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Cite as: J. Chem. Phys. **151**, 121105 (2019); https://doi.org/10.1063/1.5123306
Submitted: 04 August 2019 . Accepted: 09 September 2019 . Published Online: 30 September 2019

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Submitted: 4 August 2019 • Accepted: 9 September 2019 •
Published Online: 30 September 2019

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Note: This paper is part of the JCP Special Topic on Colloidal Quantum Dots.
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ABSTRACT

$CsPbI_3$ perovskite nanocrystals are a promising optoelectronic material when stabilized in their cubic phase. While ongoing efforts have addressed this structural challenge through a variety of meta-stabilization approaches, the postsynthesis purification of these nanocrystal dispersions has remained a challenge. In this article, we undertake a detailed investigation into the chemical, optical, and structural changes that arise during purification of $CsPbI_3$ nanocrystals. It is found that nanocrystal degradation can only be avoided through the judicious control of additives within each purification cycle. Under optimized additive-to-nanocrystal ratios, multiple purification cycles can be readily achieved, while retaining the quality and phase stability of the $CsPbI_3$. This facile purification protocol ensures the preparation of high purity and high quality $CsPbI_3$ nanocrystal inks that are suitable for better characterization or integration in optoelectronic devices. The approach has been generalized for $CsPbX_3$ ($X = Cl^-, Br^-$, and I^-).

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Inorganic perovskite nanocrystals (NCs) based on the chemical formula $CsPbX_3$ (X = Cl, Br, and I) have garnered significant interest due to their high photoluminescence quantum yield (PLQY),[1,2] narrow full-width half-maximum (FWHM) PL emission,[2] and defect-tolerant band structure.[3] $CsPbI_3$ is particularly attractive, as its optical bandgap lies in the red emitting region,[1] indicating it may find application in solar cell or red light-emitting diode devices.[4,5] However, for the full potential of these materials to be realized, a facile strategy for preventing their transformation from the cubic (α) perovskite phase to an orthorhombic (δ) phase at room temperature is required.[6] To date, a number of approaches have been employed for achieving phase stabilization, including doping $CsPbI_3$ with Cl^- ions,[7] using specific nonpolar antisolvents during purification,[4] incorporating stabilizing ligands during synthesis,[8] passivating NCs in solution via addition of bidentate ligand species,[9] partially substituting the Cs^+ cation with formamidinium$^+$,[10] and *in situ* polymer encapsulation of the NC film.[11] In general, these strategies act to either modify the effective Goldschmidt tolerance factor or the relative surface to bulk energies to enable α perovskite formation.[12]

Across all of these approaches used to stabilize α-$CsPbI_3$ NCs, a key element that has not been adequately addressed is the postprocessing of these materials to achieve purified NC inks that maintain their optical and structural properties. Instead, the purification studies of perovskite NCs are mainly focused on $CsPbBr_3$.[13–15] Generally, the purification or "washing" process for NCs involves (i) precipitating the NCs from the reaction solution (1-octadecene, ODE) with a polar antisolvent, (ii) isolating the precipitated NCs via centrifugation and decanting the supernatant containing impurities, and (iii) redispersing the NCs in a nonpolar solvent.[1] These three steps constitute a single wash cycle, with multiple wash cycles typically required to adequately purify the NCs of residual precursors, ligands, and solvents.[16] However, the need for multiple wash cycles presents a major challenge for metal halide perovskites because their surfaces tend to be passivated by weakly bound ligands, typically aliphatic ammonium/amine,[17,18] and the bulk inorganic component is partially soluble in polar solvents owing to its highly ionic bonding character. As a result, during the precipitation of such NCs with an excess of polar solvent, the stabilizing ligands on the surface of the NCs are easily removed,[19] which can result in irreversible aggregation, structural transformation of the NCs to larger sizes, and/or a phase change, resulting in the degradation of their optical properties.

Herein, we report a facile $CsPbI_3$ NC purification protocol that allows for multiple washing cycles, while retaining the quality and phase stability of the NCs. The approach is based on using additives during the washing procedure to balance the surface chemistry requirements. Toward this goal, we have assessed the effects of several different additives, including the ligands used during synthesis, the alkyl ammonium salt and a lead iodide solution. UV-vis absorption and PL spectroscopy, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and X-ray diffraction (XRD) have been used to monitor the optical properties, nanostructure, and phase stability of the NCs after multiple washes, and inductively coupled plasma-mass spectrometry (ICP-MS) and nuclear magnetic resonance (NMR) spectroscopy have been employed to evaluate the NC molar concentration and surface chemistry.

