

Antisolvent controls the shape and size of anisotropic lead halide perovskite nanocrystals

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Abstract

Colloidal lead halide perovskite nanocrystals hold enormous potential for lighting applications due to their outstanding optical properties. Precise control of the nanocrystal dimensions and composition is a prerequisite for establishing practical applications. However, the rapid nature of their synthesis precludes a detailed understanding of the synthetic pathways, thereby limiting the optimization. Here, we deduce the formation mechanisms of anisotropic lead halide perovskite nanocrystals, 1D nanorods and 2D nanoplatelets, by combining in situ X-ray scattering and photoluminescence spectroscopy. In both cases, emissive prolate nanoclusters form upon mixing of the two precursor solutions. The divergent anisotropy is induced by ensuing antisolvent addition: The intermediate nanoclusters are driven into a dense hexagonal mesophase, where they fuse to form nanorods. Contrastingly, nanoplatelets grow freely dispersed from dissolving nanoclusters, stacking subsequently in lamellar superstructures. Shape and size control of the nanocrystals are determined primarily by the antisolvent's dipole moment and Hansen hydrogen bonding parameter. Exploiting the interplay of antisolvent and organic ligands could enable more complex nanocrystal geometries in the future.

Introduction

Semiconductor nanocrystals possess unique size-dependent properties for their use in widespread applications, such as light-emitting diodes, solar cells, photocatalysis, and biomedical imaging^{1–4}. Lead halide perovskites (LHPs) are a particularly auspicious emerging class of material with advantageous characteristics, such as strong optical absorption, high photoluminescence (PL) quantum yields, and optical responses tunable throughout the visible range via size and halide composition^{5–7}. Moreover, LHPs exhibit a high propensity for forming low-dimensional nanocrystals, such as zero-dimensional (0D) quantum dots⁸, one-dimensional (1D) nanorods and nanowires^{9–11}, and two-dimensional (2D) nanoplatelets and nanosheets^{12–15}. These 1D and 2D nanocrystals show favourable anisotropic properties, such as directional and polarised light emission and superior emission in the blue spectral range^{6,7,16–18}. Previous studies have focused on developing methods to produce anisotropic LHP nanocrystals and have shown various synthetic parameters influencing size and geometry^{19–21}. Obtaining the high yield and high homogeneity essential for commercialisation or the use in hierarchically assembled materials^{22,23} requires fine-tuning the synthesis and a complete understanding of the synthetic process, also in view of potential upscaling. The most simple liquid-phase synthesis of colloidal nanocrystals progresses via a three-stage process of supersaturation, nucleation, and growth, as given by the classical LaMer model²⁴. Here, the nucleation and growth phases must be separated to control nanocrystal formation. Furthermore, a timely termination of the synthesis is essential before Ostwald ripening leads to nanocrystal size defocusing.

Using modern analytical tools, this timing has been realised for metal nanoparticles²⁵ and conventional semiconductor nanocrystals^{26,27}, whose syntheses often take tens of minutes to hours and which can be easily separated into nucleation and growth steps. However, LHP nanocrystal syntheses are typically finalised within seconds^{13,24}, severely impeding real-time analysis and, thus, a tailored anisotropic nanocrystal fabrication. Recently, a substantial slowing down of the growth of LHP nanocrystals was realised by replacing the organic ligands present during synthesis^{8,28}. This allowed for a detailed analysis of the growth mechanism, yet it also changed the final shape of the resulting nanocrystals to more isotropic shapes. Since many synthesis studies focus mainly on the final product, nucleation, growth, and potential intermediate phases are only vaguely understood²⁹. For example, it is widely believed that intermediate clusters, micelles, or complexes play a decisive role in regulating reaction kinetics by binding reactants, which are slowly released as monomers^{8,28,30,31,15} however their dimensions are rarely reported. Moreover, the labile ligand binding in LHPs potentially promotes nonclassical growth mechanisms like oriented attachment, fusion, and recrystallisation of intermediates, yet the exact mechanisms at work are elusive^{32,31}. The addition of a so-called antisolvent, i.e., a poor solvent for the as-formed nanocrystals, is assumed to act as a structure-directing agent^{33,34} and has shown to be beneficial for fabricating anisotropic nanocrystals^{6,35}. However, due to a lack of structural information during the rapid synthesis, a strategy for control of LHP nanocrystal anisotropy and size is still lacking.

To resolve this issue, elucidate the synthesis pathway of anisotropic LHP nanocrystals, and provide a guideline for their tailored fabrication, we conducted an in situ structural and spectroscopic study by simultaneous small- or wide-angle X-ray scattering (SAXS and WAXS) and PL spectroscopy using a highly brilliant storage ring-based X-ray source. We can decouple the individual steps of nanocrystal formation by simultaneously obtaining structural, crystallographic, and optical data of the synthesis with extremely high temporal resolution up to 50 ms. Accordingly, we observe that prolate and emissive nm-sized LHP nanoclusters form nearly instantaneously upon precursor mixing. Surprisingly, these are common reaction intermediates for both CsPbBr₃ 1D nanorods and 2D nanoplatelets. In suitable conditions, a subsequent antisolvent injection induces the formation of a dense, hexagonal mesophase of the intermediates, wherein they fuse to form nanorods. In the absence of this mesophase, intermediate nanoclusters and dissolved precursor ions contribute to the growth of freely dispersed nanoplatelets, representing the thermodynamically most stable structure at these conditions³⁶. These assemble into lamellar superstructures, a process which potentially enhances size homogeneity. We ascertain that two specific solvent properties are crucial for controlling the shape and monolayer (ML) thickness of anisotropic perovskite nanocrystals, namely the dipole moment μ and Hansen hydrogen bonding parameter δ_H ³⁷. We identify a narrow range of solvent conditions with significant promise for obtaining more complex LHP nanocrystal shapes. Exploring this solvent range and the interplay between solvent, organic ligands, and precursor concentrations will likely lead to a plethora of new and exciting anisotropic nanocrystal syntheses.

