Supporting Information

Direct Visualization and Determination of the Multiple Exciton Generation Rate

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Materials and Methods:

CsPbI$_3$ QDs were synthesized by a slightly altered version of the protocol first reported by Protesescu et al. in 2015\textsuperscript{17}. 0.814 g of Cs$_2$CO$_3$ was mixed with 40 mL of ODE and 2.5 ml of OA, to prepare the Cs-oleate. The mixture was subsequently stirred at 150°C in an inert atmosphere until the reaction was completed. The reactants were then dried for 1 h at 120 °C. 5 mL of ODE and 1.88 mmol of PbI$_2$ were dried in a N$_2$ atmosphere for 1 h at 120°C. After water removal, 0.5 mL of dried OA and 0.5 ml of dried OLA were added to the reaction flask increasing the temperature to 175°C. After the solvation of the PbI$_2$ was complete, 0.4 mL of the warmed up Cs-oleate solution was injected. The reaction finishes in a few seconds and after that the QD solution was quickly cooled down by an ice bath. The final product was purified using several centrifugation steps and was redispersed in hexane. For the optical measurements the samples were further diluted and transferred to a UV grade quartz cuvette with 2 mm path length.

For the TA experiments a diode pumped Mai Tai-SP oscillator (SpectraPhysics, USA), was used to seed an regenerative amplifier (SpitfirePro, SpectraPhysics) operating at 1 kHz with ~35 fs pulse width and an output power of 4 W at a wavelength of 800 nm. This was used to pump an Optical Parametric Amplifier, TOPAS-C (Light Conversion, Vilnius, Lithuania) in order to generate the pump pulses, with pulse lengths ranging from 100-150 fs. A mechanical chopper reduced the frequency to 200 Hz. The white light continuum probe beam was generated by focusing a small part of the output of the regenerative amplifier through a sapphire crystal. The probe pulse was detected after passing the sample and spectrally dispersed by a 0.5 spectrometer, SpectraPro 2500i (Acton Research Corporation, Acton, USA) and detected with an air-cooled CCD, PIXIS 256 (Princeton Instruments, Trenton, USA). For the pump photon energies of 4.4 and 4.5 eV a Pharos (Light conversion, Vilnius, Lithuania) operating at 50 kHz with a ~200 fs
pulse width and ~0.2 mJ pulse energy at an output wavelength of 1030 nm, was used to pump an OPA, Orpheus-HP (Light Conversion, Vilnius, Lithuania) to generate the pump pulse. White light continuum probe beam was generated by using part of the output of the Pharos through a YAG crystal. A mechanical chopper reduced the frequency to 50 Hz and a Thorlabs CCM200/m spectrometer was used to detect the probe beam. For both laser systems the pulse energy bandwidth was, dependent on the wavelength, between 10 and 18 meV. The performance of both systems was confirmed by comparing dynamics at 3.9 eV. All measurements have been performed at room temperature.

The transients of the photo-induced absorption signal were taken at a probe wavelength range from 770 – 780 nm, i.e. around 1.6 eV. For the transients of the photo-induced bleach signal of the ground-state exciton, a 10 nm band around 1.85 (670 nm) eV was used (i.e. an energy bandwidth of ~27 meV). The Gaussian instrument response function (IRF) has been determined from the cross-correlation of the pump and probe pulses for the different photon energies.

For absorption measurements a JascoV570 UV/VIS spectrophotometer was used.
Linear absorption / bandgap

Steady state absorption has been used to determine the bandgap (Fig. S1.)

![Steady-state absorption spectrum (black curve) and its second derivative (gray curves) for the CsPbI$_3$ QD. The minimum of the second derivative indicates the ensemble bandgap.](image)

**Figure S1.** Steady-state absorption spectrum (black curve) and its second derivative (gray curves) for the CsPbI$_3$ QD. The minimum of the second derivative indicates the ensemble bandgap.

Rate equation modeling

**Bandedge excitons (PIB)**

The dynamics of exciton cooling are described with the following rate equations. We assume in this case that $k_{MEG}$ is a fixed rate, and $k_{th}$ is dependent of the excitation photon energy and is determined by the excitation photon energy $E_{exc}$, MEG threshold $E_{th}$ (4 eV) and energy loss rate $k_{el}$ (1 eV/ps) as $k_{th} = k_{el} / (E_{exc} - E_{th})$. The results of the modeling for photon energies above $E_{th}$ up to 4.5 eV are shown in Fig. S2.

$$\frac{dN_{hot}[t]}{dt} = -N_{hot}[t](k_{th} + k_{MEG})$$  \hspace{1cm} (1)
Figure S2. Results from rate equation modeling of number of excitons at bandedge, $N_{be}$, following eqs. (2-4) of the manuscript for various energies larger than $E_{th}$, with $k_{MEG} = 1.1 \text{ ps}^{-1}$.

