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# Scalable Synthesis of Colloidal CsPbBr<sub>3</sub> Perovskite Nanocrystals with High Reaction Yields Through Solvent and Ligand Engineering

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The ligand assisted reprecipitation (LARP) technique is an accessible and facile method that can synthesize metal halide perovskite nanocrystals (PNCs) under ambient conditions. However, low product yields of less than 30 % for LARP and its contemporary methods are indicative of highly inefficient reactions. In this work we apply the principles of green chemistry to the LARP technique for synthesizing CsPbBr<sub>3</sub> PNCs and help address this issue. Through these efforts, high product yields of ~70 % are achieved using stochiometric Cs:Pb precursor ratios. This is realized by (i) substituting the conventional toluene (TOL) anti-solvent with ethyl acetate (EA) and (ii) replacing the conventionally used unsaturated oleylamine ligand with the shorter saturated octylamine ligand. These changes also result in a 60% molar reduction in total ligand concentration and a 62.5% reduction in solvent waste during purification. The synthesized PNCs are comparable to the TOL-LARP reference in crystal quality, morphology and phase, with their photoluminescence quantum yields being readily enhanced to over 80 % through additions of RNH<sub>3</sub>Br ligands. The spectral versatility of these materials is demonstrated through post-synthetic chloride and iodide halide anion exchange, which readily yields tunable CsPbX<sub>3</sub> derivatives across the visible spectrum. Our EA-LARP protocol is further shown to be readily upscaled to ~0.5 L, while maintaining good nanocrystal properties and a product yield of 60 %.

# Introduction

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The lead halide family of ABX<sub>3</sub> (A = MA<sup>+</sup>, Cs<sup>+</sup>; B = Pb<sup>2+</sup>; X = Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>) perovskite nanomaterials have generated significant interest since the inception of hybrid (organic-inorganic) methylammonium lead halide MAPbX<sub>3</sub><sup>1</sup> and all-inorganic cesium lead halide CsPbX<sub>3</sub> perovskite nanocrystals (PNCs).<sup>2</sup> These PNCs can be readily synthesized with near-unity photoluminescence quantum yields (PLQYs) that exhibits a narrow full width at half maximum (FWHM) of 12-42 nm.<sup>2,3</sup> Their highly ionic lattice also allows for tunable bandgaps across the visible spectrum (400-800 nm) through halide composition engineering.<sup>4,5</sup> These attractive material properties have found traction as potential materials in various functional devices such as photovoltaics,<sup>6,7,8</sup> light emitting diodes (LEDs),<sup>9,10,11,12</sup> photodetectors,<sup>13,14</sup> and lasers.<sup>15,16,17</sup>

Literature reports on PNCs have primarily focused on exploring various synthetic methodologies, characterizing different perovskite compositions, and improving their crystal properties.<sup>18,19</sup> While these fundamental studies only require micrograms of PNCs, their application within functional devices can require gram-scale quantities.<sup>6,20</sup> To obtain sufficient amounts of PNCs for such applications, upscaling of typical ~5-

10 mL reactions by a factor of 10 or more is required,<sup>7</sup> which can result in decreased crystal quality.<sup>3</sup> Moreover, the product yields from hot-injection (HI), 'ligand assisted re-precipitation' (LARP), ultrasonication and other non-injection methods are relatively low, with reported values typically being less than 30 %.<sup>21,22</sup> Across these synthetic approaches, the LARP technique has been shown to be among the most scalable, with ~1 L volumes producing gram-scale amounts of PNCs.<sup>6,20</sup> This has been enabled by the underlying simplicity of this synthetic approach, which utilizes solvent control to induce supersaturation and drive the formation of PNCs.<sup>3,23</sup>

Of the PNC family, CsPbBr<sub>3</sub> derivatives have been commonly synthesized through LARP.<sup>6,20</sup> An attractive facet of this synthetic approach is its ability to utilize CsBr and PbBr<sub>2</sub> in 1:1 ratios to efficiently obtain CsPbBr<sub>3</sub>. Comparatively for HI, a typical ratio of ~1:8 ratio of Cs<sub>2</sub>CO<sub>3</sub>:PbBr<sub>2</sub> is used to facilitate Pbrich conditions,<sup>2</sup> while for non-injection heat up reactions even higher ratios of ~1:10 have been reported.<sup>24</sup> The unreacted precursors are generally discarded with the solvent waste generated during purification. This process further requires anti-solvent to solvent ratios as high as 3:1, which inherently results in large volumes of solvent waste, especially if multiple washing steps are required for removing impurities.<sup>7,25</sup>

