Tailoring CsPbBr\textsubscript{3} Growth Via Non-Polar Solvent Choice and Heating Method

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Abstract

This study describes an investigation of the role of non-polar solvents on the growth of cesium lead halide (CsPbX\textsubscript{3} X = Br, I) nanoplatelets. We employed two solvents, benzyl ether (BE), and 1-octadecene (ODE), as well as two nucleation and growth mechanisms, one-pot, facilitated by microwave irradiation (MWI) based heating, and hot-injection, using conventional heating. Using BE and MWI, large mesoscale CsPbBr\textsubscript{3} nanoplatelets were produced, whereas use of ODE produced thin small crystallites. Differences between the products were observed by optical spectroscopies, which showed first band edge absorptions consistent with thicknesses of ~9 nm (~15 monolayer (ML)) for the BE-CsPbBr\textsubscript{3}, and ~5 nm (~9 ML) for ODE-CsPbBr\textsubscript{3}. Both products had orthorhombic crystal structure, with the BE-CsPbBr\textsubscript{3} revealing significant preferred orientation diffraction signals consistent with the asymmetric and two-dimensional (2D) platelet morphology. The differences in final morphology were also observed for products formed via hot-injection, with BE-CsPbBr\textsubscript{3} showing thinner square platelets with thicknesses of ~2 ML, and ODE-CsPbBr\textsubscript{3} showing similar morphologies and small crystallite sizes. To understand the role solvent plays in crystal growth, we studied lead plumbate precursor (PbBr\textsubscript{n}\textsuperscript{2n}) formation in both solvents, as well as solvent plus ligand solutions. The findings suggest that BE dissolves PbBr\textsubscript{2} salts to a higher degree than ODE, and that this BE to precursor affinity persists during growth.

Keywords: CsPbBr\textsubscript{3}, Perovskite, 2D, Platelet, Nucleation, Coordinating Solvent
Introduction

All inorganic cesium lead halides (CsPbX$_3$, X = Cl, Br, I) and hybrid methylammonium lead halides (MAPbX$_3$) are important functional materials$^{1-5}$ that can be synthesized as crystals, thin-films, and nanomaterials with varied morphologies.$^{5,6-13,14}$ Two dimensional (2D) plates and platelets are common, with thicknesses of only a few monolayers (ML) often observed, and lengths varied from nanometers to microns, which are formed during nucleation and growth, or self-assembled via solvent and or ligand mediated interactions.$^{4,15-20}$ Studies have revealed that control over ligand types and stoichiometry,$^{20}$ as well as time and temperature of the synthesis can render various morphologies.$^{3,16,17,20-31}$ Sonication,$^{32}$ solvothermal,$^{17,33,34}$ mechanochemical,$^{35}$ and microwave irradiation (MWI)$^{27}$ have also been employed to control CsPbBr$_3$ growth. Studies have shown that Ostwald ripening,$^{36,37}$ and long-ranged growth that includes oriented attachment of smaller building blocks (cubes, rods, etc.) renders 2D growth into nanoplatelets.$^{24,33,34,38}$

The role that solvent plays in CsPbBr$_3$ growth has been explored,$^{33,39-42}$ and the role it plays in the dissolution and solvation of PbX$_2$ salt into PbX$_n^{2-n}$ plumbate complexes. This is particularly interesting as the varied lead centered polyhedra formed will have different charges, molecular weights, solubility, as well as concentration and reactivity. The dynamic equilibrium between plumbates is sensitive to the Lewis basicity of the solvents and ligands involved, as well as temperature. To date, studies have focused primarily on polar solvents and their role in plumbate formation, with nitrogen or sulfur bearing solvents (e.g., DMF, DMSO) acting as stabilizers of PbX$_n^{2-n}$.43

In this report, we study whether non-polar, high boiling point solvents can tune CsPbBr$_3$ growth at both low and high temperatures, with the latter being used to compare a one-pot growth
mechanism, facilitated by microwave irradiation (MWI), and a hot-injection mechanism, via convection. The findings indicate that these solvents do tune PbX$_n^{2-n}$ formation, leading to controlled CsPbBr$_3$ growth and properties.
Experimental

