Supporting Information: Stimulated Emission through an Electron-Hole Plasma in Colloidal CdSe Quantum Rings

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S1 Synthetic Methods and Structural Analysis

S1.1 Synthesis

Chemicals 1-butanol (BuOH, anhydrous 99.8%), cadmium acetate (Cd(OAc)$_2$, 99.995%), cadmium acetate dihydrate (Cd(OAc)$_2$·2H$_2$O, 98.0%), cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O, 98%), n-hexane (anhydrous, 95%), methanol (MeOH, anhydrous 99.8%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) and sodium myristate (NaMyr, 99%) were purchased from Sigma-Aldrich. Methanol (MeOH, GPR Rectapur 99.5%) and selenium (Se, 200 mesh) were purchased from VWR and Strem chemicals, respectively.

Cadmium Myristate Precursor 1.23 g (3.99 mmol) Cd(NO$_3$)$_2$·4H$_2$O was in 40 ml MeOH dissolved while stirring. In a separate beaker glass, 3.13 g (12.5 mmol) NaMyr was dissolved in 250 ml MeOH. After complete dissolution of both salts, the cadmium containing solution was slowly added to the myristate solution. The Cd(Myr)$_2$ appears as a white precipitate and was filtered using a Büchner funnel, thoroughly washed with MeOH and dried overnight.

CdSe Nanoplatelets The 4.5ML thick CdSe nanoplatelets with a square shape were prepared in a glovebox following the synthesis procedure of Bertrand et al. with some minor modifications. In a 50 ml three-neck flask, 170 mg Cd(Myr)$_2$ and 12 mg elemental Se were added to 15ml ODE. This mixture was heated to 240 °C while quickly adding the acetate mixture (50/50 mol % of Cd(OAc)$_2$·2H$_2$O/Cd(OAc)$_2$) upon reaching 195 °C. The particles were consequently grown at 240 °C for 5 min after which the mixture was quenched with 14 ml hexane and 1 ml OA was added at 95 °C. After the solution was cooled down to room temperature, the samples were washed with a 2:1 ratio of BuOH:MeOH and centrifuged for 10 min at 3000RPM and dispersed in hexane. The required 4.5ML thick CdSe NPLs were separated by size selective precipitation from thinner 3.5ML NPLs and quantum dots (QDs) with a 2:1 BuOH:MeOH mixture.
CdSe Quantum Rings  CdSe NPLs were converted into quantum rings via the previously reported procedure of Fedin et al.\textsuperscript{2} with minor modifications.\textsuperscript{3} Elemental selenium was dispersed in oleylamine to yield a concentration of 7.9 mg Se/mL OLAM. 1ml of CdSe NPLs* was added to 3 mL ODE in an 8 mL reaction vial or round-bottom flask, together with 200 µL of the Se-OLAM dilution. The mixture was heated to 80 °C for 10 minutes to allow the hexane to evaporate. Then, the temperature was increased to 155 °C and maintained at this temperature for 10 min, after which 200 µL of TBP was added and quickly heated to 220 °C. After reaching this temperature, the mixture was allowed to cool down naturally. Finally, the mixture was washed once with a 1:2 solution of MeOH:BuOH and re-dispersed in hexane for further characterization.

*The concentration of the 4.5 ML thick NPLs was estimated from the obtained UV/VIS absorption spectrum. The 1 mL NPLs was equivalent to an absorbance of 0.2 at the first exciton transition in a 1 cm cuvette after diluting 300 times.

Structural Analysis  The HAADF-STEM images were obtained at a Talos F200X electron microscope, operating at 200 kV.
S1.2 Sizing of colloidal CdSe quantum rings

Figure S1: Electron microscopy images (HAADF-STEM) analysis of the CdSe quantum rings.

We determined the dimensions of the CdSe quantum rings used in this study analyzing the electron microscopy images (HAADF-STEM) shown in Figure S1. In Figure S1 we report the histograms of the outer dimensions of the rings in the x,y directions ($L_x, L_y$) and the width ($w$) of the quantum rings. From the analysis of 136 particles, we obtain average outer dimensions $L_x = 12.7 \pm 6.0$ nm, $L_y = 10.3 \pm 3.1$ nm and average in-plane width $w = 3.7 \pm 0.9$ nm, see also scheme in Figure 1 and Figure S2. To obtain the thickness of the QRs, several attempts were made to orientate the quantum rings with antisolvents (EtOH or a MeOH/BuOH mixture) edge-up, similarly to earlier reports on CdSe NPLs. Unfortunately, we did not observe any stacks of quantum rings, probably due to thickness differences within the particles. Therefore, the thickness of quantum rings was estimated from the contrast in HAADF-STEM imaging, as the observed contrast is linearly related to the thickness, in a similar manner as Figure 3b in our previous work. This was done by analyzing the contrast of both quantum rings and 4.5 ML thick CdSe NPLs with a thickness
of 1.3 nm. From the 76 quantum rings analyzed, an average thickness of $L_z = 2.8 \pm 0.6$ nm was found.