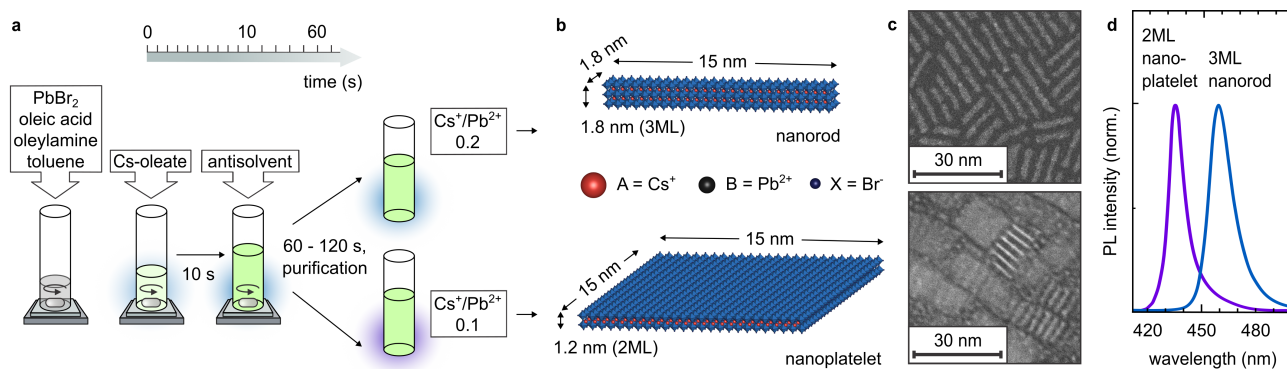


Fig. 1 | Synthesis and characteristics of the anisotropic perovskite nanocrystals. **a**, Scheme of the room temperature synthesis of CsPbBr₃ nanorods and nanoplatelets. **b**, Sketch of individual CsPbBr₃ 3ML nanorods (top) and 2ML nanoplatelets (bottom) with typical dimensions. **c**, Scanning transmission electron microscopy (STEM) images of 3ML nanorods (top) and 2ML nanoplatelets (bottom). **d**, Ex situ PL spectra of 3ML nanorods and 2ML nanoplatelets.

Results and Discussion

Synthesis scheme

Through trial and error experiments and, recently, the use of machine learning, we have developed synthesis strategies to obtain anisotropic CsPbBr₃ nanocrystals with precise control over their dimensions (Fig. 1 a)^{38,35}. The synthesis is conducted at room temperature in ambient conditions and can be described as a ligand-assisted spontaneous crystallisation. The synthesis commences with a PbBr₂-precursor in toluene, oleic acid, and oleylamine, into which a second Cs-oleate precursor is injected and thoroughly mixed for 10 s. Subsequently, acetone, a moderately polar antisolvent, is injected into this reaction mixture. After 60 – 120 s, the reaction is terminated by centrifuging and redispersing the precipitate in n-hexane. Formation of anisotropic nanocrystals is promoted by a stoichiometric deficiency of Cs⁺ ions, while the nanocrystal thickness depends on the ratio of Cs⁺/Pb²⁺ ions. Slight variations in this ratio and the acetone volume lead to the formation of either quasi-1D nanorods or quasi-2D nanoplatelets, as depicted in Fig. 1 b,c. To understand how the nanocrystal shape is controlled, we first focused on two types of nanocrystals with distinct morphological and optical characteristics: 3ML nanorods and 2ML nanoplatelets. The nanocrystals, with sizes of (1.8 × 1.8 × 15) nm³ and (1.2 × 15 × 15) nm³, respectively, as evidenced by transmission electron microscopy (TEM, Fig. 1 c and Supplementary Note 1, Supplementary Fig. 1), exhibit strongly blueshifted absorbance and photoluminescence (PL) spectra compared to bulk CsPbBr₃ (Fig. 1 d and Supplementary Fig. 2). The PL emission, centred at 460 nm (full width at half maximum (FWHM) = 18 nm) and 434 nm (FWHM = 14 nm), respectively, confirms the formation of nanocrystals with pronounced quantum and dielectric confinement and narrow size distribution^{12,11}.

The question remains, however, how to achieve control of the desired anisotropy and ML thickness based on rational principles. To investigate this, we built a small reaction cell (Supplementary Fig. 3) for integration into the beamlines of the PETRAIII storage ring at DESY, Hamburg, to simultaneously monitor PL and either small-angle X-ray scattering (SAXS) or wide-angle X-ray scattering (WAXS). This cell allows us to follow structural and optoelectronic properties during synthesis with a time resolution down to 50 ms, as shown in Fig. 2 a and detailed in Supplementary Notes 2 and 3. In the experiments, a glass capillary is loaded with PbBr₂-precursor solution (Fig. 1 a) and a magnetic stirring bar. Cs-oleate precursor solution is injected through a motorised syringe pump, starting the reaction at $t = 0$ s, and the antisolvent is injected through a separate motorised syringe pump at $t = 10$ s.

