Supplementary Information:
Thermal Stability of Mobility in Methylammonium Lead Iodide

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S1. Evaluation of Photoconductance from Time Resolved Microwave Conductivity (TRMC) Data

The microwave detector employed in our system (see Figure 1 of main text) outputs a voltage that is linearly proportional to the incident microwave power: \( V \propto P \). The change in sample conductance due to optical illumination \( \Delta G \), is related to the normalized change in microwave power (\( \Delta P / P \)) via \textbf{Equation S1}:[1–3]

\[
\Delta G = -\frac{1}{K} \frac{\Delta P}{P}
\]

(S1)

Here \( K \) is the sensitivity factor of the microwave cavity. Since \( \Delta G \) is dependent on the normalized change in microwave power (\( \Delta P / P \)), it is not necessary to know the absolute values of microwave power, just the relative change under illumination. For this reason, with a knowledge of the detector voltage in the dark \( V \), and the change in detector voltage under illumination \( \Delta V \), it is possible to determine the photo-induced conductance from \textbf{Equation S2}:[3]

\[
\Delta G = -\frac{1}{K} \frac{\Delta V}{V}
\]

(S2)

The sensitivity factor of the microwave cavity can be evaluated in several different ways,[2] one of which is to measure the reflectivity of the cavity as a function of frequency, around the resonant frequency. \textbf{Figure S1} shows an example of such a measurement.

\[ f_0 = 8.583 \text{ GHz} \]
\[ R_0 = 0.65 \]
\[ \Delta W = 13.5 \text{ MHz} \]
\[ K = 567 \text{ W} \]

\textbf{Figure S1} Example reflectivity of cavity measured as a function of frequency (points). The red line is a fit to Equation S3, with fitting parameters of \( f_0 = 8.853 \text{ GHz} \), \( R_0 = 0.65 \), \( \Delta W = 13.5 \text{ MHz} \).
The reflectivity of the cavity around the resonance frequency should be roughly Lorentzian.[2,4] The experimental data can then be fitted to Equation S3, where \( R \) is the reflectivity of the cavity at a frequency \( f \), \( R_0 \) is the reflectivity of the cavity to microwaves at the resonance frequency \( f_0 \), and \( \Delta W \) is the full width at half maximum (FWHM) of the cavity reflectivity resonance curve.

\[
R(f) = \frac{R_0 + \left(\frac{2(f - f_0)}{\Delta W}\right)^2}{1 + \left(\frac{2(f - f_0)}{\Delta W}\right)^2}
\]  
(S3)

The parameters extracted from this fit can then be used to evaluate the sensitivity factor, \( K \) via Equation S4:[2,4]

\[
K = \frac{2Q \left( \frac{1}{\sqrt{R_0}} \pm 1 \right)}{\pi f_0 \varepsilon_0 \varepsilon_r L \beta}
\]  
(S4)

\( L \) is the length of the cavity, where the length corresponds to the dimension in the direction of propagation of the electromagnetic waves. \( \beta \) is the ratio of the two remaining cavity dimensions, with the numerator / denominator depending on the polarization direction of the standing wave. In our case \( \beta = 2.25 \). \( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum permittivity and the relative permittivity of the medium of the cavity, respectively. Since our measurements are carried out in air (\( \varepsilon_r = 1 \)), the semiconductor thickness is roughly 300 nm, and the cavity length is \( L = 7.62 \text{cm} \), we have here approximated \( \varepsilon_r = 1 \). \( Q \) is the quality factor of the cavity. This is the ratio of the resonance frequency of the full width at half maximum (FWHM) of the cavity reflectivity resonance curve (\( \Delta W \)), as expressed by Equation S5:

\[
Q = -\frac{f_0}{\Delta W}
\]  
(S5)

The \( \pm \) in Equation S4 depends on whether the cavity is in the under-coupled (−) or over-coupled regime (+).[4,5]

In this report all measurements were carried out in the under-coupled regime, hence a minus sign was used in Equation S4.

