

Electronic Supporting Information:
Tuning trion binding energy and oscillator
strength in a laterally finite 2D system:
CdSe nanoplatelets as a model system for
trion properties

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S1 THEORETICAL ASPECTS

A Relative trion wave function

Similar to a helium atom or a negatively charged hydrogen ion, the three fermion components in a negatively charged exciton (trion) make them composite fermions with two sets of states. In fact, the two opposite spin electrons of an X^- trion can be in a triplet $S = 1$ or singlet state $S = 0$. The solution of the Schrodinger equation for the X^- is the following wave function: $\Phi(1, 2) = \phi(1, 2) \times \chi(1, 2)$, where ϕ is the spatial and χ is the spin part of the wave function. The appropriate way to approach the problem is to introduce even and odd combinations of opposite spins, namely, triplet and singlet states with total spin $S_Z = 0$, defined as:¹⁻³

$$|S(1, 0), S_Z = 0\rangle = \frac{1}{\sqrt{2}} \left(\left| +\frac{1}{2}, -\frac{1}{2} \right\rangle - (-1)^S \left| -\frac{1}{2}, +\frac{1}{2} \right\rangle \right) \quad (S1)$$

The Pauli exclusion principle forces the orbital part of these opposite-spin electrons to be odd for $S = 1$, and even for $S = 0$. Symmetrized and normalized spatial wave functions can be chosen as:

$$\phi(\rho_1, \rho_2) = \frac{1}{\sqrt{2}} \left(\xi_{1s}(\rho_1) \xi_{nl}(\rho_2) \pm \xi_{1s}(\rho_2) \xi_{nl}(\rho_1) \right), \quad (S2)$$

where $\xi_{nl}(\rho_i) = \sum_{n,l} C(n, l) \varphi_{n,l}(\rho)$ are the eigenvalue solution of the relative exciton Hamiltonian. In the case of a singlet state, the spin part of the wave function is antisymmetric with respect to permutation of the electrons. The spatial part of the singlet wave function is therefore symmetric with respect to permutation of the electrons ("+" in Eq. S2). On the contrary, the spatial part of the triplet wave function is antisymmetric with respect to permutation of the electrons ("- in Eq. S2). We should note that whatever S_Z is, electrons can have the same spin, in which case S_Z is equal to ± 1 , or opposite spins, in which case S_Z is equal to 0. As the orbital ground state must be even, electrons in the X^- ground state form a spin singlet state ($S = 0, S_Z = 0$) with "+" in Eq. S2.

B Calculation of oscillator strength

The predicted oscillator strength of the exciton or trion is calculated via

$f_{X,X-} = (E_p/2E_{X,X-})|\int dr \Psi_{X,X-}(r, r)|^2$ by our theory using numerical diagonalization of the matrix resulting from the projection of the Hamiltonian. $E_{X,X-}$ is the exciton or trion energy and $\Psi_{X,X-}$ the corresponding wave function, E_p the Kane parameter. The results are presented in Figures 2 and 3 (main text). For the exciton f is translated in a radiative lifetime using an (angular) average local field factor ⁴ f_{LF} deduced from the intrinsic absorption at the exciton transition in Ref. 5 and using ⁶

$$\Gamma_{X,theo}^r = \frac{4n_{out}q_e^2 E_{ph} E_p}{3\pi\epsilon_0 \hbar^2 c^3 m_0} |f_{LF}|^2 S_X, \quad (S3)$$

taking into account the symmetry of the transition related Bloch functions,⁷ we obtain the in Table 1 (main text) displayed values. E_{ph} is the photon energy, E_p the Kane parameter taken from Ref. 8, $S_X = |\langle \Psi_X | \delta_{r_e, r_h} | \Psi_X \rangle|$ the exciton e-h overlap integral from our theory and n_{out} the refractive index of the surrounding (ligands). The calculations are in very good quantitative agreement with our experimental results. Minor deviations may result e.g. from uncertainties of the dielectric function of CdSe, as the calculation of a lifetime in principle involves the dielectric function and refractive index. We also remark that calculating the radiative rate of trions from the oscillator strength is not possible with the formula above, as the left electron has to be emitted in one of the weakly confined conduction band states within an energy range of $k_B T$, and the size varying DOS or number of these states does not result in a simple analytical form like above. Hence, we did not calculate radiative rates for trions in the main text. Instead we compare for trions the resultant trion Bohr radius in Figure 2d main text, and show very good agreement with the experimental findings there, so that our theoretical model consisting of exciton and trion states is confirmed quantitatively by the size dependent exciton radiative rates and trion Bohr radii apart from the other arguments discussed in the main text.

C Impact of smallest lateral dimension on the optical properties

CdSe nanoplatelets can be synthesized with different lateral sizes and as a consequence the exciton and trion properties can depend strongly on their lateral extent.^{9,10} Therefore, varying the lateral size of these nano objects provides a rich playground for optimizing the optoelectronic properties. In order to study the effect of lateral confinement on the excitonic and trionic optical properties, we display in Figure S1a the exciton and trion energy obtained by numerically solving the exciton and trion Schrödinger equation (Eqs. 2 and 3) in the main text for different lateral aspect ratios AR . Figure S1 b and c show the trion binding energy E_{BX-} and Bohr radius a_{X-} . In contrast to Figure 2 (main text) we plot these properties as a function of the smallest dimension of the platelet L_y , for different lateral aspect ratios AR . Figures d to f show the resultant oscillator strength and ratio of exciton and trion.

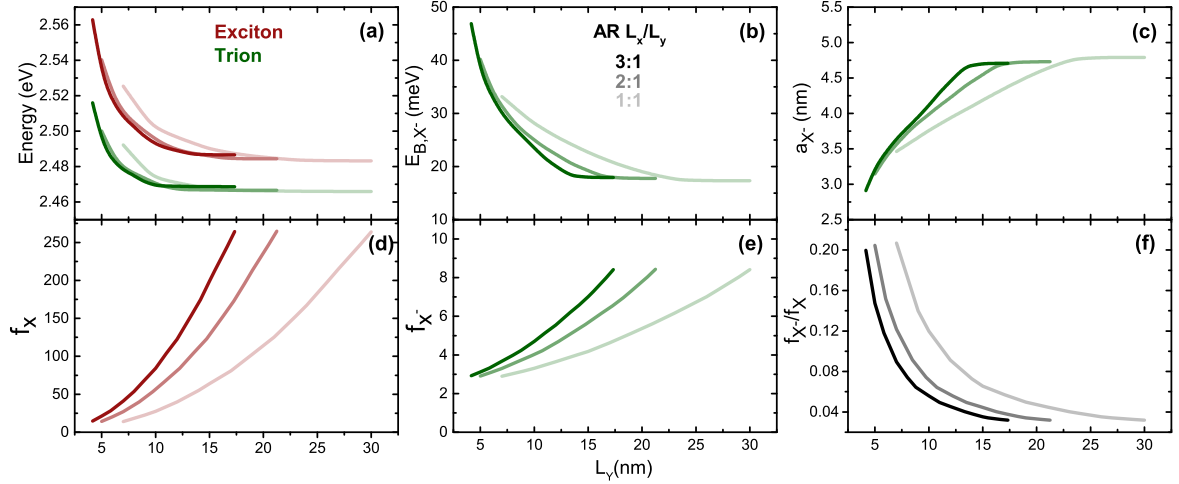


Figure S1: (a) Exciton and trion transition energy as well as trion binding energy (b) and trion Bohr radius (c) as a function of the shortest platelet dimension L_y for different lateral aspect ratios $AR = L_x/L_y$. (d), (e) exciton and trion oscillator strength as well as the ratio of both (f). The curves in a-f look horizontally shifted in L_y (with respect to their beginning) for different aspect ratios, as we plot always the same platelet area $A = L_x \cdot L_y$ range as in Figure 2 (main text). As a result quadratic platelets (1:1) have a right shifted onset for their curves.

The energy of exciton and trion, the trion binding energy E_{BX-} and the trion Bohr radius a_{X-} are very sensitive to the variation of the shortest lateral length L_y and aspect ratio R . Two regimes are recognized in our results: i) First, for small sizes, the

energies decrease, while the trion Bohr radius a_{X^-} increases with the smallest size and lateral aspect ratio. This is due to the fact that with increasing lateral size the quantum confinement becomes weaker and e.g. the trion is increasingly delocalized over the larger NPLS size. ii) For large lateral size, a saturation behavior for both the energy and the Bohr radius is observed for different aspect ratios, see Figure S1 b. In fact, for sizes beyond $L_y \geq 20nm$, the effect of confinement tends to become negligible. In this range the energy is set by the relative motion of electron and hole rather than center-of-mass motion, as we approach the ideal quantum well limit like in laterally extended TMDCs materials, in which the center of mass (CM) motion of the particle is (quasi) free.

In order to provide further insight into the effect of the shortest lateral size on the exciton and trion optical properties, we illustrate in Figure S1 d-f the dependence of the exciton and trion oscillator strength $f_i (i = X, X^-)$ and the oscillator strength ratio on the shortest lateral size L_y for different lateral ratio AR . We can clearly notice that the oscillator strength increases with L_y due to the increasing overlap integral, while there is a weaker aspect ratio dependence. We remark that e.g. for quadratic platelets a quadratic L_y^2 scaling of the exciton oscillator strength is observed, resembling the area (here $A = L_x \cdot L_y$) scaling discussed in Eq. 1 in the main text. Notably, the oscillator strength and their ratio mainly relates to the (coherence) area. The lateral aspect ratio dependence of f_X and f_{X^-} is less pronounced.

