Supporting Information for

Optical Probing of Crystal Lattice Configurations in Single CsPbBr₃ Nanoplatelets

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I. Experimental Methods

Chemicals. Cesium carbonate (Cs₂CO₃, 99.9 %), oleic acid (OA, 90 %), 1-octadecene (ODE, 90 %) and mesitylene (97 %) were purchased from Sigma Aldrich. Lead bromide (PbBr₂, 98 %) was purchased from ABCR. Oleylamine (OlAm, 80-90 %) was purchased from Acros Organics.

Nanoplatelet Synthesis. CsPbBr₃ nanoplatelets were prepared according to a recently published protocol.¹ Prior to the synthesis, the 0.1 M Cs(OA) was prepared. 408 mg of Cs₂CO₃, 1.25 mL of OA and 20 mL of ODE were loaded in a 50 mL three-neck flask and dried at 120 °C under vacuum until the solution stopped bubbling/reacting (~ 1-2 h). The Cs(OA) solution, solid at room temperature, was heated (~ 100 °C) prior to use.

For the synthesis of the CsPbBr₃ nanoplatelets, 138 mg of PbBr₂, 1 mL OA, 1 mL OlAm and 5 mL mesitylene were loaded in a 25 mL three-neck flask under inert atmosphere. The flask was then connected to a Schlenk line and the temperature was increased to 120 °C while vigorously stirring with the aid of a stirring bar. When the temperature reached 120 °C, 0.8 mL of the 0.1 M Cs(OA) solution was swiftly injected into the flask. Immediately after, the flask was plunged into an ice/water bath to quench the reaction. The crude solution was separated in 8 Eppendorf tubes (2.5 mL) and it was purified by centrifugation for 3 min at 5000 g; the precipitate was collected and redispersed in 1 mL toluene (per each vial), while the supernatant was discarded. The solution of nanoplatelets was centrifuged again for 10 min at 13400 g; this time the supernatant was collected while the precipitate was discarded. The supernatant, filtered with a 0.2 µm PTFE filter, constituted the final product.

Transmission Electron Microscopy (TEM). The NPL dispersion was diluted ten times, dropcast on a carbon/polymer-coated Cu TEM grid and let dry, leading to primarily basal agglomeration of the NPLs.² Images were recorded with a JEM-1400 Plus JEOL at 120 kV.

Preparation of Single Nanoplatelet Samples. CsPbBr₃ nanoplatelets in toluene were diluted to a concentration of ~ $3.5 \,\mu$ g/ml in nitrogen atmosphere. For dilution, anhydrous toluene (Sigma Aldrich) was used to avoid exposure of the nanoplatelets to humidity. Toluene was saturated with PbBr₂ before dilution to suppress dissolving and damaging of the nanoplatelets.³ Si substrates (6x6 mm) were prepared with location-tagged Ti/Au cross markers and cleaned. 25 μ L of the dispersion were spincoated on each substrate in a two-step process (1000 rpm and 2000 rpm for 1 min each) to prevent agglomeration of the diluted NPLs during slow drying by toluene evaporation.²

Quantum Yield (QY). Absolute QY of perovskite nanoplatelets solution was measured with a Quantaurus-QY Absolute PL quantum yield spectrometer from Hamamatsu.

Optical Characterization. Absorption spectra were recorded in a Shimadzu UV2550 double-beam spectrometer using an integrating sphere in transmission geometry to reduce scattering. Photoluminescence spectra of dispersions were measured in a Horiba Fluorolog-3 spectrometer with 374 nm laser excitation.

Photoluminescence experiments on individual nanoplatelets were conducted using a home-built micro-photoluminescence setup. The Si substrates were mounted in an Oxford Microstat HiRes2 cryostat and cooled to liquid helium temperature (~ 4 K). The nanoplatelets were excited non-resonantly by a 405 nm PicoQuant LDH D-C-405 laser diode in continuous wave mode (degree of linear polarization ~ 30 %). The laser was focused with a Zeiss LD Plan-Neofluar 63x/0.75 microscope objective; typical excitation fluences were between 25–100 W/cm². The photoluminescence spectra were dispersed in a Horiba iHR550 monochromator (1800 g/mm) and recorded by a Horiba Spectrum One CCD camera. The optical resolution of the detection system was 32 pm (161 μ eV). For polarization-resolved measurements, a linear polarization analyzer was introduced into the detection beam path.

Magneto-photoluminescence experiments were conducted under the same excitation conditions in an attocube attoDRY 1000 cryostat equipped with a superconducting vector magnet for magnetic fields up to 5 T. In this work, magnetic fields were applied in Faraday geometry. Luminescence from the individual nanoplatelets was collected with the built-in microscope system, dispersed by a Horiba TRIAX550 monochromator (1800 g/mm) and recorded with a Horiba Symphony CCD camera. The spectral resolution of the system was 40 pm (202 μ eV).