**S2. Fitting of Time Resolved Microwave Conductivity (TRMC) Figure of Merit**

The time resolved microwave conductivity (TRMC) figure of merit (\( \phi \Sigma \mu \)) is evaluated using the maximum photoconductance (\( \Delta G_{\text{max}} \)) extracted at a certain incident optical fluence (\( I_0 \)), using Equation 1 from the main text. This equation implicitly assumes that all photo-generated charge carriers contribute to the observable value of \( \Delta G_{\text{max}} \). At low fluence (\( \lesssim 10^{13} \text{ cm}^{-2} \)) this is a reasonable assumption, but at high fluence the carrier density is high-enough that a significant amount of bimolecular and Auger recombination takes place. This results in a non-
negligible fraction of charge carriers recombining during the finite duration of the laser pulse, and therefore not being detectable as photoconductance.

In TRMC data, this phenomenon is manifest as a reduction in the measured value of $\phi \Sigma \mu$ with increasing fluence at high fluence. At low-fluence, $\phi \Sigma \mu$ is observed to be roughly independent of fluence. This is a widely-observed phenomenon in TRMC experiments,[6–10] and is present in the data presented in Figure 3 of the main text. A range of models have been developed to account for this.[11–14] We here employ a simple numerical model based on carrier dynamics that can be used to evaluate a representative value of $\phi \Sigma \mu$ from fluence-dependent data.[15] In-depth details of the model are omitted here for brevity, but a short description is provided.

We start by re-labelling the experimental figure of merit as $(\phi \Sigma \mu)^{\text{exp}}$. This is the measured parameter which is observed to change as a function of fluence (e.g. in Figure 3 of the main text). We can also define the representative figure of merit, which is a material property and independent of fluence, as $\phi \Sigma \mu$. These two values are related by a parameter $R$, which we refer to as the recombination parameter. $R$ is a dimensionless parameter which can take values between 0 and 1. For a certain fluence this is expressed by Equation S6:

\[
(\phi \Sigma \mu)^{\text{exp}} = R \phi \Sigma \mu
\]

The recombination parameter as a function of time $R(t)$, can be defined by Equation S7:

\[
R(t) = \frac{n(t)}{n'(t)}
\]

Where $n(t)$ is the average carrier density in the film at a time $t$, and $n'(t)$ is what the average carrier density in the film would be in the absence of recombination. During a TRMC experiment, one could expect $n(t)$ to peak when the intensity of a laser pulse is at its highest, and $n'(t)$ to increase during the laser pulse, before remaining constant after the pulse has terminated. Implicitly, in standard TRMC analysis[2] it is assumed that when the peak value of $\Delta G$ is extracted: $n(t) = n'(t)$. For the model described, we relax this assumption via Equation S7. When employing $R$ in Equation S6, we consider it at the point when $n(t)$ is at its peak, hence corresponding to where one would extract $\Delta G_{\text{max}}$ in the evaluation of $\phi \Sigma \mu$ in a TRMC experiment (i.e. peak values of $\Delta G$ in Figure 2 of the main text).

While more sophisticated models do exist,[12,14] the model employed in this study simply describes the rate of change of overall carrier concentration due to recombination $n_r(t)$, by Equation S8:

\[
n_r(t) = -n(t)k_1 - n^2(t)k_2 - n^3(t)k_3
\]
Where $k_1$, $k_2$, and $k_3$ are the rate constants associated with monomolecular, bimolecular, and Auger recombination, respectively. These parameters are documented to have a range of potential values for this class of materials,[16] and can be used as fitting parameters in this analysis. By describing the optical powder density as having a Gaussian distribution in time, Equations S6-S8 can be solved numerically,[15] and fitted to experimental data, as shown in Figure 3 of the main text for example. For the purposes of our study we are not interested in the fitted values of $k_1$, $k_2$, and $k_3$, however we do wish to know the representative value of $\phi \Sigma \mu$. The values plotted in Figure 4(a) of the main text are extracted from such fits to three identically-prepared samples, where there error bars represent the standard deviation between extracted values.

**S3. Scanning Electron Microscope (SEM) Images**

**S3.1. Pristine MAPbI$_3$**

![Scanning electron microscope (SEM) images of thin film of pristine methylammonium lead iodide (MAPbI$_3$).](image)

*Figure S2* Scanning electron microscope (SEM) images of thin film of pristine methylammonium lead iodide (MAPbI$_3$).
S3.2. MAPbI₃ Annealed at 50°C for 96 hours

[Images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 50°C for 96 hours.]

