

## Supporting Information

### **How Photons Pump Fluence Changes the Charge Carrier Relaxation Mechanism in the Organic-inorganic Hybrid Lead Triiodide Perovskite**

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## Fluence of the absorbed photons

The fluence (F) of the absorbed photons upon excitation at 400, 600 and 800 nm was calculated using Equation S1:

$$F(\lambda) = \frac{P(\lambda)\lambda(1-e^{-\alpha(\lambda)L})}{hcf_{\text{rep}}A} \quad (\text{S1})$$

where,  $P(\lambda)$  is a pump power,  $f_{\text{rep}}$  is a repetition rate of pump (1kHz),  $A$  is the area of pump beam,  $\lambda$  is a wavelength of excitation and  $\alpha(\lambda)$  is the wavelength dependent absorption coefficient and  $L$  is the sample thickness. The  $h$  and  $c$  correspond to Planck constant and speed of light, respectively. The absorption coefficient used for the fluence calculation was reflection corrected.<sup>1</sup>

## The second- and the -third order rate equations

The analytical solution of the differential equation for second-order (electron – hole) recombination is given by linear dependence of the inverse of charge density ( $n$ ) on delay time (Equation S2):<sup>2</sup>

$$\frac{1}{n} = \frac{1}{n_0} + kt \quad (\text{S2})$$

where,  $n_0$  is initially generated charge density,  $k$  is a second-order rate constant and  $t$  is time.

Equation S3 gives the analytical solution of the differential equation for third-order (Auger) recombination:<sup>3</sup>

$$\frac{1}{n^2} = \frac{1}{n_0^2} + 2k_A t \quad (\text{S3})$$

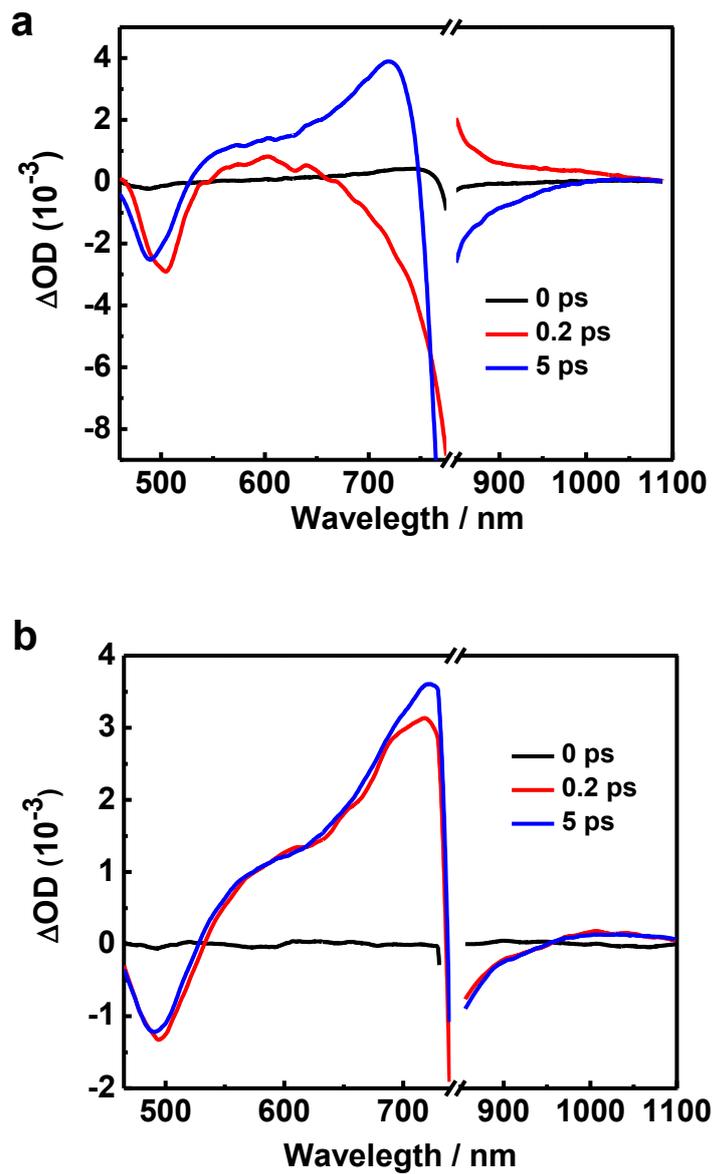
$k_A$  is the third order rate constant. The charge carrier density is proportional to  $\Delta\text{OD}$  thus we can use this value to examine the order of process occurring in the system.

Fluence ( $10^{13}$ ph/cm <sup>2</sup> )	A <sub>1</sub> (%)	$\tau_1$ (ps)	(-)A <sub>2</sub> (%)	$\tau_2$ (ps)	(-)A <sub>3</sub> (%)	$\tau_3$ (ps)	(-)A <sub>4</sub> (%)	$\tau_4$ (ps)	(-)Offset (%)
0.30	6	30	-	-	-	-	94	>1500	-
0.72	5	30	-	-	-	-	95	>1500	-
0.84	2	19	-	-	15	240	68	1410	15
1.1	4	8	-	-	14	211	55	1117	27
1.6	5	14	-	-	18	132	58	1085	19
2.1	3	10	-	-	29	122	50	937	18
2.8	3	10	-	-	28	114	52	715	10
4.2	-	-	4	8	31	101	48	550	17
6.9	-	-	19	6	29	99	37	520	15
9.4	-	-	27	6	27	98	34	458	12
12	-	-	32	7	23	102	31	458	14