**Volume and Surface Area Calculation**  To calculate the volume of the quantum rings we modify the expression of the volume of a torus. As sketched in Figure S2, defining $R$ as the distance from the center of the torus to the center of the tube and $r$ the radius of the tube, the volume of the torus is given by

$$V = (\pi r^2)(2\pi R)$$  \hspace{1cm} (S1)

![Diagram](S6)

Figure S2: Schematic depiction of the in-plane section of (a) the ideal torus and (b) the elliptical torus approximating the geometry of a quantum rings

The volume of the quantum rings can be best approximated as the product of the area of an ellipse representing the tube section and the perimeter of the ellipse described by the in-plane radii $R_x$ and $R_y$, corresponding to the distances from the center of the quantum rings and the center of
the tube in the x-y directions. The perimeter of an ellipse with semi-axis $R_x$ and $R_y$ is approximated by

$$2p = 2\pi \sqrt{\frac{R_x^2 + R_y^2}{2}}$$  \hfill (S2)

We note that knowing $L_x$, $L_y$ and the average in-plane width $w$, $R_x$ and $R_y$ can be written as

$$R_x = \frac{L_x}{2} - \frac{w}{2}$$

$$R_y = \frac{L_y}{2} - \frac{w}{2}$$

On the other hand, the area of the tube of the quantum ring can be written as

$$A = \pi \frac{w L_z}{2}$$  \hfill (S3)

Combining equation S1,S2 and S3, the volume of the quantum ring is calculated as

$$V_{QR} = \left( \pi \frac{w L_z}{2} \right) \left( 2\pi \sqrt{\frac{R_x^2 + R_y^2}{2}} \right) = 209 \text{ nm}^3$$  \hfill (S4)

Following the same arguments, we can calculate the surface area of the quantum rings as

$$S_{QR} = \left( 2\pi \sqrt{\frac{1}{2} \left( \left( \frac{w}{2} \right)^2 + \left( \frac{L_z}{2} \right)^2 \right)} \right) \left( 2\pi \sqrt{\frac{R_x^2 + R_y^2}{2}} \right) = 259 \text{ nm}^2$$  \hfill (S5)
S2 Linear Optical Properties

Absorption measurements were performed on a Perkin-Elmer Lambda 950 UV/vis spectrometer.

S2.1 Intrinsic absorption coefficient and cross section of CdSe quantum rings

We calculate the intrinsic absorption coefficient $\mu_i^0$ of the quantum rings at 309 nm using two different approaches. We first approximate the quantum rings with a nanoplatelets with the same lateral dimensions and thickness and use a Lorentz local field theory combined with an effective medium Maxwell-Garnett approach. We then numerically calculate the local field factor distribution inside the ring with a method based on the quasistatic field approximation.

Nanoplatelet approximation. As shown by Achtstein et al., colloidal nanoplatelets can be approximated as oblate ellipsoids having random orientation in the solvent medium with refractive index $n_m = \sqrt{\epsilon_m}$. We thus obtain

$$
\mu_i^0(\lambda) = \frac{2\pi}{3\lambda n_m(\lambda)} (|f_x(\lambda)|^2 + |f_y(\lambda)|^2 + |f_z(\lambda)|^2) \epsilon_{s,I}(\lambda)
$$  \hspace{1cm} (S6)

where $\epsilon_{s,I}$ is the imaginary part of the dielectric permittivity $\epsilon_s$ of bulk CdSe at $\lambda$ and $f_i$ the local field factor in the $i = (x, y, z)$ direction defined as

$$
F_i(\lambda) = \frac{1}{1 + L_i(\frac{\epsilon_s(\lambda)}{\epsilon_m(\lambda)} - 1)}
$$  \hspace{1cm} (S7)

Considering $(a,b,c)$ as half the lengths along $(x,y,z)$, the depolarization factors $L_i$ can be written as

$$
L_i = \int_0^{\infty} \frac{abc}{2(s + c^2)^{\frac{3}{2}}(s + a^2)^{\frac{1}{2}}(s + b^2)^{\frac{1}{2}}}
$$  \hspace{1cm} (S8)
We calculate the value of $\mu_i^0$ at 309 nm using the permittivity of bulk CdSe ($\epsilon_s = 7.9 + 73i$)$^6$ since at high energy the intrinsic absorption coefficient of the nanoparticles is equal to that of their bulk counterpart. Considering the refractive index of n-Hexane at 309 nm ($n_m = 1.405$) and the outer dimensions of the quantum rings (12.7 nm, 10.3 nm ,2.9 nm), we find $(L_x, L_y, L_z) = (0.13, 0.17, 0.70)$ and $(|f_x|^2, |f_y|^2, |f_z|^2) = (0.47, 0.38, 0.06)$) leading to

$$\mu_i^0(309\text{nm}) = 3.15 \times 10^5 \text{cm}^{-1}$$

Figure S3: Model geometry and meshing for the numerical calculation of the local field factor.(a) Quantum ring (left) and nanoplatelet (right) geometries enclosed in a cubic unit cell (half of the cube is removed for illustrative purposes). (b) Meshing for the cubic cell.