As stated previously, the nanoplatelets are a box-like nanostructures with a z confinement to a few monolayers and a variable lateral (x,y) confinement. Hence, depending on their lateral sizes L_x and L_y , they can be in different confinement regimes, the strong confinement regime, an intermediate regime, and a Coulomb-dominated (weak confinement) regime. For example for a $21 \times 7 \text{ nm}^2$ platelet, the 7 nm length suggests that strong confinement regime is closer, while the 21 nm length suggests weak confinement. On the other hand for $41 \times 13 \text{ nm}^2$ both lateral dimensions are in a weak confinement regime. Hence, both L_x and L_y lateral confinement are relevant to determine the various properties of CdSe NPLs. In conclusion a proper understanding of the influence of lateral confinement requires to study the optical properties as a function of platelets area and

for different aspect ratios in order to capture both, the effect of x and y confinement as well as the effect of shape (rectangular for $AR = 2$ or 3 and squared for $AR = 1$).

D Strong confinement limit for very small platelets

The smallest platelet ($3.6 \times 8.1 \text{ nm}^2$, 29 nm^2) is not in a weak or intermediate confinement, like the other, larger NPLs, since the size does not largely exceed the 2D exciton Bohr radius. Using the theoretical model explained in the main text, we find exciton and trion energies equal to 2.595 eV and 2.540 eV , which is not in good agreement with US ($E_{US} = 2.525 \text{ eV}$) and LS ($E_{LS} = 2.487 \text{ eV}$) experimental energies. The $3.6 \times 8.1 \text{ nm}^2$ is more quantum dot like, in contrast to our theoretical model in the main text, build on the assumption of a weak to intermediate confinement regime (more quantum well like than quantum dot like).

Hence we did, analog to Figure 2 (main text), a calculation of the transition energies in a strong confinement approximation, in which the confinement potential dominates compared to Coulomb interaction. Though the shape of the wave function is almost completely determined by the confinement potential and is not influenced by the Coulomb potential in a first approximation. So within the usual effective-mass and the envelope-function approximation scheme, the electrons and hole wave functions are described by the following Schrödinger equation:

$$\left(-\frac{\hbar^2}{2} \nabla \frac{1}{m_i(z_i, \rho_i)} \nabla + V_i(\mathbf{r}_i) \right) \phi_{n_i, m_i, l_i}^i(r_i) = E_{n_i, m_i, l_i}^i \phi_{n_i, m_i, l_i}^i(r_i), \quad (\text{S4})$$

with $i = (e, h)$ for the exciton and $i = (e_1, e_2, h)$ for the trion. The single-particle functions of electron and hole found in this way are used to calculate the exciton states within a configuration interaction scheme. For this purpose, we take the space spanned by the products of the single particle states, i.e. $\Psi_{X, (X-), J} = \prod_{i=e, h (i=e_1, e_2, h)} \phi_{n_i, m_i, l_i}^i(r_i)$.

Even if Coulomb coupling does not determine the shape of the exciton (trion) wave function in the strong confinement limit, it shifts the exciton (trion) energy considerably. In first-order perturbation theory, the Coulomb potential in a confined geometry

is characterized by a set of matrix elements $V_{n_i, m_i, l_i}^{n_j, m_j, l_j}$, between i and j particles defined as $V_{n_i, m_i, l_i}^{n_j, m_j, l_j} = \int d\mathbf{r}_i \int d\mathbf{r}_j |\phi_{n_i, m_i, l_i}^i(r_i)|^2 V_c(\mathbf{r}_i - \mathbf{r}_j) |\phi_{n_j, m_j, l_j}^j(r_j)|^2$. Thus, the exciton and trion energy are read respectively as: $E_{X,J} = E_g + E_{n_e, m_e, l_e}^e + E_{n_h, m_h, l_h}^h + V_{n_e, m_e, l_e}^{n_h, m_h, l_h}$ and $E_{X^-, J} = E_g + 2E_{n_e, m_e, l_e}^e + E_{n_h, m_h, l_h}^h + 2V_{n_e, m_e, l_e}^{n_{e2}, m_{e2}, l_{e2}} - V_{n_{e1}, m_{e1}, l_{e1}}^{n_{e2}, m_{e2}, l_{e2}}$.

We find 2.537 eV for the exciton energy, while 2.517 eV for the trion. This is in qualitative agreement with the 2.525 and 2.487 eV found in the experiment. (See Figure S2.) This only qualitative agreement occurs as the strong confinement theory is not expected to reproduce the results exactly, since in principle for this platelet, the x-direction (3.6 nm) is in the strong confinement, while the y-direction is in an intermediate regime, resulting in the slight over estimation observed for the X and X^- transition energies. The effect is stronger for the trion due to its larger wave function extent. As only the smallest platelet is calculated via this different theory approach, we excluded the data point in Figure 2a and c, as we do not have a continuous theory to draw continuous theory lines from strong to weak confinement regimes. The sample is further excluded from the time-dependent analysis, as is showed fast degradation, so that we were not able to record appropriate transients. (See also section S3 C.)

S2 SYNTHESIS AND CHARACTERIZATION

4.5 monolayer (ML) CdSe nanoplatelets were synthesized according to Refs. 11, 12 and 13, characterized by transmission electron microscopy (TEM) showing different average lateral sizes. (See insets Figure S1) Absorption and PL spectra as well as TEM images are shown in the same figure for selected samples. The particles were redissolved in toluene and embedded in a poly(laurylmethacrylate-co-methylmethacrylate) or PMAO polymer on fused silica substrate for low temperature PL measurements. The volume fraction in the polymer was kept below 1 % to avoid any aggregation, as shown in Ref. 14, or FRET effects.¹⁵ The orientation of the platelets is random in the matrix. A Cryovac Conti IT PL cryostat (3.5-300 K) was used for low temperature measurements.

PL excitation was done by the 420 nm second harmonic of a 840 nm, 150 fs Coherent

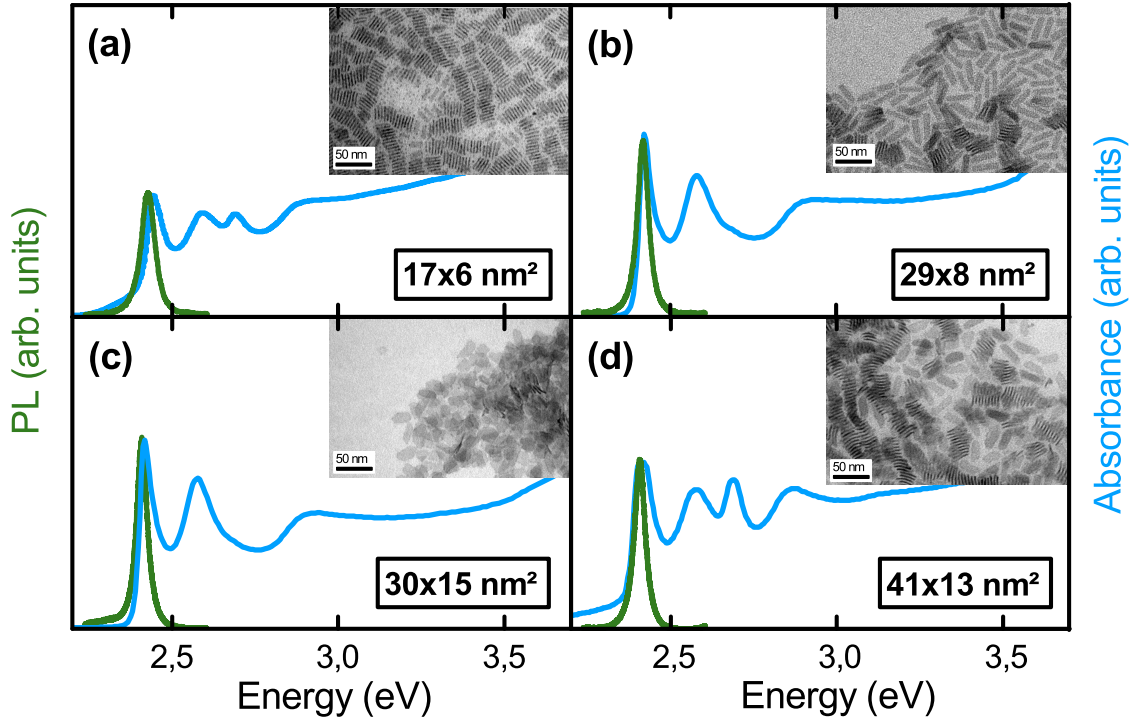


Figure S2: (a-d) Room temperature absorption and PL spectra of selected nanoplatelets along with their TEM images (inset). The average lateral sizes are noted for each NPL population.

Mira 900 HP laser through a lens, while detection was done through a 0.4 NA objective with long working distance. A Hamamatsu C5680 streak camera was used for time-resolved PL, while a Horiba IHR550 spectrometer with attached LN cooled CCD was used for time-integrated detection. The average number $\langle N \rangle$ of photons absorbed (or excitations created) per platelet and pulse is calculated via the intrinsic absorption using Ref. 4. It is low in the experiments and $\sim 3 \cdot 10^{-4}$ for the platelet size variation (see Figures S3 and S4), while for the power dependent measurements it varies as indicated in Figure S5 in Section S3. The laser with a spot size is $\sim 30 \mu\text{m}$.

S3 TIME-RESOLVED AND -INTEGRATED DATA AND MODELING OF EXCITON AND TRION BY RATE EQUATIONS AND A MASS ACTION LAW

A Rate modeling of experimental data in the trion plus exciton model

4.5 monolayer (ML) CdSe nanoplatelets were investigated. Preparation was described in section S1. Low temperature photoluminescence (PL) spectra of CdSe nanoplatelets (NPLs) in Figure S3 show a double emission.^{16–21} The energy spacing strongly depends on the lateral platelet size, and varies from 38 to 18 meV. We refer in the following to them as the lower state (LS) and the upper state (US) emission.

