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Precise Control of CsPbBr₃ Perovskite Nanocrystal Growth at Room Temperature: Size Tunability and Synthetic Insights

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ABSTRACT: Room-temperature perovskite nanocrystal syntheses have previously lacked the size tunability attainable through high-temperature methods. Herein, we outline a scalable approach whereby the nucleation and growth of CsPbBr₃ nanocrystals (NCs) can be decoupled and controlled at room temperature by utilizing different ligands. We employed octylphosphonic acid (OPA) ligands to regulate the critical radius and the NC growth rate. The subsequent addition of a bulkier didodecyldimethylammonium bromide ligand quenches the NC growth, defining the reaction duration. Management of these three variables enables precise tuning of the NC diameter between 6.8 and 13.6 nm. The photoluminescence quantum yield of the NCs remains above 80% for all sizes even after thorough antisolvent purification. The use of hydrogen-bonding OPA ligands enhances quantum confinement effects, characterized by strong, well-resolved absorption peaks. Solution and solid-state nuclear magnetic resonance spectra confirmed the effective removal of unbound ligands during purification and the presence of a hydrogen-bonded network of OPA ligands on the surface of the purified NCs. Overall, this approach has the potential to facilitate a broad range of future endeavors from studies of hot carrier dynamics to both optically and electrically driven device applications.

INTRODUCTION

Lead halide perovskite nanocrystals (NCs) have been established as excellent emissive materials in recent years due to their extremely narrow emission bandwidths and near-unity photoluminescence quantum yield (PLQY).^{1–6} Thus, they possess the potential to facilitate highly efficient displays with wide-color gamuts.^{7–14} The relatively low cost of perovskite precursor salts and their compatibility with solution-processing techniques strengthen their suitability for such commercial applications. Cesium-based perovskite NCs (CsPbX₃) are generally considered the most appealing compositions as their all-inorganic nature provides greater thermal, environmental, and light stability.^{15–17}

Currently, most reported CsPbX₃ NCs are synthesized at high temperatures (>140 °C) under an inert environment according to the “hot-injection” method.^{18,19} The size of NCs synthesized by hot injection can be controlled by the precise reaction temperature, while rapidly cooling the reaction mixture in an ice bath provides a reliable mechanism to quench the NC growth and limit size defocusing. A wide range of perovskite NC compositions have been synthesized using this method, with emission peaks ranging from around 410 nm for CsPbCl₃ to 780 nm for FAPbI₃.^{20–22}

As a result, it has proven a reliable approach, facilitating fundamental studies,^{23–25} ligand engineering,^{26–28} and highly efficient optoelectronic devices, such as light-emitting diodes (LEDs)^{29,30} and solar cells.³¹

Despite its success, the hot-injection method inherently hinders the commercial viability of perovskite NCs. Scaling up the Schlenk line setup is costly and complicated, and the difficulty is further compounded by the necessity to instantaneously inject a large volume of a precursor, followed by rapidly cooling by more than 100 °C within seconds. Alternative room-temperature processes, particularly those conducted in an ambient environment, are far more viable and economically appealing.

There has been significant progress made with room-temperature CsPbBr₃ NC syntheses over the past few years.³² Initially, ligand-assisted reprecipitation methods were employed,³³ but the low solubility of CsX salts in polar solvents has hindered reaction yields.³⁴ Moreover, the presence of the polar solvent in the reaction mixture can lead to degradation of the as-synthesized NCs. Consequently, it has proven very challenging to obtain stable NC inks of sufficient concentrations for device fabrication using this method. Instead, various researchers have explored polar solvent-free methods.^{35,36} Song et al. developed a scalable approach which

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Scheme 1. Overview of the Synthesis Protocol Employed; the Ball-and-Stick Illustrations Represent the Ligands, with Different Functional Groups (Balls) and Alkyl Groups (Sticks), While the Green Spheres Represent the Nanocrystals

mimicked the chemistry of a typical hot-injection synthesis, exploiting ligand interactions to dissolve the precursors under ambient conditions.³⁷ In this work, they dissolved Cs₂CO₃ directly in octanoic acid (OctAc), while PbBr₂ was dissolved in toluene with the aid of tetraoctylammonium bromide. Postsynthetic addition of didodecyldimethylammonium bromide (DDAB) enhanced the PLQY and colloidal stability, leading to the fabrication of LEDs with impressive EQEs of ~6 and 11.6% for CsPbBr₃ and Cs_{0.85}FA_{0.15}PbBr₃ NCs, respectively. However, the inclusion of formamidinium (FA) in the inorganic metal halide system somewhat compromises the thermal stability.³⁸