**Chemicals:** Lead iodide (PbI₂, 99%), lead bromide (PbBr₂, 99.99%), cesium carbonate (Cs₂CO₃, 97%), methyl ammonium iodide (MAI, 98%), oleyl amine (OAm, 70%, technical grade), oleic acid (OAc, 90%), 1-octadecene (ODE, 90%), benzyl ether (BE, 98%), N,N-Dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Sigma Aldrich and used as received unless otherwise noted.

**Precursor Preparation:** In a typical one-pot reaction, precursors were first prepared by adding 0.80 g of Cs₂CO₃ to 30 mL of solvent (ODE or BE), along with 2.4 mL of OAc and the mixture was heated at 120°C under vacuum until all was dissolved (0.15 M Cs-OAc). Likewise, 0.28 g of PbBr₂ or 0.34 g of PbI₂ in 20 mL solvent was heated at 120°C for 1 h under vacuum. Next, 2 mL of OAc and 2 mL OAm was added to the mixture under Ar and the mixture was heated at 120°C for another hour for a complete dispersion of a 0.03 M PbX₂ stock solution. Trials were also run using purified OAm,⁴⁴ as were reactions where Cs₂CO₃ was reacted with OAc at higher ratios.⁴⁵

**One-Pot MWI Heating and Synthesis of CsPbX₃:** In a typical one-pot MWI heated reaction, 3 mL of the as-prepared PbX₂ precursor was purged with Ar gas for 5 min at room temperature. Next, 200 μL of the cesium oleate precursor solution was heated to 85 °C and injected to PbX₂ solution followed immediately by MWI heating to 160 °C where the trajectory of the heat transfer was different between BE and ODE, and depends on the dielectric constant (ε) of the non-polar solvents.⁴⁶ The BE reaction (ε = 3.82) reached 160 °C within 100 seconds, while the ODE reaction (ε = 2.25) reached after 240 s. Upon reaching this set point, there was a rapid quenching of temperature by the active cooling of the MWI reactor. These prepared nanoplatelets were purified
by centrifuging 1 ml aliquots at 10,000 rpm for 3 min, followed by the discarding of the supernatant and redispersion in toluene aided by sonication. This procedure was repeated at least two times, except in the case of FTIR sample preparation, in which additional purification steps were used.

_Hot Injection and Conventional Heating Based Synthesis of CsPbX3._ First, a 0.15 M Cs-OAc precursor was prepared as described in the precursor preparation section and was stored at 85 °C prior to injection. To prepare the PbBr2 precursor, a mixture of 0.14 g PbBr2 powder and 10 mL BE was heated under vacuum at 120 °C for 1 h. Then, the mixture was placed under Ar and 1 mL OAm and 1 mL OAc were injected to dissolve the powder. After 1 h, temperature was raised to 140 °C. Next, 0.8 mL Cs-OAc was injected to the solution, and the reactions were let to anneal for 1, 30, and 60 min before removing the heating mantle to quench the reaction. The products were purified as described above. This method was also used for the room temperature syntheses described, except that all reactants were cooled to room temperature before initiation.

_BE-CsPbI3 synthesis via Halide Exchange of BE-CsPbBr3:_ Prior to the halide exchange (HE), BE-CsPbBr3 were purified and redispersed in toluene to the approximated concentrations.47 This solution was then combined with an aliquot from a 0.20M PbI2 stock solution so that the combined [I⁻]:[Br⁻] = 1, following a method recently developed in our lab.48 The mixture was allowed to react for 30 min, then PL emission was measured. For XRD measurement, a portion of the mixture was separated, purified and drop-casted on a zero-diffraction quartz substrate. The rest of the mixture was centrifuged and redispersed in toluene to the initial volume to remove the free Br⁻ in the solution. In the second step, PbI2 with the same ratio of 1:1 was added to the remaining solution, followed by XRD and PL measurements.
**Benesi-Hildebrand Analysis:** The competitive assay analysis was performed by first preparing a 0.1 M MAI in BE. Next, MAI aliquots were added to a diluted BE-PbI$_2$ at a ratio of [MAI]:[PbI$_2$] = 1-35. The resulting Iodoplumbate complex formation was monitored by UV-vis spectroscopy.