All spectra were corrected by the instrument response functions of all devices in the detection beam path. The Jacobian Transformation was applied to transfer the photo-luminescence spectra into the energy space.

Further Techniques. Atomic force microscopy (AFM) was conducted using a Bruker Innova device in non-contact mode.

II. Supplementary Figures

Figure S1. Distribution of single nanoplatelets (NPLs) on the substrate and linewidths.
Figure S2. Temperature dependence of luminescence and absorption in CsPbBr₃ NPLs.
Figure S3. Particle-in-a-box approximation of transition energies in CsPbBr₃ NPLs.
Figure S4. Additional emission polarization data.

Figure S5. Determination of single NPL orientation from emission polarization patterns.

Figure S6. Influence of magnetic field strength on the linewidth of Case II NPL emission.

Figure S7. Influence of population statistics on the PL fine structure of CsPbBr₃ NPLs.



Figure SI. Distribution of single nanoplatelets (NPLs) on the substrate and linewidths. **a** Exemplary micro-photoluminescence intensity map of a single nanoplatelet sample prepared as described above showing the successful preparation of individual nanoplatelets on the substrate. Five NPLs can be identified in the scanned 20x20 μ m field with a mean distance of (5.7±2.8) μ m and emission wavelengths between 486 nm and 495 nm. **b** Full width at half maximum (FWHM) of all NPLs examined in this work. Colors are matched with Figure 2 of the main text. The statistic distribution of the data shown in **b** is displayed to the right of the panel.



Figure S2. Temperature dependence of luminescence and absorption in CsPbBr₃ NPLs. **a** Temperature-dependent PL spectra of an individual CsPbBr₃ NPL showing three emission lines at 7 K. The emission shows a clear blueshift and broadening with rising temperature. The fine structure can still be observed at 30 K. **b** Temperature-dependent absorption spectra of an ensemble of CsPbBr₃ NPLs. The sample was prepared by drop-casting a dispersion of the NPLs on a quartz substrate and drying at room temperature in N₂ atmosphere. The dominant excitonic absorption peak shows a similar blueshift with rising temperature as the single NPL luminescence in **a**. For both techniques an almost linear increase of the transition energy with rising temperature is observed with a slope of 0.28(0.29) meV/K. The determined temperature coefficient is larger than previously reported values for CsPbBr₃ (0.06 meV/K),⁴ and on the order of typical values for methylammonium lead iodide (MAPbI₃).⁵ While the observed temperature blueshift is unusual for classical semiconductors, it is well known for inorganic and hybrid perovskites.⁵



Figure S3. Particle-in-a-box approximation of transition energies in CsPbBr₃ NPLs. To correlate the NPL dimensions and emission energies presented in this work, we estimated the expected transition energy of the lowest energy state of CsPbBr₃ NPLs with different thicknesses by a three-dimensional particle-in-a-box model. A suitable formula for the approximation of the fundamental optical transition (n = 1) in orthorhombic nanocrystals was adapted from Mitchell *et al.*⁶ as

$$E_1(d_x, d_y, d_z) = E_{\text{bulk}} - E_{\text{bin}} + \frac{\hbar^2 \pi^2}{2 \cdot \mu^*} \cdot \left(\frac{1}{d_x^2} + \frac{1}{d_y^2} + \frac{1}{d_z^2}\right)$$
(1)

where E_{bulk} is the fundamental bandgap of the bulk material, E_{bin} is the exciton binding energy, $\mu^* = (m_e^{-1} + m_h^{-1})^{-1}$ is the reduced exciton mass and d_x , d_y , d_z are the edge lengths of the NPL in the x-, y-, and z-direction, respectively. For simplicity, we assume the basal edge lengths of the NPLs under study to be equal ($d_x = d_y$).

From TEM images (see Figure 1 a in the main text), the thickness of the NPLs was determined to range from 4 to 8 monolayers while the average basal edge length is 11.3 nm with a range of ~ 8–15 nm (~ 14–26 ML). $E_{\text{bulk}} = 2.342 \text{ eV}^{7,8}$ and $\mu^* = 0.126 \text{ m}_0^8$ have been determined for CsPbBr₃ in recent studies. The lattice constant of the NPLs is taken to be 0.58 nm.^{1,7} With these parameters, a corridor of expected transition energies for the NPLs examined in this study can be calculated if the exciton binding energy is known (shaded grey area).

