Supporting information for

Charge Trapping Dynamics Revealed in $CH_3NH_3PbI_3$ by Ultrafast Multi-Pulse Spectroscopy

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1. Push Pulse Induced Hot Carrier Temperature Analysis

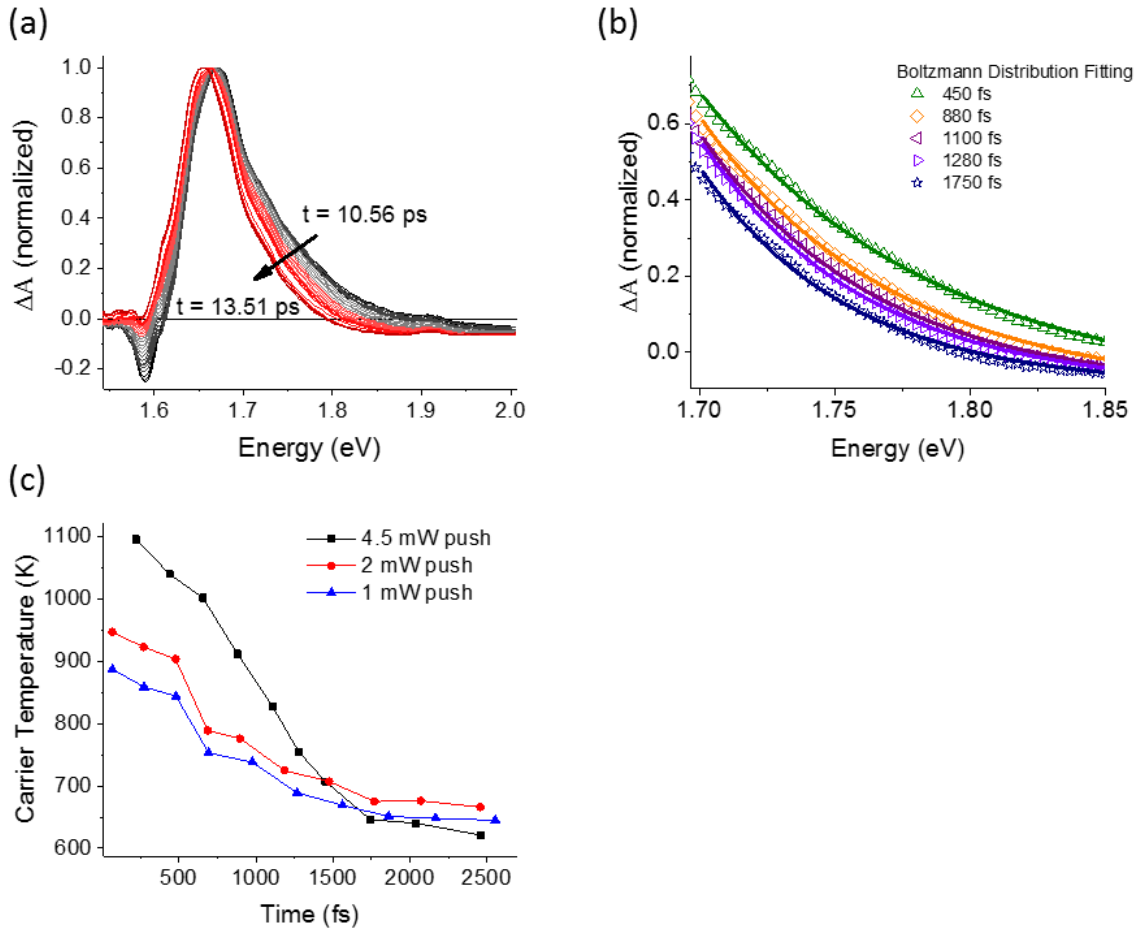

Figure S1. (a) Transient absorption spectra normalized at the band edge bleach peak beginning at the peak of the push pulse overlap with the probe (t = 10.56 ps). (b) Fitting of the high energy portion of the bleach signal to a Boltzmann distribution at time points following the push peak. (c) Comparison of carrier temperature decay with push pulse fluence.

Per the method of Price et al.,[1] fitting the high energy portion (>1.7 eV) of the band edge to a Boltzmann distribution allows the charge carrier temperature to be calculated. At higher push pulse fluences, and corresponding higher hot carrier densities, we observe an increased carrier temperature and a slower temperature decay in agreement with phonon bottleneck effect, which has previously been observed in perovskite systems. The carrier temperature at longer times (> 1500 fs) is elevated from what would be expected (~300 K) likely due to heating of the sample by the push pulse.