$CsPbI_3$ NCs were synthesized using a modified hot-injection route that involved the mixing of a Cs precursor into a PbI_2-containing solution at elevated temperature (see the supplementary material for details).[1] Briefly, the synthesis used the branched diisooctyl phosphinic acid [DPA, Fig. 1(a)] and oleylamine (OLA) as the ligand sources,[8] with the final Cs:Pb:I:DPA:OLA molar ratios being 0.25:1:2:12.5:10.[20] This synthetic approach produces a crude solution of α-$CsPbI_3$ NCs that exhibits a structural stability greater than four months (Fig. S1), making it a reliable platform for this purification study. We include the absorption and PL spectra of the unwashed NCs diluted in toluene in Fig. 1(b).

To develop an optimized purification protocol, we have trialed various antisolvents for the precipitation of $CsPbI_3$ NCs from the crude reaction solution (Table S1). Methyl-acetate has been widely accepted as an antisolvent for washing the standard oleic acid (OA) synthesized $CsPbI_3$,[4] but it was found to result in phase transformation of our washed NCs within a week, presumably because our NCs have a different surface chemistry due to the usage of DPA. For these NCs, isopropanol (IPA) was found to be the most suitable antisolvent. Following the first wash with IPA, the NC dispersion exhibited a reduction in relative absorbance and a narrowing of the PL peak FWHM from ~120 meV to ~100 meV, although its overall intensity and peak position remained similar [see Fig. 1(b)]. Such an observation indicates that the excessively small NCs were removed during the washing process without any detrimental effects on the optical properties of the remaining NCs. As seen through TEM measurements, these single-washed $CsPbI_3$ NCs were monodisperse cubic particles with an average size of 11.3 ± 1.6 nm [see Fig. 1(c)]. Furthermore, STEM revealed that the NCs exhibited an interplanar spacing of 0.62 nm, which reflects the (100) plane of α phase $CsPbI_3$.

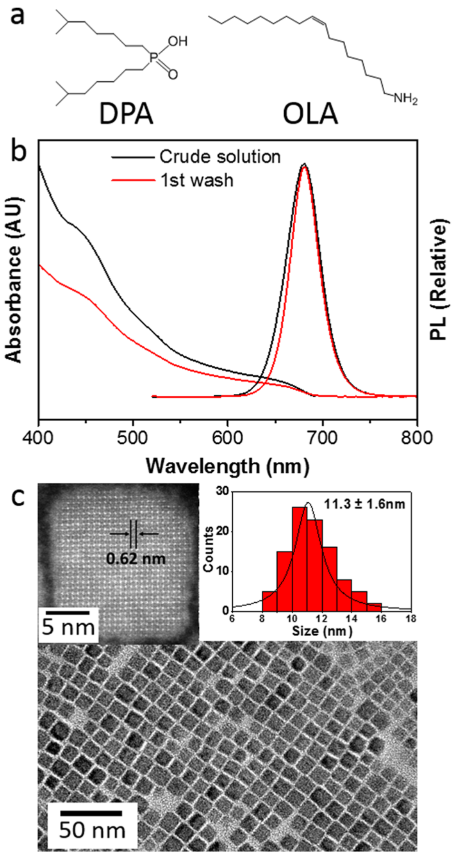

FIG. 1. (a) Chemical structures of diisooctyl phosphinic acid (DPA) and oleylamine (OLA). (b) UV-Vis absorption and photoluminescence spectra for the $CsPbI_3$ NC crude solution. (c) TEM of $CsPbI_3$ NCs synthesized with DPA after one wash cycle with the insets showing STEM of single $CsPbI_3$ NCs with the lattice spacing (left) and histogram of the size distribution of the NC ensemble (right).

Despite IPA's suitability as an antisolvent for washing the crude $CsPbI_3$ NCs, its use within multiple washing cycles was found to cause the absorption and PL intensity of the NCs to gradually decrease [Fig. 2(a)] and become almost negligible after the 3rd wash. Quantitative PL measurements were performed to determine the QY of the samples using Rhodamine 101 as a reference dye.[21] These showed that the PLQY of the NCs dropped from 62% to a mere 7% between the 1st and 3rd wash (Fig. S2). For reference, the PLQY of the crude solution was 65%. The degradation of NCs during this washing process is ascribed to the progressive loss of surface ligands, which causes subsequent aggregation or dissolution. Changes to the ligand concentrations were confirmed using ^{1}H-NMR, which showed that multiple washing steps resulted in a significant reduction in the intensity of the alkene groups of the oleylamine/ammonium ligands (Fig. S3)—the dominant surface binding species in our $CsPbI_3$ NCs.[8] This phenomenon is attributed to the highly ionic nature of the perovskite, which enables the ligands on the NC surface to be in a dynamic exchange between binding and nonbinding states.[17] Because the supernatant containing unbound ligands is discarded following each washing step, a new equilibrium between the bound and unbound ligands is established upon redispersion, resulting in a lower effective bound ligand