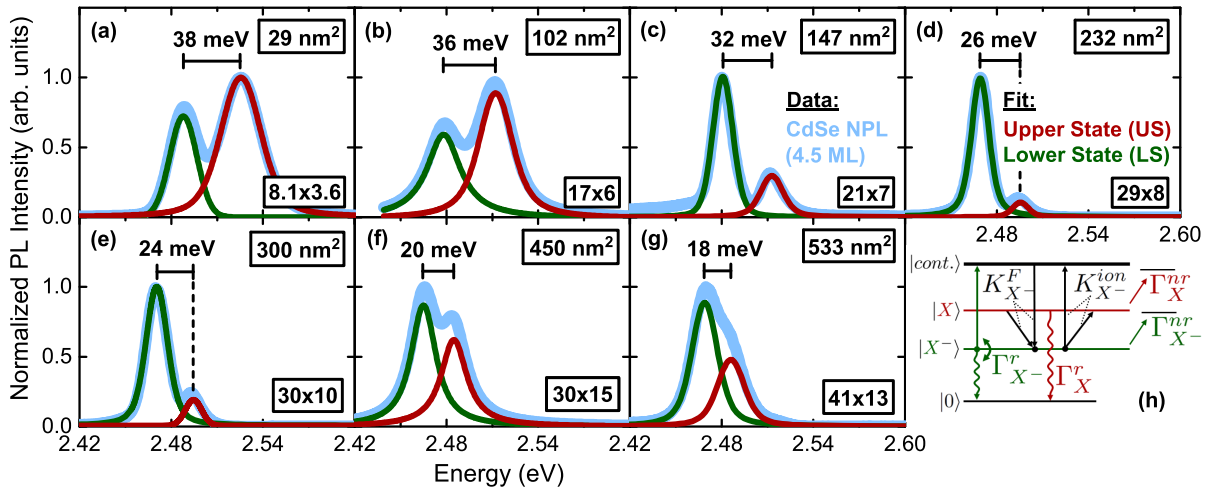


Figure S3: (a-g) Time-integrated PL emission of 4.5 monolayer (ML) CdSe NPLs for different lateral platelets size at 4 K and ~ 0.2 W/cm² (CW equivalent) 420 nm excitation. Lateral area and size ($L_x \times L_y$ in nm²) are indicated. h): Level scheme of trion model. Cave: E.g. $\Gamma_{X^-}^r$, the trion decay rate coefficient for the radiative trion decay, results in a free continuum electron in $|cont.\rangle$ and the radiative decay of an electron and hole to the (crystal) ground state $|0\rangle$, so there are two outgoing arrows related to the same rate constant. Similar behavior relates to $K_{X^-}^F$ and $K_{X^-}^{ion}$. Therefore each two arrows are involved for one rate constant.

The nature and the origin of these emission bands remains under debate both from theoretical and experimental considerations.^{16,18–20,22} Different scenarios have been discussed: i) an exciton plus negative trion,^{18,22,23} ii) exciton plus a LO phonon replica,¹⁹

iii) charge transfer excitons (excimers)¹⁶ between at least two platelets, iv) an exciton plus biexciton,²⁴ v) excited and ground state excitons²⁰ and an excitonic center of mass fine structure.¹⁰ Although in a first paper we attributed the double emission to an exciton ground and excited state,²⁰ recent further results by Shornikova and Antolinez et al.^{22,25} and their trion emission identification make it necessary to revisit our and other interpretations based on further data, as we will show in the following. Except the trion plus exciton explanation, discussed below, the other cases can be excluded by the experimental data. (See Section S4)

LS and US emission peaks: Figure S3 shows the time-integrated 4 K PL emission of CdSe NPLs with varying lateral dimensions under 150 fs pulsed 420 nm excitation of a frequency doubled Coherent Mira 900F laser, while Figure S4 shows the time-resolved emission using a Streak Camera, see Section S2 for details. The same applies for the time integrated spectra. The laser with a spot size $\sim 30 \mu\text{m}$ produces a low average number of excitations $\langle N \rangle < 3 \cdot 10^{-4}$ per platelet so that multiexcitonic effects like bimolecular Auger Recombination can be excluded in the following rate modeling. (See also section S4 iv.) In the detection spot $> 10^3$ platelets are contained so that we have an ensemble measurement with random orientation. In the following we discuss here cases i) exciton X plus a negatively charged exciton (Trion) X^- , and in section S4 the alternative scenarios ii) exciton plus LO-phonon replica, iii) exciton plus excimer, iv) exciton plus biexciton and v) excited and ground state exciton.

Exciton X plus a negatively charged exciton (Trion) X^- : We test the assumption that the lower state (LS) is an emission of charged excitons (trions) while the upper state (US) is due to a neutral exciton. Charged excitons (trions) appear frequently in 2D transition metal dichalcogenides (TMDCs) and indications for a neg. trion in CdSe platelets have been found.^{18,26} For a negative trion, the two opposite-spin electrons of an X^- trion can be in a triplet state $S = 1$ or singlet state $S = 0$. We refer to their singlet configurations in which they appear as bound states (generally below the energies of neutral excitons). The observation of triplet trions is more elusive.^{1,2,27,28} To model

the trion plus exciton emission, we evaluate the experimental time resolved PL decay (Figure S4) of our samples (Figure S3) at low temperature ($T = 4$ K) using a numerical model, which accounts for population transfer between exciton and trion states under pulsed excitation. Fitting the experimental transients numerically with that model we compare the resultant power dependence of the integrated PL intensity calculated by our theoretical model with the experimental findings for CdSe NPLs of different size (Figure S5). The model (Figure S2h) takes four levels into consideration: the crystal ground state $|0\rangle$, the electron state $|continuum\rangle$ (from e-h continuum), the excitonic $|X\rangle$, and trion state $|X^- \rangle$. In fact, due to the high exciton binding energies (~ 200 meV)²⁹⁻³¹ and resulting strong correlation in CdSe nanoplatelets, we have assumed that excitons are formed instantly upon excitation and that the ionization of an exciton to an unbound e-h pair can be neglected, as at 4 K ($k_B T = 0.34$ meV) this is a very unlikely process. (See Supplemental Material, section S3 B) The pulsed generation of excitons by 150 fs laser pulses is modeled via a generation rate $G(t)$, broadened to a gaussian pulse representing the instrument response (3.5 ps). Taking into account the radiative Γ_i^r and non radiative Γ_i^{nr} recombination rate ($i = X, X^-$) as well as the scattering rates of population transfer between the four states, the dynamics of exciton, trion and electron (see level scheme in Figure 1) can be described via:

$$\begin{aligned}
\frac{dn_X}{dt} &= G(t) - n_X \left(\Gamma_X^r + \Gamma_X^{nr} \right) - n_X n_e K_{X^-}^F + n_{X^-} K_{X^-}^{ion} n_{ph} \\
\frac{dn_{X^-}}{dt} &= -n_{X^-} \left(\Gamma_{X^-}^r + \Gamma_{X^-}^{nr} \right) - n_{X^-} K_{X^-}^{ion} n_{ph} + n_X n_e K_{X^-}^F \\
\frac{dn_e}{dt} &= n_{X^-} K_{X^-}^{ion} n_{ph} - n_X n_e K_{X^-}^F
\end{aligned} \tag{S5}$$

where, $n_X(t)$, $n_{X^-}(t)$, $n_e(t)$ are the the exciton, trion and electron densities. The non-radiative recombination rates are generally assumed to be a thermally activated process according to $\Gamma_i^{nr} = \Gamma_i^{0,nr} e^{\frac{-E_i}{k_B T}}$. Here, $\Gamma_i^{0,nr}$ is an approach frequency factor and E_i is an activation energy assumed to be identical for exciton and trion state. These activation energies are due to a concurring thermally activated non-radiative processes.^{20,29,32} However, as demonstrated in Ref. 34, the quantum yield approaches unity below 50 K

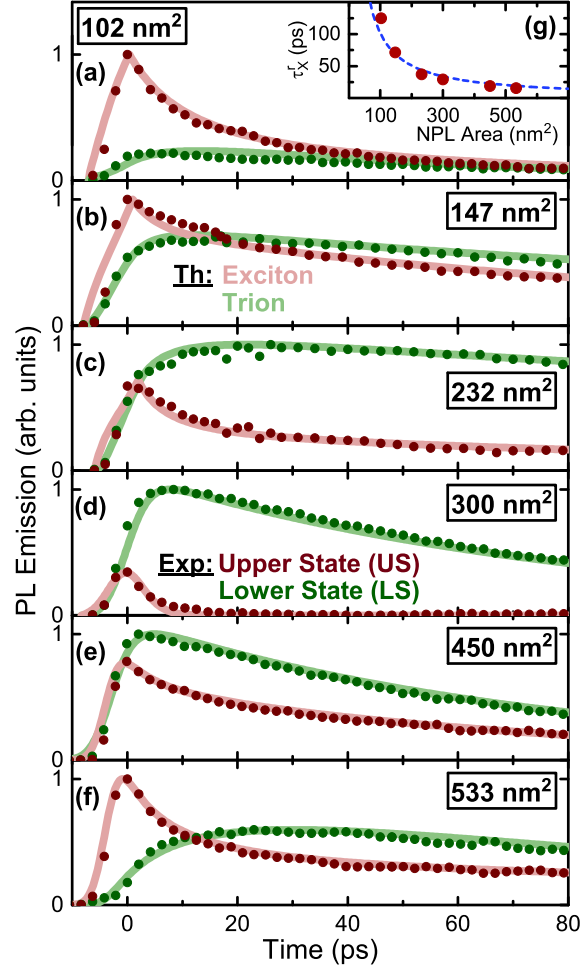


Figure S4: (a-f) Time-resolved PL dynamics at 4 K (420 nm, 150 fs 75.4 MHz repetition rate laser, 0.2 W/cm^2 excitation density producing a low average number of excitations $\langle N \rangle < 3 \cdot 10^{-4}$ per platelet) of exciton and trion for different CdSe nanoplatelets, obtained from Voigt fits (analog to Figure 1, main text) to the time dependent emission (recorded by a streak camera) at each displayed data point in time as well as fits to rate equation S5. Inset g): Radiative exciton lifetime vs. platelet area with $1/\text{area}$ fit according to Ref. 33.

in nanoplatelets^{32,34} and TMDCs,³⁵ so that numerical evaluation of our model results in a vanishing non-radiative contribution at 4 K. Alternatively the reported radiative rates (Tables 1 and S1) for exciton and trion can be considered effective decay rates, summing up the radiative plus a minor non-radiative contribution.