Almeida et al. pioneered a different approach using a phosphine oxide-enabled synthesis.³⁹ Trioctylphosphine oxide (TOPO) was first used to solvate PbBr₂ in octadecene with oleic acid. The subsequent injection of Cs-oleate in excess oleic acid released PbBr₂, triggering the nucleation of CsPbBr₃ NCs with a PLQY of up to 61%. The authors observed that the lack of amines and the hydrogen bonding of TOPO under acidic synthetic conditions suppressed Ostwald ripening. Consequently, the acidic conditions enabled impressively high reaction yields close to the theoretical maximum. However, their syntheses were mostly conducted at an elevated temperature (75 °C) as room-temperature attempts only yielded very small NCs.

Despite multiple reports of exceptional properties from low-temperature synthesized CsPbBr₃ NCs, the same excellent size control provided by hot-injection syntheses has not yet been demonstrated. Size control at room temperature is highly desirable as it provides the flexibility to easily tune and optimize toward specific applications or fundamental studies, without the need for tedious precursor preparation, Schlenk line equipment, and advanced wet chemistry expertise.

Herein, we report a room-temperature approach for the synthesis of size-tunable CsPbBr₃ perovskite NCs. The nucleation and growth stages can be effectively decoupled by reducing and controlling the NC growth rate with octylphosphonic acid (OPA) ligands. Injection of the bulky

ligand, DDAB, provides a mechanism to quench the NC growth, establishing the necessary control over the reaction duration, in addition to ensuring consistent colloidal stability and PLQY from NCs of different sizes. Together, OPA and DDAB enabled size tunability by the precise adjustment of the OPA concentration ([OPA]) and the reaction duration.

Using this method, the CsPbBr₃ NC diameter can be tuned from 6.8 to 13.6 nm, which corresponds to emission wavelengths between 501 and 517 nm. The emission peak remains a narrow full width at half-maximum (fwhm = 16 to 19 nm) regardless of NC size due to the absence of Ostwald ripening. Crucially, for all NC sizes, the PLQY after purification is maintained above 80%.

This protocol has the potential to facilitate various fundamental studies on topics such as CsPbBr₃ NC growth kinetics,⁴⁰ the size dependence of optical and electronic properties, and investigation of hot carrier dynamics.^{23,41} Moreover, the use of strong binding ligands grants high PLQY and colloidal stability even after thorough antisolvent purification, demonstrating great potential for optoelectronic device fabrication.

RESULTS AND DISCUSSION

Our room-temperature synthesis follows a polar solvent-free route. Cesium carbonate (Cs₂CO₃) was dissolved in octanoic acid (OctAc) to obtain a precursor containing cesium octanoate (0.2 M) and excess OctAc. Lead bromide (PbBr₂) was dissolved in toluene (0.09 M) by adding TOPO (0.9 M) and heating at 80 °C in air for 10 min. After cooling to room temperature, PbBr₂ remained dissolved, presumably owing to the formation of a soluble metal–ligand complex with TOPO.³⁹ OPA was then introduced to the PbBr₂–TOPO solution; hydrogen bonding between OPA and TOPO allowed OPA to be dissolved at sufficiently high concentrations. The exact concentration of OPA was adjusted to modulate NC growth, as discussed later.

To nucleate CsPbBr₃ NCs, the Cs⁺ precursor was added into the PbBr₂ solution at a 1:9 v/v ratio, which corresponds to a

Figure 1. (a) PL peak position and quantum yield data for CsPbBr₃ NCs synthesized without OPA for various growth durations, (b) TEM images of NCs of similar diameters synthesized without OPA or with 0.1 M OPA (both 300 s growth duration), and (c) CsPbBr₃ NCs synthesized with various [OPA] for a fixed 300 s growth duration. The PL spectra for the relevant samples are superimposed on each plot.

Figure 2. TEM images of CsPbBr₃ NCs synthesized with [OPA] from 0.1 to 0.6 M for a 300 s growth duration. The mean diameter of the NCs and the corresponding standard deviations are shown.

significant excess of PbBr₂ (Cs/PbBr₂ = 1:4.14). After the desired reaction duration, a toluene solution of DDAB (0.05 M) was injected. DDAB quenches the NC growth, presumably through the occupation of surface Cs⁺ vacancies by the bulky DDA⁺ species.⁴² The Cs-deficient reaction conditions are expected to promote Cs⁺ vacancies, allowing a high surface density of DDA⁺. After 5 min, the NCs were isolated by centrifugation with ethyl acetate (3:1 v/v), followed by redispersion in the fresh solvent. The NCs were washed further with methyl acetate (3:1 v/v) to obtain a fully purified NC dispersion. An overview of the synthesis is presented in Scheme 1.

