Supporting Information: Chain length dependence of thermal conductivity in 2D alkylammonium lead iodide single crystals

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S1: TDTR Fitting and Uncertainty Analysis

The experimental data for each sample (ratio vs time delay) was fit using the modeling technique described by Cahill. The sum of the squares of the difference between the experimental data and the model is minimized using fminsearch by varying only the thermal conductivity of the crystal. The nominal input parameters to the model were

As described by Cahill, the aluminum layer is split into two layers (1 and 2) in order to mimic the absorption process and to speed up the computation. The top layer is treated
Table S1: Thermal model used for data reduction

<table>
<thead>
<tr>
<th>layer #</th>
<th>material</th>
<th>k [W/m-K]</th>
<th>C [10^6 \text{J/m}^3\text{-K}]</th>
<th>h [nm]</th>
<th>(\eta \equiv k_z/k_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (top)</td>
<td>Al</td>
<td>1800</td>
<td>24.2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Al</td>
<td>180</td>
<td>2.42</td>
<td>47.5</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Ti</td>
<td>20</td>
<td>2.36</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>interface</td>
<td>0.05</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>perovskite</td>
<td>fit</td>
<td>1.29-1.80*</td>
<td>(\infty)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table S2: Thermal Transport Properties of \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4\) at 330K. * indicates average value, for addition measurement results see Fig. 6 of main text.

<table>
<thead>
<tr>
<th>Sample n</th>
<th>(\rho) [kg/m(^3)]</th>
<th>(C) [MJ/m(^3\text{-K})]</th>
<th>(k) [W/m-K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2692</td>
<td>1.47</td>
<td>0.125 ± 0.009</td>
</tr>
<tr>
<td>5</td>
<td>2512</td>
<td>1.75</td>
<td>0.123 ± 0.021</td>
</tr>
<tr>
<td>6</td>
<td>2403</td>
<td>1.62</td>
<td>0.107 ± 0.011</td>
</tr>
<tr>
<td>7</td>
<td>2215</td>
<td>1.94</td>
<td>0.099 ± 0.021</td>
</tr>
</tbody>
</table>

We use a Monte Carlo fitting procedure to report the statistics of the fitting process. The approach is to use input parameters based on Table S1 but randomly distributed about their mean according to the variance assigned to each parameter in the table, using a Gaussian distribution. This procedure is repeated 200 times for each measurement curve. The assumed uncertainties in the input parameters were are follows.
1. Uncertainties for heat capacity were assumed to be 5% for aluminum and titanium layers, and 8% for the perovskite.

2. The thickness was assumed to be 2% for aluminum and titanium (XRR is highly sensitive).

3. Through-plane thermal conductivity for aluminum and titanium was assumed to be 10%.

4. Interface conductance (layer 4) was taken as 40%.

5. Both spot sizes was assumed to be 5% (directly measured using a focused scanning slit).

6. The anisotropic ratio was taken as 10% for layers 1-3, and 100% for layer 5 (perovskite).

7. The phase of lockin amplifier was estimated using the measured out of phase noise, considering the scale of the jump in the out of phase signal, using the approach of Koh et al.

\[
\delta \phi = \frac{1}{\sqrt{N}} \frac{\delta V_{\text{out}}}{\Delta V_{\text{in}}}
\]  

Here, \(N\) is the number of out-of-phase data points considered when minimizing the jump in the out-of-phase signal. \(\delta \phi\) was calculated for each sample individually, but was typically near 0.25° for all samples. During the Monte Carlo fitting process, for each fit the experimental data was randomly rotated by a random phase chosen according to a Gaussian distribution with mean of zero and variance, \(\delta \phi\).

The results of all 200 fits are reported in the manuscript as well as their mean and standard deviation. Interestingly, we find that the ‘best fit’ for low thermal conductivity samples does not correspond to the fit using the mean value from the Monte Carlo approach - which is in fact what motivated this approach. The distribution is significantly skewed. A
typical histogram for the fitting procedure is shown below. For this reason we have reported
the mean of the distribution in the manuscript, rather than the best fit. The measurement
uncertainty is then obtained naturally as the standard deviation of the Monte Carlo fits
(reporting as the black errorbars in the main text).

Figure S1: (a) Histogram of Monte Carlo results for a \((\text{HexylA})_2\text{PbI}_4\) sample. (b) Example
Fit for \((\text{HeptylA})_2\text{PbI}_4\) showing zero order Lamb mode.
S2: Sensitivity of the Experiments

Sensitivity of the TDTR signal \((r = -V_{in}/V_{out})\) to the input and fitting parameters was calculated by numerical differentiation. The sensitivity to any parameter, \(\alpha\) is defined as

\[
S_\alpha = \frac{d \log r}{d \log \alpha} = \frac{dr}{r} \frac{d\alpha}{\alpha}
\]

and represents the fractional change in the signal in response to fractional changes of the parameter \(\alpha\). Typical sensitivity parameters for the experiment are shown below, using the input values in Table S1 and \(k_5 = 0.12, C_5 = 1.44 \text{ J/cm}^3\cdot\text{K}\). The measurement is

![Graph showing sensitivity plot for TDTR experiments in this work](image)

Figure S2: Typical sensitivity plot for TDTR experiments in this work

primarily sensitive to the thermal effusivity of the perovskite, \(\sqrt{k_5C_5}\) and capacitance of the transducer, \(C_ih_i\) for \(i = 1, 2\), and to a lesser extent shows some influence from in-plane heat spreading within the transducer, \(k_{x,i}\) \((i = 1, 2)\) and spot size (the effect of both pump and probe are combined into a single quantity, \(R_{pp}\), in the plot. For this reason, we obtained accurate estimates of the in-plane thermal conductivity of the transducer (using four point probe method and Weidemann Franz law) and the spot size of our laser with a scanning slit,
heat capacity of the perovskites use DSC, and thickness of the transducers using XRR as described above.