**Instrumentation**

Microwave irradiation heating (MWI) was performed using a Discover-SP microwave synthesizer (CEM Inc.) with magnetron frequency of 2450 MHz, where temperature, power and time were controlled by Synergy software. Each reaction was stirred in a 10 mL glass vial during which temperature was monitored by a IR sensor. To stop the reaction, samples were cooled down by compressed N$_2$ circulating inside the microwave chamber. The optical characterization was performed on a Cary 50 Bio UV-vis spectrophotometer (Varian Inc.), and photoluminescence spectroscopy was performed on a Cary Eclipse fluorescence spectrophotometer (Varian Inc.). The excitation wavelength was 400 nm. The powder X-ray diffraction (XRD) was performed using D2 PHASER XRD (Bruker Inc.) with a Cu radiation source. Samples were prepared by drop-casting purified products on a zero-diffraction quartz holder. Transmission electron microscopy (TEM) was performed on either a JEM 2100F or JEM 1400 (JEOL Inc.), operated at 200 or 120 kV, respectively. Samples were drop cast from toluene dispersions onto carbon coated copper grids. Atomic Force Microscopy (AFM) analysis was performed on an Innova SPM (Bruker Inc.) in tapping mode using samples deposited on a freshly cleaved HOPG grid. Finally, Fourier Transform Infrared Spectroscopy (FTIR) spectra was collected using a Thermo Nicolet 6700 FTIR equipped with a diamond smart iTR attenuated internal reflectance accessory, and a liquid N$_2$ cooled MCT-A detector. Samples were prepared by three rounds of purification in toluene with centrifugation.
at 4k rpm for 10 minutes in a glass tube. Samples were then drop-casted on the iTR diamond and air-dried prior to the measurement.
**Results and Discussion**

Figure 1a shows a schematic illustration of the synthetic conditioned tailored to understand CsPbBr$_3$ growth using either benzyl ether (BE) or 1-octadecene (ODE) as non-polar high boiling point solvents, cesium carbonate dissolved and complexed with oleic acid (OAc) and lead plumbate ($\text{PbBr}_2^{2-n}$)$_n$ formed via dissolving in solvent (S) and ligands (L), as described in the experimental section. The products of these reactions are denoted as BE-CsPbBr$_3$ or ODE-CsPbBr$_3$. Two nucleation and growth mechanisms were studied, so-called one-pot and hot-injection, at either high temperature or low temperature.

![Schematic Illustration](image)

**Figure 1.** (a) Schematic overview of the reaction systems used in this study. UV-vis (a) and PL emission (b) spectra of the BE- (i), and ODE-CsPbBr$_3$ products prepared via MWI heating to 160 °C.