The quenching of NC growth by DDAB addition was first verified. These reactions were conducted without OPA to demonstrate that the growth quenching mechanism is effective for different anionic ligands. Multiple reactions were conducted with various durations between Cs⁺ precursor injection and DDAB treatment (30–300 s). For these reactions, the overall time between nucleation and NC precipitation with the antisolvent was kept constant at 600 s. This was achieved by adjusting the time between DDAB and antisolvent additions for each reaction accordingly (e.g., if DDAB was added after 30 s, ethyl acetate was added after a further 570 s).

Figure 1a shows that without OPA, the emission peak shifts gradually from 514.6 to 516 nm with increasing growth duration before DDAB addition, indicating an increase in NC diameter. These results supported the successful quenching of NC growth with DDAB. There is also a decrease of PLQY from 79 to 66% with increasing growth duration, although the fwhm is reduced from 18.2 to 17.1 nm. This suggests that there is no significant size defocusing due to Ostwald ripening. However, transmission electron microscopy (TEM) (Figure 1b, top) revealed irregular rounded cuboidal NCs, which suggests that there may be poor ligand control over the NC growth without OPA. Even without OPA, NC growth is slow enough such that the NC size can be controlled by adjusting the growth duration. However, the accessible emission wavelength range is minimal, and the regularity of both size and shape is poor.

Next, the influence of OPA on the NC size was examined by comparing the outcome of syntheses performed with and without OPA. Figure 1b (bottom) shows that when 0.1 M OPA was used, the NCs had much better size regularity. Improved shape regularity is also observed, as demonstrated by the extensive hexagonal superlattice formed on the TEM grid, with 2D shapes varying between hexagonal and circular. A previous study on CsPbBr₃ NCs synthesized with phosphonic

acid ligands at elevated temperature observed similarly shaped particles, which were found to be truncated octahedrons.⁴³ This explains the shape variations seen in the TEM image here as truncated octahedrons have various orthogonal projections ranging between hexagonal and pseudo-circular depending on their orientation.

The effect of OPA was assessed in more detail by performing several syntheses with various [OPA], ranging from 0.1 to 0.6 M, for a fixed 300 s reaction duration. Figure 1c demonstrates that as [OPA] increases, the peak emission wavelength blue-shifts incrementally, tuning from 516 to 506 nm. Crucially, the PLQY increases and maintains above 80% for all concentrations. As a softer and stronger acid than OctAc, OPA can passivate under-coordinated Pb²⁺ more effectively.^{26,44} The potential for inter-ligand hydrogen bonding between bound phosphonic acid species is anticipated to provide better size control and shape regularity.^{43,45} Oleylphosphonic acid has very recently been found to improve the size control of CsPbBr₃ NC syntheses at an elevated temperature (100 °C).⁴⁶

TEM images for NCs synthesized with [OPA] from 0.1 to 0.6 M are shown in Figure 2, while the corresponding size histograms are found in Figure S1. The NC size distribution with varying [OPA] was also analyzed by the fitting of small-angle X-ray scattering (SAXS) data to provide a more statistically reliable size distribution,⁴⁷ as shown in Figure 3. The fitting of the SAXS data gave a volume-weighted size distribution, in contrast to the number-weighted distribution obtained from TEM. As a result, the mean diameters measured by SAXS were generally slightly larger.

All samples exhibit a narrow symmetrical size distribution, but the size distributions are found to be narrower for higher [OPA], suggesting that OPA enhances NC size control. Figure S2 shows powder X-ray diffraction (XRD) data for NC samples prepared with different [OPA], confirming that there were no phase changes as the NC size was decreased. The relative intensities of the diffraction peaks match exceptionally well with the diffraction pattern reported by Manna and co-workers for their truncated octahedron-shaped CsPbBr₃ NCs.⁴³

The tunability of the NC diameter with [OPA] for a fixed reaction duration suggests that OPA modulates the NC growth rate. Figure 4 verifies this by contrasting the NC diameter (extracted from fitting SAXS data^{47,48}) for different [OPA] for reactions quenched after 30 and 300 s.

As expected, Figure 4 shows that the extent of NC growth between 30 and 300 s decreases with increasing [OPA]. This indicates that the growth rate is reduced. However, intriguingly, the decreasing trend for the 30 s reactions inverts when [OPA] increases above 0.3 M, with the NC diameter increasing from 6.4 to 7.6 nm at 0.6 M. The contrasting trends of the 30 and 300 s reactions suggest that [OPA] influences the nucleation and growth phases differently. This presents an opportunity to demonstrate how the control over the growth kinetics afforded by our new protocol could uncover insights on nucleation and growth, which are concealed by the ultrafast kinetics of high-temperature syntheses.