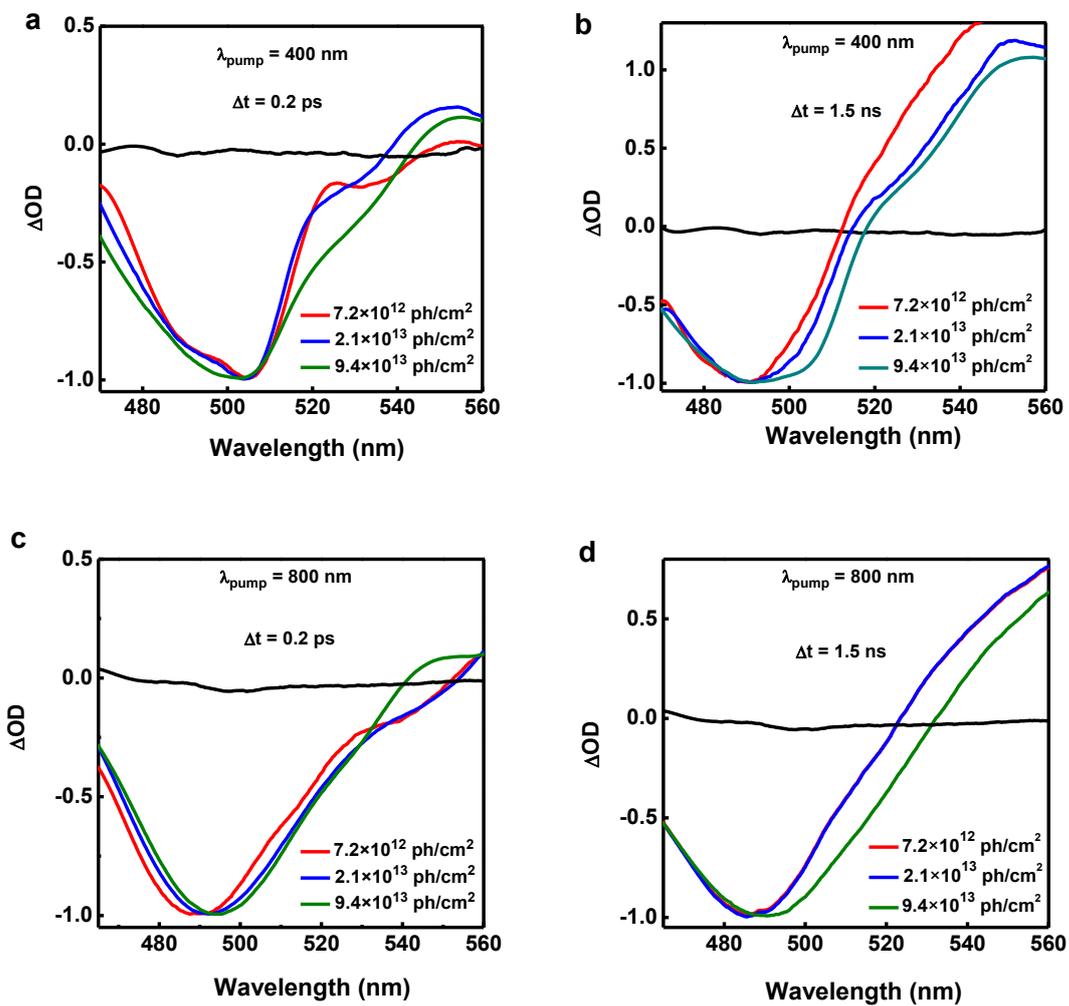
**Table S1.** Values of the time constants ( $\tau_i$ ) and normalized (to 100%) amplitudes ( $A_i$ ) of the multiexponential functions used to fit the transient absorption signals of excited FAPbI<sub>3</sub> film. The excitation was at 600 nm with different fluences of the absorbed photons, and the wavelength of observation was 775 nm. The estimated errors in  $\tau_i$  are:  $\tau_1 \pm 10$  ps,  $\tau_2 \pm 2$  ps,  $\tau_3 \pm 40$  ps,  $\tau_4 \pm 100$  ps. The transients were globally fitted using multi-exponential functions. A negative or positive sign before  $A_i$  indicates a decaying or a rising component.

Fluence ( $10^{13}$ ph/cm <sup>2</sup> )	A <sub>1</sub> (%)	$\tau_1$ (ps)	(-)A <sub>2</sub> (%)	$\tau_2$ (ps)	(-)A <sub>3</sub> (%)	$\tau_3$ (ps)	(-)A <sub>4</sub> (%)	$\tau_4$ (ps)	(-)Offset (%)
<b>0.30</b>	-	-	-	-	-	-	100	>1500	-
<b>0.72</b>	14	13	-	-	-	-	86	>1500	-
<b>0.84</b>	6	16	-	-	7	240	72	1410	15
<b>1.1</b>	4	8	-	-	10	211	53	1117	33
<b>1.6</b>	5	14	-	-	23	132	39	1085	24
<b>2.1</b>	6	10	-	-	34	122	43	937	17
<b>2.8</b>	-	-	9	8	34	113	40	713	17
<b>4.2</b>	-	-	21	8	30	101	35	550	14
<b>6.9</b>	-	-	32	6	24	99	30	520	14
<b>9.4</b>	-	-	43	6	19	98	27	428	11
<b>12</b>	-	-	41	7	19	102	26	458	14

