Supporting Information for

Radiative Monomolecular Recombination Boosts Amplified Spontaneous Emission in $HC(NH_2)_2SnI_3$ Perovskite Films

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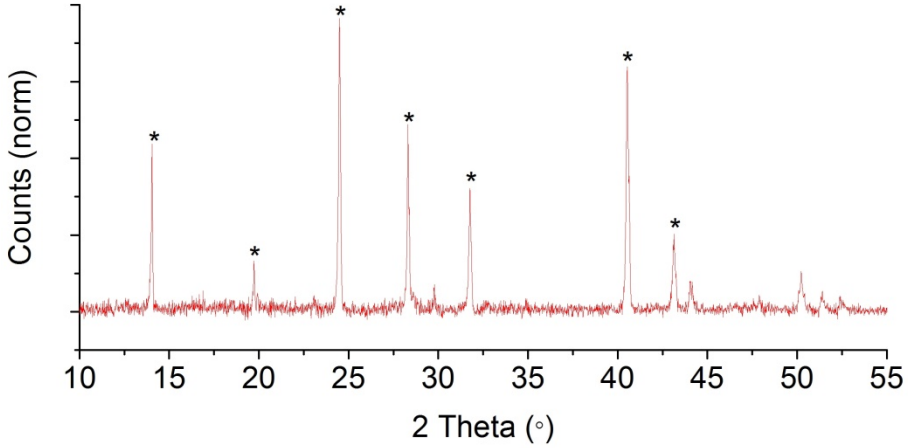
1. Film characterization

A.



B.

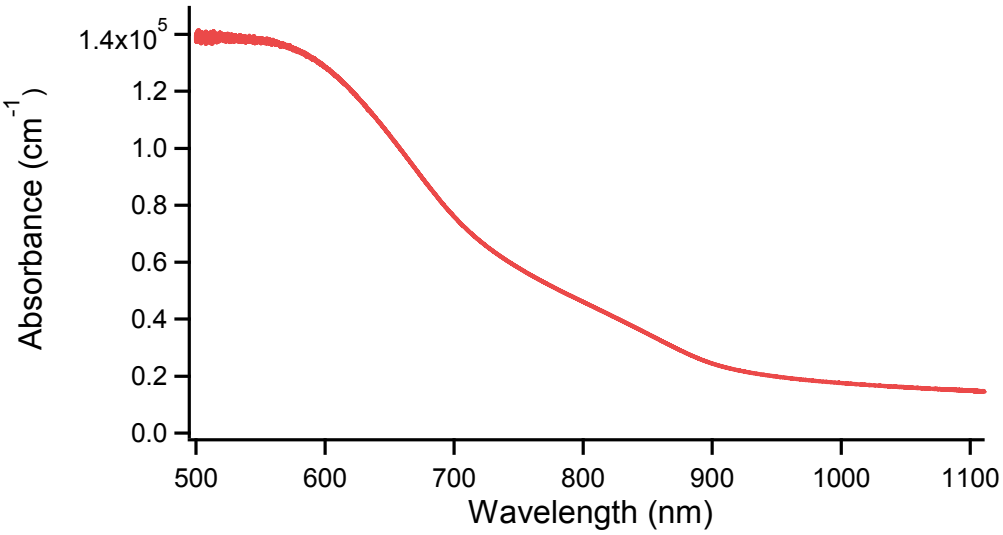


Figure S1. (A) X-ray diffraction spectra for thin films of $FASnI_3$. Peaks marked with a * correspond to the known black phase perovskite, which has been characterized in previous studies.[1,2] A PANalytical Empyrean PIXcel[1D] diffractometer with Cu anode was used to obtain XRD measurements under N_2. (B) UV-vis. spectrum of $FASnI_3$. The spectrum was taken using a Fourier-transform infrared spectrometer (Bruker, Vertex 80v). The source was a halogen lamp, which was detected by a silicon diode detector. Both transmission and reflection were measured using a transmission/reflection accessory, and the absorption coefficient was calculated as follows: $\alpha = -1/l \ln\left[T/(1-R)\right]$.