2. Hot Carrier Kinetic Analysis

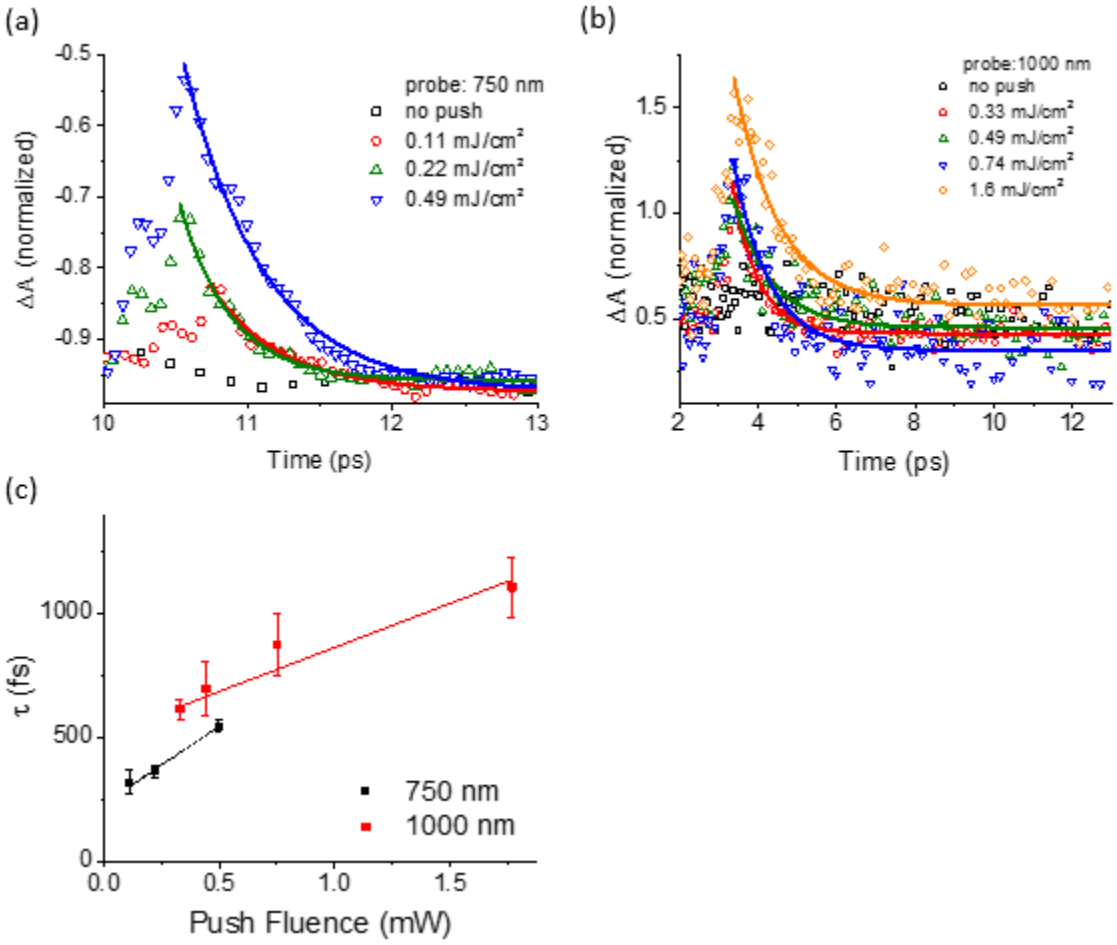

Figure S2. Push pulse induced change in transient absorption kinetics for $CH_3NH_3PbI_3$ at (a) the band edge and (b) in the NIR. Solid lines represent monoexponential fits. Lifetimes for these fits are shown in (c).