A one-pot mechanism using microwave irradiation (MWI) as the heating source was first employed, and the synthesis mixtures were heated to 160 °C. Upon cooling, the reaction solution had changed color from a light translucent yellow to a turbid orange, which if left overnight, would settle for the BE-CsPbBr$_3$ products, but not for the ODE-CsPbBr$_3$. After collection and
purification, the resulting optoelectronic properties were measured. Figure 1b shows the UV-visible absorption (UV-vis) results. The BE-CsPbBr$_3$ had a first excitonic absorption peak at 523 nm (i), while the ODE-CsPbBr$_3$ absorbed at 488 nm. Both products exhibited photoluminescence (PL), as shown in Figure 1c, with BE-CsPbBr$_3$ emitting at 527 nm (i), and ODE-CsPbBr$_3$ at 495 nm (ii). The red-shift indicates either larger sizes or thicker platelets for BE-CsPbBr$_3$. The band edge absorption is quantized by the minimum CsPbBr$_3$ dimension, especially when sizes are comparable to the exciton Bohr radius ($a_B$), which for CsPbBr$_3$ is ~ 7 nm. Using the studies reported by others,$^{19,22,24,52}$ we estimate a thickness of >15 monolayers (ML), where ML is defined a linear chain of corner sharing PbBr$_6^{4-}$ octahedra with thickness of 0.59 nm, for the BE-CsPbBr$_3$, corresponding to approximate thickness of 8 ~ 9 nm. We note that the absorption is broad, indicating a polydisperse sample and distribution in thicknesses. Using the same approach, the ODE-CsPbBr$_3$ would have a minimum feature size of ~ 9 ML, or ~5.3 nm.

Figure 2: Representative TEM micrographs of ODE-CsPbBr$_3$ (a) and BE-CsPbBr$_3$ products (b-e) Size analysis histogram of BE-CsPbBr$_3$ showing platelet 2D dimensions (f).
The dimensions and morphology of the two products were characterized using transmission electron microscopy (TEM). Figure 2a shows a micrograph for the ODE-CsPbBr$_3$ products, which has small square-like lateral morphology with a length of ~9.7 ± 0.8 nm, which combined with the optical data above is ~5 nm thick, and is consistent with other ODE based CsPbBr$_3$ platelets. In contrast, the BE-CsPbBr$_3$ products had larger 2D platelet-like morphology, as shown in Figure 2b-e, and supporting Figures S1. The large platelet morphology of the products was highly reproducible; however, the lateral dimensions were polydisperse. For example, the platelets largest length varies from 20 - 500 nm. The platelets were indeed thin, as suggested by the UV-vis, as illustrated in the TEM micrographs where the platelets orient on top of another.

The thickness was also probed by atomic force microscopy (AFM). Figure S2 shows a typical AFM image of BE-CsPbBr$_3$ platelets dropcast from a toluene dispersion onto a HOPG grid. At the resolution shown, domains consisting of many platelets are imaged. Importantly, sharp edges can be observed, and cross-section analysis reveals overall thickness profiles of the domains (Fig. S2). The heights measured vary slightly, from 3-5 nm, which are thinner than the ML estimate from the main absorption band above, suggesting that thinner platelets were sampled. We note that some products dispersions showed significant aggregation, and after drop casting, domains revealed stacks or clusters of platelets that revealed larger heights. To understand this, scanning electron microscopy (SEM) was used to image those dropcast substrates. Figure S3 shows the platelets and the 2D morphology, as well as grouped discrete aggregates, which were difficult to separate, and was attributed to either residue BE in the purified product, or the result of excess purification steps, as described below.
Figure 3: Representative powder XRD of BE-CsPbBr$_3$ (i) and ODE-CsPbBr$_3$ products (ii), as compared to an orthorhombic CsPbBr$_3$ standard (97851-ICSD).