First, we analyzed the nucleation phase. According to the thermodynamic theory for the nucleation of colloidal particles, the minimum size of nuclei that are stable with respect to dissolution is known as the critical radius, r_c , which is given by⁴⁹

Figure 3. NC size distributions extracted from SAXS measurements performed on CsPbBr₃ NC dispersions synthesized with [OPA] from 0.1 to 0.6 M for a 300 s growth duration. The mean NC diameter and the corresponding standard error of the mean are shown on each plot.

Figure 4. Diameter of CsPbBr₃ NCs (obtained from SAXS) synthesized with [OPA] from 0 to 0.6 M for 30 or 300 s growth durations. The error bars show the standard error of the mean.

$$r_c = \frac{2\gamma V_m}{N_A k_B T \ln S}$$

Given that Avogadro's number, N_A , the Boltzmann constant, k_B , the molar volume, V_m , and the temperature, T , are constant for this synthesis, the size of nuclei formed should be governed by the surface energy, γ , and the supersaturation, S . Consequently, it can be inferred that decreasing γ by increasing

Figure 5. (a) Peak PL wavelengths (red) and PLQY (blue) of CsPbBr₃ NCs synthesized with [OctAc] or [OPA] from 0 to 0.6 M for 30 s growth durations; (b) absorbance and PL spectra of CsPbBr₃ NCs synthesized with OPA (0.3 M) for growth durations of 5 or 30 s and (c) with OctAc (0.4 M) or OPA (0.3 M) for a growth duration of 5 min.

either the surface ligand density or ligand binding strength should reduce the size of nuclei. This explains the reduction of NC diameter for the 30 s reactions as [OPA] increases to 0.3 M.

The reversal of the trend above 0.3 M must instead be correlated to the other variable, supersaturation. Supersaturation is defined as the ratio between the bulk concentration of monomers in solution, [M], and the equilibrium concentration (i.e., solubility) of the monomers, [M]₀. Therefore, either a decrease in the concentration of monomers or an increase in their solubility would be required to reduce supersaturation, leading to the increased *r_c* observed above 0.3 M OPA.

An initial analysis of the expected interactions between OPA and other species in the reaction mixture does not appear to present a mechanism which could stabilize either monomer [Cs(OctAc) or PbBr₂]. An increase in [OPA] would be expected to increase the competition for TOPO coordination, instead destabilizing PbBr₂ and reducing the critical radius further. However, an examination of the interaction between OPA and the Cs precursor Cs(octanoate) led to a critical hypothesis, as illustrated by the following equilibrium

As OPA is a stronger acid than OctAc, this equilibrium should lean toward the right when [OPA] ≈ [OctAc]. We calculated that [OctAc] in the reaction mixture is 0.63 M, so as [OPA] → 0.6 M, Cs(OPA) should be present at a significant concentration, comparable to Cs(OctAc). This is significant because OPA is a diacid; hence, Cs(OPA) has a remaining hydroxyl group, while Cs(OctAc) does not. As a result, Cs(OPA) can still form hydrogen bonds with TOPO, as described by a further equilibrium

Therefore, we hypothesize that at high [OPA], the average solubility of Cs-containing monomers would be increased substantially due to hydrogen bonding between Cs(OPA) and TOPO. We further speculate that because PbBr₂ is in excess in the reaction mixture, the supersaturation of Cs monomers has a more decisive influence on the nucleation dynamics than PbBr₂ monomers.

To test our hypothesis, NC syntheses with a 30 s duration were conducted using OctAc in the PbBr₂ precursor instead of OPA. Figure 5a shows that for OctAc, the peak PL wavelength consistently decreases as [OctAc] is increased from 0 to 0.6 M,

with no inversion of the trend. This supports the influential role of hydrogen bonding between Cs(OPA) and TOPO at high [OPA].

The hydrogen-bonding capability of Cs(OPA) monomers here could be considered analogous to the hydrogen bonding between FA(oleate) and TOPO highlighted by Ashton et al., which showed a disruptive influence in their FAPbBr₃ NC synthesis.⁵⁰ This emphasizes the importance of understanding and manipulating the interactions between species in the reaction mixture in order to impose control over the properties of the final NC ink.