Intermediate nanocluster formation after precursor mixing

As soon as Cs-oleate is added to the PbBr₂-precursor, a bright blue emission, located at 446 nm (FWHM = 40 nm), and indicative of strongly quantum-confined CsPbBr₃ nanoclusters, is detected (Fig. 2 b)^{39–41}. Simultaneously, a growing WAXS signal (Fig. 2 c) is observed, with a Bragg reflection emerging at $q = 2.1 \text{ \AA}^{-1}$, i.e., at the position of the (040) and (202) reflections of orthorhombic CsPbBr₃ (Supplementary Figs. 4 and 5)⁴². The simultaneous emergence of the PL and WAXS signals indicates that crystalline perovskite forms immediately after precursor mixing. After 5 s, both signal intensities reach a plateau (Fig. 2 d), suggesting the initial burst of nucleation is caused by supersaturation in response to the injection of the second precursor and quickly terminated, as previously reported²⁸. A Scherrer analysis of the WAXS signal (Supplementary Note 2 and

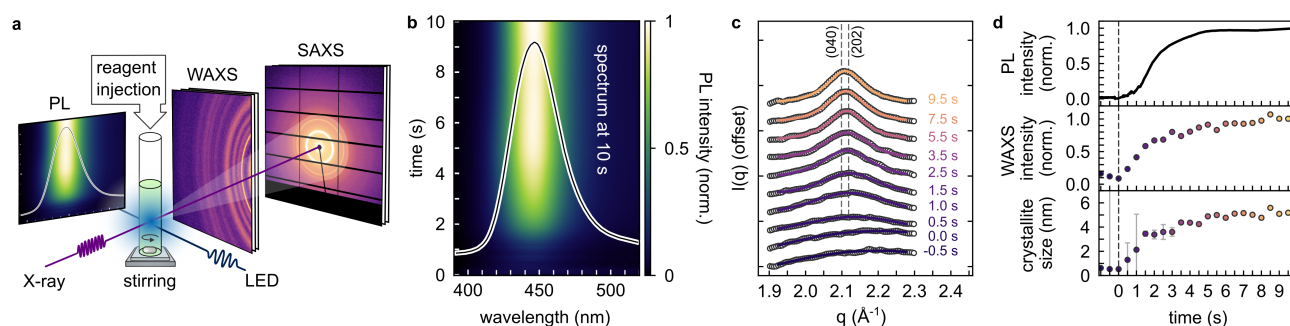


Fig. 2 | In situ WAXS and PL spectroscopy reveal the formation of nanoclusters during Cs-oleate and PbBr₂-precursor mixing. **a**, Sketch of the in situ reaction cell for simultaneous SAXS, WAXS, and PL spectroscopy. **b**, In situ PL data recorded in between injection of Cs-oleate into the PbBr₂-precursor ($t = 0$ s) and antisolvent addition ($t = 10$ s). The PL maximum position at 446 nm and FWHM = 40 nm do not change over time, while the PL intensity increases rapidly, saturating after 5 s. **c**, Simultaneously recorded in situ WAXS data, showing the formation of the (040) and (202) CsPbBr₃ Bragg reflections between 0.5 and 2 s after Cs-oleate injection. **d**, PL intensity, WAXS peak intensity, and crystallite size as derived from a Scherrer analysis.

Fig. 2d) reveals that nanoclusters reach a crystallite domain size of (5.1 ± 0.3) nm after 5 s. However, as the PL emission wavelength does not shift during this synthesis phase, shown in Supplementary Fig. 6, at least one nanocluster dimension must maintain its size within the strongly quantum-confined regime. Importantly, these crystallites are still smaller than the final nanocrystals, and their PL spectra do not match those of either nanorods or nanoplatelets (Supplementary Fig. 7). Accordingly, we identify these LHP nanoclusters as reaction intermediates²⁸.

The rapid formation of nanoclusters and evolution of their physical dimensions were followed in more detail by in situ SAXS measurements (Supplementary Note 3), shown here from slightly before Cs-oleate injection up to the moment before antisolvent injection at $t = 10$ s (Fig. 3a). After Cs-oleate injection ($t = 0$ s), an immediate increase in SAXS intensity at low q is observed, followed by saturation within a few seconds, in agreement with PL and WAXS data in Fig. 2b-d. A fit to the signal of the PbBr₂-precursor before mixing (solid line at $t = -0.5$ s) shows that the PbBr₂-precursor is dispersed in the form of micellar nanoclusters, with 1.2 nm diameter PbBr₂-cores enclosed in 2.8 nm thick ligand micelles (see Supplementary Fig. 8 and Supplementary Table 2). We analyse the time-dependent SAXS data with a two-component model form factor, accounting for the micellar cluster structure of the PbBr₂-precursor as the first component and the newly forming LHP nanoclusters as freely dispersed ellipsoids as the second component (Fig. 3b,c, Supplementary Figs. 9 to 11 and Supplementary Tables 3 and 4). This model describes the SAXS data very well, allowing us to quantify the nanocluster formation in terms of size and density. As shown in Fig. 3d, the number density of nanoclusters rapidly increases within 1-2 s. It then slowly decays, indicating a phase of coalescence or Ostwald ripening. The nanoclusters are prolate ellipsoids and their remaining growth proceeds slowly within 10 s from initially (1.8 ± 0.2) nm $\times$ (4.3 ± 0.2) nm to a final size of (2.1 ± 0.2) nm $\times$ (5.9 ± 0.4) nm. Importantly, the short axes, which dominate confinement, retain their sizes. This explains the stationary PL maximum observed in Fig. 2b. In addition to in situ SAXS, we verified the presence of prolate intermediate nanoclusters through ex situ TEM imaging of the crude reaction solution obtained after precursor mixing (Fig. 3f). We observe a monolayer of size-uniform nanoclusters arranged in a regular hexagonal assembly with a spacing of (5.01 ± 0.13) nm (Fig. 3g and Supplementary Fig. 12). Remarkably, both of our synthesis schemes show identical intermediate nanocluster sizes at this stage (Fig. 3e), i.e., the syntheses of nanorods and nanoplatelets proceed via the same prolate intermediates.