Developing greener reaction pathways with lower waste factors remains to be addressed in this field. Towards this pursuit, we have developed a modified LARP protocol using ethyl acetate (EA-LARP) as the non-solvent and systematically optimized the reaction conditions to obtain high yields of ~10 nm CsPbBr<sub>3</sub> nanocuboids (NCu). To the best of our knowledge, the preliminary work by Seth and Samanta has been the only other

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to report on the use of ethyl acetate as an anti-solvent for  $CsPbBr_3 LARP$  synthesis.<sup>26</sup> In that work, the authors showed that ethyl acetate's use resulted in blue-emitting ~2.6 nm sized  $CsPbBr_3$  quantum dots, which could be ripened into aggregated nanoplates and nanobars of ~100 nm in dimension. However, the role of ethyl acetate as a non-solvent and the ensuing reaction dynamics were not well understood.

To this end, here we have carried out detailed investigations into solvent reaction ratios, ligand ratios, amine species and reactant concentrations for EA-LARP. Moreover, we have probed the early reaction dynamics of TOL-LARP and EA-LARP with time-dependent absorbance and photoluminescence measurements to show enhanced kinetics induced by EA. Tuning of the alkylammonium ligands was found to dramatically impact the final reaction yields, which could reach a level of ~70 %. Through post-synthetic treatments we further showed that CsPbBr<sub>3</sub> PNCs with photoluminescence quantum yields of >80 % and with high colloidal stability could be achieved, as well as demonstrating anion-exchanged CsPb(Br<sub>x</sub>Cl<sub>1-x</sub>)<sub>3</sub> and CsPb(Br<sub>x</sub>l<sub>1-x</sub>)<sub>3</sub> derivatives. Up-scaling of the reactions was demonstrated to ~500 mL final volumes with no significant loss of quality from its small-scale counterparts.

## **Results & Discussion**

The LARP reaction scheme is depicted in Figure 1. In this process, the DMF precursor solution (good solvent) containing the metal halide salts (CsBr, PbBr<sub>2</sub>) and organic ligands (OA, OLA) are added to a vigorously stirred solution of an antisolvent (e.g. TOL, EA). The sudden decrease in solubility for the metal halide salts by several orders of magnitude results in the rapid nucleation and formation of CsPbBr<sub>3</sub> PNCs.<sup>3</sup> The organic ligands help to control both crystal growth and facilitate their colloidal dispersion, with oleylammonium (OLA<sup>+</sup>) and either a bromide (Br<sup>-</sup>) or oleate (OA<sup>-</sup>) counter-ion being the most commonly used examples. OA is primarily used to protonate the OLA and control the acid-base equilibria to maintain colloidal stability.<sup>27</sup>

The addition of EA as a secondary anti-solvent to the TOL-LARP crude solution assists in precipitating the CsPbBr<sub>3</sub> NCu during centrifugation to improve the purified yield from 12 % to 18 %. EA's low dipole moment facilitates the removal of impurities while minimizing irreversible aggregation and anion defect formation.<sup>28,29</sup> Other protic solvents, such as isopropanol (IPA) or polar aprotic solvents, such as acetone tend to destabilize the colloids and cause irreversible aggregation and/or degradation (Figure S1a,b). In comparison, aprotic solvents with lower dipole moments such as methyl acetate (MeOAc), ethyl acetate (EA) and dichloromethane (DCM) better precipitate the PNCs during centrifugation without inducing severe aggregation, with the alkyl acetate solvents being found to be the most effective (Figure S1b,c). As expected from a good anti-solvent, it is found that the OLA/OA ligand salt pair is much less soluble in EA than in TOL (Figure S2).

Motivated by this observation, we developed the modified EA-LARP synthesis, in which the traditionally used TOL was replaced by EA with the aim of enhancing precipitation to minimize

solvent waste during processing and increase product yields. An optimized TOL-LARP protocol and its CsPBBr31PNCS Served 73565 reference benchmark. Extensive examination into the interdependent role of DMF:EA, OLA:OA ratio and total ligand concentrations were carried out to understand the synthetic limits of the EA-LARP reaction system (see Supporting Information for details). It was found that at a DMF:EA ratio of 1:10 or less, a mixture of NCu and nanoplatelets (NPL) of 3-5 unit cells thick formed, while at higher ratios NCu were the dominant product (Figure S3). Meanwhile, [OLA] >0.15 M in the final growth solution also favored NPL formation, with NCu forming at [OLA] < 0.06 M (Figure S4). The optimized synthetic conditions consist of a 1:15 DMF:EA solvent reaction ratio with both CsBr and PbBr<sub>2</sub> concentrations at 0.040 M and the ligand concentration within the DMF precursor being at 4.0 v/v % (0.127 M) OA and 2.0 v/v % (0.061 M) OLA (Figure S5-6). Importantly, the purification of PNCs using EA-LARP is vastly simplified compared to TOL-LARP, requiring only a direct centrifugation of the crude reaction mixture followed by redispersion of the precipitate in TOL (Figure S7).



