

Supporting Information: Long-Lived Hot Carriers in Formamidinium Lead Iodide

Nanocrystals

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Fit Param. ⟨N⟩	$\frac{A_1}{\sum_1^3 A_i}$	τ_1 (ps)	$\frac{A_2}{\sum_1^3 A_i}$	τ_2 (ps)	$\frac{A_3}{\sum_1^3 A_i}$	τ_3 (ps)	T_0 (K)	t_{avg} (ps)
0.25	0.70	0.26	0.19	4.6	0.11	42	309	5.7
0.5	0.19	0.22	0.52	5.3	0.29	39	331	14.1
2	0.2	0.53	0.47	5.6	0.33	41	385	16.2

Supplementary Table S1: Fitting parameters of the triple-exponential model (2) applied to describe the curves of the carrier temperature versus delay time for the three pump fluences measured.

T(K)	405	603	806	997	1156	1430	1694
⟨N⟩	Cooling Rate per Carrier (meV ps ⁻¹)						
0.25	0.31	1.7	22.5	85.3	245	227	-
0.5	0.22	1.3	4.3	9.3	11.5	24.7	59.3
2	0.08	0.5	2.3	6.7	8.7	18.3	27.2

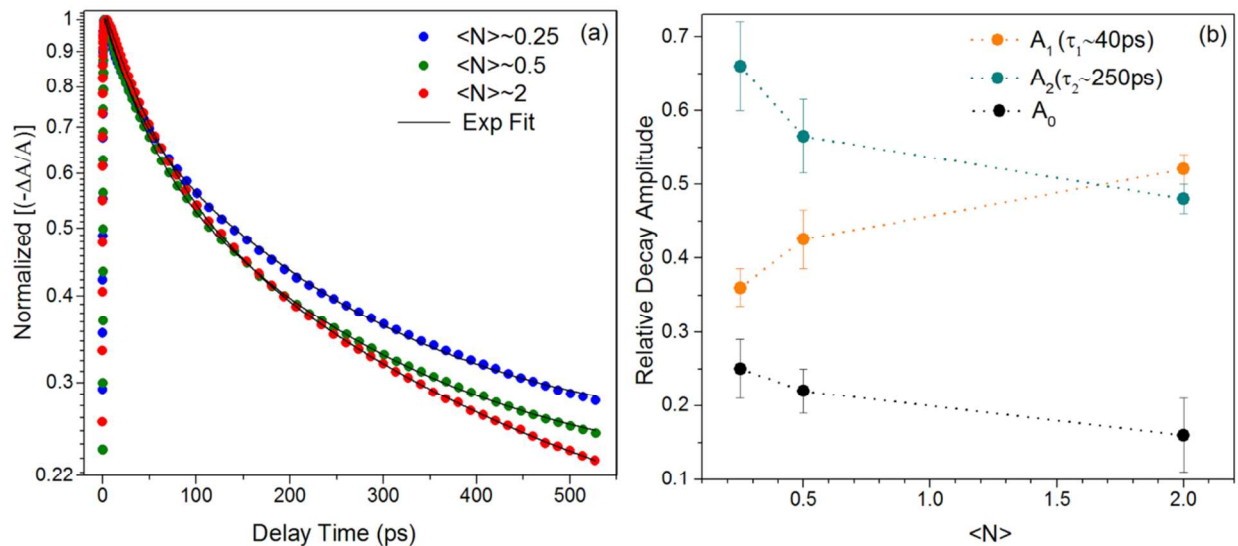
Supplementary Table S2: Average cooling rate per carrier for different carrier temperatures and pump fluences.