Nanorod growth via hexagonal mesophase formation

Up to this point in the synthesis, there is essentially no difference between the 2ML nanoplatelet and 3ML nanorod synthesis. Accordingly, the divergence must be induced by the subsequent antisolvent injection. To explore this, we use the moderately polar acetone as the antisolvent, with a larger relative volume added in the 3ML nanorod synthesis in comparison to the nanoplatelet synthesis (see Methods and Supplementary Table 5). This results in a pronounced change in the SAXS signal (Fig. 4a and Supplementary Fig. 13a), which differs substantially for nanorods and nanoplatelets. For the nanorod synthesis (Fig. 4a), intense peaks in the SAXS intensity appear immediately after antisolvent injection, indicating the formation of a superstructure of nanoclusters, i.e., a mesophase. These peaks are located at the positions of $q_{100} = 0.150 \text{ \AA}^{-1}$, $q_{110} = \sqrt{3} \cdot q_{100}$, and $q_{200} = 2 \cdot q_{100}$, and correspond to the diffraction pattern of a two-dimensional hexagonal structure,

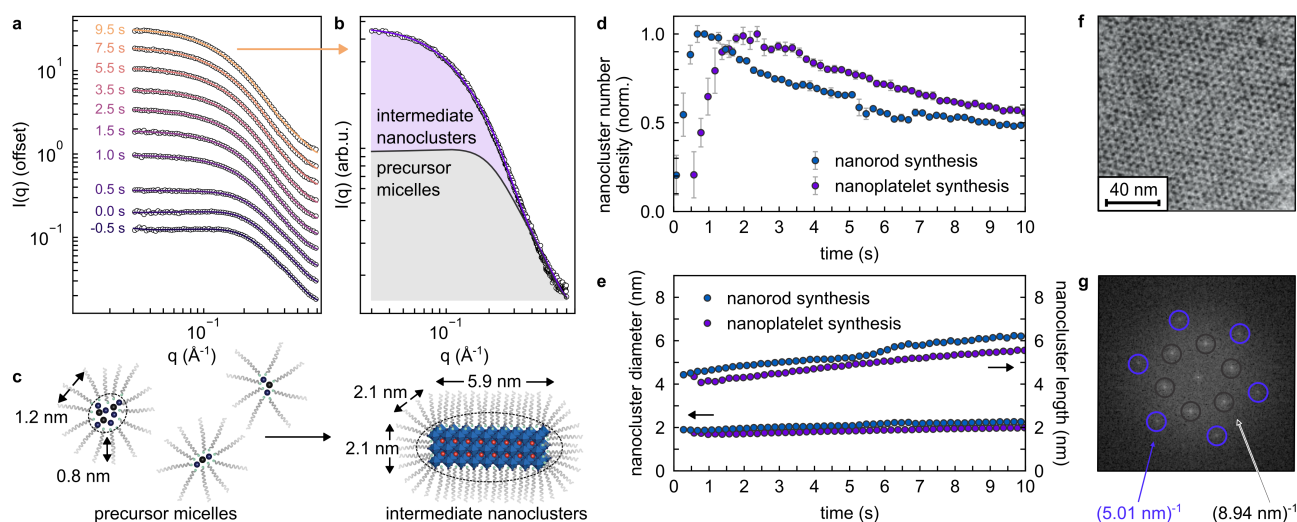


Fig. 3 | Intermediate nanoclusters are identical in 3ML nanorod and 2ML nanoplatelet synthesis, according to SAXS and TEM data. **a**, SAXS intensity recorded in between injection of Cs-oleate into the PbBr_2 -precursor ($t = 0$ s) and antisolvent addition ($t = 10$ s). Solid lines indicate fits to the data. **b**, Decomposition of the SAXS intensity into signals of precursor micelles and intermediate nanoclusters, illustrated for $t = 9.5$ s, immediately before antisolvent addition. **c**, Dimensions of the precursor micelles and intermediate nanoclusters obtained from SAXS data analysis. **d**, Number density of nanoclusters as a function of time from SAXS data analysis for nanorod and nanoplatelet synthesis, respectively. **e**, Diameter and length of the intermediate nanoclusters from SAXS data analysis. **f**, TEM image of a reaction solution dropcasted on a substrate after precursor mixing. **g**, Fast Fourier transform (FFT) of the TEM image in **f** indicates a hexagonal assembly with 5.01 nm and 8.94 nm distance to the nearest and next-nearest nanocluster.

e.g., the dense packing of long cylinders with a hexagonal lattice constant of $d = 4\pi/(\sqrt{3}q_{100}) = (4.8 \pm 0.1)$ nm. This spacing corresponds to the short axis of prolate intermediates (1.8 nm) plus an intercalated double layer of ligands (3.0 nm)³⁸. The SAXS intensity shown in Fig. 4a reveals an additional peak between 0.04 and $0.07 \text{ \AA}^{-1}$, which is not part of the 2D hexagonal (hk0) series. It indicates the formation of a periodic structure along the long axis of the intermediates as they grow to nanorods. Here, the nanorods stack end-to-end with a spacing that increases over time and finally reaches $2\pi/q_{001} = (13.7 \pm 0.2)$ nm (Supplementary Fig. 14). The PL intensity decreases within 5 s after acetone injection, then gradually recovers throughout the measurement time (Fig. 4b), with the final PL spectrum being slightly redshifted compared to the intermediate nanoclusters (Supplementary Fig. 7).

Nanoplatelet growth followed by lamellar mesophase formation

In contrast, upon injection of a smaller volume of acetone as in the nanoplatelet synthesis, the emergence of superstructure peaks in the SAXS intensity is delayed by 60 s (Fig. 4e and Supplementary Fig. 13b). The emerging X-ray pattern differs considerably, as an (h00) peak series with integer multiples of $q_{100} = 0.143 \text{ \AA}^{-1}$ appears. This signifies the formation of a lamellar mesophase with repeat distances of $2\pi/q_{100} = (4.4 \pm 0.1)$ nm, compatible with stacked 1.4 nm thick nanocrystals separated by an intercalated double layer of ligands (3.0 nm). The SAXS intensity additionally shows another (00l) peak series starting at smaller q -values, indicating the formation of an even larger lattice (Fig. 4e and Supplementary Fig. 14). The final repeat distance of this peak series corresponds to $2\pi/q_{001} = (12.1 \pm 0.4)$ nm, implying the presence of 9.1 nm large nanoplatelets with a ligand shell, arranged side by side. Here, anisotropic nanocrystals, and not intermediate nanoclusters, assemble in a mesophase. The PL signal of the intermediate nanoclusters in the nanoplatelet synthesis, centred at 451 nm, shows a similarly sharp decrease as in the nanorod synthesis. However, instead of a PL signal at > 450 nm, a new PL peak centred at 433 nm, resembling the emission of 2ML nanoplatelets^{38,13}, emerges 20 s after acetone injection and increases in intensity for another 60 s before reaching a plateau at a slightly lower value.