K_{X-}^F, K_{X-}^{ion} are the formation and the ionization rate constants of the trion, given by the Saha equation in 2D:³⁶

$$\frac{n_e \times n_X}{n_{X-}} = \frac{g_e g_X}{g_{X-}} \frac{m_e M_X}{2\pi \hbar^2 M_{X-}} k_B T e^{\frac{-E_{BX-}}{k_B T}} = \frac{K_{X-}^{ion}}{K_{X-}^F} \quad (\text{S6})$$

g_e , g_X and g_{X^-} are the degeneracy factors of the electron, exciton and trion in the nondegenerate regime, where Boltzmann statistics applies. $M_X = m_e + m_h$ and $M_{X^-} = 2m_e + m_h$ are the mass of the exciton and trion, respectively, with m_e (m_h) the electron (hole) effective mass. E_{B,X^-} is the trion binding energy, equal to the energy separation $E_{B,X^-} = \Delta E = E_{US} - E_{LS}$ between X (US) and X^- (LS). The ionization rate of a trion to an unbound electron and exciton is given by: $K_{X^-}^{ion} = \gamma_{X^-}^0 n_\Delta$, $\gamma_{X^-}^0$ the phonon-assisted scattering rate between the two levels, $n_\Delta = 1/(e^{(\Delta E/k_B T)} - 1)$ the Bose occupation number of phonons for an energy spacing ΔE taken from Figure S3. (We calculate the trion binding energy, equal to ΔE also theoretically in the main text.) We assume a background charge density of one electron per platelet, which is involved in the trion formation, see reasoning at the end of this paragraph. It is assumed to stem from residual charges on the platelets, e.g. from the host matrix or a desorbed charged oleic acid ligand leaving a net negative charge behind. But to investigate the nature of this process is not the focus of our paper. (See also further comments at the end of this section.)

Due to the low excitation densities in our experiments, which are even for the power dependent measurements below $\langle N \rangle < 5 \cdot 10^{-2}$ per platelet, we do not take into account multiexcitonic effects like bimolecular Auger recombination in the rate modeling, as discussed above. Nonradiative trion Auger decay is not included, as: 1) The QY of NPLs is near unity at 4 K in CdSe platelets,^{32,34} ruling out significant contribution as for the excitons. 2) On the other hand an electron shakeup²⁵ from the trion state to an highly excited state (by the full total trion energy), which is still a laterally quantized electron state in the conduction band, has low probability. This is because the trion wave function is s-like, while these highly excited states beyond d-, f-like states have multiple knots in their wave function, and hence transition (overlap) integrals and subsequently rates are expected to be (very) low.

We are thus left with three adjustable parameters, the exciton radiative rate Γ_X^r , the trion radiative rate $\Gamma_{X^-}^r$, and scattering rate $\gamma_{X^-}^0$, and exploiting the experimental evidence for $\gamma_{X^-} \gg \Gamma_X^r, \Gamma_{X^-}^r$.²⁰ Hence, for low T the PL decay is a function of only these parameters for fits. Table 1 summarizes the fit results displayed in Figure S4 (a-f). We

Table S1: The experimental fitting parameters of the rate equation model (Eq.S5) for nanoplatelets of different size as well as the exciton radiative rates (theo.), as obtained from theory in the main text.

Size (nm ²)	17 × 6	21 × 7	29 × 8	30 × 10	30 × 15	41 × 13
Area (nm ²)	102	147	232	300	450	533
ΔE (meV)	36	32	26	24	20	18
$\Gamma_X^r (ns^{-1})$	8	14	27	35	53	64
$\Gamma_{X-}^r (ns^{-1})$	1.6	1.9	2.5	3.3	4.1	4.6
$\gamma_{X-}^0 (ns^{-1})$	62	77	111	96	78	32
$\Gamma_{X,theo}^r (ns^{-1})$	11	16	26	34	50	62

see that the rate constants (Table 1 and identical table S1 here) get higher and the overall dynamics of the exciton and trion gets faster for larger NPLs.

The integrated PL intensity measured as a function of the pump power or average number of photons absorbed $\langle N \rangle$ per NPL is displayed in Figure S5 (a-c). (We studied selected samples of the full size range only.) The average number of photons absorbed (or excitations created) per platelet is calculated via the intrinsic absorption using Ref. 4. For comparison, we plot in panels (d-f) the results of our rate equation model based on the fit results in Table 1. We see good agreement. In all cases at low excitation power, the PL signal, scaling with population times radiative rate constant, increases linearly, as expected for excitonic transitions. At high excitation densities the trion and

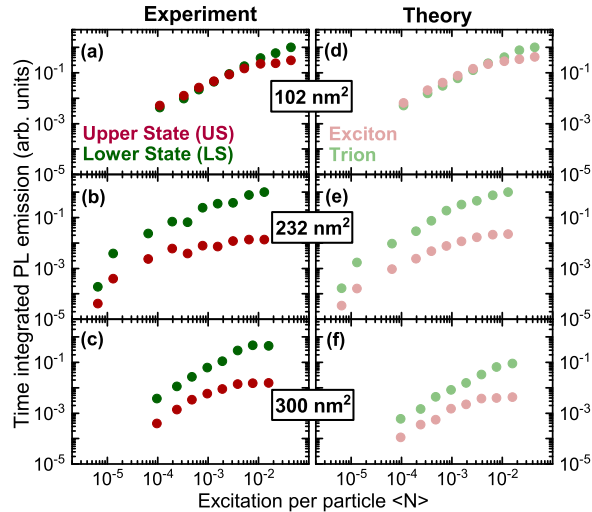


Figure S5: Time integrated luminescence of the exciton and trion as a function of $\langle N \rangle$ from experiment at 4 K (a-c) and exciton-trion modeling (d-f).

exciton PL begins to saturate, since the trion (LS) intensity will be limited by the initial

(background) concentration of electrons in the platelets. The saturation of the exciton state (US) at high excitation density is not expected at first glance. Due to the low number of excitations per nanoplatelet $\langle N \rangle \ll 1$ multiexcitonic effects or state filling up to higher states^{37,38} can not account for it. As the observed saturation is well reproduced in our model, it results from the dynamical equilibrium between excitons, trions and resident electrons, given by the mass action law. The agreement of theory and experiments both in time resolved and integrated data directly substantiates the trion based (LS) emission, in contrast to the other models (discussed below), which can not reproduce both time resolved and integrated data at the same time. Minor deviations may arise e.g. from slight photo darkening phenomena at elevated excitation densities.

For our rate equations we use a density of one background electron per nanoplatelet. This is substantiated by the following estimation using Astakhov et al.,³⁹ which relates the trion to exciton radiative rate ratio to the trion Bohr radius $\Gamma_{X-}^r / \Gamma_X^r \approx n_e \pi a_{X-}$. Using either the parameter ranges of the experiments in Table 1 and the experimental trion Bohr radius in Figure 2 (main text) or the theory predictions results in approx. 1 electron per nanoplatelet, as used in the rate equations above as uniform density delocalized over the whole platelet. There are no indications for localized defect formation, especially not as the radiative rates of the trions in Table 1 scale with the platelet area, so that trions and original electrons are not expected to be defect bound, where such a scaling would not occur due to localization.

B Mass action law for exciton formation

In the rate equation we have assumed that excitons are formed directly upon excitation due to the high exciton binding energies (~ 200 meV,^{29,30} discussed in the main text) in CdSe nanoplatelets, the ionization of an exciton to an unbound e-h pair is neglected and hence continuum excitation by laser excitation leads to direct exciton generation. This can be justified by using the Saha equation for the e-h to exciton dynamics. In fact, with respect to the mechanism leading to an equilibrium between free excitons n_X , free

electrons n_e , and free holes n_h we apply the Saha equation;^{36,40–42}

$$\frac{n_h n_e}{n_{X_0}} = \frac{g_e g_h}{g_X} \frac{m_h m_e}{M_X} \frac{K_B T}{2\pi\hbar^2} \exp\left(\frac{-E_{BX}}{K_B T}\right) = \frac{K_X^{ion}}{K_X^F} \quad (S7)$$

Here, g_e , g_h , and g_{X_0} are the degeneracy factors of electron, hole, and exciton in the nondegenerate regime, where our measurements take place and where Boltzmann statistics applies. K_X^{ion} is the ionization rate of an exciton to an unbound e-h and K_X^F is the formation rate of an exciton from an unbound e-h pair. Since the exponential term in Eq. 1 decays rapidly to zero due to the large value of exciton binding energy ($E_{BX} \sim 200$ meV). Hence K_X^{ion} goes to zero and K_X^F is high, and results in sub time resolution (detection system) formation of excitons. Therefore we can safely neglect (for the temperature we are interested, 4K) the generation of the free electrons and holes from excitons and we assume a direct generation of excitons under optical excitation.