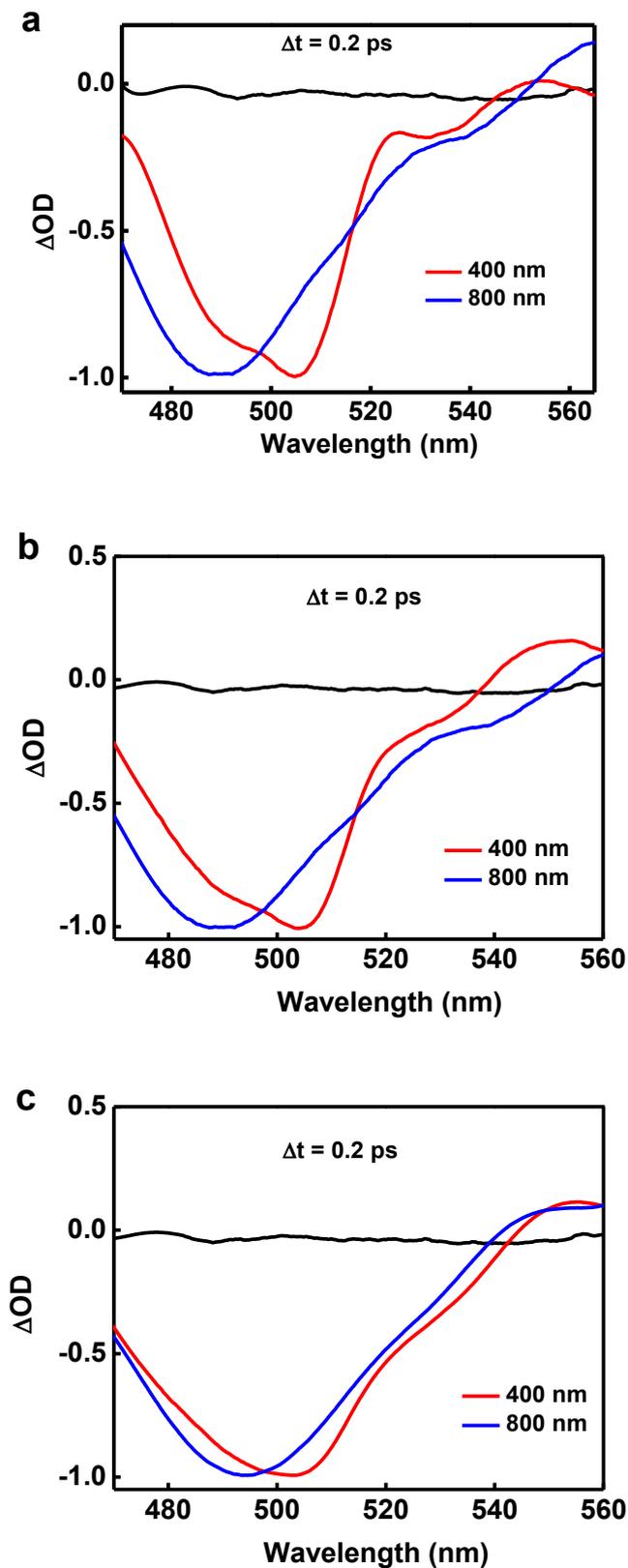
**Table S2.** Values of the time constants ( $\tau_i$ ) and normalized (to 100%) amplitudes ( $A_i$ ) of the multiexponential functions used to fit the transient absorption signals of excited FAPbI<sub>3</sub> film. The excitation was at 800 nm with different fluences of the absorbed photons, and the wavelength of observation was 775 nm. The estimated errors in  $\tau_i$  are:  $\tau_1 \pm 10$  ps,  $\tau_2 \pm 2$  ps,  $\tau_3 \pm 40$  ps,  $\tau_4 \pm 100$  ps. The transients were globally fitted using multi-exponential functions. A negative or positive sign before  $A_i$  indicates a decaying or a rising component.



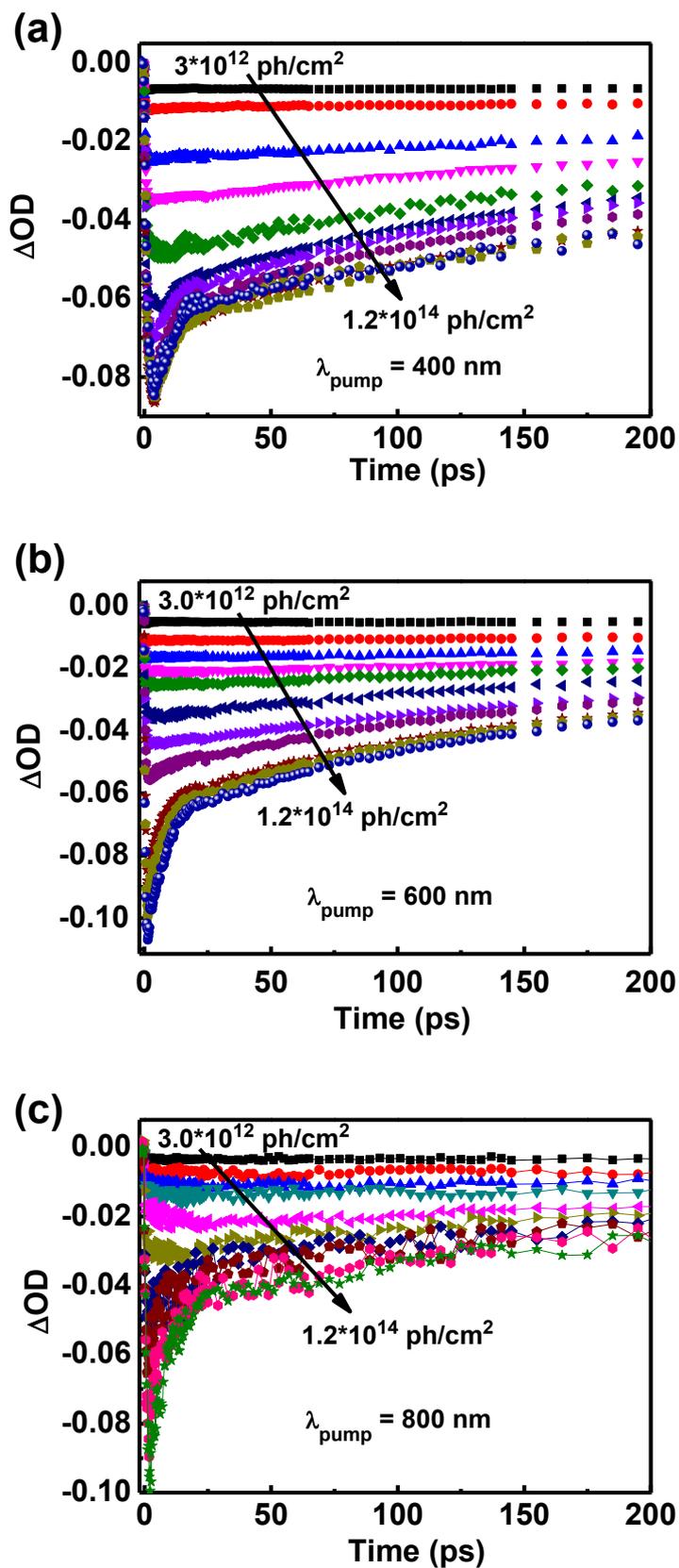
**Figure S1.** Transient absorption spectra of FAPbI<sub>3</sub> film gated at three representative pump-probe delay times upon excitation at (a) 400 nm and (b) 800 nm. The fluence of the absorbed photons was  $1.2 \cdot 10^{13}$  ph/cm<sup>2</sup>.