2. Determination of Average Carrier Density

In an optical-pump THz-probe experiment, the observed signal $\Delta T/T$ is proportional to the photoconductivity σ and thus the product of the charge-carrier mobility μ and the charge-carrier density n.

$$\sigma = \phi\mu n \tag{S1}$$

Assuming that the charge-carrier mobility is constant, then $\Delta T/T$ or ΔT is directly proportional to the carrier density. If every absorbed photon results in the creation of an electron-hole pair, then the carrier density should also be proportional to the laser fluence, and $-\Delta T$ should have a linear dependence on the fluence. While this relationship holds for $FASnI_3$ thin films excited at fluences below ~50 μJ/cm^2, a significant deviation from linearity is observed at higher fluences, as seen in Figure S2, most likely due to absorption saturation during the 35-fs excitation pulse.

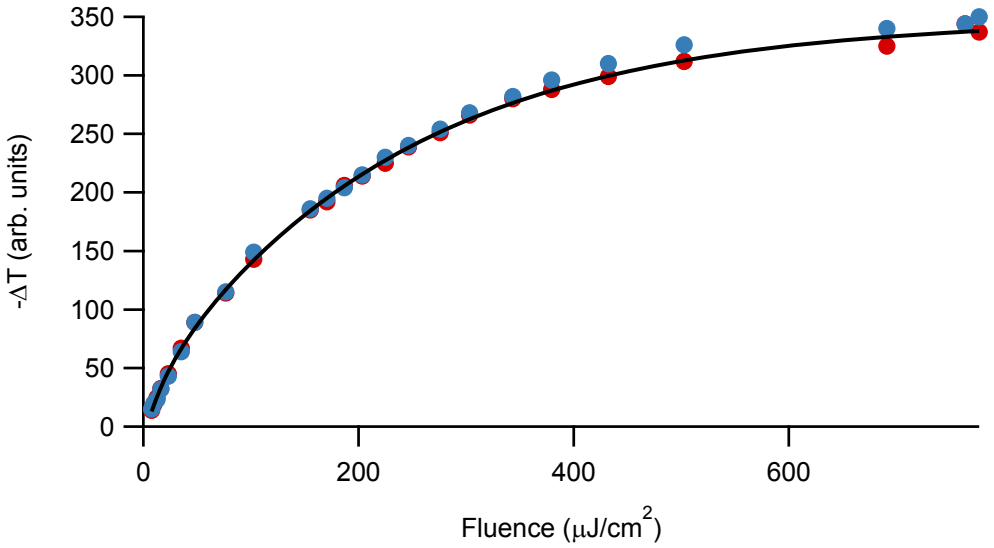


Figure S2. Dependence of $-\Delta T$ on laser fluence at 800 nm. Because $-\Delta T$ is proportional to the carrier density, this relationship was used to determine the average carrier density in the films at the fluences investigated as described below.

To correct for this deviation, an arbitrary function (a double exponential) was fit to the data in Figure S2 to obtain an expression for ΔT as a function of fluence, $\Delta T(fluence)$. The charge-carrier density at a fluence of 8μJ/cm^2, which is well within the linear regime of Figure S2, was then determined using the following equation

$$n = \phi \frac{E\lambda\alpha(\lambda)}{hcA_{eff}}\left(1 - R_{pump}\right), \tag{S2}$$

where φ is the photon-to-charge branching ratio, E is the excitation energy, λ is the excitation wavelength, α(λ) is the absorption coefficient at the excitation wavelength, A_{eff} is the effective

overlap area between the optical pump and THz probe beams, and R_{pump} is the reflectance of the thin film at the excitation wavelength. Carrier densities at higher fluences were then determined using the following relationship

$$n = \frac{\Delta T\left(fluence\right) n_{8\mu J/cm^2}}{\Delta T\left(8\mu J/cm^2\right)}, \tag{S3}$$

where $\Delta T(8\mu J/cm^2)$ is the value of $\Delta T(fluence)$ at a fluence of 8 $\mu J/cm^2$.