Figure 1. A schematic visually depicting the basic synthetic steps of the TOL-LARP and EA-LARP methods described herein; the nucleation and growth of PNCs, their precipitation from solution and subsequent purification to isolate colloidally stable PNCs dispersed in toluene.

Quantitative absorption and relative PL spectra of the PNCs synthesized under optimized TOL- and EA- LARP conditions are shown in Figure 2a,b. These exhibit nearly identical absorption and PL profiles that are characteristic of high quality CsPbBr<sub>3</sub> NCu, with optical bandgaps determined from Tauc analysis of ~2.4 eV (Figure S8). Purification across both syntheses results in a quantitative reduction in collected product, with a much larger product loss for the TOL-LARP synthesis. Moreover, a reduction in the FWHM of the PL is observed due to likely size-selection during purification. A comparison of the PLQYs of the purified samples, as measured by using a Rhodamine 6G reference, show similar values of 25 % for TOL-LARP and 21 % for EA-LARP. A summary of the optical properties related to Figure 2a,b are included in Table S1.

Structural characterization of purified TOL-LARP and EA-LARP CsPbBr<sub>3</sub> PNCs with high resolution transmission electron microscopy (HR-TEM) show that both syntheses produce NCu PNCs, with average edge lengths measuring at  $8.4 \pm 2.5$  nm and  $9.2 \pm 2.7$  nm and aspect ratios of  $1.4 \pm 0.4$  and  $1.5 \pm 0.4$ , respectively (Figure 2c,d). It should be noted that the commonly observed black dots from TEM imaging of PNCs are also present, which are attributed as Pb-rich particles degrading under the focused electron beam.<sup>30</sup> To better estimate the particle

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dimensions, atomic force microscopy (AFM) was used to measure the particle heights of sparsely deposited PNCs on silicon substrates. The height profiles are step-functions with average height intervals of ~4.8  $\pm$  1 nm for TOL-LARP and ~5.5  $\pm$  1 for EA-LARP (Figure S9). This confirms that the PNCs are of cuboid geometry.

Selected area electron diffraction (SAED) patterns for both LARP crystals appear to show similar crystal structures, although these measurements cannot definitively distinguish a cubic ( $\alpha$ -CsPbBr<sub>3</sub>) or orthorhombic ( $\gamma$ -CsPbBr<sub>3</sub>) phase (Table S2).<sup>31</sup> Further structural analysis was carried out using XRD analysis of purified CsPbBr<sub>3</sub> PNC thin films (Figure S10). The XRD patterns show that the PNCs from both LARP methods exist in a perovskite phase ( $\alpha$ - and/or  $\gamma$ -CsPbBr<sub>3</sub>),<sup>32,33</sup> with no adventitious Cs<sub>4</sub>PbBr<sub>6</sub> present (Figure 2e). Scherrer analysis provides an estimation of the average crystal size to be 10.8 nm and 11.7 nm for TOL-LARP and EA-LARP, respectively (Figure 2f). These values are similar to dynamic light scattering (DLS) size estimates of 9.6 nm and 10.6 nm (Figure S11), and are consistent with the trend of slightly larger crystal sizes for EA-LARP as found in TEM and AFM measurements.



**Figure 2.** (a) TOL-LARP and (b) EA-LARP optical density (solid line) derived from absorbance measurements and PL (dotted line) spectra of their optimized PNC crude and purified CSPbBr<sub>3</sub> solutions. Insets show photographs of the respective crude and purified CSPbBr<sub>3</sub> solutions. (c) TOL-LARP and (d) EA-LARP low/high resolution TEM images of their purified PNCs with measured lattice spacings, SAED pattern and size histogram of crystal edge lengths. (e) XRD patterns of the deposited CSPbBr<sub>3</sub> nanocrystal films from purified TOL- and EA-LARP solutions, as well as (f) Voigt peak fitting for the dominant peak.