**Figure S3** Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 50°C for 96 hours.

S3.3. MAPbI₃ Annealed at 60°C for 96 hours

[Images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 60°C for 96 hours.]

**Figure S4** Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 60°C for 96 hours.
S3.4. MAPbI$_3$ Annealed at 70°C for 96 hours

Figure S5 Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 70°C for 96 hours.

S3.5. MAPbI$_3$ Annealed at 80°C for 96 hours

Figure S6 Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 80°C for 96 hours.
S3.6. MAPbI₃ Annealed at 90°C for 96 hours

Figure S7 Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 90°C for 96 hours.

S3.7. MAPbI₃ Annealed at 100°C for 96 hours

Figure S8 Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI₃) thermally annealed at 100°C for 96 hours.
S3.8. MAPbI$_3$ Annealed at 110°C for 96 hours

![SEM images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 110°C for 96 hours.]

**Figure S9** Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 110°C for 96 hours.

S3.9. MAPbI$_3$ Annealed at 120°C for 96 hours

![SEM images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 120°C for 96 hours.]

**Figure S10** Scanning electron microscope (SEM) images of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 120°C for 96 hours.
S3.10. Pristine PbI$_2$

**Figure S11** Scanning electron microscope (SEM) images of thin film of pristine lead iodide (PbI$_2$).
S4. X-ray Diffractograms

Figure S12 Normalized X-ray diffraction (XRD) spectra of thin films of pristine methylammonium lead iodide (MAPbI$_3$), lead iodide (PbI$_2$), and films of MAPbI$_3$ subjected to extended thermal annealing at various temperatures. All measurements were carried out in air at room temperature. Annealed samples were annealed for 96 hours under ambient pressure N$_2$ at the labelled temperature.
S5. X-ray absorption near edge structure (XANES)

![Figure S13. Lead (Pb) LIII edge XANES spectra for thin films of pristine MAPbI₃, MAPbI₃ annealed for 96 hours at 70°C, 80°C, 100°C, pristine PbI₂ and Pb foil for comparison.](image)

S6. Extended X-ray Absorption Fine Structure (EXAFS) Fitting Parameters

|        | MAPbI₃ | 70°C | 80°C | 100°C | PbI₂ |
|--------|--------|------|------|-------|------|
| $N_{\text{Pb-I}}$ | 6      | 6    | N/A  | 6     | 6    |
| $E_0$ (eV) |        |      |      | 4.6±1.6 |      |
| $R_{\text{Pb-I}}$ (Å) | 3.119±0.011 | 3.133±0.017 | N/A | 3.145±0.012 | 3.147±0.014 |
| $\sigma^2$ (Å²)   | 0.014±0.002 | 0.015±0.003 | N/A | 0.013±0.002 | 0.015±0.002 |

*Table S1. Pb LIII edge extended X-ray absorption fine structure (EXAFS) fitting parameters for thin films of pristine MAPbI₃, MAPbI₃ annealed for 96 hours at 70°C, MAPbI₃ annealed for 96 hours at 100°C, and pristine PbI₂. No satisfactory fit was obtainable for the 80°C sample. N is the number of neighboring atoms, $E_0$ is the absorption edge energy, $R_{\text{Pb-I}}$ is the interatomic distance and $\sigma^2$ is the variation in the neighbor distance. $E_0$ was fixed to -4.584.*
S7. $k^2$-weighted EXAFS data in R space

S7.1. Pristine MAPbI$_3$

Figure S14. Experimental and fitted magnitude of the $k^2$ weighted Fourier transform in R space for the EXAFS data of thin film of pristine methylammonium lead iodide (MAPbI$_3$)

S7.2. MAPbI$_3$ Annealed at 70°C for 96 hours

Figure S15. Experimental and fitted magnitude of the $k^2$ weighted Fourier transform in R space for the EXAFS data of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 70°C for 96 hours.
**S7.3. MAPbI$_3$ Annealed at 100°C for 96 hours**

![Graph](image1)

*Figure S16.* Experimental and fitted magnitude of the k$^2$ weighted Fourier transform in R space for the EXAFS data of thin film of methylammonium lead iodide (MAPbI$_3$) thermally annealed at 100°C for 96 hours.