The crystalline nature of the CsPbBr$_3$ products were studied by powder X-ray diffraction (XRD). Figure 3 shows the XRD analysis of the BE- (i) and ODE-CsPbBr$_3$ (ii), as compared to an orthorhombic CsPbBr$_3$ bulk standard. Both products index with the orthorhombic standard with minimal variation to Bragg angles, but intensity ratios differed, as did the extent of Scherrer broadening. For example, the BE-CsPbBr$_3$ (i) showed pronounced preferred orientation of the planes diffracting at $2\theta = 30.4$ and 30.7°, which correspond to (004) and (220) of the crystal. Clearly, the intensities do not match the standard, and suggest not only that each platelet grows in the same orientation, but that each platelet is highly crystalline. It’s important to note that preferred orientation in XRD can be a result of crystal growth, as well as an artifact produced by the way a
sample self-assembles during drying, as well as by substrate type and sample-to-substrate interactions.\textsuperscript{53} We suspect that each of these factors influence the XRD shown here. The samples were prepared via drop-casting from a concentrated solution, and we assume they form into the irregular clusters shown by SEM (Fig. S3). Nonetheless, a number of control experiments were performed to better understand the peak intensities and the origin of the preferred orientation. To test whether the intensity ratios could be an artifact of platelet drying on the XRD substrate, samples that were both drop cast from solution, and from dried powders, each of which showed similar intensities. In another control, a concentrated carbon black slurry with colloidal carbon (\(\sim 20\) nm) was added to a toluene solution of purified \(\text{BE-CsPbBr}_3\), sonicated, and dropcast, with the aim of using the carbon to inhibit platelet stacking during drying. This however resulted in similar XRD signatures (Fig. S4), suggesting that crystal orientation plays at least some role, and that growth occurs in the (004) and (220) directions of the platelets, of which (220) can be indexed to the longer dimension of the platelet. The thickness of the platelets, and thus the planes of atoms in that direction, are outweighed in terms of number, and have lower Bragg intensities. The ODE-CsPbBr\(_3\) on the other hand (ii), had intensity ratios consistent with that of bulk, as well as broadening consistent with the smaller dimensions.

The halide concentration of the platelets could also be fine-tuned, either by introducing iodide (I) into the synthetic solutions, or via halide exchange (HE), resulting in \(\text{BE-CsPbBr}_{3-x}\text{I}_x\). Here, we focused on only the BE solvent, since there are numerous examples of halide control in ODE-based products.\textsuperscript{54} Figure S5 shows the PL for \(\text{BE-CsPbBr}_{3-x}\text{I}_x\), synthesized by varying the [Br]:[I\textsuperscript{-}] feed ratio, with the corresponding XRD shown in Figure S6. The XRD signatures were consistent with those platelet morphologies shown above and increased I-rich content is indicated by shifts in 2\(\theta\). Products formed at low I\textsuperscript{-} concentrations showed the platelet like preferred orientation,
however this was lost at high I content. Alternatively, HE could be used to transform the BE-CsPbBr\(_3\) via addition of I\(^{-}\) rich precursors\(^{54}\) or small organohalide molecules.\(^{55,56}\) Using a protocol recently developed in our lab,\(^ {48}\) we found that the BE-CsPbBr\(_3\) platelets could undergo HE without disrupting the crystal structure, and allowed for a broader control of composition than direct synthesis (Fig. S7). A more detailed study of the synthesis of mixed halides and of halide exchange in BE-CsPbBr\(_3\) are beyond the scope of this paper and will be reported elsewhere.

The novel component of this study is understanding the role of BE in the formation of CsPbBr\(_3\), and we next prepared BE-CsPbBr\(_3\) not with MWI heating, but and instead via hot-injection. In contrast to MWI based heating, in which all precursors are in ‘one-pot’ and growth is facilitated or activated by heating, ‘hot-injection’ introduces the final precursor at an elevated temperature, inducing burst nucleation and growth of what is typically a smaller and more monodispersed product. Figure 4 shows a set of TEM micrographs for BE-CsPbBr\(_3\) products collected after hot injection and \(~1\) min annealing at \(140^\circ\)C (a-c), and after annealing for \(30\) min (d). One observation made after synthesis was that the product had soluble and insoluble fractions after \(1\) min (Fig. S8a). A TEM of the soluble portion is shown in Figure 4a, with small square crystals with edge lengths of \(l = 6.8 \pm 1.1\) nm visible. The insoluble portion (5b-c) shows larger square platelets with edge lengths of \(l = 11.1 \pm 3.5\) nm. Both fractions showed smaller clusters or nuclei with diameters of \(d \sim 3.5\) nm and very uniform inter-cluster distances, see arrow. Based on the optical signature, which showed a band edge absorption at \(500\) (a-c) and \(510\) nm (d), these had thicknesses of \(~2\) ML, respectively (Fig. S8), making them much thinner than the MWI based products.
Figure 4: (a-d) Representative TEM micrographs of BE-CsPbBr$_3$ products via hot-injection in BE. Samples collected from soluble (a, $l = 6.8 \pm 1.1$ nm) and non-soluble fractions (b-c, $l = 11.1 \pm 3.5$ nm) of the synthesis solution after centrifugation. Early reaction times show a high concentration of small clusters (arrow, $d \sim 3.5$ nm). The sole non-soluble product after 30 min annealing (d, $l_1 = 17.4 \pm 2.6$ nm, $l_2 = 10.4 \pm 1.6$ nm).