Inductively coupled plasma - mass spectrometry (ICP-MS) reveals that the elemental ratio of Cs:Pb:Br for the TOL-LARP and EA-LARP PCNs are not the stoichiometric 1:1:3, but ~0.81:1.00:2.59 and ~0.86:1.00:2.70, respectively. This is consistent with PbBr<sub>2</sub> terminated particles.<sup>[34]</sup> The elemental mass data from ICP-MS are combined with absorption and TEM

particle size measurements to determine the molar extinction coefficient for the CsPbBr3 PNCs (see Supporting and the second for details). For the TOL and EA-LARP methods, the calculated molar extinction coefficients ( $\epsilon$ ) at 335 nm are  $\epsilon_{335} = 3.08 \times 10^6$  $cm^{\text{-1}}M^{\text{-1}}$  and 3.96×10 $^{6}$   $cm^{\text{-1}}M^{\text{-1}},$  respectively, which is also consistent with previous reports (Table S3).<sup>35,36</sup> Using these extinction coefficients, we determine the final PNC concentrations in the purified dispersions and then calculate the product yields for the TOL-LARP and EA-LARP protocols. These values are found to be  $18.2 \pm 1.5$  % and  $40.2 \pm 4.3$  %, respectively. The latter exhibits more than a two-fold (x2.2) increase in the PNC yield, while simultaneously reducing the volume of solvent waste by as much as 62.5 %. When considering the amount of solvent waste generated for the amount of PNC material, this respectively translates to 0.10 mg and 0.62 mg of purified CsPbBr3 per mL of waste solvent generated; a dramatic increase in material efficiency for the EA-LARP procedure introduced here.

To understand and compare the reaction mechanisms of LARP using TOL and EA, we use in-situ time-dependent absorption (TD-Abs) and photoluminescence measurements (TD-PL) to monitor the optical evolution of a single injection step into TOL (Figure 3a,b) and EA (Figure 3c,d). By monitoring the relative absorbance over time at 450 nm, it can be readily seen from the TD-Abs measurements that nucleation and growth processes in TOL-LARP are much slower compared to EA-LARP, completing within ~20 s versus only ~5 s, respectively. Tauc plots further reveal that the initial ~2.49 eV bandgap for TOL-LARP stabilizes at ~2.37 eV after 20 s (Figure S12), while for EA-LARP the bandgap is comparatively smaller and decreases from ~2.33 eV to stabilize at ~2.30 eV after only 5 s. From both estimates of absorbance and band gap energies versus reaction time (Figure 3e), EA-LARP's reaction kinetics appear to be 2-4 times faster than for TOL-LARP. The TD-PL measurements and their summarized dynamics shown in Figure 3f, similarly reveal the faster reaction kinetics in EA-LARP compared to TOL-LARP. Interestingly, it is seen that for the TOL-LARP a two-stage process is observed, with an initial formation stage followed by a secondary "enhancement" stage in which the emission wavelength remains constant but the PL intensity increases.

In the above temporally resolved experiments, a single precursor injection was conducted at a dilute concentration to understand the nucleation and growth process. However, in LARP synthesis the precursor is injected drop-wise to ensure homogeneous mixing and avoid the precipitation of Cs<sub>4</sub>PbBr<sub>6</sub> products.<sup>[37]</sup> As such, for both TOL- and EA- LARP reactions, we also study the effect of a gradual addition of 10 µL precursor aliquots in 20 s intervals (Figure S13, see Supporting Information). As seen from the evolution of the TD-Abs measurements at 450 nm in Figure 3g, the slow growth dynamics of the TOL-LARP causes the nucleation and growth stages to overlap between the precursor injections. Meanwhile, for EA-LARP, the more rapid growth dynamics causes the absorption to saturate shortly after each injection, indicating that each injection causes a distinct nucleation and growth event.

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existing particles to grow, while also inducing their aggregation at the higher PNC concentrations.<sup>1</sup>We consider that the underlying cause of these differences lies in EA's lower solubility of both the metal salts and ligand pairs compared to toluene.

The dramatic enhancement in reaction rates and product yield of EA-LARP holds great promise for potential application of such materials. However, for this to be realized the low PLQY values obtained for purified PNCs using LARP need to be enhanced. Previous works have indeed shown that post-synthesis surface with passivation approaches thiocyanate salts.<sup>[40]</sup> tetrafluoroborate salts,<sup>[41]</sup> and didodecylammonium bromide with lead bromide<sup>[34]</sup> can enhance the PLQY to near-unity. Most recently, Quarta et al. reported that exposure of oleylammonium bromide terminated CsPbBr<sub>3</sub> PNCs synthesized using hot-injection to butyl/octyl-amine ligand resulted in an improved colloidal stability and an increase in the PLQY from 69 % to >90 %.<sup>[42]</sup> It was suggested that this resulted from the amine undergoing proton transfer with the native OLA<sup>+</sup> species, before strongly binding to the crystal surface.