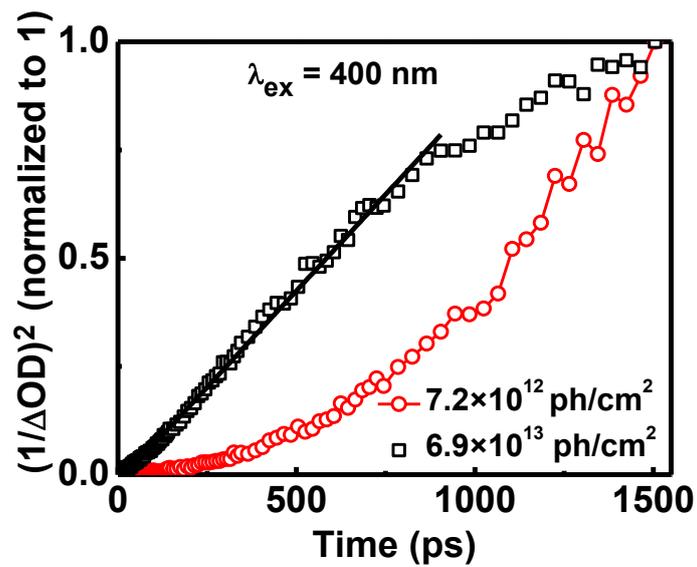
**Figure S2.** TA spectra of FAPbI<sub>3</sub> excited at (a, b) 400 nm and (c, d) 800 nm at 0.2 ps and 1.5 ns pump-probe delay times, with indicated fluences of absorbed photons. The bleach bands were normalized to -1.



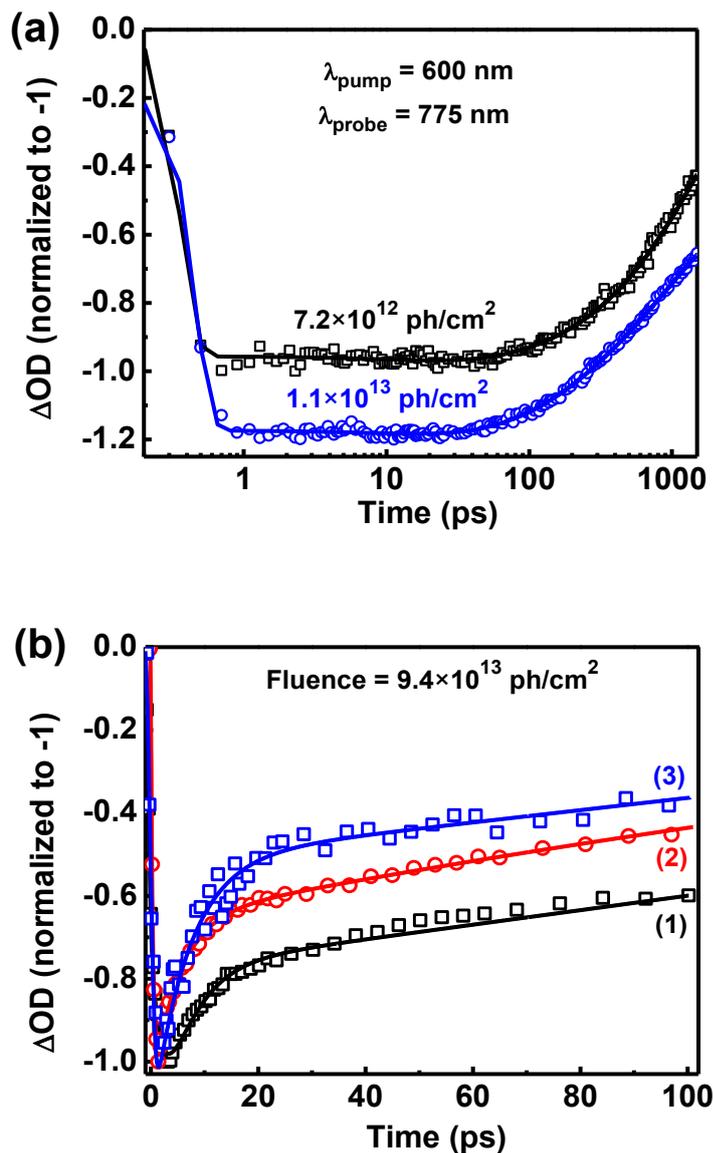
**Figure S3.** TA spectra of FAPbI<sub>3</sub> upon excitation at indicated wavelengths at 0.2 ps pump-probe delay time, with different fluences of the absorbed photons: (a)  $7.2 \times 10^{12}$ , (b)  $2.1 \times 10^{13}$  and (c)  $9.4 \times 10^{13}$  ( $\Delta t = 0.2$  ps). The bleach bands were normalized to -1.