Figure 5 shows the powder XRD for BE-CsPbBr$_3$ soluble (i) and insoluble (ii) products from hot-injection, as compared to ODE-CsPbBr$_3$ (iii). Compared to the MWI BE-CsPbBr$_3$ products (Fig. 4), these showed more cubic crystal characteristics, with the insoluble products (ii) showing some preferred orientation. The ODE-CsPbBr$_3$ similarly showed cubic similarities, but with slight 20 shifts that may suggest some orthorhombic features.
Figure 5: Representative powder XRD of BE-CsPbBr$_3$ hot-injection products for soluble (i), and insoluble (ii) fractions and ODE-CsPbBr$_3$ (iii) after ~1 min annealing. Reference patterns for cubic (1533063-COD, red) and orthorhombic CsPbBr$_3$ (97851-ICSD, blue).

We hypothesize that the reason why BE and ODE produce different morphologies is due to the different fractions of precursor types at the time of nucleation, as well the affinity of the solvent to Pb$^{2+}$. Figure 6 shows the electronic absorption of PbBr$_2$ solid dissolved in BE (i) and ODE (iv), and mixtures of BE+OAm+OAc (ii), as well as ODE+OAm+OAc (iii). The absorptions observed are categorized broadly as exfoliated PbBr$_2$ solids, which may be two dimensional in nature,$^{50}$ and multiple PbBr$_{n+2}$ lead plumbate complexes which are often defined as PbBr$_6^{2-}$, PbBr$_3^-$, and PbBr$_4^{2-}$. Comparing (i) to (iv) reveals that BE is more effective at dissolving PbBr$_2$ to PbBr$_{n+2}$ than ODE. This was also physically observed in the experiment, where BE dissolved the PbBr$_2$ salt with less visible solids than ODE, in which a high percentage of insoluble salt was still
observed. Secondly, the addition of OAm and OAc further dissolves the solids in the case of ODE and shifts the absorption wavelengths in BE. Both solvent plus ligand mixtures show high concentrations of PbBr$_2$,$^{2-n}$, likely the result of ligand coordination to Pb$^{2+}$ and substitution of one or more bromides (see below), with ODE+OAm+OAc still showing a considerable percentage of insoluble PbBr$_2$. Whether or not this solid PbBr$_2$ is incorporated into forming the nano CsPbBr$_3$ is likely dependent on the effect of the synthetic temperature on dissolution equilibrium.

Figure 6: The UV-vis of [PbBr$_n$]$_{2-n}$ formed via PbBr$_2$ dissolved in BE (i), BE+OAc+OAm (ii), ODE+OAc+Oam (iii), and ODE (iv) at 140 °C under vacuum for 1h and then cooled to room temperature. Approximate absorption regions for different [PbBr$_n$]$_{2-n}$ complexes are shown. Spectral ranges used vary due to solvent absorption.