Supplementary Note S1: Estimation of Auger Recombination Lifetime

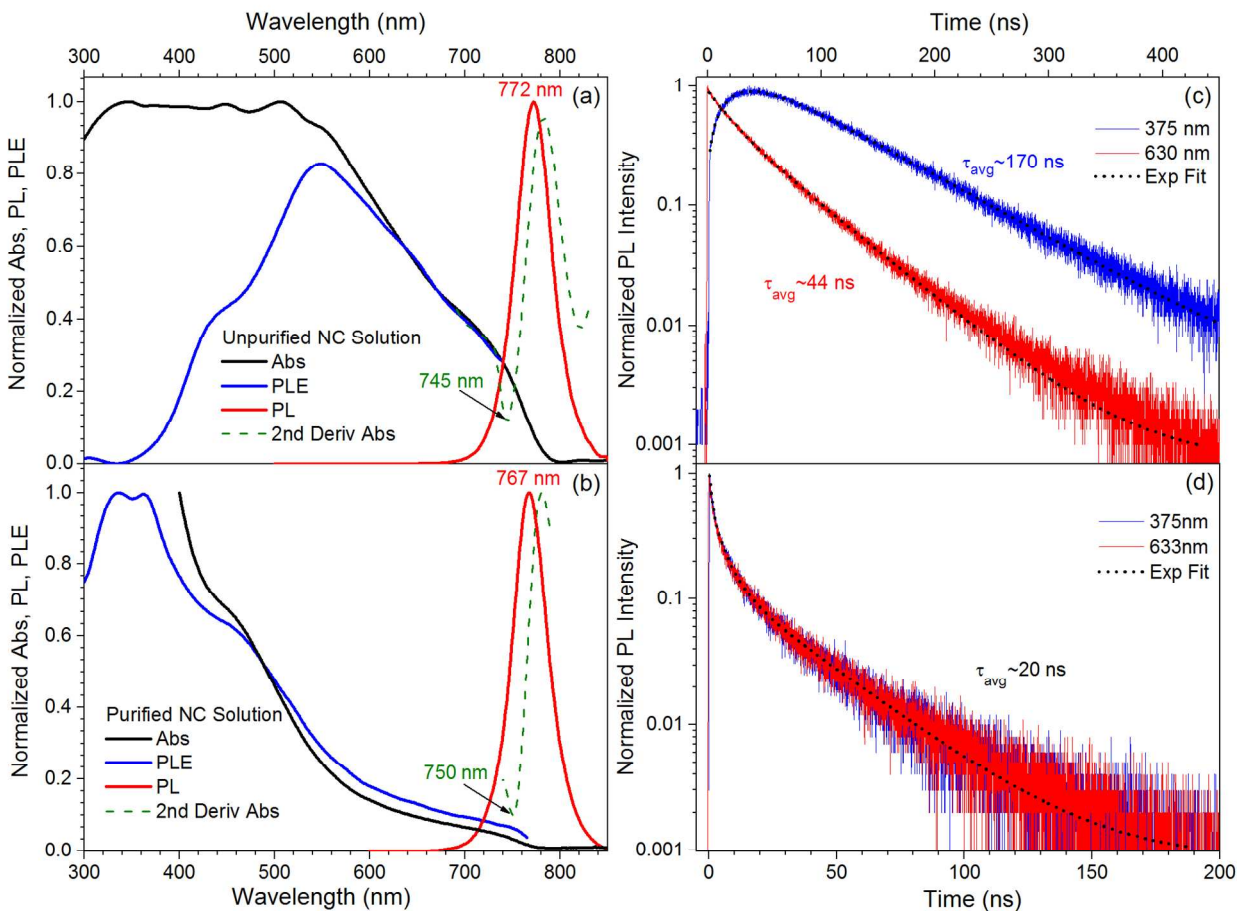
TA bleaching transients from FAPbI₃ NC films at different fluences are displayed in Supplementary Figure 1(a). The bleaching exhibits a recovery that can be described by:

$$-\frac{\Delta A}{A} = A_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (\text{S1})$$

With A_0 a background term that accounts for long relaxation processes that are beyond the temporal resolution of our system. Fits with the model (1) yield values of ~ 40 ps and ~ 250 ps for the time constants τ_1 and τ_2 . The relative amplitudes of the three terms appear dependent on the energy of the pump beam, as observed in Supplementary Figure 2(b) with the contribution of the fast τ_1 process monotonically increasing with fluence at the expense of the two slower channels. The excitation dependence and the timescales i.e. few tens of picoseconds, for channel τ_1 appear consistent with recent findings in hybrid MAPbBr₃ (24) and inorganic CsPbI₃ (18) and CsPbBr₃ (33) perovskite nanocrystals, attributing the process to Auger recombination of bi- or multiexciton species. Similar results with overall faster transients i.e. τ_1 of ~ 25 ps and τ_2 of ~ 150 -200 ps and similar dependence of the relative amplitudes with fluence were obtained from colloidal solutions of the FAPbI₃ NCs. On the other hand the two other TA channels exhibit an almost identical quenching behavior with excitation fluence, which indicates that they are associated with recombination channels of the same species, most probably single NC excitons. Tentatively, the background term is predominantly assigned to the slow radiative recombination of the NC excitons while the faster τ_2 channel accounts for non-radiative quenching of the NC excitons.



Supplementary Figure S1: (a) Fluence-dependent bleaching recovery from a spin-casted FAPbI₃ NC film. Exponential fits with model (1) are also displayed. (b) Relative amplitude of the three contributions of model (1) as a function of NC carrier population.



Supplementary Figure S2: Absorption, PL and PLE spectra of **(a)** unpurified, **(b)** purified solutions of FAPbI₃ NCs. The NC gap is estimated by the minimum of the second derivative of the absorbance obtaining values of ~ 745 nm (~ 1.66 eV) and ~ 750 nm (~ 1.65 eV) for unpurified and purified NCs, respectively. **(b)** PL transients under quasi-resonant, red and non-resonant, UV excitation, along with triple-exponential curve fits, from which the average PL lifetimes are obtained and displayed in the graph.