S3: Bayesian Statistical Analysis

We compute the probability distribution $P(G, k_0|H, \{k_i^{\text{exp}}\})$, given a hypothetical model, $H$ and a set of experimental observations $\{k_i^{\text{exp}}\}$. The model, $H$, is that the expected value of the thermal conductivity is

$$k_H = \left(\frac{1}{GL_n} + \frac{1}{k_0}\right)^{-1}. \quad (3)$$

Note that the value of $L_n$ for any particular $n$ is known nearly exactly from XRD. We compute $P(G, k_0|H, \text{data})$ using the following algorithm

1. The initial ‘Prior distribution’, $P(G, k_0|\emptyset)$ is taken as uniform and equal to one (i.e. there is no built in bias to the model before data is taken into account). Normalization is not enforced until the end of the algorithm. Numerically, we compute the distribution on a discrete mesh with $50 < G < 1,000 \text{ MW/m}^2\text{-K}$, and $0.1 < k_0 < 200 \text{ W/m-K}$, both logarithmically spaced.

2. For each experimental thermal conductivity point (here, ‘point’ means the mean of the Monte Carlo fitting on each sample), the probability distribution, $P(G, k_0|H, \{k_i^{\text{exp}}, m = 1..i\})$ is updated using Bayes’s theorem

$$P(G, k_0|H, \{k_i^{\text{exp}}, m = 1..i\}) = P(k_i^{\text{exp}}|G, k_0)P(G, k_0|H, \{k_i^{\text{exp}}, m = 1..i - 1\}) \quad (4)$$

The probability of observing a particular data point, $k_i^{\text{exp}}$, during the experiment for any given value of $G, k_0$ is taken as a Gaussian distribution with variance determined from the Monte Carlo fitting approach

$$P(k_i^{\text{exp}}|G, k_0) = \frac{e^{-\frac{(k_i^{\text{exp}} - k_H)^2}{2\sigma^2}}}{\sqrt{2\pi\sigma}}; \quad (5)$$
For simplicity, the variance for all samples is taken as $\sigma = 0.019 \text{ W/m-K}$.

3. Bayes’s theorem (above) is applied iteratively until all experimental observations (i.e. the 41 measurements reported in the main manuscript) have been considered.

The final probability distribution, $P(G, k_0|H, \{k_i^{\text{exp}}\})$, is shown below. The relative probability of the best fit stacked interface model can be directly compared to the best fit chain-length independent model using the ratio, $\max P(G \to \infty, k_0|H, \{k_i^{\text{exp}}\}) / \max P(G, k_0 \to \infty|H, \{k_i^{\text{exp}}\})$ which yields $10^0/10^{-8.987} \approx 10^9$ indicating that it is a billion times less likely that a stacked interface model captures the data than a simpler model that just assumes there is no chain length dependence. As outlined in the main text, one can examine the limit of $P(G, k_0 \to \infty|H, \{k_i^{\text{exp}}\})$ to force the model to simulate a stacked interface resistance model, in which case the renormalized distribution and it’s integrated probability are shown below.

Figure S3: Logarithm of the calculated probability distribution, $P(G, k_0|H, \{k_i^{\text{exp}}\})$. Here we have not normalized the distribution.
Figure S4: Probability distribution for a stacked interface resistance model, $P(G_k \rightarrow \infty | H, \{k_i^{\text{exp}}\})$ (upper) and its integrated probability (lower). Data markers indicate the edges of the 95% confidence interval on $G$.

**S4: Surface Morphology**

We have observed that after exfoliation with Scotch tape, the samples are very smooth and showing only occasional step heights that correspond to one or a few monolayers worth of
thickness change. Figure S5a shows an AFM image over a 1\( \mu \)m square after exfoliation. The associated RMS roughness is calculated to be \( Rq = 0.41 \) nm. Figure S5b shows the appearance of steps each approximately integer multiples of 1.5 nm.

![AFM images](image)

Figure S5: Atomic Force Microscopy for (ButylA)\(_2\)PbI\(_4\) (left) 1\( \mu \)m square region showing smoothness of the exfoliated crystal. (right) larger region shown shallow steps in the exfoliated crystals.

**S5: Crystal/Location Breakdown of Thermal Conductivity Data**

The figure below is identical to the one in the manuscript, but shows which crystals and location correspond to which measurement result.
Figure S6: Sample by sample breakdown of the thermal conductivity. Each unique crystal (usually 3 per n) is given a different tint. Each location (usually 3) is given a different column.
References