Next, we explored the NC growth phase. The NC growth rate is generally considered limited by either the diffusion of monomers to the surface or the rate of the reaction on the NC surface.⁵¹ In this case, the effective quenching of NC growth by the addition of the bulky DDAB ligand strongly suggests that the surface reaction limits the growth. Hence, surface–ligand interactions should also affect the growth considerably before DDAB addition.

We first analyzed the initial stage, between 5 and 30 s, after nucleation but before any discernible growth. Figure 5b shows that although the band edge absorption and PL emission wavelengths remain the same, there is a significant enhancement of the excitonic absorption peaks between 5 and 30 s and a slight narrowing of the PL fwhm (~1 nm). This suggests that some size focusing occurs. We hypothesize that when OPA is used, the initial postnucleation phase is characterized by a surface ligand exchange of Cs(OctAc) for Cs(OPA). The corresponding release of free TOPO would increase the solubility PbBr₂, thus increasing *r_c* and destabilizing the smallest nuclei with respect to redissolution. Imran et al. recently observed similarly prominent excitonic peaks from CsPbBr₃ NCs when the monodispersity was improved.⁵²

To investigate this further, we compared CsPbBr₃ NCs synthesized using OPA (0.3 M, 120 s) with NCs of similar emission wavelengths that were synthesized using OctAc (0.4 M, 300 s) in place of OPA. The absorption spectra in Figure 5c demonstrate that without OPA, the excitonic features are far less prominent. Also, the PL spectra suggest that there is a corresponding narrowing of the NC size distribution with OPA as the fwhm is reduced from 20 to 18 nm. Both these observations highlighted the greater control exerted over the NC growth by OPA.

The above observation may also explain the difference in the NC morphology observed in the TEM images in Figure 2. NCs that grow substantially after nucleation exhibit shapes

Figure 6. Optical characterization of CsPbBr₃ NCs synthesized with [OPA] = 0.3 M and various growth durations: (a) NC diameter and PLQY plots, (b) PL spectra, (c) absorbance spectra, (d,e) relative TA spectra up to 1000 ps, and (f,g) normalized kinetics of the TA signal at the wavelength of the two excitonic peaks observed for each sample.

resembling the truncated octahedrons promoted by OPA, while those that do not grow much larger retain the cubic shape promoted by OctAc during nucleation.

Modulation of [OPA] has been shown to offer decent NC size tunability. However, to fully exploit the capability of this method, it is important to explore a wider range of growth durations. The plot in Figure 4 suggests that [OPA] = 0.3 M could allow access to the widest range of NC diameters. To investigate this, we conducted multiple syntheses for [OPA] = 0.3 M with various growth durations. Figure 6a demonstrates that for growth durations ranging from 30 to 2400 s, the NC diameter is tuned from 6.8 to 13.6 nm, while PLQY remains >80%. The NC diameters were extracted from SAXS data, as plotted in Figure S3. Figure 6b shows the corresponding red shift of the PL emission peak with increasing growth duration.

To illustrate the efficacy of NC growth quenching by DDAB when OPA is used, identical reactions are conducted, with only the delay between DDAB and antisolvent additions changed. A relatively high [OPA] (0.3 M) was employed so that NCs were more strongly confined, and thus, small increases in the diameter would result in significant red shifting of the PL peak. Figure S4 shows that delaying antisolvent addition by 2400 s results only in a slight narrowing of the emission peak, which is accompanied by an increase of PLQY from 80 to 86%. This contrasts sharply with the over 10 nm red shift observed over the same duration without DDAB (Figure 6b).

Intriguingly, the absorbance spectra in Figure 6c exhibit multiple prominent excitonic features. The positions of the excitonic peaks are marked to highlight the difference between samples. The prominence of the first excitonic feature (at the band edge) increases as the growth duration decreases along with a blue shift in the PL peak position. This correlates with stronger quantum confinement as the NC diameter approaches and drops below the exciton Bohr diameter. The same trend was observed for the second and third excitonic peaks.

If the observed excitonic peaks correspond to nanoplatelets, they should only appear at specific quantized energies, determined by the number of crystal layers within each phase (n). Thus, the existence of such quasi-2D phases can be ruled out by the gradual shifting of the peaks with different reaction durations. These peaks could instead indicate a separate distribution of NCs within the sample which is more strongly confined in one dimension, such as nanoplates. To assess this possibility, a size-selective purification was conducted. A lesser quantity of the methyl acetate (MeOAc) antisolvent than normally used was added during the second purification cycle such that after centrifugation, there were significant quantities of NCs in both the precipitate and the supernatant. Thus, separating and fully purifying the supernatant and precipitate with the regular quantity of MeOAc yielded two NC inks, containing fractions of smaller and larger NCs, respectively. Figure S5 shows a comparison of the absorbance and PL spectra of the two separated fractions. All excitonic peaks remained prominent in both fractions and are all blue-shifted in the smaller NC fraction. This implies that the excitonic features all originate from the same NC population as an additional population of nanoplates should have preferentially remained in the supernatant due to their higher surface area.