In the strongly confined NPLs the exciton binding energy is significantly increased by quantum and dielectric confinement compared to the bulk value.^{9,10} For our data, a value of $E_{\text{bin}} \approx 120 \text{ meV}$ yields the best agreement between the model and the observed transitions energies of the NPLs (Figure 2 b of the main text). This value is in good agreement with previously reported exciton binding energies for CsPbBr₃ NPLs with a thickness of 6 monolayers.¹¹



Figure S4. NPL emission polarization statistics. a, b Photoluminescence spectra of individual CsPbBr₃ nanoplatelets at different angles of the polarization analyzer with respect to the optical table surface normal. Black circles are measured data, color-shaded areas are Lorentzian peak fits to the data and colored solid lines are the cumulative peak fitting results. c Zero-field fine structure splitting of all examined NPLs of Case II (green) and Case III (blue) defined as the energy difference between the highest (E_c) and lowest (E_a) energy emission peaks of each individual NPL. Each solid circle represents one NPL, the overlayed box plots indicate the median and first and third quartile, whiskers indicate minimum and maximum values of each type of NPL. d, e Polar plots of the extracted relative photoluminescence intensity of the spectra in **a**, **b**. Solid lines are fits to Malus's law. Colors are matched with the shaded areas in a, b. f Relative polarization orientation of the photoluminescence peaks of the individual NPLs. The polarization orientation of each peak was extracted by fitting the data to Malus's law. The polarization orientation angle of the lowest energy peak of each NPL (E_a) was assigned to zero on the relative polarization orientation axis. The naming and coloring scheme of the individual emission peaks uses the convention introduced in Figure 4 of the main text with indices representing the orthorhombic crystal axis assigned to the respective emission.



Figure S5. Determination of single NPL orientation from emission polarization patterns. In polarization-resolved photoluminescence measurements, Si substrates with individual CsPbBr₃ NPLs were mounted in the spatial yz_{lab}-plane of the laboratory (right). As the NPLs are lying flat on the substrate (see main text) their absolute orientation is determined solely by the rotation around the x_{lab} axis which coincides with the luminescence observation direction, indicated by the angle θ with respect to z_{lab} (i.e., the table normal). In the detection path, a linear polarization analyzer is inserted and aligned in the yzlab-plane (center). The NPL emission polarization is probed by rotating the transmission axis of the analyzer around the x_{lab}-axis by an angle φ with respect to the table normal. The resulting angular distribution of the NPL emission intensity is visualized in polar plots (left). Due to the direct correlation between the CsPbBr₃ NPL triplet exciton emission and the orthorhombic crystal axes discussed in the main text, the orientation θ of the NPL on the substrate can directly be inferred from the polarization patterns. Here, this correlation is visualized for two exemplary datasets from Figure 3 of the main text. In the top scheme, the emission pattern of a NPL in the $T_{[010]}$ crystal configuration (main text, Figure 3 c/d) is shown. The polarization angle of the emission related to the corth crystal axis (red) is φ_{0101} = 50°. Due to the 45° alignment of the a_{orth} and c_{orth} crystal axes with respect to the NPL facets in the T_[010] configuration, the orientation of the NPL can be concluded to be $\theta_{0101} = 5^{\circ}$ with respect to z_{1ab} . In the bottom scheme, the polarization angle of the emission

related to the b_{orth} dipole of a NPL in T_[100] configuration (main text, Figure 3 e/f) is $\varphi_{[100]} = 20^\circ$. Due to the parallel alignment of the crystal b_{orth} axis and the NPL facets in this crystal configuration, the orientation of the NPL on the substrate can be determined as $\theta_{[100]} = 20^\circ$. Note that the observable polarization of the a_{orth} and b_{orth} emissions resembles the projections of the corresponding crystal axes on the observation plane (i.e., the yz_{lab} or NPL basal plane) as indicated by dashed blue and red arrows, respectively.

While the crystal configuration of a single CsPbBr₃ NPL can be identified by the photoluminescence spectra alone (i.e., the number of observable emission lines), measuring the emission polarization patterns further facilitates the absolute orientation of the NPL to be determined by pure optical measurements.