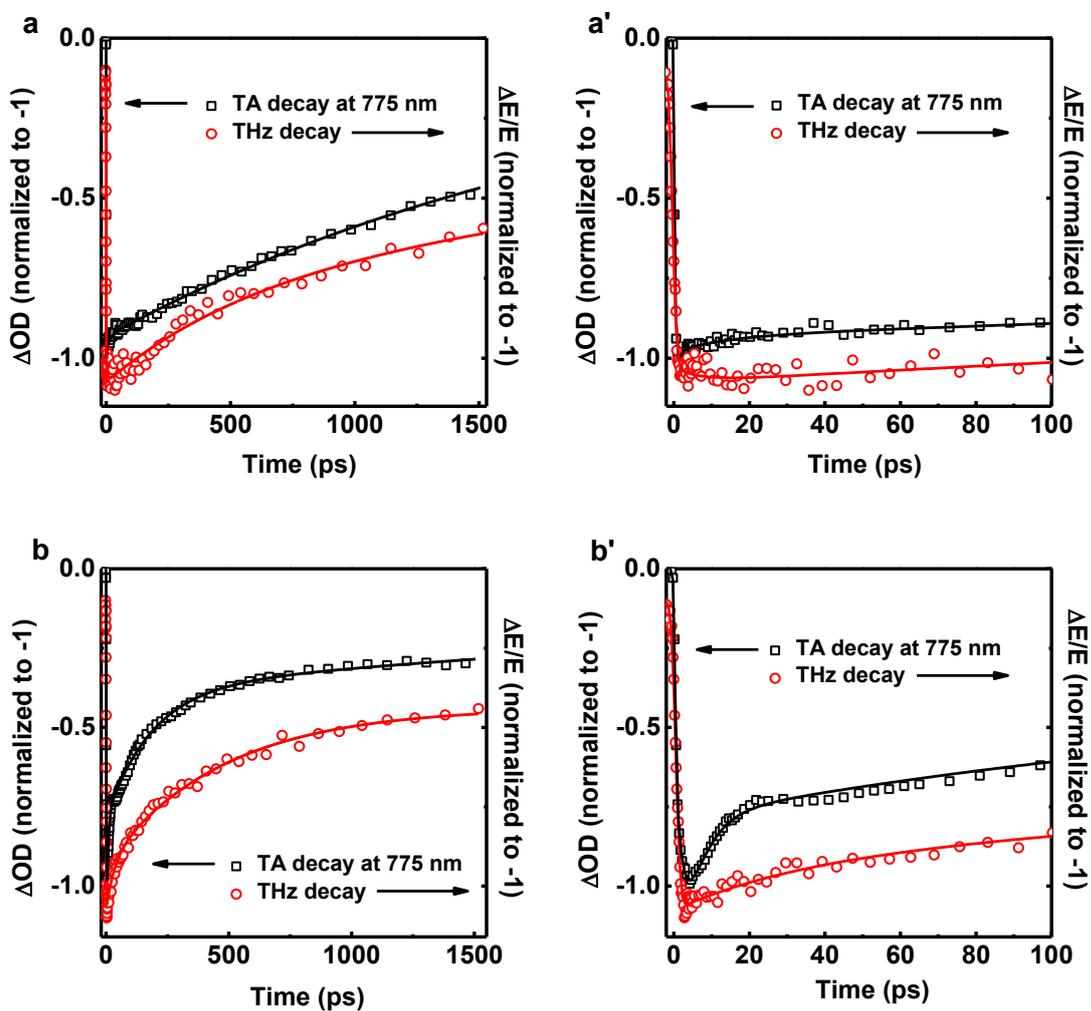
**Figure S4.** Transient absorption decays of FAPbI<sub>3</sub> film ( $\lambda_{\text{obs}} = 775 \text{ nm}$ ) upon excitation at (a) 400 nm, (b) 600 nm and (c) 800 nm at different fluences of absorbed photons.



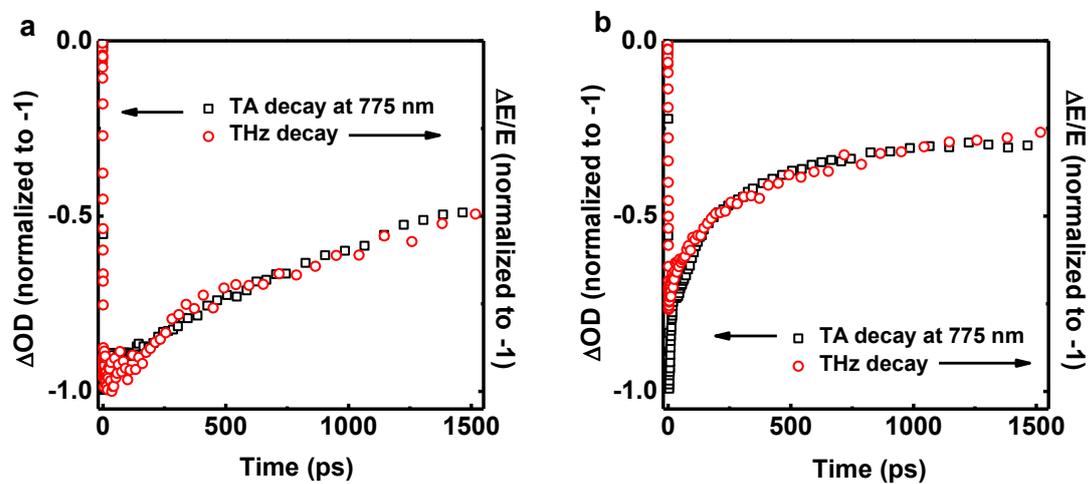
**Figure S5.** The inverse of  $\Delta OD^2$  with pump-probe delay time for the FAPbI<sub>3</sub> film upon excitation at 400 nm and observing at 775 nm.