C Impact of the dark-bright fine structure in the trion model

Fine structure:

Owing to the strong confinement in nanoplatelets the splittings between the lowest dark and next bright exciton level is a few meV, so that at low temperatures of a few Kelvin the nanocrystals emission is contributed by the two lowest energy levels only. In fact, in CdSe NPLs, the exciton ground state is a dark state with angular momentum projection ± 2 on the quantization axis, it is separated by a few meV from the first excited bright exciton state with angular momentum projection ± 1 . Bright excitons can relax to the dark state by spin-flip of either the electron or the hole. This process is assisted by emission or absorption of acoustic phonons.^{17,18,43–45} In order to take into account the effect of an exciton dark state on the dynamics of the exciton and trion we include the exciton scattering between bright and dark states. We use a series of coupled rate equations for a four-level system describing each of the bright and dark excitons as well as the trion, as illustrated in Fig. S6b. We consider multiple relaxation channels including population relaxation (Γ_i^r , $i=XB, XD, X^-$), scattering between bright states and long-lived dark

states (Γ_{BD} and Γ_{DB}), as well as exciton-trion population transfer ($K_{X^-}^{ion}$ and $K_{X^-}^F$). These processes are captured by the following expressions

$$\begin{aligned}
\frac{dn_{XB}}{dt} &= G(t) - n_{XB} \left(\Gamma_{XB}^r + \Gamma_{XB}^{nr} \right) - n_{XB} n_e K_{X^-}^F + n_{X^-} K_{X^-}^{ion} n_{ph} \\
&\quad - \Gamma_{BD} n_{XB} + \Gamma_{DB} n_{XD} \\
\frac{dn_{XD}}{dt} &= -n_{XD} \Gamma_{XD}^r + \Gamma_{BD} n_{XB} - \Gamma_{DB} n_{XD} \\
\frac{dn_{X^-}}{dt} &= -n_{X^-} \left(\Gamma_{X^-}^r + \Gamma_{X^-}^{nr} \right) - n_{X^-} K_{X^-}^{ion} n_{ph} + n_{XB} n_e K_{X^-}^F \\
\frac{dn_e}{dt} &= n_{X^-} K_{X^-}^{ion} n_{ph} - n_{XB} n_e K_{X^-}^F,
\end{aligned} \tag{S8}$$

where n_{XB} and n_{XD} correspond to the optically bright and dark state populations, characterized by their radiative rates Γ_{XB}^r and Γ_{XD}^r . The conversion rate from the bright to dark state and from the dark to the bright state is given by: $\Gamma_{BD} = \gamma_{BD}^0 (n_{\delta E_{BD}} + 1)$ and $\Gamma_{DB} = \gamma_{BD}^0 n_{\delta E_{BD}}$, where γ_0 is the zero temperature relaxation rate, which refers to the spin flip rate and $n_{\delta} = \frac{1}{e^{(\delta E_{BD}/K_B T)} - 1}$ is the Bose Einstein phonon occupation, $\delta E_{BD} \sim 5 \text{ meV}$ is the bright dark energy splitting.¹⁸ We use additional data on the dark-bright splitting from Ref. 18 for the following modeling.

To study the role of the dark exciton ground state (XD) on the bright exciton (XB) and trion X^- decay kinetics we plot in Fig. S6 (a) the normalized population (or PL emission) of the trion state calculated numerically by solving the above rate equation for fixed values of $\Gamma_{XB} = 34.5 \text{ ns}^{-1}$, $\Gamma_{XD} = 0.0396 \text{ ns}^{-1}$,¹⁸ $\Gamma_{X^-} = 3.0 \text{ ns}^{-1}$, $\gamma_{X^-}^0 = 95.5 \text{ ns}^{-1}$ and different values of scattering rate γ_{BD}^0 for a $30 \times 10 \text{ nm}^2$ (300 nm^2) platelet. We can clearly notice that with increasing γ_{BD}^0 from 35 ns^{-1} to 95 ns^{-1} , the trion decay becomes slightly faster, since the dynamics of the exciton and trion are interconnected. The presence of a dark state influences the trion kinetics slightly as seen in a comparison of the with and

Table S2: Resulting parameters utilized for modeling the exciton and trion dynamics in Figure S6.

	$\Gamma_{XB}^r [\text{ns}^{-1}]$	$\Gamma_{XD}^r [\text{ns}^{-1}]$	$\Gamma_{X^-}^r [\text{ns}^{-1}]$	$\gamma_{X^-}^0 [\text{ns}^{-1}]$	$\gamma_{BD}^0 [\text{ns}^{-1}]$
$30 \times 10 \text{ nm}^2$	15	0.0396 ¹⁸	1.25	95.5	35 ¹⁸

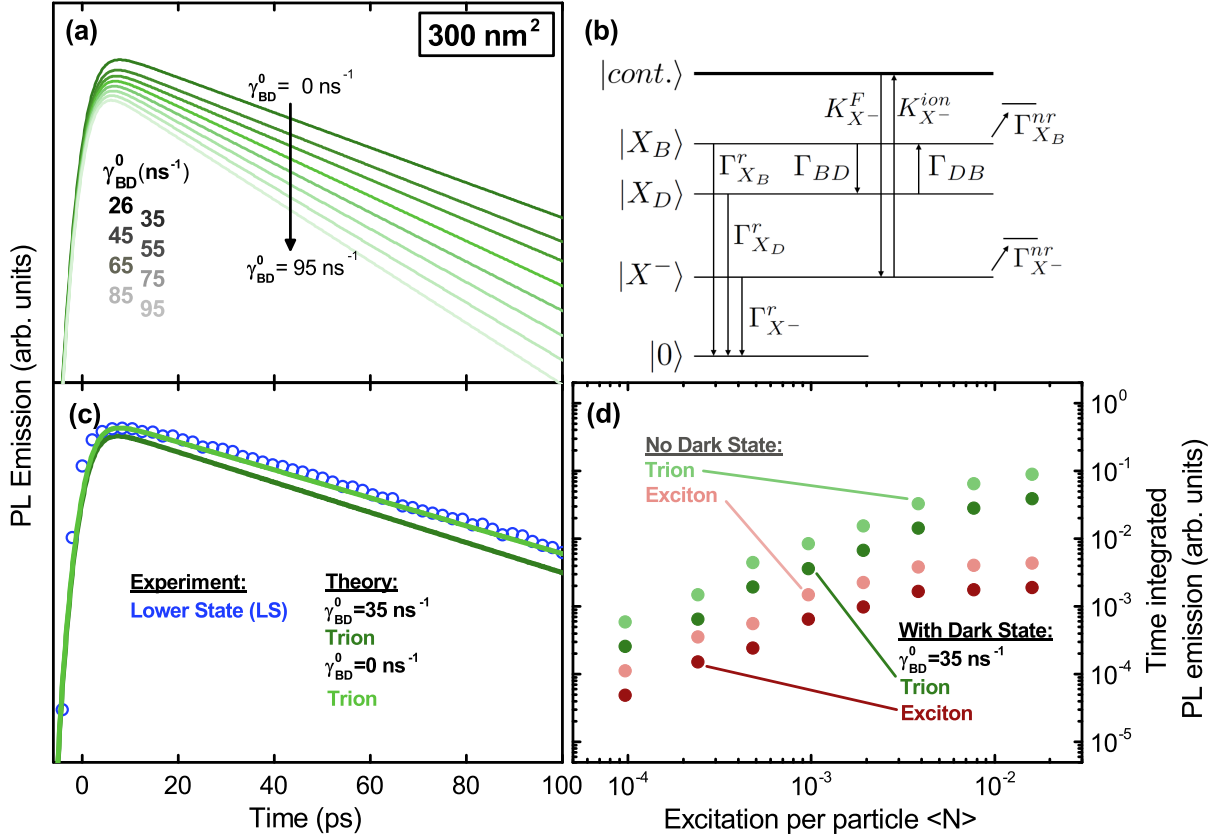


Figure S6: Impact of dark-bright splitting on the kinetics of 4.5 ML CdSe NPLs with $30 \times 10 \text{ nm}^2$ (300 nm^2) lateral size and for fixed value of $\Gamma_{X_B}^r = 15 \text{ ns}^{-1}$, $\Gamma_{X^-}^r = 1.25 \text{ ns}^{-1}$, $\Gamma_{X_D}^r = 0.0396 \text{ ns}^{-1}$ and $\gamma_{X^-}^0 = 95.5 \text{ ns}^{-1}$ and different values of the scattering rate γ_{BD}^0 . Modeling by the dark-bright rate equation system. a) Trion emission modelling with parameters in Table S2. b) Level scheme. c) Decay dynamics of the lower state for different γ_{BD}^0 in comparison to experimental transient PL of the lower state with $\gamma_{DB}^0 = 35 \text{ ns}^{-1}$ and without scattering into the dark state $\gamma_{DB}^0 = 0 \text{ ns}^{-1}$. d) Resultant power dependence (as a function of the average number of excitations per platelet) of time-integrated PL emission with ($\gamma_{DB}^0 = 35 \text{ ns}^{-1}$) and without the dark state ($\gamma_{DB}^0 = 0 \text{ ns}^{-1}$).

without dark (exciton) state (see Figure S6 c) as well as the experimental transient. For a typical $\gamma_0 = 35 \text{ ns}^{-1}$,¹⁸ we fit our parameters to reproduce the experimental results (c) and find that as compared to the case without dark state the radiative decay rates of the exciton and trion decrease not dramatically, from 34.5 ns^{-1} to 15 ns^{-1} , and from 3.0 ns^{-1} to 1.25 ns^{-1} (Table S2), while the behavior of the total emission of e.g. the trion and exciton is not strongly altered and the emission does not decrease dramatically (d). We clearly notice that the trion to exciton ratio is constant in both cases ($\Gamma_{X^-}/\Gamma_{X_B} = 0.08$). Hence it is clearly shown, that introducing a dark state will not have a strong impact on the behavior of the integrated PL measurements.