As the $FASnI_3$ films are highly absorbing and were excited with a pulsed laser source, it is more meaningful to report an average carrier density, which is averaged over the thickness of the film l and the 1/e lifetime of the photoexcited carriers $t_{1/e}$.

$$\left\langle n \right\rangle = n_{total} \times \frac{1}{l}\int_0^l e^{-\alpha x} dx \times \frac{1}{2t_e}\int_0^{2t_{1/e}} e^{-k_1 t} dt \approx 0.24 n_{total}, \tag{S4}$$

where n_{total} is the total carrier density as calculated from equation S3, α is the absorption coefficient at the excitation wavelength, x is the optical path length, k_1 is the monomolecular recombination rate, and t is time. Substituting values of l = 380 nm, $\alpha = 4.6\text{x}10^4$ cm^{-1}, $k_1 = 1.2\text{x}10^9$ s^{-1}, and $t_{1/e}$ = 0.83 ns yields an average carrier density of $0.24 n_{initial}$.

3. Additional PL Spectra

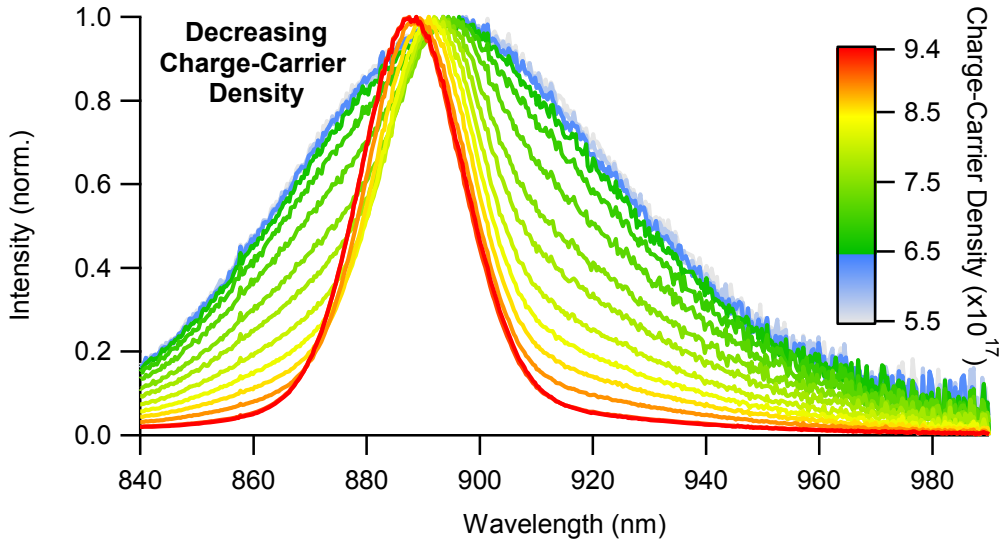


Figure S3. Normalized PL spectra obtained at various fluences following 800 nm excitation. The highest fluence spectrum was taken first and the others were acquired subsequently while constantly illuminating the sample with 35-fs pulses at a repetition rate of 1 kHz.

4. Charge-carrier mobility calculation

The charge carrier mobility μ is given by

$$\mu = \frac{\Delta S A_{eff}}{Ne}, \tag{S5}$$

where ΔS is the sheet conductivity of the perovskite thin film, A_{eff} is the effective area of the overlap of optical pump and THz probe pulse, N is the number of photoexcited charge carriers, and e is the elementary charge.

Assuming that the film thickness is much smaller than the THz wavelength, the sheet photoconductivity ΔS of a thin film between two media of refractive indices, n_{A} and n_{B}, can be expressed as[3,4]

$$\Delta S = -\varepsilon_0 c\left(n_A + n_B\right)\left(\frac{\Delta T}{T}\right), \tag{S6}$$

where $\Delta T/T$ is the experimentally determined change in transmitted THz electric field amplitude. In our experiment, $n_{\text{A}} = 1$ for vacuum and $n_{\text{B}} = 2.13$ for the z-cut quartz substrate.