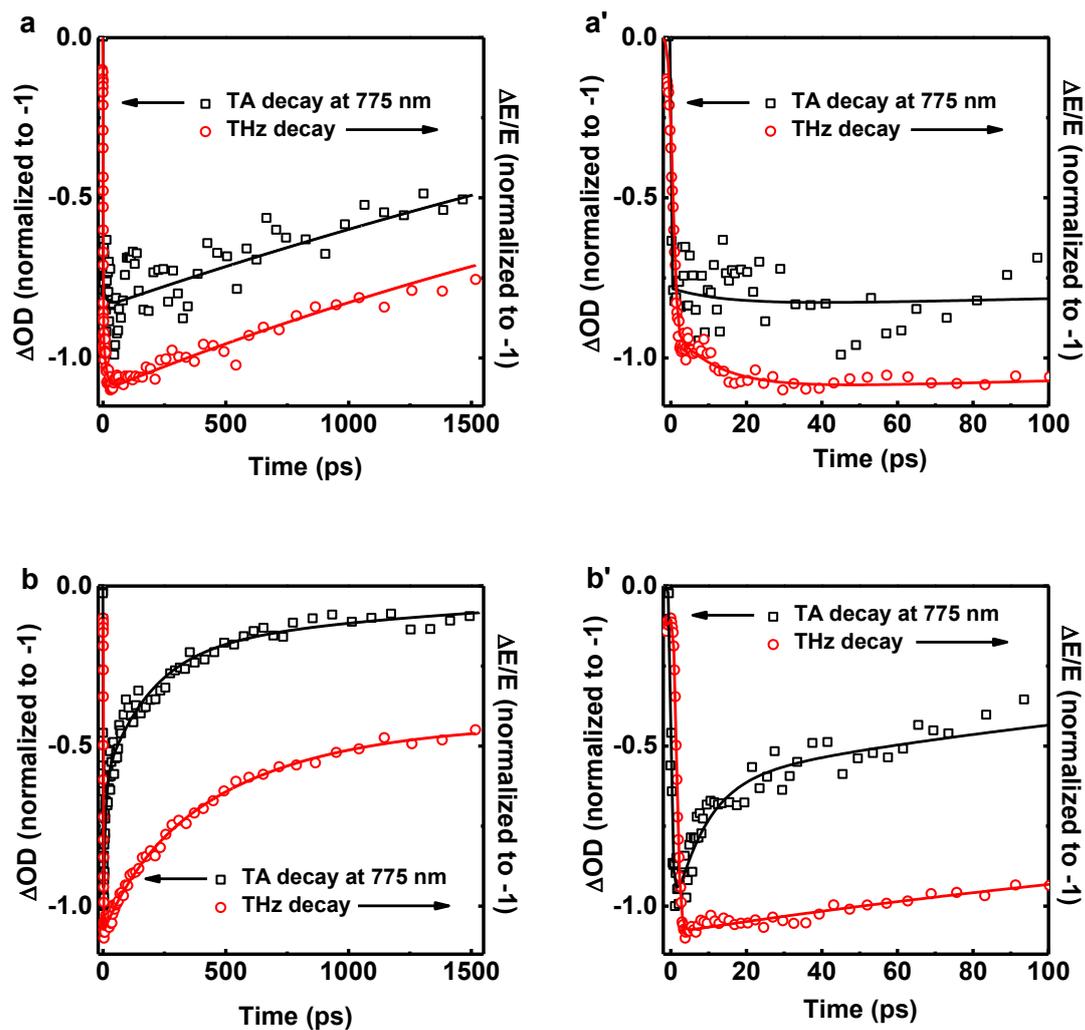
**Figure S6.** (a) Transient absorption decays in terms of  $\Delta OD$  change of FAPbI<sub>3</sub> upon excitation at 600 nm and observing at 775 nm. (b) Transient absorption decays of FAPbI<sub>3</sub> film upon excitation at (1) 400 nm, (2) 600 nm and (3) 800 nm ( $\lambda_{\text{obs}} = 775$  nm). Solid lines are from the best multi-exponential fits of the experimental data. For clarity, the TA decay signal in (a) was offset on the y axis.



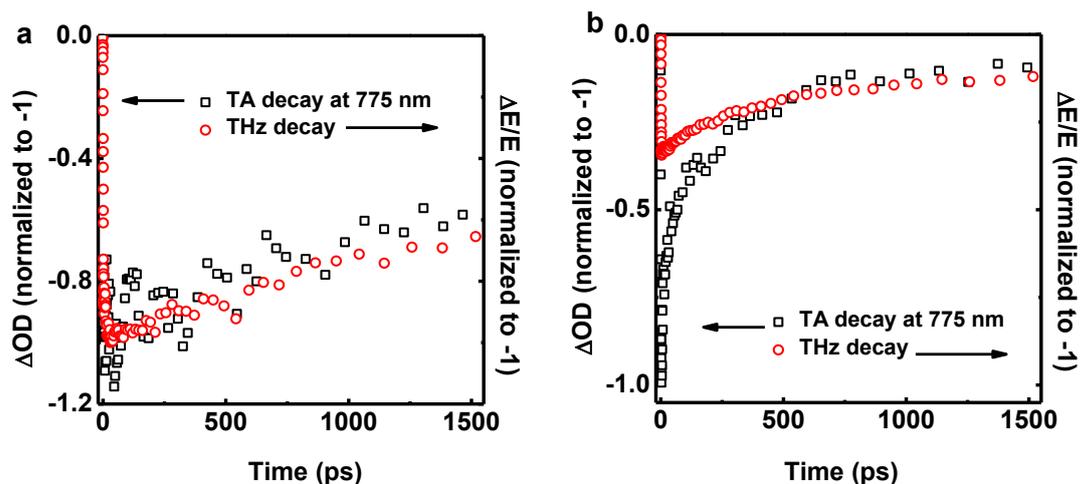
**Figure S7.** Normalized decays of transient absorption intensity (TA, probed at 775 nm, solid circles) and THz signal (solid squares) upon excitation at 400 nm with fluences of the absorbed photons ( $\text{ph}/\text{cm}^2$ ): (a, a')  $7.2 \times 10^{12}$  and (b, b')  $9.4 \times 10^{12}$ . The solid lines are to guide the eye.