**Numerical static field calculations of the local field factor of the quantum rings.**

To numerically calculate the absorption of CdSe nanocrystals, we apply our previously developed method based on the quasistatic field approximation.$^7, 8$ The numerical simulations are performed using the finite-element modelling software COMSOL Multiphysics 5.4 (Electrostatics module). We consider nanocrystals with two different geometries (quantum rings and nanoplatelets in Figure S3a) that are much smaller than the wavelength of the light (309 nm) and consist of an isotropic, homogeneous material with permittivity $\epsilon_s = 9 + 7.3i$ for CdSe. The dimensions of the particles are the same as mentioned in Supporting Information S1 ($L_x = 12.7$ nm, $L_y = 10.3$ nm, $L_z = 2.9$ nm and $w = 3.7$ nm) according to the HAADF-STEM analysis. The particles are embedded in a medium with permittivity $\epsilon_m = 1.97$ corresponding to n-Hexane. The potential problem $\nabla(\epsilon \cdot \nabla V) = 0$ is solved within
a cubic unit cell (Figure S3a), with boundary conditions that represent the external field \( \mathbf{E}_e \). We apply Dirichlet boundary conditions at the two faces (one at +1V and one at -1V) of the cube that have their normal parallel to the external electric field, and Neumann boundary conditions at the remaining four interfaces that have their normal perpendicular to the electric field. The model is meshed using a built-in algorithm, that generates tetrahedral elements (Figure S3b) with maximum element size \( w/8 \) inside the particle and a maximum element growth rate of 1.3. The values \( f_{ij}(\mathbf{r}) \) are found by dividing the \( i^{th} \) component of the electric field inside the particle \( E_i(\mathbf{r}) \) by the amplitude of the applied external field \( E_j \). This approach allows us to calculate the three square of local field factors \( f_x^2(\mathbf{r}) \), \( f_y^2(\mathbf{r}) \) and \( f_z^2(\mathbf{r}) \) as shown in the Figure 1 of the main text for the QRs and in Figure S4 for the oblate spheroidal nanoplatelet with semiaxes \( \frac{L_x}{2} = 6.35 \text{ nm} \), \( \frac{L_y}{2} = 5.15 \text{ nm} \) and \( \frac{L_z}{2} = 1.45 \text{ nm} \). By taking the volume integral of the local field factors, we obtain the volume-averaged local field factors \( |f_x|^2 \), \( |f_y|^2 \) and \( |f_z|^2 \), which are proportional to the intrinsic absorption of the particles accordingly to Equation S6. The calculated values for the QRs are \( |f_x|^2 = 0.45 \), \( |f_y|^2 = 0.33 \) and \( |f_z|^2 = 0.09 \). Notably, these values are comparable with the ones obtained for the nanoplatelets \( (|f_x|^2 = 0.47, \ |f_y|^2 = 0.37 \text{ and } |f_z|^2 = 0.06) \). Moreover our results show that the numerical calculation for the nanoplatelets is in excellent agreement with the analytical results obtained for the oblate spheroid using the effective medium approach.

Finally, using the numerical calculated volume-averaged local field factors \((|f_x|^2, |f_y|^2, |f_z|^2) = (0.45, 0.33, 0.09))\), we calculated for the QRs

\[
\mu_i^0(309\text{nm}) = 3.01 \times 10^5 \text{cm}^{-1}
\]
Once calculated $\mu_i^0(309nm)$ the intrinsic absorption spectrum is obtained by rescaling the absorption spectrum $A_0(\lambda)$ using

$$\mu_i^0(\lambda) = A_0(\lambda) \frac{\mu_i^0(309nm)}{A_0(309nm)} \quad (S9)$$

**The Absorption Cross Section** Considering the volume of a single CdSe quantum ring $V = 2.09 \times 10^{-19} cm^3$ and the intrinsic absorption coefficient $\mu_i^0$ the absorption cross section at a given wavelength is defined as $\sigma_i(\lambda) = \mu_i^0(\lambda) \times V$. From this expression we found

$$\sigma_{309} = 3.01 \times 10^5 cm^{-1} \times 2.09 \times 10^{-19} cm^3 = 6.29 \times 10^{-14} cm^2$$

$$\sigma_{400} = 1.22 \times 10^5 cm^{-1} \times 2.09 \times 10^{-19} cm^3 = 2.54 \times 10^{-14} cm^2$$

$$\sigma_{510} = 0.66 \times 10^5 cm^{-1} \times 2.09 \times 10^{-19} cm^3 = 1.38 \times 10^{-14} cm^2$$

$$\sigma_{625} = 0.40 \times 10^5 cm^{-1} \times 2.09 \times 10^{-19} cm^3 = 0.84 \times 10^{-14} cm^2$$

### S2.2 Deconvolution of the Linear Absorption Spectrum

We model the linear absorption spectrum of the quantum rings by describing partially localized exciton absorption$^{9,10}$ and we use the parameters extracted from the fit to calculate relevant properties of excitons in these systems.

