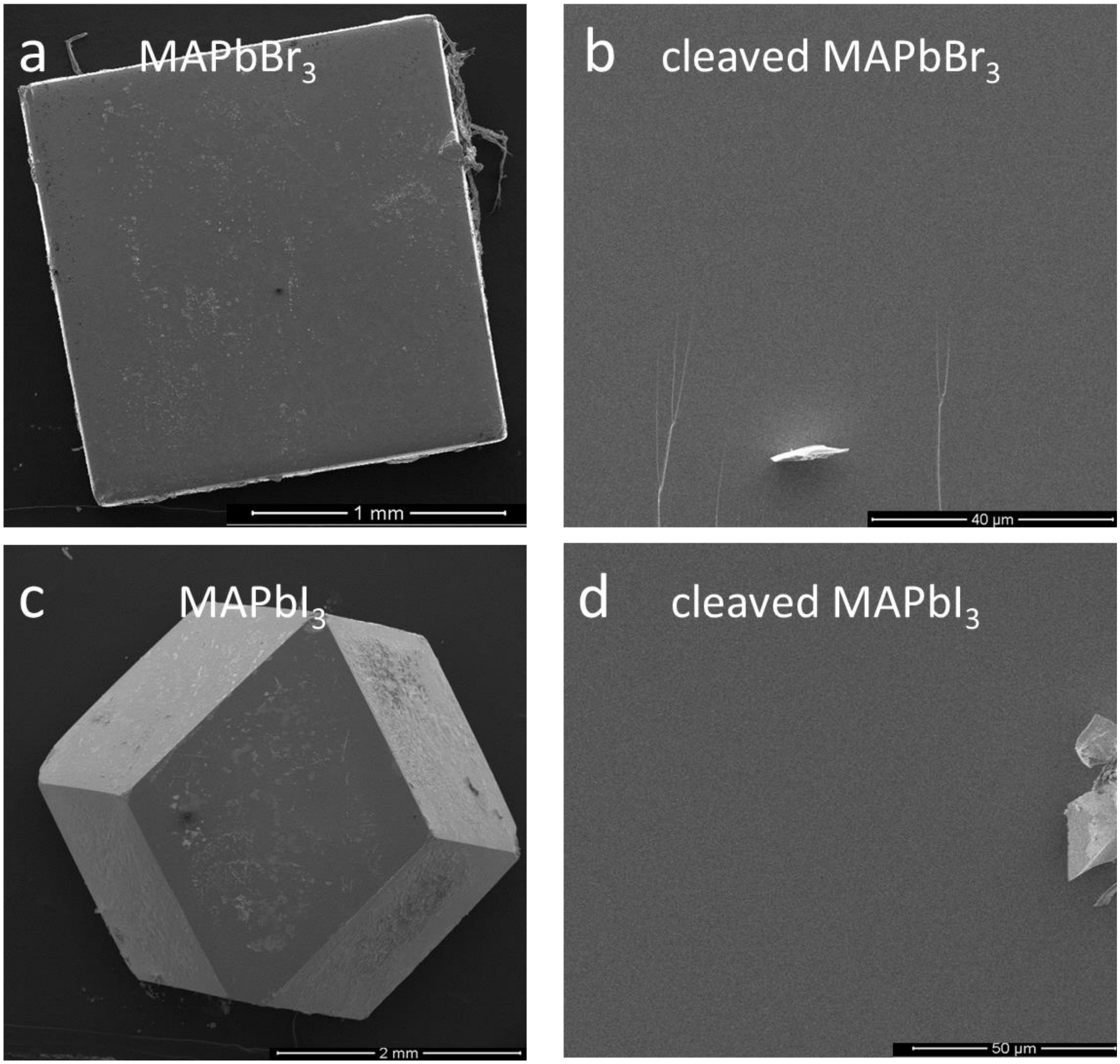
**Supplementary Figure 1. Picture of crystallization setup.** This picture demonstrates, that all 8 vessels containing 1 M $MAPbBr_3$ in DMF produced less than 5 crystals, in particular, 3 of them produced an individual $MAPbBr_3$ crystal. Time-accelerated video of one of these individual crystals growth is presented in Supplementary Movie 2.