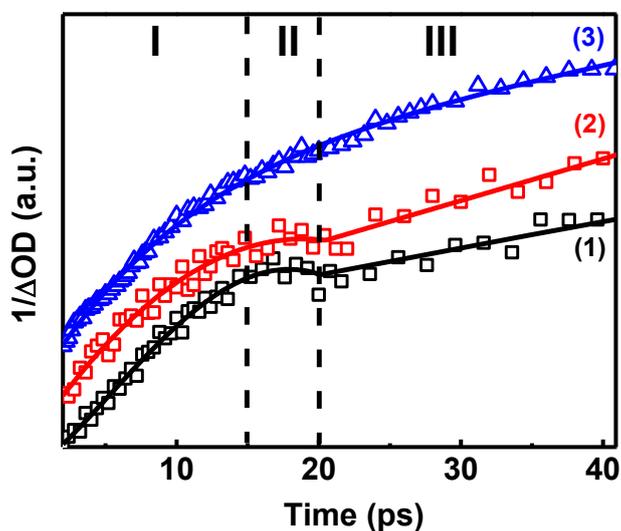
**Figure S8.** Normalized (to the long time decay component) transient absorption intensities (TA, probed at 775 nm, solid circles) and THz signals (solid squares) upon excitation at 400 nm with fluences of the absorbed photons (ph/cm<sup>2</sup>): (a)  $7.2 \times 10^{12}$  and (b)  $9.4 \times 10^{12}$ .



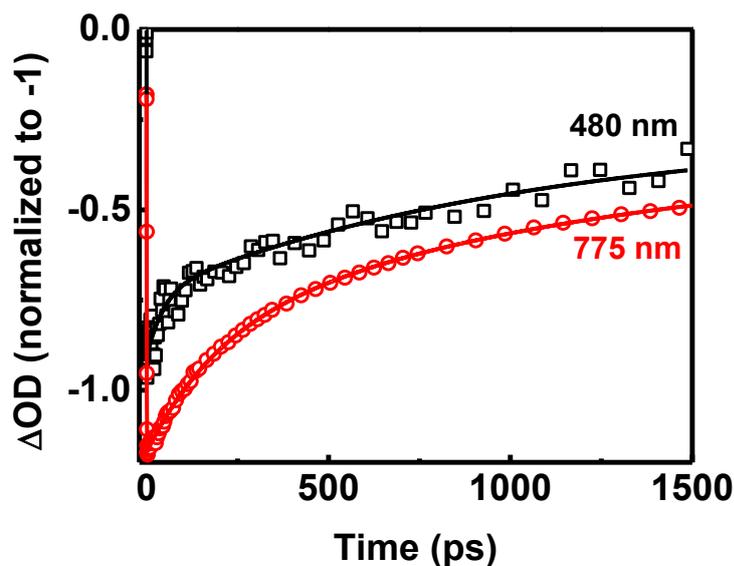
**Figure S9.** Normalized decays of transient absorption intensity (TA, probed at 775 nm, solid circles) and THz signal (solid squares) upon excitation at 800 nm with fluences of the absorbed photons ( $\text{ph}/\text{cm}^2$ ): (a, a')  $7.2 \times 10^{12}$  and (b, b')  $9.4 \times 10^{12}$ . The solid lines are to guide the eye.



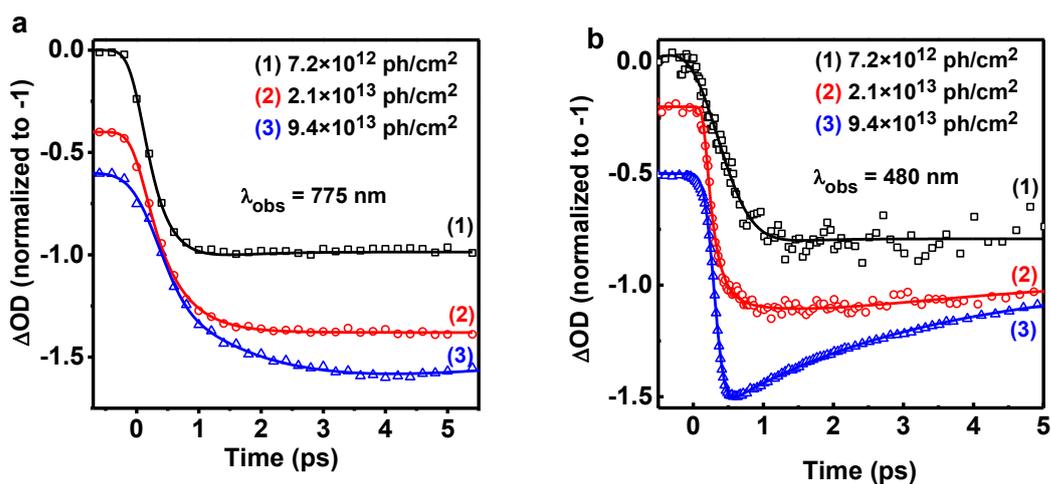
**Figure S10.** Normalized (to the long time decay component) transient absorption intensities (TA, probed at 775 nm, solid circles) and THz signals (solid squares) upon excitation at 800 nm with fluences of the absorbed photons ( $\text{ph}/\text{cm}^2$ ): (a)  $7.2 \times 10^{12}$  and (b)  $9.4 \times 10^{12}$ .