**Fitting function** We fit the absorption spectrum of the CdSe quantum rings by considering weak exciton localization by means of asymmetric broadening.$^{9–11}$ The absorption spectrum is obtained as a superposition of exciton lines ($p$) and free carrier transitions ($C$):

$$A(E) = p_X(E) + C(E) \quad (S10)$$
where $p_X$ is the absorption line of an exciton with linewidth $\gamma$ and asymmetric broadening $\eta$ due to localization:

$$p_X(E) = \frac{1}{2\eta} \left[ erf \left( \frac{E - E_x}{\gamma/2\eta} \right) + 1 \right] \exp \left( \frac{\gamma^2}{4\eta^2} - \frac{E - E_x}{\eta} \right) \quad (S11)$$

and $C$ the absorption associated with free carrier transitions:

$$C_X(E) = \frac{A_C}{2} \left[ erf \left( \frac{E - E_X}{\gamma_C} \right) \right] \quad (S12)$$

Here $E_x$ and $\Delta E_{b,X}$ are the absolute exciton energy and the exciton binding energy, respectively. Therefore, including the contribution of the heavy-hole (hh), light hole (ll) and split-off (so) bands, the total absorption spectrum $\alpha$ can be written as:

$$\alpha(E) = A_{HH}(p_{HH}(E)+C_{HH}(E)) + A_{LH}(p_{LH}(E)+C_{LH}(E)) + A_{SO}(p_{SO}(E)+C_{SO}(E)) \quad (S13)$$

with $A_{HH}$, $A_{LH}$ and $A_{SO}$ the weight of the HH, LH and SO band respectively.

Figure S5: Intrinsic absorption coefficient spectrum (black) and respective fit (red).
The fit parameters are listed in Table S1 and the fit is shown in Figure S5.

Table S1: Parameters extracted from the fit of the linear intrinsic absorption spectrum of CdSe quantum rings using a sum of exciton and free carrier absorbance for HH, LH and SO transitions.

|                | HH          | LH          | SO          |
|----------------|-------------|-------------|-------------|
| $E_X$ (meV)    | 1973.8 ± 0.1| 2044.2 ± 0.7| 2422.1 ± 0.8|
| $\eta$ (meV)  | 11.02 ± 0.01| 11.73 ± 0.2  | 54.63 ± 0.07|
| $\gamma$ (meV)| 55.35 ± 0.04| 43.82 ± 0.54| 281.07 ± 0.58|
| $\Delta E_{b,X}$ (meV) | 108 ± 1    | 301 ± 1     | 410 ± 7     |
| $\gamma_C$ (meV) | 33.44 ± 0.58| 123.73 ± 1.80| 250.62 ± 9.6|
| $A_C$          | 7.05 ± 0.09 | 18.42 ± 0.84| 16.29 ± 3.05|
| $A$ (cm$^{-1}$) | 3844 ± 14   | 2098 ± 36   | 3065 ± 705  |

**Exciton parameters** Using the exciton binding energy, we can calculate the Bohr radius of the HH exciton as $a_B = \frac{\hbar}{\sqrt{2m_e \Delta E_{b,X}}} = 2.05$ nm. The full occupation of a quantum ring of area $S$ will occur at $\langle N_f \rangle = \frac{S}{\pi a_B^2} = 20$.

**S2.3 Determination of $\langle N \rangle$**

The number of excitons per quantum rings $\langle N \rangle$ is calculated as the product of the photon flux $J_{ph}$ and the absorption cross section $\sigma$ as determined in section S2.2. $J_{ph}$ depends on the pump photon energy, the area of the pump beam, the pulse repetition rate and the power measured at the sample position. This combination yields the relationship as follows:

$$J_{ph} = \frac{P(\text{mW}) \times 10^{-3}}{E_{ph} \times 1.6 \times 10^{-19} \times \frac{1}{A_b f}}$$

In this relation, $E_{ph}$ is the photon energy in eV, $f$ is the chopper frequency (500 Hz) and $A_b$ is the beam area. The latter is determined using a Thorlabs CCD camera beam profiler as $A_b = 2\pi\sigma_x\sigma_y$ where $\sigma_i$ is the standard deviation in the x,y directions.
S2.4 Luminescence Lifetime of CdSe Quantum Rings

In Figure S6 we report the PL intensity decay of the CdSe quantum rings dispersed in n-Hexane after photo-excitation with a 400 nm pulsed laser diode at 1 MHz. We fit the decay of the PL intensity with a triple exponential function:\(^1\)

\[
I(t) = I_0 + I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}} + I_3 e^{-\frac{t}{\tau_3}}
\]  
\(\text{(S14)}\)

The fit parameters are reported in Table S2.