It is notable that even for NCs with diameters significantly greater than the exciton Bohr diameter (7 nm), the second and third excitonic features can be resolved. These features only disappear completely when the diameter reaches 13.6 nm, and the absorption spectrum resembles that of bulk CsPbBr₃. This emphasizes the exceptional impact of the enhanced monodispersity imposed by OPA.

Transient absorption (TA) spectroscopy was employed to supply further insight into the photophysical properties of the two smallest NC samples: 0.3 M OPA with 30 and 120 s growth durations. Figure 6d,e shows that there are two well-

Figure 7. Solution ^{31}P (left) and ^{13}C (right) NMR spectra for CsPbBr_3 NC solutions before purification (0 W) and after one (1 W) or two (2 W) purification cycles. The assignments of each resonance are labeled accordingly. Signals marked by † are attributed to toluene or toluene- d_8 solvent impurities.

resolved peaks around 471 and 502, and 487 and 509 nm, for the 30 and 120 s samples, respectively. These can be correlated to the two excitonic peaks in the steady-state absorbance (Figure 6c).

Figure 6f,g shows the normalized kinetics corresponding to the TA signals for each excitonic peak in each sample. The ultrafast energy transfer from the higher-energy excitonic state to the lower-energy state is consistent with the monomodal steady-state PL peaks observed in Figure 6b. Rossi et al. reported that these peaks can be attributed to excitonic transitions, while the induced absorption in-between corresponds to a formally forbidden excitonic transition. They explained that the prominence of additional excitonic transition peaks was indicative of strong quantum confinement and an NC ensemble with a narrow size distribution.^{53,54} The NC size distributions in Figure S5 confirm the tight size distribution in all six samples here. This serves as excellent validation that our protocol enables robust control of the NC properties. Thus, not only will the simple open-air synthesis improve the accessibility of high-quality NC samples to fellow researchers but also the well-resolved excitonic peaks will facilitate investigations of hot carrier dynamics, which are of great interest in semiconductor research.^{55,56}

So far, we have demonstrated the influence of ligands on NC growth, but it is also pertinent to investigate which ligands ultimately remain in the NC ink through purification. For electronic device applications, it is crucial to remove as much unbound ligand as possible to minimize resistivity in thin films. Figure 7a shows that without any antisolvent purification (0 W), there are two sharp peaks in the ^{31}P solution nuclear magnetic resonance (NMR) spectrum, attributable to TOPO and OPA. After one antisolvent purification cycle (1 W), both peaks are shifted toward one another, indicating less hydrogen-bonding interaction between TOPO and OPA,³⁹ presumably due to a decrease in their respective concentrations. After the second antisolvent purification (2 W), no peak is observed even after a significantly longer measurement. Thus, it can be concluded that two purification cycles sufficiently removed the excess free TOPO and OPA ligands from the NC ink. The ^{13}C NMR spectrum similarly confirms the removal of OctAc after one cycle, evidenced by the disappearance of the C—OOH resonance around 170 ppm (Figure 7b).

Despite enabling efficient analysis of free ligands, analyzing the presence of OPA on the NC surface by solution NMR is more difficult and time-consuming. Instead, we utilized solid-state NMR to directly analyze the NC powder, obtained after the second centrifugation step with MeOAc. The solid-state ^{31}P proton-decoupled NMR spectrum for the synthesized CsPbBr_3 NCs is shown above the ^{31}P — ^1H heteronuclear correlation (HETCOR) NMR plot in Figure S6a. There is a single resonance in the 1D ^{31}P spectrum, which was assigned to octylphosphonate, $[\text{CH}_3(\text{CH}_2)_7\text{PO}_2\text{OH}]^-$, as it is shifted 12 ppm upfield from the ^{31}P resonance of pure OPA (Figure S6b). The correlation between the ^{31}P resonance and the hydrogen-bonded P—OH proton peak around 12 ppm (P—OH^h) indicates that inter-ligand hydrogen bonding is present between OPA molecules on the NC surface, as analyzed in detail by our previous work.⁴⁵ As speculated earlier, these interactions could contribute to the greater control exerted by OPA ligands on NC growth compared to OctAc.