Inspired by these works, while also noting that <sup>1</sup>H-NMR and FTIR measurements verify alkylammonium surface passivation of our purified PNCs (Figure S16-17), we explored a series of RNH<sub>3</sub>Br salts as a post-synthetic additive to passivate surface defects and enhance colloidal stability.42,43 To this end, oleylammonium bromide (OLABr), hexadecylammonium bromide (C<sub>16</sub>NH<sub>3</sub>Br), dodecylammonium bromide (C<sub>12</sub>NH<sub>3</sub>Br), octylammonium bromide (C<sub>8</sub>NH<sub>3</sub>Br) and butylammonium bromide (C<sub>4</sub>NH<sub>3</sub>Br), were fully solubilized in anhydrous-IPA and added to a standardized dispersion of CsPbBr<sub>3</sub> PNCs (see Supporting Information for details). All species show a drastic increase in PL intensity for small ligand additions, before equilibrating at a lower intensity at the higher concentrations (Figure 4a,b). The initial increase inherently suggests an improvement in surface passivation under optimal ligand concentrations, while the decrease is believed to arise from using IPA as a carrier solvent, which quenches the PL by inducing aggregation. Notably, compared to all tested RNH<sub>3</sub>Br species, OLABr is seen to be the least effective in maintaining a high PL intensity. Meanwhile, C<sub>12</sub>NH<sub>3</sub>Br proved to be the most effective additive, with the longer C16NH3Br species yielding poorer PL stability, despite providing stronger steric interactions. The latter is correlated to the poorer solubility of C<sub>16</sub>NH<sub>3</sub>Br in toluene.

Using TD-PL spectroscopy, we compare the effectiveness of using  $C_{12}NH_3Br$  to treat purified dispersions of PNCs synthesized using both LARP methods (see Supporting Information for details). As can be seen from Figure 4c-f, both samples exhibit a significant increase in the PLQY, with TOL-LARP PNCs increasing from 25 % to 90 %, and those synthesized using EA-LARP increasing from 21 % to 82 %. These enhancements were tracked following an initial 20 µg addition of  $C_{12}NH_3Br$  to 25 µM, then a secondary addition of 100 µg after 40 s to 150 µM. The initial ligand addition quickly saturates the PL intensity to >80 % of its maximum after the 2<sup>nd</sup> addition without any major changes to the PL peak shape or position (Figure S18). Assuming complete surface adsorption, we determine that the first



The PL spectra of samples measured after each precursor addition have also been measured (Figure S14, see Supporting Information for details). It is seen that as the PNC concentration across both reactions increases with the added precursor volume, the PL peak maximum redshifts (Figure 3h). This can arise from PNC growth, either from monomer growth or through Ostwald ripening,<sup>[38]</sup> or enhanced self-absorption of the PL at increasing PNC concentrations.<sup>[39]</sup> To contrast these mechanisms, the solutions with 50  $\mu\text{L}$  of added precursor are diluted five-fold, returning them to an equivalent CsPbBr<sub>3</sub> concentration as observed after the initial 10  $\mu$ L addition. The dilution blue-shifts the PL maximum for EA-LARP to a value close to that observed for the latter solution. This suggests that for this synthesis, existing PNCs do not undergo significant growth after each precursor addition, but instead form new aggregates of particles (Figure S15). In comparison, TOL-LARP shows only a partial blue-shift post-dilution. When considered in conjunction with the scattering arising from these solutions at higher precursors volumes, this suggests that concurrent precursor additions for TOL-LARP PNCs causes new particles to form and



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addition can itself contribute an additional 1.9 ligands per nm<sup>2</sup> to the pre-existing surface ligands. This value is consistent with the reported surface ligand densities of 2.3-6.7 required to stabilize PNC surfaces.<sup>9,35,44</sup>



**Figure 4.** (a,b) PL peak intensity of standardized CsPbBr<sub>3</sub> PNC dispersions with successive additions of RNH<sub>3</sub>Br salts in anhydrous IPA at 1mg/mL. TD-PL spectra of the two-step addition of 20 µg then 100 µg of  $C_{12}$ NH<sub>3</sub>Br (total 120 µg) to purified into 10 µL of purified (C) TOL-LARP and (d) EA-LARP CsPbBr<sub>3</sub> PNCs solutions with the time scale being in seconds. '\*' indicates 390 nm scattering from the LED source. (e) The peak intensity and peak position of (c) and (d) plotted against time. (f) Photographs of the samples under ambient and  $\lambda = 365$  nm UV-light, before and after C<sub>12</sub>NH<sub>3</sub>Br addition.