![Figure S6](image)

Figure S6: Decay of the PL intensity after photo-excitation with a 400 nm pulsed laser diode at 1 MHz

| Parameter | Value       |
|-----------|-------------|
| $I_0$     | 0.00107 ± 0.00001 |
| $I_1$     | 0.338 ± 0.002  |
| $\tau_1$ (ns) | 4.20 ± 0.07  |
| $I_2$     | 0.412 ± 0.002  |
| $\tau_2$ (ns) | 25.7 ± 0.32   |
| $I_3$     | 0.130 ± 0.003  |
| $\tau_3$ (ns) | 93.7 ± 1.3    |

Table S2: Parameters extracted from the fit of the PL intensity decay using a triple exponential function

Considering the multi-exponential character of the decay, we can define an average life-
time $\tau_{\text{avg}}$ as:

$$\tau_{\text{avg}} = \frac{I_1 \tau_1 + I_2 \tau_2 + I_3 \tau_3}{I_1 + I_2 + I_3} = 27.5 \text{ ns} \quad \text{(S15)}$$

We assign this average lifetime to single exciton recombination in CdSe quantum rings. Compared to core-only 3.5 and 4.5 ML CdSe NPLs, where the average lifetime is 3-6 ns,\textsuperscript{12,13} and 8.5 ML CdSe (10.8 ns),\textsuperscript{14} $\tau_{\text{avg}}$ is longer in QRs. Moreover, we point out that the time window analyzed in the TA and fPL experiments amounts to only 2 ns, a value much smaller than the single exciton recombination time in quantum rings.
S3 Ultrafast Spectroscopy

S3.1 Transient Absorption

Samples were excited using 120 femtosecond pump pulses with varying wavelengths created from the 800 nm fundamental (Spitfire Ace, Spectra Physics) through non-linear conversion in an OPA (Light Conversion TOPAS). Equally short probe pulses were generated in a 2 mm CaF$_2$ crystal using the 800 nm fundamental. The pulses were delayed relative to the pump using a delay stage with 33 fs bi-directional accuracy. The probe spectrum in our experiments covers the UV-VIS window from 350 nm up to 750 nm. Pump and probe pulses were linearly polarized using appropriate polarization optics, in particular a broadband quartz-MgF$_2$ quarter wave plate (Newport) is used for the probe and a Bérek compensator or calcite polarizer (Newport) is used to rotate or fix the pump polarization. The photon flux is calculated from the average power, the repetition rate and the beam area. The latter is obtained through a Thorlabs CCD beam profiler, and defined as $A_{\text{beam}} = 2\pi \times \sigma_x \sigma_y$ where $\sigma_i$ is the standard deviation in the $i = x, y$ direction.

S3.2 Low fluency $\Delta A$ maps

Figure S7: (a) Transient absorption map $\Delta A$ after photo-excitation at 510 nm creating an average number of electron-hole pairs $\langle N \rangle = 0.5$. (b) Transient absorption map $\Delta A$ after photo-excitation at 625 nm creating an average number of electron-hole pairs $\langle N \rangle = 0.4$. 
S3.3 SO/CB transition in TA maps: Bleach or Shift

In order to clarify the origin of the SO/CB bleach in the $\Delta A$ map, we integrate the SO/CB band. If the bleach originated from a mere spectral shift, the integral around the transition should be zero. To set the boundaries of the integral, we look at the second derivative of the absorption spectrum reported in Figure S8a. The SO/CB transition can be recognised in the region between 480 and 565 nm. We thus integrate the $\Delta A$ map obtained creating $\langle N \rangle = 14.5$ electron-hole pairs (See Figure 1c of the main manuscript) around the SO/CB band between 480 and 565 nm. In Figure S8b we report the integrated $\Delta A$ signal as a function of time, showing a clear decay trace and thus confirming that the bleach at the SO/CB transition is originating from occupation of the CB electron state, as discussed in the main manuscript.

![Figure S8: (a)Second derivative of the absorbance spectrum $A_0$. (b)Integral of the $\Delta A$ signal between 480 and 565 nm corresponding to the SO/CB bleach when pumping the quantum rings at 510 nm generating $\langle N \rangle = 14.5$ electron-hole pairs](image)

S3.4 Early-time Low Fluency $\Delta A$ Dynamics

From the $\Delta A$ map reported in Figure S7a we can extract the dynamics of the HH/LH-CB (625 nm) and SO-CB (510 nm) following excitation at 510 nm, as reported in Figure 3a-b of the main text. A detailed scheme of the pump-probe experiment is reported in Figure S9a. The HH/LH and SO bands are coupled to the same electron state in the CB. This means that when an electron occupies the CB level it will show up as (or contribute to) a bleach for both
Figure S9: (a) Scheme of the pump-probe experiment for photo-excitation at 510 nm. (b) Normalized $\Delta A$ traces probed at the HH/LH - CB transition (red) and the SO/CB transition (black) after excitation at the SO/CB (510 nm) creating $\langle N \rangle = 0.5$.