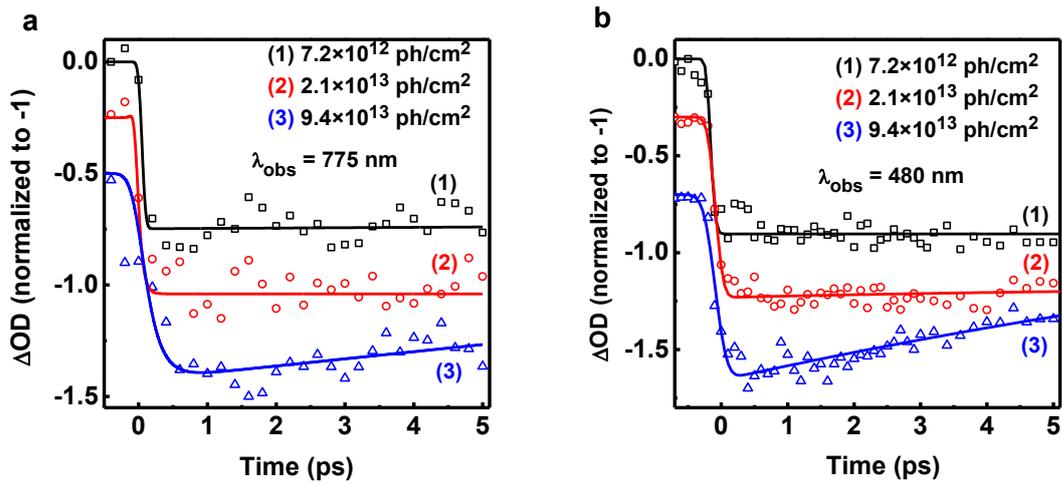
**Figure S11.** The inverse of  $\Delta\text{OD}$  with pump-probe delay time for the  $\text{FAPbI}_3$  film upon excitation at (1) 400 nm, (2) 600 nm and (3) 800 nm and observing at 775 nm. The fluence of absorbed photons was  $6.9 \times 10^{13}$ . The solid lines are to guide the eye.



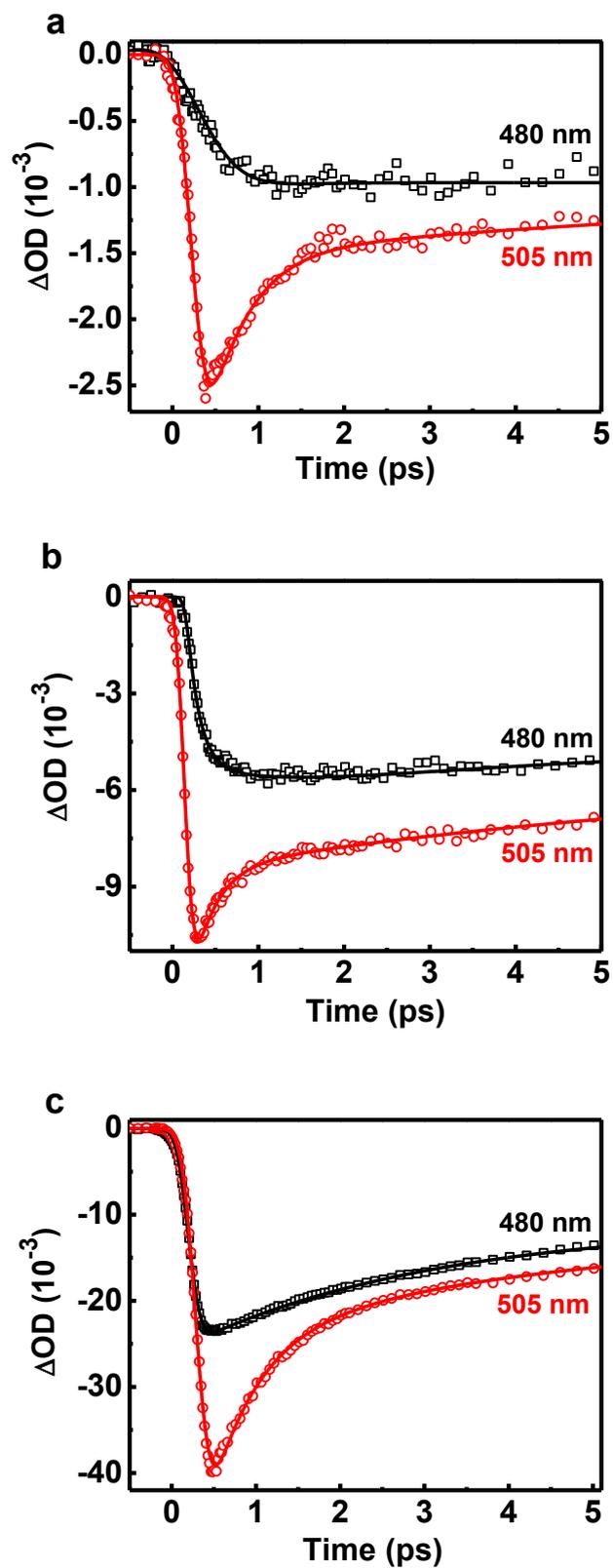
**Figure S12.** Normalized decays of transient absorption intensity probed at indicated wavelengths upon excitation at 400 nm with the fluences of the absorbed photons of  $1.1 \times 10^{13}$ . The solid lines are the best multiexponential fits.



**Figure S13.** Transient absorption kinetics of FAPbI<sub>3</sub> upon excitation at 400 nm and at observation wavelengths of (a) 480 nm and (b) 775 nm.



**Figure S14.** Transient absorption kinetics of FAPbI<sub>3</sub> film upon excitation at 800 nm and at observation wavelengths of (a) 480 nm and (b) 775 nm.



**Figure S15.** TA decays of FAPbI<sub>3</sub> upon excitation at 400 nm with fluences (ph/cm<sup>2</sup>): (a)  $7.2 \times 10^{12}$ , (b)  $2.1 \times 10^{13}$  and (c)  $9.4 \times 10^{13}$ .

1. P. Piatkowski, B. Cohen, C. S. Ponseca, Jr., M. Salado, S. Kazim, S. Ahmad, V. Sundstrom and A. Douhal, *J. Phys. Chem. Lett.*, 2016, **7**, 204-210.
2. J. S. Manser and P. V. Kamat, *Nature Photon.*, 2014, **8**, 737-743.
3. C. La-o-vorakiat, T. Salim, J. Kadro, M.-T. Khuc, R. Haselsberger, L. Cheng, H. Xia, G. G. Gurzadyan, H. Su, Y. M. Lam, R. A. Marcus, M.-E. Michel-Beyerle and E. E. M. Chia, *Nature Commun.*, 2015, **6**, 8903.