This insight suggests that BE coordinates and solvates PbBr$_2$ better than ODE, which is understandable considering it’s π-rich nature. Researchers have studied the solvent effect of
perovskite formation previously, especially as it relates to thin film formations of methyl ammonium halides (MAPbX₃) using polar solvents.⁴² And, we note that BE has been used in nanoparticle synthesis before, especially in the recent synthesis of Qdot heterostructured libraries.⁵⁷,⁵⁸ By using a competitive assay between solvents and halides, a Benesi-Hildebrand analysis can be used to approximate coordination strength by way of estimating equilibrium constant (K) and Guttmann donor number (DN), which measures PbBr₂ⁿ⁻펫 concentration and type in the presence of excess halides by way of UV-vis.⁴²,⁴³,⁴⁹,⁵⁹ For instance, Loo and co-workers compared solvent dielectric constants and DN with either crystal growth or thin-film growth mechanisms, and showed that while ε values did not predict growth, that DN > 15 consistently resulted in thin film growth, whereas higher numbers consistently showed crystal growth.⁴² Thus, higher DN solvents, typical polar and strong Lewis bases, coordinate favorably with Pb²⁺, resulting in PbBr₂ⁿ⁻ϕ with higher n, resulting in more crystal growth (ideal building blocks), whereas DN < 15, coordinate weakly with Pb²⁺, resulting in lower n, and more amorphous or thin-film growth.⁴² To date, most analysis is compared to polar solvents, like DMF and DMSO, both of which bind strongly to Pb²⁺ and decrease plumbate equilibrium.⁴²,⁴³,⁴⁹ Both BE and ODE are considerably less polar that many of these solvents used for perovskite growth. Figure S9 shows a Benesi-Hildebrand assay used to compare BE and ODE, to DMF, where PbI₂ and MAI were used in place of PbBr₂ and MABr. Both assays resulted in equilibrium (K) values comparable to other non-coordinating solvents, where KBE ~ 74 M⁻¹ and KODE ~ 84 M⁻¹, indicating that BE binds stronger to PbBr₂ⁿ⁻ϕ than ODE, but much weaker than DMSO (KDMSO ~10, Fig. S9). The composition of the final organic capping monolayer of BE-CsPbBr₃ was also studied via Fourier Transform Infrared (FTIR) spectroscopy, and shown in Figure S10. Vibrations attributed to BE adsorbed to the CsPbBr₃ interface were consistently observed, further suggesting coordination.
While the DN and K values aid in understanding the \( \text{PbBr}_2 \) dissolution, the cesium oleate precursor is also important, and can have different temperature dependent and stoichiometry related solubility. Control experiments fully solubilizing cesium oleate (\( \text{Cs}^+\text{-OAc} \)) at room temperature were performed, which used high OAc-to-Cs molar ratios, following a method recently described.\(^{45} \) The products of that control synthesis using MWI had more soluble final products, but the platelet morphology and XRD intensity ratios persisted (Fig. S11). This Cs precursor was also used in the hot-injection synthesis described above.

![Figure 8](image)

**Figure 8:** An idealized mechanism schematic for the growth of CsPbBr\(_3\) using BE or ODE solvents.

Considering the procedural steps employed in this study, and the findings above, Figure 8 idealizes the mechanism for CsPbBr\(_3\) growth. The dissolution of PbBr\(_2\) salt (a) in a solvent (\( S = \text{BE or ODE} \)) produces two intermediates, two dimensional, exfoliated (PbBr\(_2\)), solid layers solvated by S, as described recently,\(^{50} \) and the PbBr\(_n\),\(^{2-n} \) plumbates of various coordination, such as PbBr\(_4\), PbBr\(_3\), etc.\(^{51,60} \) Here, the PbBr\(_n\),\(^{2-n} \) may have a Br\(^-\) substituted by S, which is not charged (b). Upon addition
of ligands ($L = \text{OAm, OAc, OAm+OAc}$), the equilibrium shifts to forming a higher percentage of $\text{PbBr}_n^{2-n}$ afforded by strong $L\text{-to-Pb}^{2+}$ coordination (c), which breaks the PbBr2 into smaller fragments or lower molecular weight polyhedra. Upon the addition of Cs$^+$ (d), the $\text{PbBr}_n^{2-n}$ polyhedra are electrostatically attracted to one another, forming $2-n\text{Cs}^+\text{PbBr}_n^{2-n}$ complexes, but still under the coordination of excess $L$ and $S$. In this study, steps a-c (precursor preparation) occurs over the course of an hour, whereas step (d) occurs over a few minutes before heating in the case of MWI heating, or within seconds during hot-injection. Upon heating, the $2-n\text{Cs}^+\text{PbBr}_n^{2-n}$ complexes loose coordinating $S$ as well as $L$ and are consumed producing CsPbBr$_3$ perovskite platelets (e). Loss of coordinating solvent during heating is often observed in the formation of perovskite thin films from polar solvents, however in this study, loss of solvent refers to those molecules that were either coordinating to the crystal or separating intermediate plumbates. It is possible that both BE DN numbers likely reside in the thin-film growth regime, as described above, resulting in large mesoscale platelets are observed with prolonged MWI heating and smaller square platelets are formed via quick hot-injection, while ODE produces smaller crystallites of similar sizes for both heating conditions. Also of importance is the temperature used, as it will influence the equilibrium between $\text{PbBr}_n^{2-n}$ types and CsPbBr$_3$ crystalization in the presence of $S$ and $L$, promoting $\text{PbBr}_n^{2-n}$ at lower temperatures.