HH/LH-CB and SO-CB. On the other hand a hole has two options and ensuing outcomes. If it occupies the SO level, it will only contribute to the bleach of the SO-CB transition at 510 nm, and not to the HH/LH-CB transition at 625 nm. If the hole occupies the HH/LH level on the other hand, it will contribute to bleach of the HH/LH-CB transition and not to the SO-CB level. Comparing the bleach signal at 510 (SO-CB) and 625 (HH/LH-CB) hence allows us to distinguish electron from hole dynamics. Any similarity between both traces is due to electron dynamics, any difference is due to holes relaxing between energy levels or getting trapped.

By pumping at 510 nm, we prepare the system in the state as shown in Figure S9a, i.e. the hole in the SO level and the electron directly in the CB level. As a result, (Figure S9b and Figure 3a of the main text), both the HH/LH-CB and SO-CB bleach curves show a rapid ingrowth due to the occupation of the electron in the CB. After this rapid ingrowth, the HH/LH and SO dynamics are markedly different, pointing to hole dynamics, by showing a clear anti-correlation. Specifically, the SO-CB shows a sub-picosecond decay concomitantly to the ingrowth of the HH/LH-CB signal on the same timescale. Since the two bands share the same electron level, a difference in their kinetic behavior is to be ascribed to hole dynamics. The anti-correlation can thus be explained as hole cooling via rapid phonon emission from the SO valence band to the HH/LH valence band level. The anti-correlation
also rules out trapping since the gain of population of the HH/LH hole level is matched by the loss of the SO hole level. Once the hole cooling is completed, the two traces line up (see Figure 3b of the main text), indicating that the curves at later times, as shown in Figure 3b of the main paper, describe the electron dynamics.

S3.5 Recombination Kinetics

In order to get insights on the recombination dynamics of carriers in the first nanosecond(s), we analyze the recombination dynamics at the HH/LH bleach following excitation at 510 nm. To avoid possible contribution of spectral shifts we integrated the ∆A signal along the whole HH/LH band from 600 – 635 nm.

Double exponential fit  First, we fit the recombination kinetics using a double exponential function:

\[ y(t) = y_0 + Ae^{-k_1t} + Be^{-k_2t} \]

The result of the fit is reported in Figure S10(a). Such a function provides a good fit to the whole data set that spans an average number of electron-hole pairs \( \langle N \rangle \) between 0.5 and 18. As highlighted in Figure S10(b)-(c), the decay is characterized by two recombination rates, \( k_1 \) corresponding to ca. 25 ps followed by a faster one (\( k_2 \)) leading to a lifetime of 250-340 ps. We note that for \( \langle N \rangle < 10 \) the weight of \( k_1 \) amounts to ca. 30 % of initial amplitude. This component was assigned by Xiao et al. to carrier capture at surface defects originating from the etching procedure.\(^{15}\)

Second Order Recombination Fit  Excluding the first 20 ps of the decay to avoid the electron trapping component, we apply a second order recombination model to the decay of the HH/LH integrated bleach. In this picture the decay of ∆A is proportional to the decay
Figure S10: Double exponential fit. (a) Double exponential fit of the recombination kinetics at the $HH/LH$ bleach for an average number of excitons $<N>$ between 0.6 and 19 following photo-excitation at 510 nm. Decay rate (b) $k_1$ and (c) $k_2$ as a function of $<N>$, together with (d) the respective relative weight calculated as the prefector A and B normalized for the decay initial amplitude.
of the density of carriers, following the second order equation:

\[-\frac{d^2 n}{dt^2} - k_1 n - k_2 n^2 = 0\]

From the steady-state PL decay we get an average recombination lifetime of 27.4 ns, a value much longer than the time-window consider here. Consistently, we put \( k_1 \), the recombination rate linear with \( n \), to zero. The solution to equation S3.5 is thus

\[ n(t) = \frac{n_0}{1 - k_2 n_0 t} \]

where \( n_0 \) is the initial density of a carriers. We thus fit the whole set of data with \( k_2 \) as a global parameter. In Figure S11(a) we report the values of \( n_0 \) extracted from the fit as a function of the experimental number of electron-hole pairs \( \langle N \rangle \) calculated from the cross section. Clearly, for \( \langle N \rangle > 10 \) there is a change in the slope of the curve. Since the model holds when \( \Delta A \) is in linear dependence with the density of carriers \( n \), for our analysis we focus on the data set for \( \langle N \rangle \) between 0.6 and 7.1. We point out that the change in the slope of \( n_0 \) could be due to the fact that, for higher electron-hole density pairs, the recombination time \( 1/(k_2 n_0) \) starts to become comparable to the initial electron trapping time (Figure S21).
S11(b)). From this analysis, see Figure 4d of the main text, the fit yields a second order recombination rate \( k_2 = (7.7 \pm 0.1) \times 10^{-3} \) cm\(^2\)/s. For comparison, in Table S3 we report the second order recombination rate for various 2D materials, see discussion in the main manuscript.