Effects of antisolvent addition

The two synthesis pathways proceed fundamentally differently after the addition of the same antisolvent in different volumes (Fig. 4c and g and Fig. 4d and h). This can be rationalised as follows: Firstly, the addition of acetone increases the polarity of the reaction mixture and therefore, the solubility of precursor ions in the solution is enhanced. At the same time, the ligand shell of the nanoclusters is disturbed⁴³, and surface defects

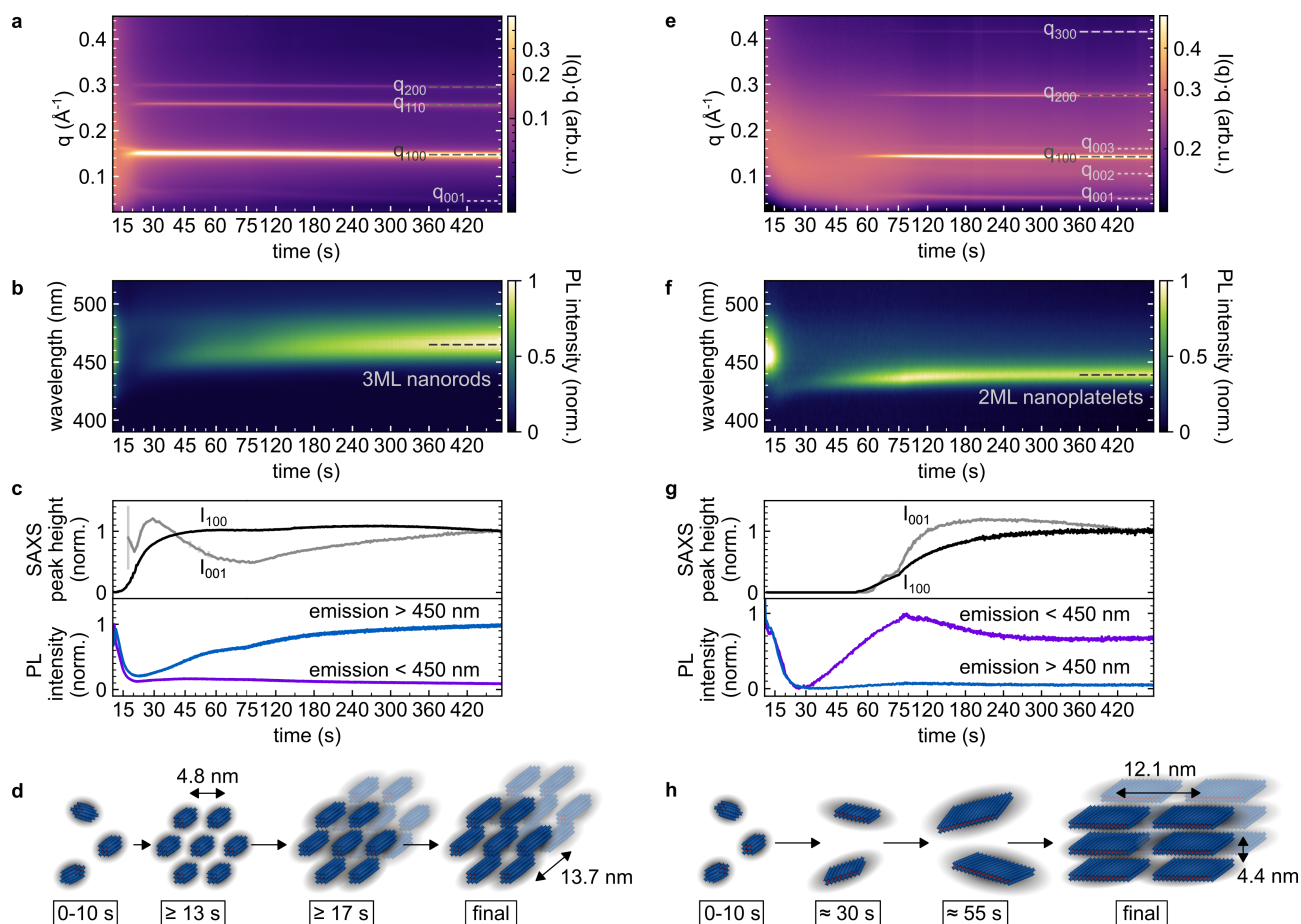


Fig. 4 | Antisolvent injection induces mesophase formation, enabling fusion of intermediate nanoclusters into nanorods. **a**, In situ SAXS intensities of a 3ML nanorod-forming reaction mixture after antisolvent injection as a function of scattering vector and time. **b**, In situ PL intensities of a 3ML nanorod-forming mixture as a function of wavelength and time. The initially broad PL of intermediate nanoclusters is strongly reduced by antisolvent injection. Later, the characteristic emission of 3ML nanorods at > 450 nm is recovered. **c**, SAXS and PL intensities extracted from (a) and (b), summarised. **d**, Sketch of hexagonal mesophase formation and transformation of prolate intermediate nanoclusters to nanorods. **e**, In situ SAXS intensities of a 2ML nanoplatelet-forming reaction mixture after antisolvent injection. **f**, In situ PL intensities of a 2ML nanoplatelet-forming mixture. The initial PL from intermediate nanoclusters is suppressed in favour of a sharp peak at 433 nm, characteristic of the formation of 2ML nanoplatelets. **g**, SAXS and PL intensities extracted from **e** and **f**, summarised. **h**, Sketch of the sequence of growth of freely dispersed nanoplatelets from intermediate nanoclusters and subsequent stacking of nanoplatelets.

are introduced⁴⁴. Both effects reduce the stability of the intermediate nanoclusters, which are partly dissolved, releasing ions into the solvent mixture. This is supported by the observation of a strong reduction in PL intensity of the intermediates (Fig. 4c and g) and their WAXS signal (Supplementary Fig. 5) upon the addition of the antisolvent.