S4 ALTERNATIVE LO-PHONON REPLICA, EXCIMER, BIEXCITON AND S- AND P-EXCITON HYPOTHESES

In this section, we will argue, that alternative scenarios for the double emission (as listed above), ii) exciton plus a LO phonon replica,¹⁹ iii) charge transfer excitons (excimers)¹⁶ between at least two platelets, iv) an exciton plus biexciton,²⁴ v) excited and ground state excitons²⁰ and an excitonic center of mass fine structure¹⁰ can be ruled out based on experimental time-resolved, time-integrated and power-dependent data. For this we use the comprehensive dataset presented in section S3 of this supporting information and Figure 1 of the main text. These data represent a comprehensive dataset of these measurements at 4 K in the following.

i) Trion plus exciton – See section S3

ii) LO-phonon replica

Here the double emission is assumed to stem from a zero-phonon peak and its first LO phonon replica. In Ref. 19, Tessier et al. have observed a double emission line with 25 meV energy spacing and as it nearly matches the LO phonon energy in CdSe nanoplatelets,⁴⁶ they concluded that the red-shifted emission line is LO-phonon replica related. In Figures 1 (main text) and S2, we plot the time-integrated PL emission of the investigated 4.5 monolayer (ML) CdSe NPLs for different lateral platelets size at 4 K. In line with recent results,^{16–21} the energy spacing strongly depends on the lateral platelet size, and varies from 38 to 18 meV by a factor of ~ 2 with increasing lateral platelet size from $8.6 \times 3.6 \text{ nm}^2$ (29 nm^2) to $41 \times 13 \text{ nm}^2$ (533 nm^2). Using Raman measurements it has been shown that all in-and out-of-plane LO-phonon modes have energies between 22-25 meV.^{46,47} Hence, we can exclude that this energy spacing is related to a zero-phonon peak and its first LO phonon replica. This is in line with Diroll et al.,¹⁶ who demonstrated that the energy spacing does not correlate with the Raman determined

LO-phonon energy for platelet thickness variation. Also the time resolved data presented in Figure S4 contradict the LO replica, as the dynamics of both states is strongly dissimilar.

iii) Excimers

We exclude the formation of excimers (excitons delocalized over two platelets, stacking atop each other) plus neutral exciton emission (for the upper emission) as the reason for the double emission, as presented by Diroll et al.,¹⁶ since the conditions are different. Our sample platelets are embedded very dilute and isolated in a host polymer, as demonstrated in Ref. 14. Hence we do not have stacking and the related excimer formation can not occur. This is in contrast to Diroll et al., where concentrated solutions have been investigated, leading to predominant stacking. Another point relates to the strongly extended nature of charge transfer (CT) excitons. We calculated the e-h envelope function overlap integrals and related radiative rates (not shown here.) They are considerably lower for a CT exciton than for an exciton in one nanoplatelet due to the large inter platelet spacing of ~ 4 nm (given by the ligand length). Hence, a charge transfer state spanning two platelets would result in much slower relaxation, that is not observed experimentally.²⁰

iv) Exciton plus biexciton

Among the considered options for the (LS) state is the biexciton.^{24,48} Using again coupled rate equations to describe the dynamics of exciton and biexciton levels including the Saha equation and fitting the observed PL decay with that model, we can fit the PL dynamics reasonably. However, the excitation density dependence obtained from the modeling of the transients in Figure S7 shows a near quadratic increase for the biexciton, while a near linear for the exciton, in contrast to the experimental results in Figure S5. At high densities the experimental curves (Figure S5) tend to saturate, while the biexciton model shows no saturation as shown here below. A further argument against biexcitons is the

low excitation density $\langle N \rangle < 3 \cdot 10^{-4}$ at which the transient PL is recorded, as Poisson statistics results in a negligible probability for absorption of two photons within one laser pulse. We thus exclude that the lower energy (LS) state is related to biexciton emission.

In depth discussion: We use coupled rate equations, taking three levels into consideration (see sketch above Figure S7: The crystal ground state $|0\rangle$, the exciton $|X\rangle$, and the biexciton $|XX\rangle$, as well as the non-resonant generation rate $G(t)$ of excitons, assuming sub time-resolution population transfer (cooling)⁴⁹ to the exciton level. The populations $n_X(t)$ and $n_{XX}(t)$ are given by the coupled rate equations:

$$\begin{aligned}\frac{dn_X}{dt} &= G(t) - n_X \left(\Gamma_X^r + \Gamma_X^{nr} \right) - 2n_X^2 K_{XX}^F + 2n_{XX} K_{XX}^{dis} + n_{XX} \Gamma_{XX}^r \\ \frac{dn_{XX}}{dt} &= -n_{XX} \Gamma_{XX}^r - n_{XX} K_{XX}^{dis} + n_X^2 K_{XX}^F\end{aligned}\tag{S9}$$

with Γ_{XX}^r the biexciton decay rate, $K_{XX}^{dis} = \gamma_0^{XX} n_\Delta$ the dissociation rate of the biexciton, where γ_0^{XX} between both states. The biexciton K_{XX}^F formation rate is given by $F(T) = K_{XX}^{dis}/K_{XX}^F$, with the equilibrium constant $F(T)$ obtained by the mass action law between excitons and biexcitons.⁵⁰

$$\frac{n_{X0}^2}{n_{XX}} = \frac{g_X^2}{g_{XX}} \frac{M_X^2}{M_{XX}} \frac{k_B T}{2\pi\hbar^2} e^{\frac{-\Delta_{XX}}{k_B T}} = F(T)\tag{S10}$$

Δ_{XX} is the biexciton binding energy, the energy difference of both states. As we have seen in Figure S2 the energy spacing decreases with increasing lateral size. g_{XX} is the degeneracy factor of the Biexciton, $M_{XX} = 2M_X$ the biexciton mass.

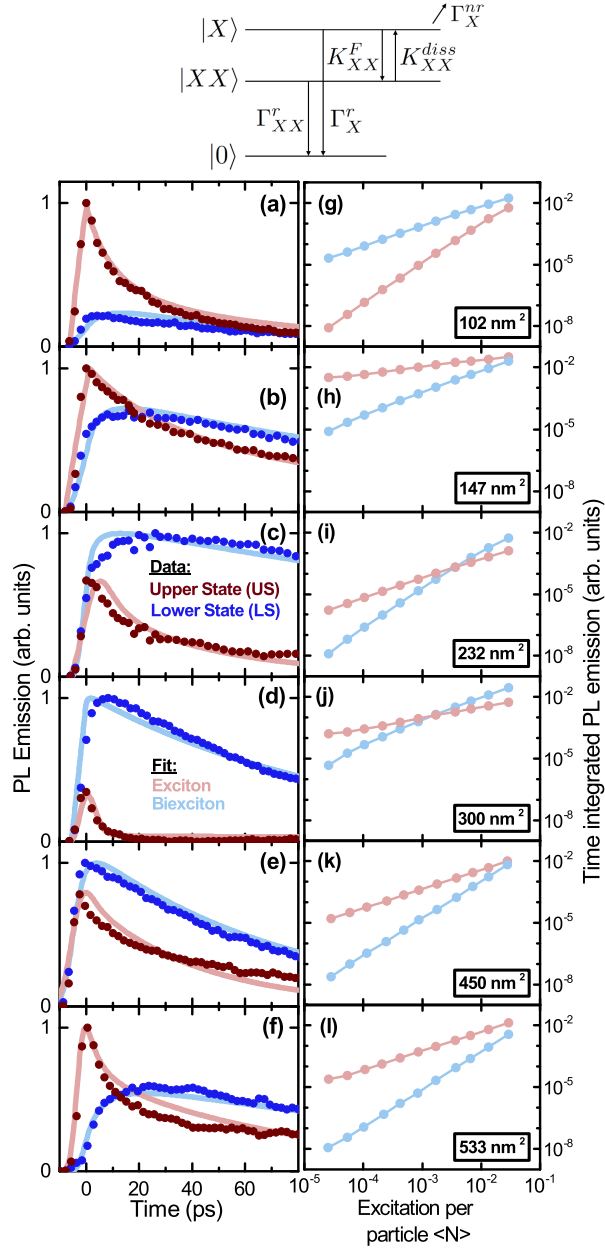


Figure S7: a-f) Time-resolved PL dynamics of the exciton (blue line) and biexciton (pink line) at 4K for different size of CdSe nanoplatelets (from $17 \times 6 \text{ nm}^2$ to $41 \times 13 \text{ nm}^2$) calculated by numerically solving the rate equation (eq. S9) and the parameters displayed in table S3. Experimental data as in Figure S4 with average excitation $\langle N \rangle < 3 \cdot 10^{-4}$ per platelet. LS (blue line), US (dark red line) refer to the experimental data. Above: Energy level scheme used for our rate equation model (eq. S9). (g-l) Time integrated luminescence of the exciton and biexciton as a function of the average number of excitations per platelet $\langle N \rangle$ for g) $17 \times 6 \text{ nm}^2$ and h) $21 \times 7 \text{ nm}^2$ i) $29 \times 8 \text{ nm}^2$, j) $30 \times 10 \text{ nm}^2$, k) $30 \times 15 \text{ nm}^2$, l) $41 \times 13 \text{ nm}^2$ lateral dimensions, modeled by eq. S9.