The surface binding of DDAB is confirmed by X-ray photoelectron spectroscopy (XPS) of thin films prepared from two OPA— CsPbBr_3 NC samples of different diameters. Figure S7a,b shows the N 1s peaks recorded. The N/Pb ratios for the 10.4 and 8.3 nm NCs were similar, calculated to be 0.119:1 and 0.122:1, respectively. These values are consistent with the presence of DDA^+ on the surface of the NCs. The Cs/Pb/Br ratio for the 10.4 nm NCs is 0.76:1:3.41, while for the 8.3 nm NCs, it is 0.69:1:3.43. The severe cesium deficiency further supports our hypothesis that the DDA^+ species occupy Cs vacancies, with the coordination of the accompanying bromide ions leading the bromide-rich surface.

CONCLUSIONS

In this work, we have demonstrated precise control over the nucleation and growth of CsPbBr_3 NCs at room temperature. Through the decoupling of these two processes, we can unveil that [OPA] modulates nucleation through two competing mechanisms; OPA ligands better stabilize the surface of nuclei, but the $\text{Cs}(\text{OPA})$ monomers formed are stabilized by hydrogen-bonding interactions with TOPO. OPA also has a strong influence on nucleation thermodynamics as [OPA] governs the growth kinetics and the final NC morphology.

Combining the control over the growth rate offered by OPA with the control over the growth duration obtained by

quenching with DDAB ligands, the NC diameter is tunable from 6.8 to 13.6 nm, corresponding to PL peak wavelengths from 501 to 517 nm. The PLQY is maintained above 80% for all sizes, while the PL fwhm remains narrow, between 16 and 19 nm. Moreover, NCs with OPA bound to the surface exhibit enhanced quantum confinement effects, such as multiple well-resolved excitonic transitions, highlighting the excellent quality of the NC inks prepared and their suitability for fundamental photophysical studies. Our approach is the first to achieve broad size tunability at room temperature. This enhanced versatility further improves the accessibility of high-quality perovskite NCs, which could facilitate a wide range of optically and electrically driven applications.

■ EXPERIMENTAL SECTION

Materials. Lead bromide (PbBr₂, 99.99%), cesium carbonate (Cs₂CO₃, >99.9%), octanoic acid (OctAc, 98%), TOPO (99%), DDAB (98%), ethyl acetate (EtOAc, anhydrous, >99.9%), methyl acetate (MeOAc, anhydrous, >99.9%), toluene (anhydrous, >99.8%), and heptane (anhydrous, 99%) were purchased from Sigma-Aldrich. OPA (98%) was purchased from TCI. All chemicals were used without further purification.

Precursor Preparation. Cs₂CO₃ (32.6 mg, 0.1 mmol) was dissolved in OctAc (1 mL) with stirring at room temperature to form a Cs-octanoate solution. PbBr₂ (550 mg, 1.5 mmol) was dissolved in toluene (10 mL) by adding TOPO (5.8 g, 6.44 mL, 15 mmol) and heating at 80 °C for 15 min. OPA or octanoic acid was added to the lead halide precursor solution and dissolved with stirring. DDAB (23.2 mg, 0.05 mmol) was dissolved in toluene (1 mL).

Nanocrystal Synthesis. For the synthesis of CsPbBr₃ NCs, 55 μ L of the Cs-octanoate solution was injected into a 0.5 mL PbBr₂ solution at room temperature (approx. 25 °C) with vigorous stirring. After the desired growth duration, 156 μ L of the DDAB solution was added. After a further 300 s, the precipitate was collected by centrifugation with 1.5 mL of ethyl acetate at 10,000 rpm and redispersed in 100 μ L of heptane. The dispersion was centrifuged at 5000 rpm, and the precipitate was discarded. The supernatant was retained, and 300 μ L of methyl acetate was added to fully precipitate the NCs. The precipitate was collected by centrifugation at 10,000 rpm and redispersed in 100 μ L of heptane. Another 300 μ L of methyl acetate was added to fully precipitate the NCs again, followed by centrifugation at 10,000 rpm and redispersion in 100 μ L of heptane. The dispersion was centrifuged at 5000 rpm, and the supernatant was extracted as the fully-purified CsPbBr₃ NC ink.

Optical Absorption Spectroscopy. Stable NC dispersions were diluted by a factor of between 500 and 1000. Absorbance spectra were recorded in Quartz cuvettes with a Shimadzu UV-3600 spectrophotometer using 0.1 nm steps and an integration time of 0.1 s.