Evidently, saturated primary alkylammonium additives significantly improve the optical properties of CsPbBr<sub>3</sub> PNCs post-synthesis compared to OLA<sup>+</sup> derivatives. To see whether they can also provide these benefits during EA-LARP synthesis, their respective amine counterparts (hexadecylamine ( $\mathsf{C}_{16}\mathsf{NH}_2)$ , dodeclyamine  $(C_{12}NH_2)$ , octylamine  $(C_8NH_2)$  and butylamine  $(C_4NH_2)$ ) were substituted for OLA while maintaining the same molar ratio (Figure 5a,b, see Supporting Information for details). All variants show higher reaction yields than TOL-LARP, with similar or higher yields than EA-LARP with OLA (Figure S19-21, Table S4). Unexpectedly, C<sub>8</sub>NH<sub>2</sub> gave the highest product yield of ~70 %, an improvement of ×3.85 over TOL-LARP. This corresponds to 1.08 mg of CsPbBr<sub>3</sub> PNCs per mL of waste solvent generated, which is an order of magnitude greater than for TOL-LARP (0.10 mg/mL). The main optical features of interest for their purified solutions and yields are tabulated in Table S5. Notably, unlike for the EA-LARP synthesis with OLA, which led to gradual precipitation over time, using C<sub>8</sub>NH<sub>2</sub> led to negligible precipitation of purified PNCs, with low additions of C<sub>8</sub>NH<sub>3</sub>Br at ~0.20 mg/mL providing optimal stability to their structural and optical properties (Figure S22,23). These PNC dispersions could exhibit a PLQY of >80 %.

TEM imaging of the purified EA-LARP CsPbBr<sub>3</sub> PNCs with  $C_{16}NH_2$ ,  $C_{12}NH_2$ ,  $C_8NH_2$  and  $C_4NH_2$  show average particle edge lengths of





Figure 5. The optical density (solid curve) derived from absorbance measurements and normalised PL (dotted curve) spectra of the (a) crude and (b) purified EA-LARP synthesized CsPbBr<sub>3</sub> PNCs using different saturated amines substituting for OLA. TEM images of purified samples made with (c) C<sub>4</sub>NH<sub>2</sub>, (d) C<sub>3</sub>NH<sub>2</sub>, (e) C<sub>12</sub>NH<sub>2</sub> and (f) C<sub>16</sub>NH<sub>2</sub>; insets showing histograms of the crystal edge lengths and HR-TEM images.

To demonstrate scalability, we performed the modified EA-LARP synthesis with OA and  $C_8NH_2$  at 60 times the original scale (Figure 6, Figure S25). Our upscaled EA-LARP resulted in purified PNCs with almost identical optical (Figure 6a,b) and structural (Figure 6c) properties compared to its small scale counterpart. Moreover, a final post-purification yield of 60 % was determined. This is vastly superior compared to our optimized standard TOL-LARP reaction, for which even mild scaling of the reaction by a factor of ×6, resulted in product yields of 8-12 % and mixed PNC morphologies. We believe that this yield reduction arises from the slow kinetics in this system, which gives rise to an extended growth stage upon scaling that leads to larger PNCs that are removed during purification.

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**Figure 6.** (a) The relative optical density (solid curve) between the respective crude and purified, and PL (dotted curve) spectra, of the small scale and upscaled CsPbBr<sub>3</sub> PNC solutions. (b) The normalised absorbance and PL spectra. (c) The XRD spectra of the purified solutions against reference spectra. (d) Photograph of the purified and concentrated (~15 mg/mL) upscaled CsPbBr<sub>3</sub> solution under ambient and  $\lambda$  = 365 nm UV-light.

Having demonstrated scalable synthesis of CsPbBr<sub>3</sub> PNCs using EA-LARP, we now show that these can also readily undergo halide exchange with Cl<sup>-</sup> or l<sup>-</sup> to tune their optical properties across the visible spectrum.<sup>4,5</sup> This is done by simply adding the respective halide exchange solutions to dispersions of CsPbBr<sub>3</sub> PNCs with an initial PL peak emission centered at 516 nm and a FWHM of 21 nm (Figure 7a-c). Under chloride-rich compositions, the PNC emission selectively blue-shift to 414 nm with a FWHM of 12 nm. Conversely, iodide rich compositions red-shift the PNC emission to as high as 684 nm with a FWHM of 35 nm. These exchange processes are monitored using TD-PL spectroscopy. It is found that Cl<sup>-</sup> exchange has vastly slower kinetics than for I<sup>-</sup> (Figure 7d). This is consistent with previous reports that suggest different exchange mechanisms across the halides, with I<sup>-</sup> being surface limited and CI<sup>-</sup> being diffusion limited.45