**Table S3: Bimolecular rate \( k_2 \) values reported in the literature for various 2D colloidal materials.**

|                | \( k_2 \) (cm\(^2\)/s) |
|----------------|--------------------------|
| Kunneman et Al\(^{16}\) CdSe NPLs | 0.13 \times 10^{-3} |
| Tomar et Al\(^{17}\) CdSe NPLs | 0.97 \times 10^{-3} |
| Kumar et Al\(^{18}\) Monolayer MoSe\(_2\) | 300 \times 10^{-3} |
| Sun et Al\(^{19}\) Monolayer MoS\(_2\) | 43 \times 10^{-3} |
| Yuan et Al\(^{20}\) Monolayer WS\(_2\) | 410 \times 10^{-3} |
|        | Bilayer WS\(_2\) |
|        | Three-layer WS\(_2\) |
| Delport et Al\(^{21}\) Iodaide Ruddlesden-Popper Perovskites | 0.11 – 0.49 \times 10^{-3} |

**S3.6 Broadening of \( \Delta A \) at shorter wavelength**

In Figure S12 we report the normalized \( \Delta A \) spectra at 3ps following excitation at 510 nm for increasing electron-hole pairs, showing a pronounced broadening of the HH/LH transition lower wavelengths (higher energies). This behaviour matches the broadening of the fPL spectra (See Figure 1d and 4a of the main manuscript) in the same range of wavelength, pointing towards the presence of hot charge carriers.

**S3.7 Femtosecond Photoluminescence**

For the detection of the broadband PL transients on a sub-picosecond timescale, we used the transient grating PL technique.\(^{22}\) The output of a femtosecond Ytterbium fiber laser, (Tangerine SP, Amplitude Systemes; operating at 58 kHz with pulses < 150 fs) was split into pump and gate parts. For the pump part, second harmonic (515 nm) and third harmonic
Figure S12: Normalized $\Delta A$ spectra at 3 ps following excitation at 510 nm for increasing number of average number of excitations $\langle N \rangle$ (from 0.5 to 18).

(343 nm) generation was used in the experiments and focused to a 50 $\mu$m$^2$ spot onto the sample. During the measurement, the sample was continuously stirred in a 1 mm cuvette to avoid photo-induced degradation effects or charging of the nanoparticles. The PL signal from the sample was collected and refocused onto the gate medium, a 1 mm fused silica crystal, using a pair of off-axis parabolic mirrors. For the gate part, about 40 $\mu$J of the 1030 nm output was split using a 50/50 beam splitter to generate the two gate beams and focused onto the gate medium at a crossing angle of approximately 8° and overlapped with the PL in a boxcar geometry. The two gate beams, which spatial and temporal overlap inside the gate medium, generate a laser-induced grating. This transient grating acts like an ultrafast optical shutter to temporally resolve the broadband PL signals by diffracting the gated signal from the PL background. Two achromatic lenses collimated and focussed the gated signals onto the spectrometer entrance (Princeton Instruments SP 2150), and the gated PL spectra were measured by an intensified CCD camera (Princeton Instruments, PIMAX3). A 380 nm or 550 nm long- and 850 nm short-pass filter were used to remove the residual pump and intense 1030 nm gate, respectively. The time delay between pump and gate beams was controlled via a motorized optical delay line. For each transient PL spectrum, 120 000 shots at each gate time delay were accumulated.
S3.8 Low fluency fPL map

In Figure S13 we report the fPL map after excitation at 515 nm generating 0.7 electron-hole pairs.

Figure S13: fPL map after photo-excitation at 515 nm creating an average number of electron-hole pairs $\langle N \rangle = 0.7$
S3.9 Carrier Temperature from Femtosecond PL

**Fit of the Femtosecond PL spectra.** The extraction of the carrier temperature is based on the concept that temperature describes the distribution of charges over the energy levels at hand. This distribution is in principle a Fermi-Dirac (FD) distribution for electrons and holes with a complex energy dependence. However, if we look only at those carriers residing at high energy (relative to the quasi-Fermi levels) this dependence can be simplified to the Boltzmann tail approximation:

\[
FD(E) \propto \exp\left(-\frac{E}{k_B T_{\text{eff}}^\text{eff}}\right)
\]

This approach has been followed extensively in literature for the extraction of the carrier temperature from femtosecond transient absorption experiments.\(^{17,23}\) However, the involvement of photo-induced absorptions, strong shifts and renormalizations and the congested fine structure (including excitons and free charge transitions) at the band edge, this is not so straightforward. Instead, we opted to apply this concept to the luminescence spectra, an approach followed also for \textit{e.g.} CdSe nanoplatelets by Pelton \textit{et al.}\(^{24}\)

**Bi-exponential Fit of the cooling curves T(t).** By fitting the PL spectra using the approach described in the section above, we extracted the decay of the carrier temperature as a function of time, see Figure 4b of the main text. We fit the cooling curves T(t) using a biexponential function:

\[
T(t) = T_0 + A_1 e^{-\frac{t}{\tau_0}} + A_2 e^{-\frac{t}{\tau_1}}
\]

where \(T_0\) was fixed at 298 K.