**Supplementary Figure 2. SEM images of the surface and cleaved crystals.** SEM of (a) surface of MAPbBr$_3$, (b) cleaved MAPbBr$_3$, (c) surface of MAPbI$_3$ and (d) cleaved MAPbI$_3$. Excess precursors from solution can be observed on the surface of the crystals. No grain boundaries are found on the surface or core of cleaved crystals indicating the single crystalline nature of both crystals. The dusts in (b,d) indicate the good focus of electron beam.

**Supplementary Table 1. Single crystal XRD data.**

| **Compound** | **MAPbBr$_3$** | **MAPbI$_3$** |
|---|---|---|
| $D_{calc.}$/ g cm$^{-3}$ | 3.582 | 3.947 |
| $\mu$/mm$^{-1}$ | 55.601 | 105.893 |
| Max Size/mm | 0.98 | 0.58 |
| Mid Size/mm | 0.09 | 0.56 |
| Min Size/mm | 0.05 | 0.53 |
| $T$/K | 250(2) | 250(2) |
| Crystal System | cubic | tetragonal |
| Space Group | Pm3m | I4/m |
| $a$/Å | 5.9173(6) | 8.8310(5) |
| $b$/Å | 5.9173(6) | 8.8310(5) |
| $c$/Å | 5.9173(6) | 12.6855(7) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$/° | 90 | 90 |
| V/Å$^3$ | 207.19(6) | 989.30(12) |
| $Z$ | 1 | 4 |
| $Z'$ | 0.02083 | 0.125 |
| $\Theta_{min}$/° | 10.617 | 6.981 |
| $\Theta_{max}$/° | 71.520 | 72.151 |
| Measured Refl. | 1572 | 2093 |
| Independent Refl. | 64 | 278 |
| Reflections Used | 64 | 274 |
| $R_{int}$ | 0.0659 | 0.0971 |
| Parameters | 4 | 9 |
| Restraints | 0 | 0 |
| Largest Peak | 4.507 | 8.090 |
| Deepest Hole | -6.787 | -17.741 |
| GooF | 1.336 | 1.491 |
| $wR_2$ (all data) | 0.2197 | 0.3021 |
| $wR_2$ | 0.2197 | 0.3010 |
| $R_1$ (all data) | 0.0868 | 0.1034 |
| $R_1$ | 0.0868 | 0.1029 |

Single crystals of both materials have been obtained and their unit cells have been verified by single crystal X-ray diffraction. The unit cell dimensions as well as the space groups (cubic, space group Pm3m, a = 5.9173(6) Å for MAPbBr$_3$ and tetragonal, space group I4/m, a = b = 8.8310(5) Å, c = 12.6855(7) Å for MAPbBr$_3$) are in excellent agreement with literature reports[1-3].

## Supplementary Note 1

The free energy of a system of unit volume containing a number $n_S$ of solvent molecules in the solution and numbers $n_A$ and $n_C$ of, respectively, isolated A-molecules, and the complexes is

$$\begin{aligned} G = &-\varepsilon n_P + \gamma \cdot S_P - \varepsilon_C \cdot n_C + T n_C \cdot \ln\left(n_C v_C\right) + T n_A \cdot \ln\left(n_A v_A\right) + T n_S \cdot \ln\left(n_S v_S\right) \\ &- T \cdot \left(n_A + n_S + n_C\right) \cdot \ln\left(n_A v_A + n_S v_S + n_C v_C\right) \end{aligned}, \qquad (1)$$

where $\varepsilon$ is the cohesive energy of A-molecules in the particle, $\gamma$ is the surface energy per molecule, $\varepsilon_C$ is the binding energy of the complexes, $S_P$ is the number of A-molecules on the surfaces of A-particle, $T$ is the solution temperature and $v_S$, $v_C$ and $v_A$ are the characteristic volumes of the solvent molecule, the complex, and the A-molecule, respectively. It is convenient to introduce total concentrations of A- and solvent molecules $m_A = n_A + n_P + n_C$ and $m_S = n_S + j \cdot n_C$, respectively, where $j$ is the number of solvent molecules in the A-solvent complex. Expressing $n_S$ and $n_A$ in terms of the total concentrations allows rewriting equation (1) in the form

$$\begin{aligned} G = &-\varepsilon n_P + \gamma \cdot S_P - \varepsilon_C \cdot n_C + T n_C \cdot \ln\left(n_C v_C\right) + T\left(m_A - n_P - n_C\right) \cdot \ln\left(\left(m_A - n_P - n_C\right) v_A\right) \\ &+ T\left(m_S - j n_C\right) \cdot \ln\left(\left(m_S - j n_C\right) v_S\right) \\ &- T\left(m_A + m_S - n_P - j n_C\right) \cdot \ln\left(v_A m_A + v_S m_S - v_A n_P + n_C \cdot \left(v_C - v_A - j v_S\right)\right) \end{aligned} \qquad (2)$$