The number of photo-excited charge carriers N can be determined using the following equation:

$$N = \varphi \frac{E\lambda}{hc}\left(1 - R_{pump}\right)\left(1 - T_{pump}\right), \tag{S7}$$

where E is the energy contained in an optical excitation pulse of wavelength λ, R_{pump} is the reflectivity of the sample at normal incidence of the excitation beam, T_{pump} transmittance of the pump beam, and φ is the ratio of free charge carriers created per photons absorbed (the photon-to-charge branching ratio).

Substituting Equations S7 and S6 into Equation S5, the following equation is obtained:

$$\varphi\mu = -\varepsilon_0 c\left(n_A + n_B\right)\frac{A_{eff} hc}{Ee\lambda\left(1 - R_{pump}\right)\left(1 - T_{pump}\right)}\left(\frac{\Delta T}{T}\right). \tag{S8}$$

Because $0 \leq \varphi \leq 1$, the effective mobility φμ represents a lower limit, which becomes identical to the actual mobility for full photon to free carrier conversion. To allow accurate determination of φμ, we ensured that excitation conditions were in the linear regime. It should also be noted that the determined charge carrier mobility arises from the contributions of both electrons and holes and that these contributions cannot be separated.

5. Fits to THz photoconductivity transients

As described in the main text, the overall recombination dynamics can be described by the following equation:

$$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n\,, \tag{S9}$$

where n is the charge-carrier density, k_1 is the monomolecular rate constant, k_2 is the bimolecular rate constant, and k_3 is the Auger rate constant.

As the experimentally observed quantity in optical pump-THz probe measurements, $\Delta T/T = x(t)$, is proportional to the photoconductivity, it is also proportional to the carrier density.

$$n(t) = \varphi C x(t) \tag{S10}$$

The photon-to-charge branching ratio φ indicates the fraction of absorbed photons which are converted to charge carriers. The proportionality factor $C = \tilde{n}_0 / x(0)$ is the ratio of the absorbed photon density $\tilde{n}_0$ to the initial THz response at time zero $x(0)$, where

$$\tilde{n}_0 = \frac{E\lambda\alpha(\lambda)}{hcA_{eff}}\left(1 - R_{pump}\right). \tag{S11}$$

The absorbed photon density is a function of the absorption coefficient α and reflectance R_{pump} of the sample at the excitation wavelength λ and of the effective overlap A_{eff} of the optical pump beam and THz probe beam. At high excitation fluences, $x(0)$ is no longer proportional to $\tilde{n}_0$. The value of C is therefore determined using a value of $x(0)$ within the regime where $x(0)$ is linearly proportional to the excitation fluence.

An expression for the time-dependent THz dynamics can be obtained by substituting Equation S10 into Equation S1:

$$\begin{aligned}\frac{dx}{dt} &= -C^2\varphi^2 k_3 x^3 - C\varphi k_2 x^2 - k_1 x \\ &= -A_3 x^3 - A_2 x^2 - A_1 x\end{aligned} \tag{S12}$$

with $A_i = C^{i-1}\varphi^{i-1}k_i$. The coefficients A_1, A_2, and A_3 are determined via a global fit to a fluence dependent set of THz transients. As the photon-to-free-carrier conversion ratio φ is unknown, we can

only determine the values $\varphi^2 k_3$, φk_2 and k_1 from our fits. These equal the actual decay rate constants k_3, k_2 and k_1 in case the material exhibits full photon-to-free-charge conversion and are lower limits when $\varphi < 1$.

To account for the spatially varying charge density profile, the fit routine takes into account the exponential charge density profile created by the pump beam by dividing the sample into 50 equally thick slabs and computing the decay function for all of these individually.

6. References

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