Secondly, as long as the nonpolar ligand shell is still intact, the solubility of LHP nanoclusters as a whole is largely reduced by the addition of polar solvent^{45,46}. Thus, the rapid addition of a large volume of acetone results in an instantaneous formation of a hexagonal mesophase formed by densely packed prolate nanoclusters, in essence, a phase separation. The destabilisation of the intermediate nanoclusters follows the mesophase formation temporally, indicating that ion and ligand release takes at least a few seconds while phase separation is almost instantaneous. In turn, the rod-like nanocrystals form within the hexagonal mesophase in the presence of the destabilised intermediates, presumably by fusion and recrystallisation, as suggested by increasing PL emission and WAXS intensity (Supplementary Fig. 5). By varying the precursor concentration as well as the antisolvent volume, we find that an increased relative concentration of intermediate nanoclusters leads to assembly in the mesophase, similar to observations for CdS magic-sized clusters⁴⁷, but not to nanorod growth, as the destabilizing effect of the antisolvent is then insufficient (see Supplementary Fig. 15). We also verified that hexagonal mesophase formation occurs when the LHP nanoclusters are present and does not form in mixtures containing only ligands or one precursor salt (Supplementary Fig. 16).

At lower acetone volumes and/or precursor concentrations, the effect of enhanced LHP ion solubility dom-

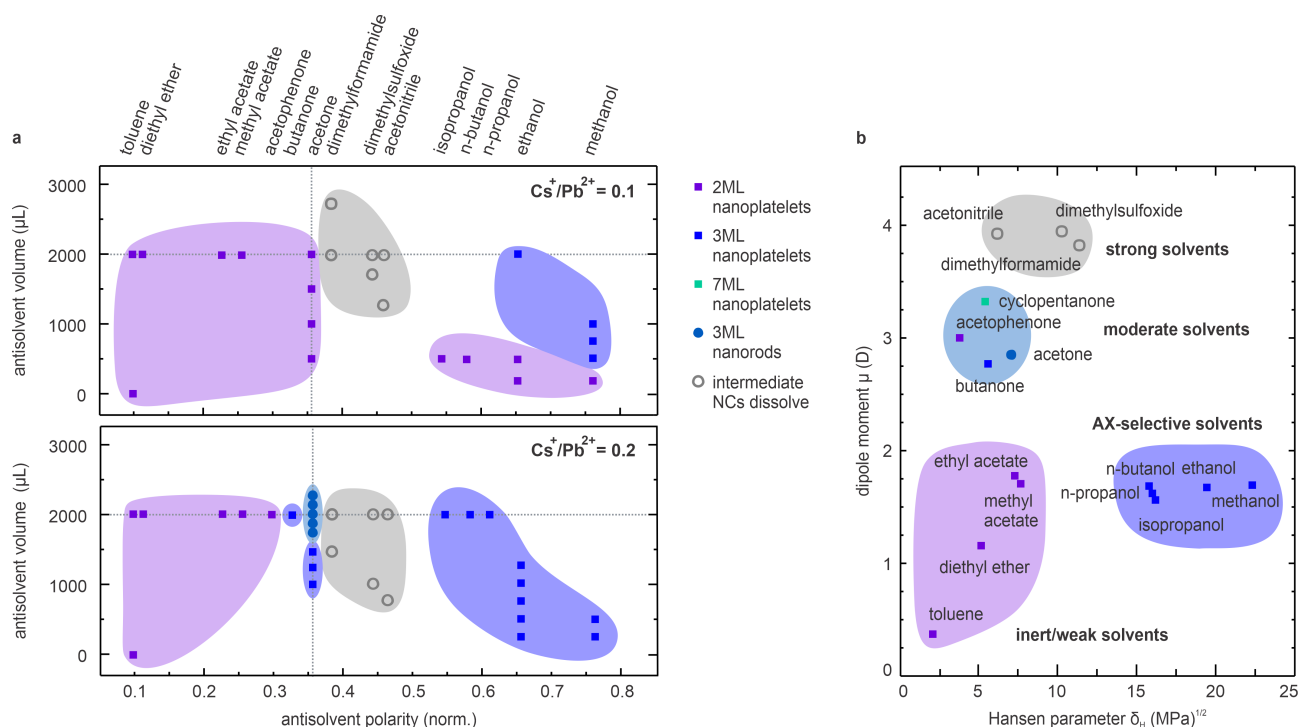


Fig. 5 | Variation of antisolvent properties controls the dimensionality and thickness of anisotropic CsPbBr₃ nanocrystals **a**, Shape and thickness of the obtained perovskite nanocrystals depending on Cs⁺/Pb²⁺ ratio, relative antisolvent polarity and antisolvent volume. Acetone, the antisolvent used in the standard procedure of the nanorod and nanoplatelet synthesis and the typically injected volume are marked for reference (grey dashed lines). The type of nanocrystal product from each synthesis is indicated in the legend. **b**, Shape anisotropy and ML thickness of perovskite nanocrystals classified by antisolvent properties (inert, weak, moderate, strong, and AX-selective solvents), legend as given in **a**. Inert and weak solvents yield 2ML nanoplatelets, AX-selective solvents yield 3ML nanoplatelets, whereas strong solvents dissolve intermediate nanoclusters and do not yield any perovskite product. Moderate solvents show a diverse reaction outcome, with only acetone producing 3ML nanorods.