**Total number of excitons (PIA)**

The dynamics of the total number of excitons after and excitation pulse can be described by the following rate equations.

\[
\frac{dN_{\text{hot}}[t]}{dt} = -N_{\text{hot}}[t](k_{th} + k_{MEG})
\]

\[
\frac{dN_{\text{cool}}[t]}{dt} = N_{\text{hot}}[t](k_{th} + 2k_{MEG})
\]

\[
N_{\text{total}}[t] = N_{\text{hot}}[t] + N_{\text{cool}}[t],
\]
The same rates are used as for the bandedge exciton modeling. The results can be found in Fig. S3.

**Figure S3.** Results from rate equation modeling of the number of excitons after an excitation pulse following Eqs. (4-6) for $k_{MEG}$ is 1.1 ps$^{-1}$. 
Schematic explanation of PIA and PIB

Figure S4. a) Photo-induced absorption (PIA) is probed at a photon energy below the bandgap. A hypothetical delta-like pump pulse at \(t = 0\) generates hot excitons, which will give an instantaneous increase in absorption of the probe signal, with the intensity reflecting the number of excitons. The dashed line horizontal line indicates the signal where the number of excitons \(N_{ex}\) equals the number of absorbed photons of the pump pulse \(N_{abs}\). If the excitons cool down to the bottom of the band (bottom panel), and under assumption that there are no other processes active and the induced absorption cross-section is independent of the excess energy, no change of absorption is expected. If carrier multiplication takes place (top panel) the instantaneous rise is followed by slower rise, with a rise-time determined by \(\tau_{MEG}\) and \(\tau_{th}\).

b) The band edge absorption is probed at a photon energy matching the bandgap. After an excitation pulse, the band edge absorption will start to bleach as a result of cooled down excitons, with the intensity of the bleach signal directly reflecting the number of excitons. In the case there is no MEG (bottom panel), the bleach signal will rise with the time determined by the cooling time of the excitons \(\tau_{Cool}\). In the case MEG takes place (top panel), the bleach signal will rise with the characteristic time \(\tau_{MEG}\). In both techniques the signal with MEG will be double of that of the non-MEG case. We note that in a real system there will be contributions of both cases.
Figure S5. Absorption cross-section as function of wavelength. The absorption cross-section was determined from linear absorption measurements and the concentration of QDs. The values are similar as found in earlier work (S1).

The average number of absorbed photons per QD has been determined for all excitation wavelengths by the product of the pump fluence and absorption cross-section and are given in Table S1.

| Photon energy (eV) | $<N_{abs}>$ | Photon energy (eV) | $<N_{abs}>$ |
|-------------------|------------|-------------------|------------|
| 1.9               | 0.09       | 3.7               | 0.26       |
| 2.1               | 0.1        | 3.9               | 0.25       |
| 2.3               | 0.15       | 4.1               | 0.23       |
| 2.5               | 0.21       | 4.2               | 0.23       |
| 2.6               | 0.23       | 4.3               | 0.15       |
| 3.2               | 0.3        | 4.4               | 0.14       |
| 3.3               | 0.3        | 4.5               | 0.14       |
| 3.5               | 0.27       |

Table S1
Values for the average amount of absorbed photons per QD for all excitation photon energies.
Fits of PIB traces

**Figure S6.** Fits of the fringes with sine function of the PIB traces for the two largest photon energies.
Bi-exciton shift determination

Figure S7. Bi-exciton shift. Fits of the differential absorption spectra with the sum of two Gaussian functions following the methodology in Ref. 36. The width and central energy of the Gaussian for the induced bleach were determined by a fit of this feature at 100 ps after pumping. The bi-exciton shift, given by the difference between the central energy of both Gaussians, is 56 meV.

References:

S1 Liu, Q.; Wang, Y.; Sui, N.; Wang, Y.; Chi, X.; Wang, Q.; Chen, Y.; Ji, W.; Zou, L.; and Zhang, H. Exciton Relaxation Dynamics in Photo-Excited CsPbI3 Perovskite Nanocrystals. Sci. Rep. 2016, 6, 29442