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Supporting Information for:

Third-Order Nonlinear Optical Properties Methylammonium Lead Halide Perovskite Films

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I. Experimental Design



Figure S1. The layout of the laser system and beam configuration for performing transient grating spectroscopy. FM = folding mirror, BS = beamsplitter, CM = curved mirror, OC = optical chopper, CS = cover slip, BB = beam block, PD = photodiode, $\lambda/2$ = half waveplate. For the studies here, E_{LO} is blocked, producing a homodyne E_{sig} in the specified direction.

II. Ellipsometry Raw Data



Figure S2. Ellipsometry data for A, CH₃NH₃PbBr₃ and B, CH₃NH₃PbBr₂I films.

Steady-state optical ellipsometry data were collected on all films. The values of *n* (real) and *k* (imaginary) part of the refractive index were extracted at wavelengths from 200 nm to 2000 nm. The value of *k* is often termed "extinction" and is proportional to the absolute extinction spectrum, which can be found in ref 1. The two types of films had very similar thicknesses, and thus peak extinction values near the lowest exciton are both $\sim 8 \times 10^4$ cm⁻¹.

III. Additional Transient Grating Data



Figure S3. Transient grating intensity vs. pump intensity for (A)-(B) $CH_3NH_3PbBr_3$ (orange) and (C) $CH_3NH_3PbBr_2I$ (brown) films. The solid line indicates a slope of three, expected for unsaturated third-order signals. The deviation from the line is most evident and at the lowest pump intensity for the $CH_3NH_3PbBr_3$ film under resonant conditions (B and C).

IV. Absorption Fitting

Absorption spectra were fitted with a Elliott model as in Yang et al.² The portion of the spectrum near the band edge was fitted. The exciton and continuum components were extracted and plotted with the full fit and the data (Figure S3A-B). For the CH₃NH₃PbBr₃ films, the exciton portion was extracted vs. temperature (Figure S3C), and the amplitude plotted (Figure S3D). There was no discernible trend in the exciton feature vs. temperature for CH₃NH₃PbBr₂I, which shows a much smaller exciton feature overall.



Figure S4. Absorption spectra with fit (green), exciton portion (red) and continuum portion (blue) for **A**, CH₃NH₃PbBr₃ and **B** CH₃NH₃PbBr₂I films. **C**, The exciton spectrum vs. temperature and **D**, amplitude vs. temperature for the CH₃NH₃PbBr₃ film.

References

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