inates. These reaction conditions result in the growth of nanoplatelets. The nanoplatelets grow laterally in size while freely dispersed and only later begin to stack in a lamellar phase due to a combination of solvation forces⁴⁸, van der Waals interactions between large platelet facets⁴⁹, and attractive dispersion forces between alkyl chains of surface ligands⁵⁰. Nanoplatelet stacking becomes apparent as a set of peaks at regular intervals in the SAXS intensity (Fig. 4e) and a reduction of the PL intensity due to increased reabsorption and scattering (Fig. 4g, Supplementary Fig. 17, Supplementary Table 6). The platelet shape is likely the thermodynamically stable polymorph since 2ML nanoplatelets also form very slowly without antisolvent injection (Supplementary Fig. 18). In this case, variation of the precursor concentration moderately affects the reaction rates (Supplementary Fig. 19 and Supplementary Table 7). Thus, we identify two processes contributing to 2ML nanoplatelet growth: direct supply of available precursor material from solution and supply from dissolution of intermediate nanoclusters, which serve as an ion reservoir and regulate the reaction kinetics.

Shape and size control by tuning solvent properties

So far, our analysis highlights that antisolvent injection is the decisive step that initiates either nanorod or nanoplatelet formation. To understand the role of the antisolvent in more detail, we screened other potential antisolvents, varying the antisolvent polarity and volume fraction (Fig. 5, Supplementary Note 6, Supplementary Tables 9 and 10, and Supplementary Fig. 20). Solvents with polarity equal to or less than acetone also result in 2ML nanoplatelets, provided the volume fraction is similar (Fig. 5a, top panel). At very high polarities, i.e., for alcohols, the platelet shape remains, but the thickness increases to 3ML nanoplatelets. Furthermore, an intermediate polarity regime exists, where the intermediates dissolve without forming a stable perovskite phase. Nanorods were only obtained under very specific conditions by using acetone as an antisolvent (Fig. 5a, bottom panel). We, therefore, further elucidated the special role of acetone in comparison to other antisolvents. For this purpose, we adopt the idea of classifying solvents according to their dipole moment, Hansen hydrogen bonding parameter and donor number³⁷. Solvents can be classified as inert, weak, moderate, strong, or AX-selective according to their effect on the ion solubility of lead halide perovskites. We find a striking clustering of

synthesis products (Fig. 5 b) in this parameter space. Weak solvents (diethyl ether, ethyl acetate, methyl acetate) and small amounts of acetone accelerate 2ML nanoplatelet formation, reducing reaction times (Supplementary Fig. 17) while monodispersity and optical properties of the nanoplatelets are maintained. Strong solvents, mainly characterised by a large dipole moment and/or high donor number (dimethylformamide, dimethylsulfoxide and acetonitrile) immediately dissolve the intermediate nanoclusters and prevent further LHP growth. Owing to a high electron-pair donor ability, these Lewis basic solvents strongly coordinate Pb^{2+} ions, inhibiting perovskite crystallisation³⁴. Solvents with a high Hansen hydrogen bonding parameter, such as alcohols, are termed AX-selective due to their ability to coordinate organic A cations³⁷. In our case, they also coordinate the weakly bound oleylamine ligands⁴³ from the surface of the intermediate nanoclusters. Thereby, they enable the formation of thicker (3ML) nanoplatelets with very narrow, blue emission (462 nm, FWHM = 14 nm, Supplementary Figs. 21 and 22), likely via seeded growth from intermediate nanoclusters⁵¹. By reducing the injected volume of AX-selective solvents, again, 2ML nanoplatelets are obtained, suggesting that the hydrogen bonding ability, as well as the polarity of the solvent mixture, allows for ML thickness control. This is remarkable, as previous experiments only focused on the precursor ratio, specifically the A/B cation ratio, to control the resulting nanoplatelet thickness^{14,38,35}.

Moderate solvents like acetone occupy a narrow region in the μ - δ_H diagram (Fig. 5 b), characterised by an intermediate hydrogen bonding ability and dipole moment. This combination makes acetone rather unique. On the one hand, acetone destabilises the intermediate particles moderately. On the other hand, acetone is well known to allow for an efficient transfer of ligand-coated nanocrystals from polar to nonpolar solvents by mediating surface tension mismatch in colloidal dispersions⁵². Both properties are needed for the nanorod synthesis, which proceeds via rapid mesophase formation according to our SAXS data. Indeed, other moderate antisolvents (butanone, cyclopentanone, acetophenone) which have been added to the screening after analysis of the solubility parameter space, lead to the formation of a variety of different perovskite nanocrystals, including 7ML nanoplatelets and 5ML nanorods, see Supplementary Fig. 23.

The broad screening of synthesis conditions combined with precise structural information during synthesis allowed us to obtain thickness and shape control of the final nanocrystals with excellent color-tunability (Supplementary Fig. 24). We expect that thicker nanorods and nanoplatelets could be synthesised via an analogous approach by adapting the precursor ratio and types of ligands to form larger intermediate nanoclusters. Employing similar moderate solvents, mesophase formation could be controlled to favour nanorod growth.

In conclusion, combining in situ optical spectroscopy and X-ray scattering, we reveal the formation mechanism of anisotropic CsPbBr_3 nanocrystals. We find that crystalline intermediate nanoclusters form immediately upon precursor mixing and play a crucial role in the growth of the final LHP nanocrystals. The intermediate nanoclusters serve either as reservoirs for the growth of nanoplatelets or as building blocks in mesophase-templated nanorod growth, depending on the antisolvent. In the first case, nanoclusters gradually dissolve and contribute to the formation of quasi-2D nanoplatelets as the thermodynamically most stable shape of LHP nanocrystals at low $\text{Cs}^+/\text{Pb}^{2+}$ ratio. In the second case, the antisolvent has a more profound impact and induces the formation of a well-ordered mesophase, resulting in a quasi-1D nanorod shape of LHP nanocrystals that is predefined by the geometry of the mesophase. We identify the dipole moment and Hansen hydrogen bonding parameter of the antisolvent as the most critical parameters in determining the final LHP nanocrystal shape. Solvents with moderate dipole moment and hydrogen bonding add further control in addition to established ligands and precursor ratios, providing ample room for extending the range of shape and size control of LHP nanocrystals.