TA Spectroscopy. TA data were obtained using a commercial TA Ultrafast Systems HELIOS spectrometer. The spectrometer was powered by Coherent Libra, which produced an approx. 50 fs pulsed laser with an 800 nm fundamental wavelength at a 1 kHz repetition rate. The output beam was split into two. The first beam was frequency-doubled using a β -barium borate (BBO) crystal (400 nm), which acted as the pump beam. The second beam was delayed by a mechanical stage and focused into a sapphire crystal to generate a white light continuum, which acted as the probe beam. The pump beam was mechanically modulated at 500 Hz by using an optical chopper to obtain a pump-induced change of probe transmission. The measurements were performed at transmission geometry.

PL Spectroscopy. Stable NC dispersions were diluted by a factor of between 500 and 1000. PL spectra were recorded in Quartz cuvettes with a Horiba FluoroMax-4 spectrophotometer using an excitation wavelength of 365 nm with 0.1 nm steps and an integration time of 0.1 s.

PLQY Measurement. The PLQY measurement was done using a Labsphere integrating sphere. The sample was placed inside and excited with a cobolt 445 nm continuous-wave diode laser. The

output of the integrating sphere was coupled through an optical fiber to a charge-coupled device (Newton 920 CCD, Andor) in which the photon count was captured.

High-Resolution Transmission Electron Microscopy. High-resolution TEM (HR-TEM) images were taken with a JEOL 2100F instrument using an accelerating voltage of 200 kV and a beam current of 146 μ A. The NCs were deposited on a Cu-200 mesh on formvar TEM grids by submerging the grid in a diluted NC dispersion and allowing the solvent to evaporate.

Small-Angle X-ray Scattering. A Xenocs Nano-inXider equipped with a Dectris Pilatus 3 hybrid pixel detector was used to perform SAXS. The effective scattering vector magnitude was measured in the range of $0.0821 < q < 4.47 \text{ nm}^{-1}$ in SAXS. The samples were measured in sealed glass capillaries under vacuum at room temperature. Particle size distributions were obtained (form-free) from scattering curves using the Monte Carlo-based software package McSAS using a convergence criterion of 5, with 20 calculating repetitions, and 500 contributions.⁴⁸

Powder X-ray Diffraction. All XRD data were accumulated using a Bruker D8 Advance X-ray diffractometer equipped with a Cu K α X-ray tube operating at 40 kV and 30 mA. These diffraction patterns were obtained in air at room temperature using the Bragg–Brentano geometry. The NC samples were prepared by collecting the final precipitate after antisolvent purification.

Solution NMR Spectroscopy. Solution ¹H, ¹³C, and ³¹P NMR experiments were completed at 9.40 T [$\nu_0(^1\text{H}) = 400.13 \text{ MHz}$; $\nu_0(^{13}\text{C}) = 150.92 \text{ MHz}$; $\nu_0(^{31}\text{P}) = 242.96 \text{ MHz}$] using a Bruker Avance I spectrometer with a Bruker 5 mm BBO probe. The ³¹P experiments employed a proton-decoupled one-pulse sequence, with a $\pi/6$ pulse length of 2.7 μ s. The ¹H experiments employed a one-pulse sequence, with a $\pi/2$ pulse length of 10 μ s. A recycle delay of 1 s was used throughout. Samples were prepared with the toluene-*d*₈ solvent and were referenced internally.

Solid-State NMR Spectroscopy. Solid-state ¹H and ³¹P NMR experiments were completed using a Bruker Avance III HD 600 MHz spectrometer with a Bruker 4 mm HXY MAS probe. The ¹H and ³¹P MAS NMR were obtained at a MAS frequency of 14 kHz, and the resulting data were externally referenced with respect to ammonium dihydrogen phosphate [(NH₄)₂HPO₄ (s); $\delta_{\text{iso}} = 0.99 \text{ ppm}$] and adamantane [C₁₀H₁₆ (s); $\delta_{\text{iso}} = 1.82 \text{ ppm}$]. The 1D ³¹P experiments employed a proton-decoupled one-pulse sequence, with a $\pi/2$ pulse length of 4.6 μ s and a recycle delay of 180 s. The 1D ¹H experiments employed a proton-decoupled one-pulse sequence, with a $\pi/2$ pulse length of 3.4 μ s and a recycle delay of 3 s. The 2D ³¹P–¹H HETCOR NMR experiments employed a proton-decoupled CP correlation sequence utilizing the same ¹H parameters as the one-pulse sequence and a contact pulse length of 5000 μ s.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c04569>.

TEM NC size histograms, powder XRD spectra, SAXS NC size distributions, solid-state ³¹P–¹H HETCOR NMR spectra, and N 1s XPS spectra (PDF)

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Notes

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