Figure S6. Influence of magnetic field strength on the linewidth of Case II NPL emission. **a**–**c** Magneto-photoluminescence spectra of three different individual CsPbBr₃ NPLs showing Case II emission at magnetic field strengths between 0 T and 5 T. In **a** and **b**, colored lines are raw data; in **c**, light grey circles are raw data and colored lines are guides to the eye. **d** Change of the FWHM of the emission spectra of the Case II NPLs shown in **a**–**c** and in Figure 5 c of the main text, where Δ FWHM = FWHM(*B*) – FWHM(0 T) with the magnetic field strength *B*. Dashed lines indicate the expected magnetic field-induced energy splitting $\Delta E - \Delta E_0$ according to equation 1 and 2 of the main text with *g* = 2.1 and the indicated intrinsic energy splitting ΔE_0 in case that the emission line comprises two degenerate ($\Delta E_0 = 0.0$ meV) or irresolvable ($\Delta E_0 = 0.2$ meV) exciton states. Neither a systematic increase of the emission linewidth nor an energy splitting that the two observed emission lines of such NPLs stem from two non-degenerate exciton transitions as discussed in the main text.



Figure S7. Influence of population statistics on the PL fine structure of CsPbBr₃ NPLs. To estimate the influence of thermal population statistics on the identification of Case II and III NPLs we analyzed the observed relative intensities of the fine structure emissions of our NPLs and compared them to the expected relative population according to a Boltzmann distribution. **a**-**d** Exemplary emission spectra of the NPLs shown in Figure 3 c/e in the main text and Figure S4 a/b. Light grey data points represent raw data measured at 4 K without the linear polarizer (see section I). Solid black lines represent cumulative Lorentzian peak fits to the raw data. With the extracted linear polarization directions of the individual peaks (see referenced figures), the spectra can be corrected for the polarization response of the detection system (i.e., a beam splitter and the grating monochromator). For that, each individual emission peak was scaled with the respective transmittivity of the detection system at the determined polarization angle and the resulting polarization corrected spectrum was then built by summing up the individual peaks (green solid lines). Additionally, red solid lines indicate the expected spectral shape of each NPL based on the individual energy splitting extracted from the fit of the raw data (black solid lines) and presuming Boltzmann occupation with a temperature of 5 K. Clearly, the relative intensities of both the Case II and III NPLs do not follow a Boltzmann distribution. Especially for several Case III NPLs (c, d), the intensities of the higher energy transitions are even higher than that of the lowest energy transition. The same procedure as demonstrated in **a**-**d** can be applied to all NPLs with known polarization characteristics.

Further, for all Case III NPLs the polarization direction of the highest and lowest energy emission peaks is assumed to be equal from the results of this work. Hence, the relative intensities of these peaks can be considered even without correction of the polarization response of the detection system. **e** Resulting intensity ratios of several emission peak pairs according to the described evaluation procedures. E_a , E_b and E_c denote the lowest to highest energy peaks according to Figure S4. The black solid line represents the expected Boltzmann occupation at 5 K. We do not see any correlation of the observed peak intensities with the thermal distribution.

To further ensure that high energy peaks are not overseen in Case II NPLs due to low emission intensities, we evaluated the root mean square (RMS) noise value of measurements on Case II NPLs. f RMS noise values of spectra showing only two emission peaks (green diamonds). The grey shaded area marks the expected relative intensity of the third (highest energy) emission peak according to a Boltzmann distribution of occupied states at 5 K with an energy splitting between 1.75 meV (upper solid black border) and 2.58 meV (lower solid black border). The energy splitting boundaries were taken as the first and third quartile from Figure S4 c (blue data). The intermediate solid black line denotes the Boltzmann occupation for the median energy splitting observed for Case III NPLs (~ 2.1 eV). The red shaded area marks the same statistical values for the experimentally observed intensity ratios between the lowest and highest energy emission in the given energy splitting range as shown in e. While for roughly half of the datapoints the RMS noise value is higher than the expected peak intensity for Boltzmann occupation, the highest energy emission peak would still be detectable for a significant amount of observed twopeak spectra. More strikingly, all noise values are well below the experimentally observed relative intensity of the highest energy peak in Case III NPLs. We hence conclude that thermal occupation does not dominate the relative peak intensity distribution of the triplet emission observed in our work and that the absence of a third emission peak in Case II NPLs cannot primarily be explained by low thermal occupation. Possible deviations from simple Boltzmann statistics can occur at low temperatures, e.g., when the relaxation times between the individual triplet exciton states are not significantly shorter than the exciton recombination time.

Besides population statistics, different oscillator strengths could potentially influence the relative intensities of the triplet exciton transitions. However, the three orthogonal dipoles in CsPbBr₃ are expected to have equal oscillator strengths from a theoretical point of view.¹² Further, we do not see any indication that oscillator strengths should vary between the NPLs studied (namely, between Case II and III NPLs) in a way such that the highest energy peak would be rendered undetectable only in some of them. While we can therefore not fully rule out the oscillator strength of the triplet transitions to interplay with the relative peak intensities, we argue that they do not interfere with the detectability of the highest energy emission peak.

III. References

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