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Methods

Nanocrystal synthesis

First, the Cs-oleate precursor was prepared by dissolving Cs_2CO_3 (0.1 mmol, 32.6 mg) in oleic acid (10 mL) while stirring at 85 °C for up to three hours until a clear solution was obtained. Similarly, the PbBr_2 -precursor was prepared by dissolving PbBr_2 (0.1 mmol, 36.7 mg) in toluene (10 mL), oleic acid, and oleylamine (100 μL each) under stirring at 85 °C for up to three hours until a clear solution is obtained. Precursors were stored at room temperature under ambient conditions. For the automated synthesis, a certain volume of PbBr_2 -precursor (300 μL for 3ML nanorods, 400 μL for 2ML nanoplatelets) was added to the glass capillary of the custom-built in situ reaction cell. Under vigorous stirring, the Cs-oleate precursor (30 μL for 3ML nanorods, 20 μL for 2ML nanoplatelets) was injected with a motorised syringe pump. After 10 s, the antisolvent acetone (400 μL for 3ML nanorods, 267 μL for 2ML nanoplatelets) was injected through a second motorised syringe pump. The reaction mixture was stirred for up to 8 min and then centrifuged at 4000 rpm for 3 minutes (Eppendorf MiniSpin Plus, $r = 60$ mm). The supernatant was discarded, and the precipitate, containing the anisotropic CsPbBr_3 nanocrystals, was redispersed in n-hexane (500 μL) for further ex situ characterisation. Precursor and antisolvent volumes for manually conducted ex situ syntheses are listed in Supplementary Table 10. Chemicals are listed in Supplementary Table 11.

SAXS and WAXS

In situ SAXS data were recorded at beamline P62⁵³ (PETRAIII, DESY, Hamburg) at an X-ray energy of 20 keV (wavelength $\lambda = 0.62 \text{ \AA}$). A custom-built reaction cell with magnetic stirring and reagent injection served as the sample environment, as described in detail in Supplementary Fig. 3. An Eiger2 X 9M detector (Dectris) in vacuum was used at 1.87 m distance with 50 ms exposure time per frame. In situ WAXS data were recorded at the second experimental hutch EH2 of beamline P07⁵⁴ (PETRAIII, DESY, Hamburg) at an X-ray energy of 104 keV (wavelength $\lambda = 0.12 \text{ \AA}$). A XRD 4343CT detector (Varex Imaging) at 0.77 m distance was used with 0.5 s per frame. SAXS and WAXS data were transformed to intensity as a function of scattering vector $q = \frac{4\pi}{\lambda} \sin \theta$. 2θ is the scattering angle. The signal of toluene and the antisolvent were subtracted as a background. SAXS data were fitted as detailed in Supplementary Note 3.

In situ PL spectroscopy

In situ photoluminescence spectra were recorded in the same custom-built reaction cell, simultaneously with SAXS and WAXS measurements. A 385 nm LED (Roschwege RSW-P01-385-2) filtered by a 10 nm FWHM bandpass filter (Thorlabs FBH380-10) was coupled into a reflection probe fibre (Thorlabs RP20) as the excitation. The emitted light captured by the reflection probe fibre was passed through a 400 nm long-pass filter (Thorlabs FELH0400) and recorded with a CCD-based UV-visible spectrometer (Ocean Optics Flame-S for in situ SAXS/PL, Ocean Insight QE-Pro for in situ SAXS/WAXS/PL measurements). Subsequent frames were binned for further analysis. Emission at wavelengths smaller and larger than 450 nm was analysed by summing the intensities in bins from 415-450 nm and 450-470 nm, respectively.

Ex situ absorbance and PL spectroscopy

Ex situ PL spectra and UV-Vis absorbance spectra of purified and diluted CsPbBr_3 nanocrystals were measured in a commercial FluoroMax-4Plus spectrometer equipped with a xenon arc lamp and an F-3031 transmission accessory (HORIBA Scientific). The excitation wavelength for photoluminescence spectra was set to 380 nm.

Electron Microscopy

STEM images were recorded using a probe-corrected FEI Titan Themis 60-300 operated at 300 kV with a semi-convergence angle of 16.6 mrad. The inner and outer collection angles of the annular dark field detector were 33 and 198 mrad. No further filtering was applied to the obtained micrographs. Specimen preparation was carried out by drop casting onto TEM grids (Quantifoil R2/2, 2 nm ultrathin carbon). TEM images at lower magnifications were recorded on a JEOL JEM-1100 microscope operated at an acceleration voltage of 80 kV. Specimen preparation was carried out by drop casting onto TEM grids (Electron Microscopy Sciences, Cu with 10/1 nm Formvar/carbon).

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Author contributions

K.F. and N.A.H. contributed equally to this work. A.S.U. and B.N. supervised the project. N.A.H., C.L. and V.M. synthesised the nanocrystals. K.F., C.L., X.S., S.H., A-C.D., O.G. and B.N. designed the simultaneous SAXS/WAXS/PL experiment and K.F., N.A.H. and C.L. carried out the measurements. N.A.H. recorded TEM images, absorption and PL spectra and analyzed the respective data. T.L. and B.M. recorded STEM images under supervision of K.M.-C.. K.F. and N.A.H. carried out laboratory SAXS measurements. K.F. analyzed the SAXS and WAXS data and the in situ PL data. K.F., N.A.H., A.S.U. and B.N. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information for this article is given at the end of the document.

Competing interests

The authors declare no competing interests.