For \(<N>=0.7\), the T vs time curve is well fitted by using a single exponential with \(\tau_0=270\pm30\) fs. This value is in good agreement with the hole cooling rate calculated at low fluency from the \(\Delta A\) map kinetics shown in Figure 3a (300\pm15 fs), see discussion in the main manuscript. As such, we can define \(\tau_0\) as the intrinsic cooling time of carriers in this
system. We thus fixed the value of $\tau_0$ and fit the T vs time curves for $<N>= 1.9$ and $3.9$ with equation S17. In table S4 we report the fit coefficients. The fit are reported in Figure 4b of the main text. As shown in table S4 $\tau_1$ amounts to several ps, showing already that for

**Table S4: Parameters extracted from the fit of the PL intensity decay using a triple exponential function**

|      | $<N>=0.7$ | $<N>=1.9$ | $<N>=3.9$ |
|------|-----------|-----------|-----------|
| $A_1$ | $349\pm35$ | $228\pm50$ | $864\pm48$ |
| $\tau_0$ (ps) | $0.270\pm0.03$ | $0.270$ | $0.270$ |
| $A_2$ | - | $488\pm31$ | $722\pm25$ |
| $\tau_1$ (ps) | - | $7.1\pm0.9$ | $20.9\pm1.7$ |

increasing fluency the phonon emission rate slows down significantly. Nevertheless, we point out that this approach lacks physical basis and it is meant uniquely as an indication that the net charge carrier cooling rate slows down with increasing fluency. We thus proceed in calculating the phonon emission rate as shown in the section below and discuss in the main text.
S3.10 Electron - LO Phonon Scattering

Phonon Emission Time from Transient PL The cooling process can be model assuming that the energy loss rate \( \frac{dU}{dT} \) is dominated by carrier-phonon interactions\(^{25,26} \) described as

\[
\frac{dU}{dT} \approx \frac{3k_B dT_{eff}}{2} \approx \frac{\hbar \omega_{LO}}{\tau_{ph}} \left[ \exp\left( -\frac{\hbar \omega_{LO}}{k_B T_{eff}} \right) - \exp\left( -\frac{\hbar \omega_{LO}}{k_B T_L} \right) \right]
\]

where \( T_L \) is the lattice temperature fixed at 300 K and \( \hbar \omega_{LO} \) the phonon energy of CdSe (26 meV).\(^{26} \) \( \tau_{ph} \) is the phonon emission time, \( i.e. \) the average time needed to emit one LO phonon with energy 26 meV.

We can re-write the expression above to describe \( \tau_{ph} \) directly:

\[
\tau_{ph}(t) = \frac{2\hbar \omega_{LO}}{3k_B \frac{dT_{eff}}{dt}(t)} \left[ \exp\left( -\frac{\hbar \omega_{LO}}{k_B T_{eff}(t)} \right) - \exp\left( -\frac{\hbar \omega_{LO}}{k_B T_L} \right) \right]
\] (S18)

where the explicit time dependence of \( \tau_{ph}, T_{eff}(t) \) and its derivative are written out. The input required to calculate \( \tau_{ph} \) is thus given by Figure 4b which presents us with exactly this \( T_{eff}(t) \), from which we calculate also directly \( dT_{eff}/dt \). All the other parameters are known and as such we can calculate \( \tau_{ph}(t) \) at the varying time delays.

Theoretical Estimate of the Phonon Emission Time Considering the energy of the LO phonon \( \hbar \omega_{LO} \), the scattering time constant \( \tau_0 \) can be estimated from the relation:

\[
\frac{1}{\tau_0} = \frac{e^2 \sqrt{2m\hbar \omega_{LO}}}{4\epsilon_0 \pi \hbar^2} \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right)
\] (S19)

where \( m \) is the effective electron mass, \( \epsilon_0 \) is the permittivity of the vacuum and \( \epsilon_s \) and \( \epsilon_\infty \) the static and high-frequency dielectric constant of the medium. Following Sippel et al.\(^{26} \) using \( m = 0.13m_0, \epsilon_\infty=6.3 \) and \( \epsilon_0=9.3, \tau_0 = 31 \text{ fs} \), a value that agrees well with the \( \tau_{ph} \) we extracted from the cooling curves at \( \langle N \rangle=0.7 \), see main manuscript.
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