The rate equations describe the generation of the exciton, the decays of the exciton and biexciton as well as interconversion between them. For the excitonic level three processes increasing its occupation are possible: Direct generation of the exciton via optical

Table S3: The fitting parameters utilized in the biexciton rate equation model (Eq. S9) for nanoplatelets of different size.

Size (nm ²)	17 × 6	21 × 7	29 × 8	30 × 10	30 × 15	41 × 13
Area (nm ²)	102	147	232	300	450	533
$\Gamma_X^r(ns^{-1})$	18	27.2	50.2	60	76	91
$\Gamma_{XX}^r(ns^{-1})$	7.6	11	18	24	38	46
$\gamma_0^{XX}(ns^{-1})$	35	68	118	120.5	130	138

excitation, recombination or dissociation of a biexciton (see scheme in Figure S7). On the other hand, the exciton recombination and the biexciton formation are depopulating this level. For the biexciton only its formation rate populates this level. The possibility of a direct biexciton creation from the system ground state is not taken into account due to the very low probability of such a two photon absorption process according to poissonian statistics given the low average number $\langle N \rangle < 3 \cdot 10^{-4}$ of absorbed photons per platelet and pulse.

There are two crucial parameters of the rate equation model—the relative biexciton to exciton radiative rate ratio (Γ_{XX}^r/Γ_X^r) and the zero temperature scattering rate between exciton and biexciton state γ_{XX}^0 , which is typically considered higher than the biexciton and trion rates ($\gamma_{XX}^X \gg \Gamma_X^r, \Gamma_{XX}^r$). Table S1 reports the numerical fit results for them. Again vanishing non-radiative rates are found at 4 K as discussed in the main text. We can see a clear monotonic rise in recombination rate versus lateral size, while the ratio of biexciton decay rate to the exciton Γ_{XX}^r/Γ_X^r stays nearly constant. Table S3 and Figure S7 show the size dependence of the decay rate and the impact of the Γ_{XX}^r/Γ_X^r ratio on the shape of the theoretical curves. Although there is agreement with the fitted time-resolved data in Figure S7, the fit results in table S3 result in strongly different power dependencies (Figure S7.(g-l)) as compared to the experiments in Figure S5. In the low-density limit (in which the transients are recorded), the biexciton intensity increases superlinearly, while a linear growth of both emission intensities is observed in experiments. At high densities the experimental curves (Figure S5) tend to saturate, while the biexciton model shows no saturation. A further argument against biexcitons is the low excitation density $\langle N \rangle < 3 \cdot 10^{-4}$ as Poisson statistics results in a negligible probability for absorption of

two photons within one laser pulse. We thus exclude that the lower energy (LS) state is related to biexciton emission.

Further details on the biexciton state: A biexciton is a bound state of two electrons and two holes. It is often described approximately as a bound state of two excitons, where the interaction between the excitons is treated as a perturbation. This approximation is justified if the binding energy of the biexciton (the energy difference between the two free excitons and the Biexciton) is much smaller than that of the exciton. If this is the case, the relaxation process of the biexciton reflects various features of exciton relaxation. Radiative decay of the biexciton is then described as an annihilation of one of the two excitons in it. It is very efficient because the annihilation can occur at any unit cell within the large wave function extent of the biexciton. This is called the giant oscillator-strength effect. Phonons are supposed to interact with a biexciton as if they interact with two excitons in this perturbational treatment, where the change in the internal motion of the biexciton by lattice deformation, etc., is neglected. Actually, since the CdSe NPLs are characterized by high exciton binding energies (of 200 meV), we can safely assume in our rate equation (Eq. S9) that the biexciton is formed by two interacting excitons.³¹

v) Excited and ground state excitons

In the next part we test the double emission attribution to the S- and P-type ground and excited state exciton emission only.²⁰ Recently, Richter⁹ and Specht et al.¹⁰ showed that there can exist a substructure of exciton states. S-like ground and and P-like excited exciton states (scheme above Figure S8) are now included in the rate equations.

The model fits the experimental transients (Figure S8 (a-f)) reasonably well and there is i) a faster excited state (higher rates) as compared to the ground state and ii) an LO phonon bottleneck between US and LS state, resulting in the highest γ_0 for the 29x8 nm² (232 nm²) platelet like in the other models. Further increasing radiative rates with increasing lateral platelet size are obtained, in line with a GOST effect.³³ Figure S8 (g-l) displays the resultant time integrated PL intensity ($I_{X,S}$, $I_{X,P}$) as a function of $\langle N \rangle$ from the model. It deviates at higher densities considerably from the experimental power de-

dependencies in Figure S5. As shown Figure S8 (g-l) both S - and P -exciton lines display a linear dependence, while a saturation behavior is observed in experiments, ruling out the model due to the higher density behavior. In contrast, the trion model is capable of reproducing the experimental data very well, especially the saturation, based on a finite background density of charges for trion formation. Hence, an excitonic fine structure alone can be excluded to be the reason for the observed double emission. A trion based lower state emission and exciton upper emission however can explain all discussed observations. However, based on Ref. 10, the exciton state has a substructure due to weak lateral center of mass quantization in the nanoplatelets, which is not resolved in experiments due to inhomogeneous broadening (lateral size dispersion) and finite line width.

In depth discussion: S-like ground and and P-like excited exciton states (scheme above Figure S8) are now included in the rate equations:

$$\begin{aligned}\frac{dn_{X,P}}{dt} &= G(t) - n_{X,P}(\Gamma_{X,P}^r + \Gamma_{X,P}^{nr}) - n_{X,P}\gamma_0(n_\Delta + 1) + \\ &\quad + \gamma_0 n_\Delta n_{X,S} \\ \frac{dn_{X,S}}{dt} &= -n_{X,S}(\Gamma_{X,S}^r + \Gamma_{X,S}^{nr}) - \gamma_0 n_\Delta n_{X,S} + n_{X,S}\gamma_0(n_\Delta + 1)\end{aligned}\quad (\text{S11})$$

Here $n_{X,P/X,S}$ is the density of P- and S-excitons with radiative rate $\Gamma_{X,P/X,S}^r$ and $\Gamma_{X,P/X,S}^{nr}$, respectively, for non-radiative rates, defined near Eq. S5. This rate vanishes at 4 K analogously to the discussion there. $\gamma_0 n_\Delta$ the thermally activated ($X_S \rightarrow X_P$) and $\gamma_0(n_\Delta + 1)$ the ($X_P \rightarrow X_S$) scattering and relaxation rates. γ_0 is the zero temperature scattering rate between X_P and X_S . n_Δ is the Bose-Einstein statistics factor for LO-phonon mediated scattering between LS and US. Table S4 shows the obtained model fit parameters from the transients in Figure S8 (a-f).

The model fits the experimental transients (Figure S8(a-f)) reasonably well and there is i) a faster excited state (higher rates) as compared to the ground state, ii) an LO phonon bottleneck between US and LS state, resulting in the highest γ_0 for the 29x8 nm² (232 nm²)

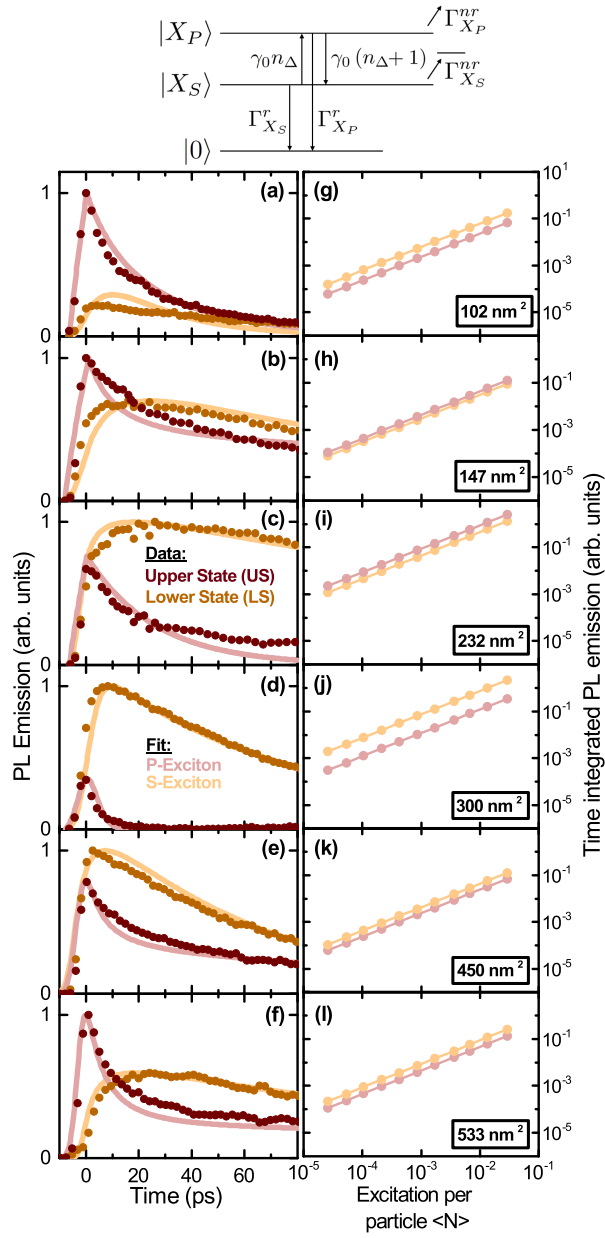


Figure S8: (a-f) Time-resolved PL dynamics at 4 K and fits of the S-exciton and P-exciton state model for varying lateral size. Experimental data as in Figure S4. Sketch: Energy level scheme used. (g-l) Time integrated luminescence of the exciton and biexciton as a function of the average number of excitations per platelet $\langle N \rangle$ for g) $17 \times 6 \text{ nm}^2$ and h) $21 \times 7 \text{ nm}^2$ i) $29 \times 8 \text{ nm}^2$, j) $30 \times 10 \text{ nm}^2$, k) $30 \times 15 \text{ nm}^2$, l) $41 \times 13 \text{ nm}^2$ lateral dimensions, as obtained from modeling by eq. S11.

platelet like in the other models. Further increasing radiative rates with increasing lateral platelet size are obtained, in line with a GOST effect.³³ Figure S8 (g-l) displays the resultant time integrated PL intensity ($I_{X,S}$, $I_{X,P}$) from the model.