**Figure 7.** (a) The relative optical density (solid curve) between the respective crude and purified, and PL (dotted curve) spectra, of the small scale and upscaled CsPbBr<sub>3</sub> PNC solutions. (b) The normalised absorbance and PL spectra. (c) The XRD spectra of the purified solutions against reference spectra. (d) Photograph of the purified and concentrated (~15 mg/mL) upscaled CsPbBr<sub>3</sub> solution under ambient and  $\lambda$  = 365 nm UV-light.

# Conclusions

DOI: 10.1039/C9NR10726F In this work we have adopted green chemistry principles to develop a modified LARP synthesis for CsPbBr<sub>3</sub> perovskite nanocrystals with high reaction yields and low-solvent waste. This was achieved by substituting the typically used toluene non-solvent by ethyl acetate, which enhanced reaction kinetics and allowed for the rapid aggregation of formed perovskite nanocrystals. The latter enabled purification with no additional anti-solvent to induce precipitation. Substitution of the typically used oleylamine by the saturate octylamine species, further led to improved colloidal stability and increased reaction yields to ~70 %, which is at least 2.3 times larger than for any other reported method. Post-synthetic treatments with simple alkylammonium bromides were shown to further improve PLQYs to over 80 %. Moreover, the synthesized CsPbBr<sub>3</sub> readily underwent anion-exchange with chloride or iodide to access a wide range of  $CsPbX_3$  (X = Cl, Br, I) nanocrystals. As a result of these factors, the presented synthetic protocol provides a simple reaction pathway toward scalable and high-quality PNCs for use in fundamental material studies and their application in functional optoelectronic devices.

# **Experimental Section**

#### Materials

Cesium bromide (CsBr, 99.999 %), lead (II) bromide (PbBr<sub>2</sub>, 99.999 %), lead (II) iodide (PbI2, 99.999 % trace metal basis), lead (II) chloride (PbCl<sub>2</sub>, 99.999 % trace metal basis), oleylamine (OLA, 70 % technical grade), oleic acid (OA, 90 % technical grade), hexadecylamine ( $C_{16}NH_2$ , 98 %), dodecylamine ( $C_{12}NH_2$ , 98 %), octylamine (C<sub>8</sub>NH<sub>2</sub>, 99 %), butylamine (C<sub>4</sub>NH<sub>2</sub>, 99.5 %), dimethyl formamide (DMF, 99.8 % anhydrous), methyl acetate (MeOAc, 99.5 % anhydrous), ethanol (EtOH, anhydrous >99.5 %) were sourced from Sigma-Aldrich. Toluene (TOL,  $\geq$ 99.9 %), ethyl acetate (EA, ≥99.5 %), dichloromethane (DCM, ≥99.5 %), hydrobromic acid (HBr, 47 %), were sourced from Merck. Ethanol (EtOH, 99.5 %), was sourced from Ajax Finechem. Toluene-d<sub>8</sub> (TOL-d<sub>8</sub>, 99.5 %) was sourced from Cambridge Isotope Laboratories. Cesium bromide (CsBr, 99 %), lead bromide (PbBr<sub>2</sub>, 98+ %), were sourced from Alfa-Aesar. All reagents were used without further purification; the exceptions are oleylamine and oleic acid, which were degassed at 120 °C for 30 min.

## Characterisation

Ultraviolet-Visible (UV-Vis) absorption spectroscopy of colloidally dispersed PNCs in toluene were analyzed with a Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer. Photoluminescence (PL) spectroscopy of colloidally dispersed PNCs in toluene were analyzed with a Horiba Fluoromax-4 Spectrofluorometer. PLQY measurements were determined with a Rhodamine-6G (PLQY = 0.95) reference dye in anhydrous ethanol. Dynamic light scattering (DLS) measurements were performed with a Brookhaven NanoBrook Omni analyzer with a 640 nm diode laser. Fourier-transform infrared (FTIR)