We are interested in both the equilibrium size of A-particles and the concentration $n_C$ of A complexes with solvent. Therefore we choose $n_P$ and $n_C$ as independent variables. Minimization of the free energy with respect to these variables leads to the equations

$$\begin{aligned}&\frac{\partial G}{\partial n_{\mathrm{P}}}=-\varepsilon+\gamma\cdot\frac{2}{R}-T\cdot\ln\left(n_{\mathrm{A}}v_{\mathrm{A}}\right)=0\\&\frac{\partial G}{\partial n_{\mathrm{C}}}=-\varepsilon_{\mathrm{C}}+T\cdot\ln\left(n_{\mathrm{C}}v_{\mathrm{C}}\right)-T\cdot\ln\left(n_{\mathrm{A}}v_{\mathrm{A}}\right)-jT\cdot\ln\left(n_{\mathrm{S}}v_{\mathrm{S}}\right)=0\end{aligned}\tag{3}$$

The first line gives an equality of the chemical potentials of A-molecules in the particle $\mu_{\mathrm{AP}}=-\varepsilon+2\gamma/R$ and in the solution $\mu_{\mathrm{AS}}=T\cdot\ln\left(n_{\mathrm{A}}v_{\mathrm{A}}\right)$. The second line states that chemical potential of the complex is equal to the sum of chemical potentials of A-molecule and $j$ solvent molecules involved in complex formation $\mu_{\mathrm{SS}}=T\cdot\ln\left(n_{\mathrm{S}}v_{\mathrm{S}}\right)$. Solving the equations

$$\begin{aligned}&-\varepsilon+\gamma\cdot\frac{2}{R}=T\cdot\ln\left(n_{\mathrm{A}}v_{\mathrm{A}}\right)\\&-\varepsilon_{\mathrm{C}}+T\cdot\ln\left(n_{\mathrm{C}}v_{\mathrm{C}}\right)=T\cdot\ln\left(n_{\mathrm{A}}v_{\mathrm{A}}\right)+jT\cdot\ln\left(n_{\mathrm{S}}v_{\mathrm{S}}\right)\end{aligned}\tag{4}$$

with respect to $n_{\mathrm{A}}$ and $n_{\mathrm{C}}$ gives

$$\begin{aligned}&n_{\mathrm{A}}=\frac{1}{v_{\mathrm{A}}}\exp\left(\frac{1}{T}\left(-\varepsilon+\gamma\cdot\frac{2}{R}\right)\right)\\&n_{\mathrm{C}}=\frac{1}{v_{\mathrm{C}}}\left(n_{\mathrm{S}}v_{\mathrm{S}}\right)^{j}\exp\left(\frac{1}{T}\left(\varepsilon_{\mathrm{C}}-\varepsilon+\gamma\cdot\frac{2}{R}\right)\right)\end{aligned}\tag{5}$$

These equations contain the particle radius $R$, which can be expressed in terms of $n_{\mathrm{P}}$. Therefore, these equations can be solved numerically. However, we can understand qualitatively the temperature effect on $n_{\mathrm{P}}$ by considering the particle size to be far from its critical value (where the surface energy is really important) when we may set $\gamma\approx 0$. In that limit the number fraction of precipitated molecules is

$$n_{\mathrm{P}}v_{\mathrm{A}}=m_{\mathrm{A}}v_{\mathrm{A}}-\frac{v_{\mathrm{A}}}{v_{\mathrm{C}}}\left(n_{\mathrm{S}}v_{\mathrm{S}}\right)^{j}\exp\left(\frac{\left(\varepsilon_{\mathrm{C}}-\varepsilon\right)}{T}\right)-\exp\left(-\frac{\varepsilon}{T}\right).\tag{6}$$

## Supplementary References

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