Interestingly, if the reaction is held at step d for long periods of time (days) at room temperature (f), then differences between BE and ODE can also be observed. Kinetically, the BE-CsPbBr$_3$ formed slower and resulted in thinner CsPbBr$_3$ (Fig. S12), where smaller crystallites are formed that have well defined inter-crystal distances, which we attribute to repulsion from coatings of charged PbBr$_n^{2-n}$ at the interface. A TEM image of these is shown in Figure S13. The slower kinetics and smaller crystal size ($d \sim 3$ nm) in the case of BE at room temperature again suggests
strong coordination to PbBr$_{n}^{2-n}$, the release of which is more sensitive to temperature. ODE on the other hand formed uniform rod like structures with lengths < 15 nm. This final point suggests that judicious selection of both solvent as well as modest temperature changes may allow for a wealth of morphologies to be formed and controlled, which is part of our ongoing work and will be reported elsewhere.

**Conclusion**

Taken together, a synthesis route for CsPbBr$_3$ nanoplatelets has been described in which choice of non-polar solvents and heating method can be used to control morphology. The findings demonstrate that combining BE, a one-pot mechanism, and MWI heating prove effective at influencing nucleation and growth to the point of forming highly crystalline platelets, with lateral dimensions of 20-500 nm, and relatively thick, ~15 ML, thicknesses. These platelets show preferred orientation in XRD signatures along the (220) and (004) planes. Synthesis via hot-injection with BE also leads to platelets, but a more uniform square shapes, ~17 nm lengths, and ~2 ML thicknesses. On the contrary, use of ODE results in small crystallites, ~10 nm, in both heating approaches. The ability of the solvent, and solvent plus ligand mixtures to dissolve PbBr$_2$ salt into varied PbBr$_{n}^{2-n}$ plumbates was studied, and showed that BE is more effective, due in large part to its π-donating character and coordination to Pb$^{2+}$. The compositions of the BE-CsPbBr$_3$ could be tailored by adding iodine either via synthesis upon addition of PbI$_{n}^{2-n}$ during synthesis, or via halide exchange.

**Associated Content**

The Supplemental Information is available free of charge. Experimental details, control studies, and supplemental Figures S1-S13.
Author Contributions
H.Z. and T.H.C. performed the synthesis, optical and XRD analysis, K.R.K. performed halide exchange studies, A.J.H performed AFM and SEM studies. H.Z. and M.M.M. conceived of the study and wrote the manuscript with input from all other authors.

Notes
The authors declare no competing financial interest.

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References


TOC Graphic

\[ [\text{PbBr}_3]_x \cdot (\text{OAm})_m + \text{Cs(OAc)}_n + \text{OAm} + \text{OAc} \rightarrow \text{CsPbBr}_3 + \text{MWI} + \text{Benzyl Ether} \]