On the other hand the calculated integrated PL intensities for the S- and P-state as a function of $\langle N \rangle$ deviate at high densities considerably from the experimental power

Table S4: Fit parameters obtained from the S- and P-exciton model.

Size (nm ²)	17×6	21×7	29×8	30×10	30×15	41×13
Area (nm ²)	102	147	232	300	450	533
$\Gamma_{XP}^r(ns^{-1})$	6.7	13	20	40.3	47.5	58
$\Gamma_{XS}^r(ns^{-1})$	2.5	3.4	5.7	7.8	9.5	13
$\gamma_0(ns^{-1})$	47	76	105	89	58	29

dependencies in Figure S5. As shown Figure S8 (g-l) both lines display a linear dependence while a saturation behavior is observed in experiments. Further, while at low densities the time-integrated intensity ratio of both emissions is constant (Figure S5), at elevated intensities the time-integrated intensity ratio changes strongly in experiments, whereas the model fit (Figure S8) predicts intensities still following parallel lines in logarithmic representation. State filling can also not account for the experimentally observed saturation, as at the densities are far below one excitation per platelet.

In contrast, the trion model is capable of reproducing the experimental data very well, especially the saturation, based on a finite background density of charges for trion formation. Hence, an excitonic fine structure alone can be excluded to be the reason for the observed double emission. A trion based lower state emission and exciton upper emission however can explain all discussed observations. However, based on Ref. 10, the exciton state has a substructure due to weak lateral center of mass quantization in the nanoplatelets, which is not resolved in experiments due to inhomogeneous broadening (lateral size dispersion) and finite line width.

S5 COMPARISON OF THE PLATELET RESULTS WITH LITERATURE

We remark, that as shown in the Supporting Materials section S4, alternative explanations (exciton plus LO-phonon replica, excimer, biexciton, S- and P-excitons) for the double emission can be ruled out based on time-resolved, time-integrated and pump-

power dependent data. The exciton plus trion emission and our presented modeling in contrast is consistent with all present experimental observations from this paper:

- 1) The energy spacing of the two states; we showed by theoretical calculations, that it corresponds to the trion binding energy (18-36 meV).
- 2) The temporal PL dynamics of the double emission.
- 3) A linear increase of the oscillator strength of both exciton and trion emission with size, observed in experiments, is explained by our theory.
- 4) A low oscillator strength and radiative rate of the lower, trion emission, all in good agreement with theory and explained by weaker localization of the third carrier, as compared to the exciton. This allows to observe energetically higher lying exciton emission due to a bottleneck and much higher oscillator strength of the exciton. This sets the platelets apart from e.g. stronger confined quantum dots, where the trion to exciton oscillator strength ratio is closer to unity (compare trend in Figure 2h, main text) and lowest state emission is observed only.
- 5) The existence of an LO-phonon bottleneck between the states and resultant resonance effects of the transition rate with varying platelet size.
- 6) Saturation effects in the power dependence of the two emissions based on Saha equilibria and a finite background charge density.

The presented trion plus exciton model for CdSe nanoplatelets is also compatible with reported findings in literature:

- i) The low energy transition (trion) is weak or indiscernible in low temperature absorption, as the trion transition oscillator strength is much lower (by more than an order of magnitude) than for the exciton. (See also Figure 2 and Table 1 of the main text.) Arguments for that can be found in the low temperature absorption in Ref. 18, where indications for a weak low energy shoulder are observed. Although the thickness of that sample is 1 ML more, the ratio of the area under curve of the two peaks (trion by exciton) is below 0.1, in line with the predictions of our model (0.07 for 4.5 ML). A further argument relates to the trion formation process: The matrix element for the application of

Fermi's Golden Rule is different for direct photo-creation of a trion by an above bandgap excitation (e-h pair) in presence of an excess electron as compared to photon absorption by exciton generation and subsequent trion formation. The latter is the more probable process as in the resonant case the exciton oscillator strength is higher and in a non resonant excitation, like in our case, coulomb correlation to an exciton is fast, since it is a second order process, as compared to a third order process for direct trion formation from three carriers. Therefore, in absorption, exciton absorption dominates (reasoned also by the presented calculations, showing considerably lower oscillator strength of trions), while in emission both excitons and subsequently formed trions decay radiatively.

ii) The (nearly) vanishing degree of circular polarization of the lower state (trion) emission in magnetic fields¹⁸ up to 10 T²² and the related g-factors.²⁶ In Ref. 18 and 22 Shornikova et al. demonstrated using an external magnetic field that the alteration of the recombination dynamics is very different for the two emission bands. While the PL decay of the exciton line is strongly affected by a magnetic field, no magnetic field effect is found for the dynamics of the low-energy line, a behavior typical for trions in colloidal nanocrystals.^{51,52} They interpret this as an indication of trions with a bright ground state.

iii) The existence of electron shakeup lines in single platelet emission spectra clearly supports the negative trion attribution.²⁵

iv) Biadala et al.¹⁷ have recently calculated a lower radiative exciton recombination rate (as compared to Table 1 of the main text) and explained it with the existence of a dark (forbidden) exciton ground state split by a few meV from the higher bright exciton state. However their model does not take the presence of a lower trion state with low oscillator strength into account, so that lower values are not unexpected. In our study the ratio Γ_{X-}^r/Γ_X^r can get slightly larger in the presence of a lowest dark excitonic state, however it will not have relevant impact on our integrated PL measurements, especially not on our parameter ranges. This is tested with respect to the dynamic behavior of trion and exciton in section S3 C.

v) Cobaltocene (electron donor) treatment of nanoplatelets results in a reduction of PL

intensity with donor concentration (Ref. 16). This may be explained by the increasing trion formation probability and their lower oscillator strength, resulting in decreased QY.

vi) An increase of the trion to exciton oscillator strength ratio with hydrostatic pressure can be explained by a different change of the screening of exciton and trion due to alteration of the dielectric surrounding once the ligands are compressed (higher epsilon), see also Figure 3 (main text). The observed increase of the energy spacing with pressure, can be interpreted as the result of a negative hydrostatic deformation potential constant⁵³ in addition to a well width shrinkage changing the confinement of exciton and trion differently.

vii) The increase of the trion emission with increasing stacking, as observed in concentrated solutions in literature (Ref. 16), can be explained by efficient Förster Resonant Energy Transfer in nanoplatelets,⁵⁴ increasing with the stack column length. In a stack of increasing length the excitonic excitations can hop¹⁵ to a charged platelet, acting as an effective excitation sink, as it provides a lower energy (trion) state for the population. The FRET probability for excitons is high due to the high oscillator strength and co-planar orientation of donor and emitter dipoles,⁷ so that excitonic excitation hops efficiently from platelet to platelet in a stack. Trions in contrast have lower oscillator strength (as discussed above) and can couple only (weakly) to other trion states in platelets beneath, but totally not to exciton states there because of the energetic resonance condition for Förster transitions. There is an energy mismatch. Therefore the excitation gets localized to the platelet, which contained the free electron before the exciton was transferred to it. This exciton to trion population transfer and subsequent trion localization due to a high tunneling barrier by imposed by the ligands between platelets produces enhanced trion emission as compared to exciton emission, so that the trion to exciton emission ratio increases with aggregation and stacking.

viii) We also remark, that the trion as lowest state is also compatible with the existence of long lived trap states,⁵⁵ as e.g. a trion is strongly polarizable by ambient, fluctuating charges in the dielectric surrounding (organic shell), further decreasing its oscillator strength temporarily or producing some metastable dark or grey state. As trions are po-

larizable and composite charge carriers, they produce both real and imaginary response in a optical pump-THz probe experiment, so that on long timescales, when the exciton population has decayed, real and imaginary part of the induced transient absorption decay similarly (See Ref. 56).

viii) A last argument for a trion origin of the low energy emission comes from recent findings that better passivation of the platelets leads to a reduction of the trapped background electrons and lower trion emission.⁵⁷ The results are also in line with electron donor addition experiments, showing reduced (total) PL emission with increasing donor concentration,¹⁶ as the the trion oscillator strength is lower than the exciton oscillator strength and hence for that room temperature experiment the ratio of radiative to non-radiative recombination is worse.

However, some observations may look contradictory to the exciton plus trion origin of the double emission and the observed properties at first glance, but are not: ix) It may be argued against trion formation that: Trions have low binding energies,^{58,59} smaller than the ΔE range observed. However Califano et al.⁶⁰ report binding energies of 30-50 meV for strong confined CdSe quantum dots, while for larger dots lower values of ~ 15 meV have been observed. Hence the values for our strongly z-confined nanoplatelets are not unexpected. As seen in the main text, the trion binding energy from our calculations are in-line with our experiments (See also Figure 2 main text).

x) The trion lifetime should be shorter than the exciton lifetime.^{16,61} As we prove in Figure 2 (main text), the latter is not necessarily correct for different lateral platelet sizes, as the oscillator strength ratio varies with lateral size.

Hence we can state that the trion plus exciton state model is consistent with all these eventualities and present data.

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