**S7.4. Pristine PbI$_2$**

![Graph](image2)

*Figure S17.* Experimental and fitted magnitude of the k$^2$ weighted Fourier transform in R space for the EXAFS data of thin film of pristine lead iodide (PbI$_2$).
References

[1] Kroeze J E, Savenije T J, Vermeulen M J W and Warman J M 2003 Contactless Determination of the Photoconductivity Action Spectrum, Exciton Diffusion Length, and Charge Separation Efficiency in Polythiophene-Sensitized TiO 2 Bilayers J. Phys. Chem. B 107 7696–705

[2] Savenije T J, Ferguson A J, Kopidakis N and Rumbles G 2013 Revealing the Dynamics of Charge Carriers in Polymer:Fullerene Blends Using Photoinduced Time-Resolved Microwave Conductivity J. Phys. Chem. C 117 24085–103

[3] Labram J G, Venkatesan N R, Takacs C J, Evans H A, Perry E E, Wudl F and Chabinyc M L 2017 Charge transport in a two-dimensional hybrid metal halide thiocyanate compound J. Mater. Chem. C 5 5930–8

[4] De Haas M P and Warman J M 1982 Photon-induced molecular charge separation studied by nanosecond time-resolved microwave conductivity Chem. Phys. 73 35–53

[5] Infelta P P, de Haas M P and Warman J M 1977 The study of the transient conductivity of pulse irradiated dielectric liquids on a nanosecond timescale using microwaves Radiat. Phys. Chem. 1977 10 353–65

[6] Oga H, Saeki A, Ogomi Y, Hayase S and Seki S 2014 Improved Understanding of the Electronic and Energetic Landscapes of Perovskite Solar Cells: High Local Charge Mobility, Reduced Recombination, and Extremely Shallow Traps J. Am. Chem. Soc. 136 13818–25

[7] Savenije T J, Kroeze J E, Wienk M M, Kroon J M and Warman J M 2004 Mobility and decay kinetics of charge carriers in photoexcited PCBM/PPV blends Phys. Rev. B 69 155205

[8] G. Labram J, R. Venkatesan N, J. Takacs C, A. Evans H, E. Perry E, Wudl F and L. Chabinyc M 2017 Charge transport in a two-dimensional hybrid metal halide thiocyanate compound J. Mater. Chem. C 5 5930–8

[9] Crovetto A, Nielsen R, Pandey M, Watts L, Labram J G, Geisler M, Stenger N, Jacobsen K W, Hansen O, Seger B, Chorkendorff I and Vesborg P C K 2019 Shining Light on Sulfide Perovskites: LaYS 3 Material Properties and Solar Cells Chem. Mater. 31 3359–69

[10] Hutter E M, Gélvez-Rueda M C, Bartesaghi D, Grozema F C and Savenije T J 2018 Band-Like Charge Transport in Cs 2 AgBiBr 6 and Mixed Antimony–Bismuth Cs 2 AgBi 1–x Sb x Br 6 Halide Double Perovskites ACS Omega 3 11655–62

[11] Dicker G, de Haas M P, Siebbeles L D A and Warman J M 2004 Electrodeless time-resolved microwave conductivity study of charge-carrier photogeneration in regioregular poly(3-hexylthiophene) thin films Phys. Rev. B 70 045203

[12] Ferguson A J, Kopidakis N, Shaheen S E and Rumbles G 2008 Quenching of Excitons by Holes in Poly(3-hexylthiophene) Films J. Phys. Chem. C 112 9865–71

[13] Reid O G, Malik J A N, Latini G, Dayal S, Kopidakis N, Silva C, Stingelin N and Rumbles G 2012 The influence of solid-state microstructure on the origin and yield of long-lived photogenerated charge in neat semiconducting polymers J. Polym. Sci. Part B Polym. Phys. 50 27–37

[14] Hutter E M, Eperon G E, Stranks S D and Savenije T J 2015 Charge Carriers in Planar and Meso-Structured Organic–Inorganic Perovskites: Mobilities, Lifetimes, and Concentrations of Trap States J. Phys. Chem. Lett. 6 3082–90

[15] Labram J G and Chabinyc M L 2017 Recombination at high carrier density in methylammonium lead iodide studied using time-resolved microwave conductivity J. Appl. Phys. 122 065501

[16] Herz L M 2016 Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites Annu. Rev. Phys. Chem. 67 65–89