3. Comparing Pump-Push-Probe Model Assumptions

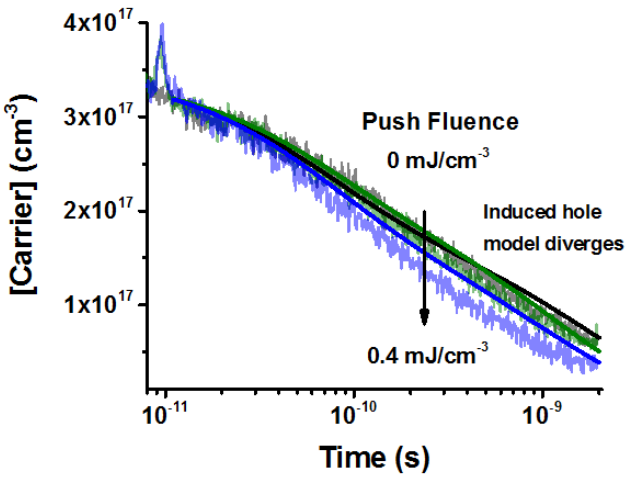

Figure S3. Pump-push-probe data with model fits where the kinetic rate constants are fixed to the values listed in Table 1, and the carrier populations are constrained by $n_e = n_h + n_T$.

Due to the sub-gap pump transient absorption data implying that a 1500 nm laser pulse can excite valence band electrons to mid-gap trap states, we fit the fluence dependent push data in a similar manner to that described in the main text, except here we have applied the constraint $n_e = n_h + n_T$ and only allow n_h and n_T to vary, while holding the rate constants and trap state density fixed to the values in Table 1. The poor fit implies that the data cannot be modelled by assuming that the push pulse only interacts with valence band electrons.

4. Transient Absorption and PPP kinetics for TOPO Passivated Samples

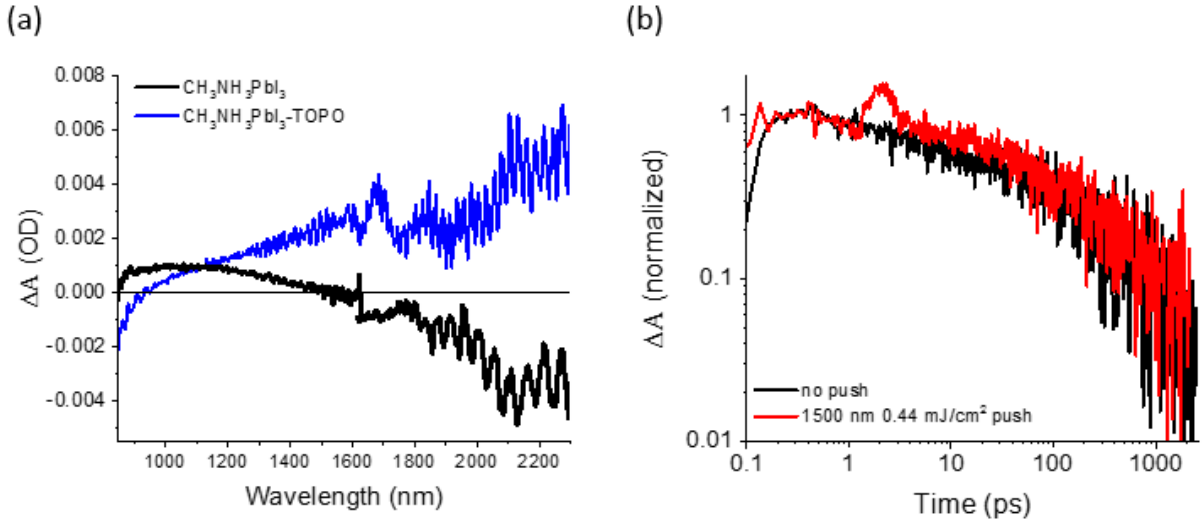

Figure S4. (a) Comparison of excited state NIR transient absorption spectra for $CH_3NH_3PbI_3$ with (blue trace) and without (black trace) TOPO treatment. (b) PPP kinetics at 1000 nm for a TOPO passivated $CH_3NH_3PbI_3$ sample comparing no push (black) and a 1500 nm push pulse (red).