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spectroscopy was performed with a Thermo Scientific Nicolet 6700 FT-IR spectrometer, with a Smart iTR<sup>™</sup> Attenuated Total Reflectance (ATR) Sampling Accessory attachment. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) was performed on a Bruker Avance III 600 MHz Cryoprobe spectrometer. Inductively coupled plasma - mass spectrometry (ICP-MS) was performed on an Agilent 7700 ICP-MS instrument. X-ray Diffraction (XRD) spectra were recorded using a Bruker D8 Advance X-ray diffractometer with a Lynxye XE 1D detector using a Cu source  $(K_{\alpha} = 1.54060 \text{ Å})$  radiation at 40 kV, 40 mA. XRD films were prepared by drop-casting the purified nanocrystal solutions dispersed in toluene and gently dried under flowing gas. Atomic force microscopy (AFM) measurements were recorded using a PicoPlus Agilent 5500 Scanning Probe Microscope in air, with nanocrystal samples spin-deposited on silicon substrates. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G<sup>2</sup> T20 Transmission Electron Microscope equipped with a  $LaB_6$  electron source operated at 200 kV. Images were acquired by either a Gatan Orius SC200D CCD camera or a Gatan Orius SC600 CCD camera. Time-dependent absorption (TD-Abs) and time-dependent photoluminescence (TD-PL) spectra were recorded by the commercial spectrometer from the company of StellarNet in the U.S, with CCD camera (Silver-Nova-TEC-X2), under a Halogen lamp (SL1) or 390 nm excitation (SL1-LED), respectively.

#### Synthetic Procedures

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Standard TOL-LARP synthesis of CsPbBr<sub>3</sub> nanocrystals. An optimized LARP protocol based on the work by Li et al. was used as a CsPbBr<sub>3</sub> reference sample.<sup>3</sup> Briefly, an anhydrous DMF precursor solution was prepared containing 0.040 M of CsBr, 0.040 M of PbBr<sub>2</sub>, 10 v/v % of OA, 5 v/v % of OLA and heated to 80 °C to ensure a clear, homogeneous solution. Typically, 1.0 mL of the precursor was then added dropwise into a vigorously stirred solution of toluene in a DMF:TOL ratio of 1:10 for 2 min under ambient conditions to precipitate CsPbBr<sub>3</sub> PNCs. Ethyl acetate was then added as a secondary anti-solvent into the crude PNC solution to assist in precipitation, with a final crude:EA ratio of 1:3 being used. This solution was then centrifuged at 8000 rotations per minute (rpm) for 5 min. The supernatant was discarded and the pellet dispersed in 1.0 mL of toluene, which was then also centrifuged at 3000 rpm for 2 min to remove any residual larger impurities. This supernatant was taken for further measurements and stored under ambient conditions in the dark.

**Modified EA-LARP synthesis of CsPbBr<sub>3</sub> nanocrystals.** The modified ethyl acetate based LARP (EA-LARP) protocol uses the same procedure as the reference toluene based LARP (TOL-LARP) process described above but with the following modifications. The ligand content was reduced to 4 v/v % of OA and 2 v/v % of OLA. TOL was replaced with EA and a 1:15 DMF:EA ratio was employed. No additional anti-solvent was required, and the crude PNC solution was directly centrifuged at 5000 rpm for 5 min, with the remaining purification steps as above. For the different EA-LARP variants using saturated primary amines, OLA is replaced with an equimolar quantity to

retain the acid to amine molar ratio at 2:1. No other changes to the standard EA-LARP reaction conditions <sup>1</sup>ອກອັງ ເມາກີເອລີເບັດກິ protocol were made.

**Upscaled EA-LARP synthesis of CsPbBr**<sub>3</sub> **nanocrystals.** For upscaling, the DMF precursor solution was prepared using lower grade purity CsBr and PbBr<sub>2</sub> materials from Alfa-Aesar, which did not significantly differ to using higher purity grades. 30 mL of DMF precursor was prepared using OA and C<sub>8</sub>NH<sub>2</sub> and injected into a stirred 450 mL volume of EA. Purification followed similarly as before, except the second centrifuge step's speed was increased to 8000 rpm.

**Synthesis of ammonium bromide salts.** The ammonium salts were synthesized in-house adapting previous protocols.<sup>46,47</sup> Generally, the different amines were dissolved in EtOH and a molar excess of aqueous HBr (47 %) added to ensure full conversion. This was left to mix for several hours. The liquid phase was removed with a rotary evaporator and then recrystallized several times before being filtered and dried under vacuum. The ammonium salts were determined to be pure with FTIR and <sup>1</sup>H-NMR.

# **Conflicts of interest**

There are no conflicts to declare.

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Application of green chemistry to obtain 70% reaction yields of high quality CsPbBr<sub>3</sub> perovskite nanocrystals through solvent and ligand engineering.