5. Sub-gap Pump Transient Absorption Kinetics

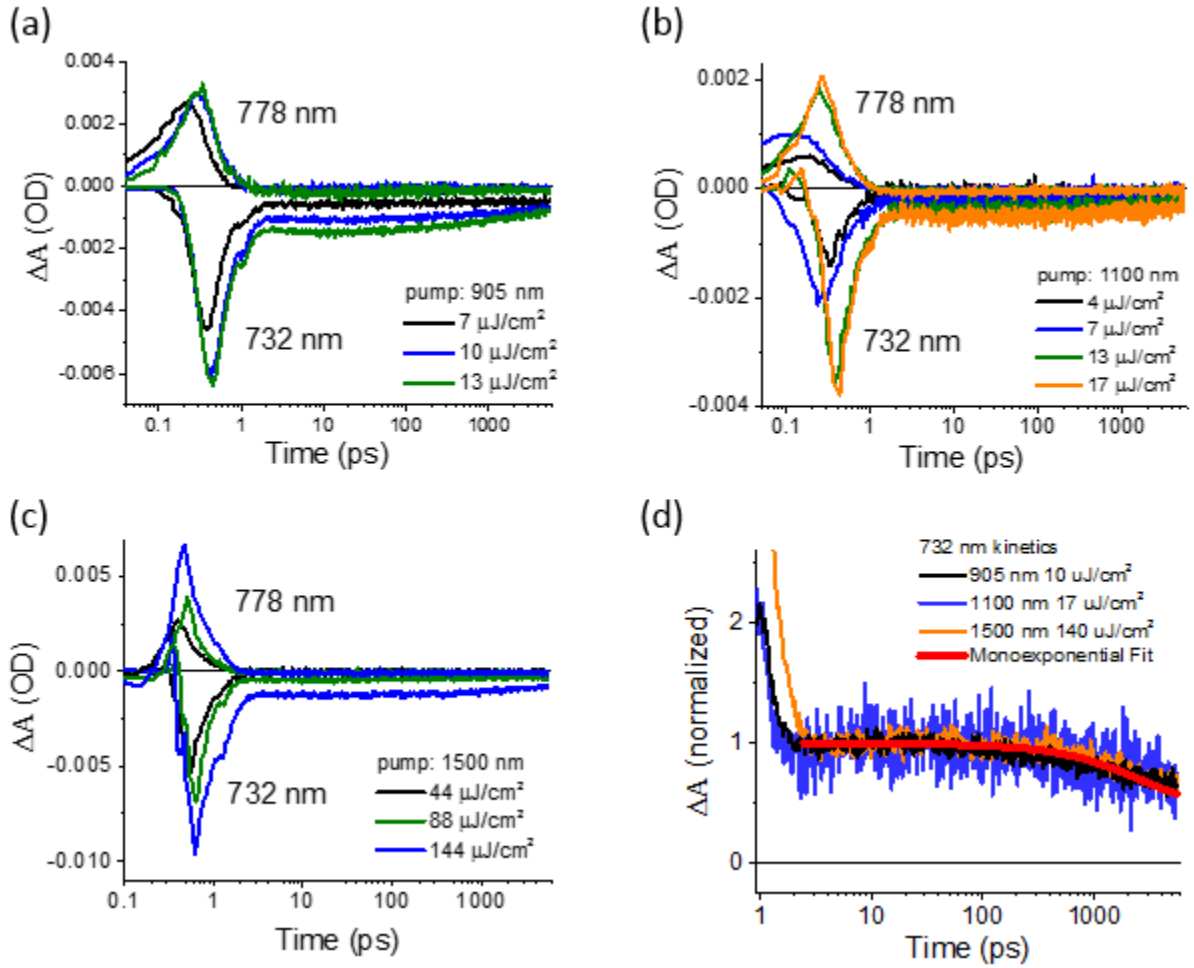

Figure S5. Raw kinetics for the low energy induced absorption at 778 nm and the band edge bleach at 732 nm for a (a) 905 nm, (b) 1100 nm, and (c) 1500 nm pump. (d) Kinetics for the band edge bleach normalized following decay of the fast component showing pump energy independent recombination. Red line shows monoexponential fit for 1100 nm data.

6. Statistical Analysis of Transient Absorption Fitting Parameters

	k_2	k_A	k_T	k_R	N_T
k_2	**1**	**-0.8963**	**-0.43745**	**-0.84003**	**0.86541**
k_A	**-0.8963**	**1**	**-0.94832**	**0.79010**	**-0.94654**
k_T	**-0.43745**	**-0.94832**	**1**	**0.39588**	**-0.74752**
k_R	**-0.84003**	**0.79010**	**0.39588**	**1**	**-0.89326**
N_T	**0.86541**	**-0.94654**	**-0.74752**	**-0.89326**	**1**

Table S1. Correlation matrix for parameters from Table 1 in the main text.

References

1. Price, M. B.; Butkus, J.; Jellicoe, T. C.; Sadhanala, A.; Briane, A.; Halpert, J. E.; Broch, K.; Hodgkiss, J. M.; Friend, R. H.; Deschler, F., Hot-carrier cooling and photoinduced refractive index changes in organic-inorganic lead halide perovskites. *Nat. Commun.* **2015,** *6*, 8420.