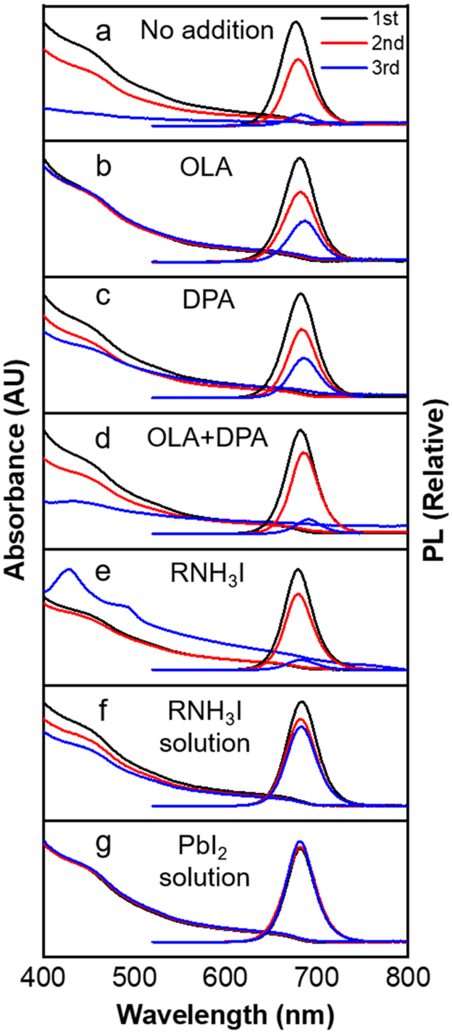

FIG. 2. UV-Vis absorption and PL spectra of NCs after the 1st, 2nd, and 3rd washing cycle with (a) no additive additions, (b) OLA, (c) DPA, (d) OLA and DPA, (e) hexadecylammonium iodide (RNH$_3$I), (f) RNH$_3$I with OLA and DPA, referred to as "RNH$_3$I solution," and (g) PbI$_2$ with OLA and DPA, referred to as "PbI$_2$ solution."

concentration. After multiple wash cycles, the progressive ligand loss eventually causes insufficient surface passivation on the NCs, leading to degradation of their structural and optical properties.

One simple strategy for addressing this ligand loss has been demonstrated for CsPbBr$_3$ NCs by compensating additional OLA and OA ligands during the purification process.[17] Here, we have assessed a similar strategy by using the native ligands in the form of OLA, DPA, or a mixture of both as additives within the toluene redispersion before the next wash cycle (see the supplementary material). When OLA was added, the absorption was preserved, but the PL intensity exhibited a gradual loss [Fig. 2(b)]. A similar trend in PL reduction was observed with the addition of DPA [see Fig. 2(c)], although the absorption was not preserved after multiple washes due to partial NC dissolution. When the two ligands were added together, the relative PL intensity loss and reduction in absorption was greater than for any of the individual ligands. This observation is in accordance with a previous report that indicated acid-base pairs (i.e., OLA$^+$-DPA$^-$) can effectively dissolve CsPbX$_3$ NCs.[22]

Evidently, during NC synthesis, iodide is also present in the reaction mixture. As such, we have also assessed the role of additional alkyl ammonium iodide within the solution. We synthesized hexadecylammonium iodide for this purpose owing to its higher purity compared to the OLA analog used within the synthesis. However, the addition of this RNH$_3$I to the washing process yielded additional absorption peaks at lower wavelengths and enhanced scattering [Fig. 2(e)], indicating a partial α-to-δ phase transformation.

Regardless of the additives introduced during the washing procedure, the first wash (precipitation directly from the crude solution) always gave the best absorption and PL characteristics. This suggests that mimicking the "crude solution condition" is the key for washing NCs multiple times. Therefore, we prepared an "RNH$_3$I solution" in toluene that featured a combination of RNH$_3$I+DPA+OLA in a similar molar ratio to the synthesis solution of 1:5:5. Unfortunately, the introduction of the RNH$_3$I solution into the washing process was still found to result in NC instability [Fig. 2(f)].

Given the lead-rich synthetic conditions, we then formulated a "PbI$_2$ solution" with a Pb:I:DPA:OLA molar ratio of 1:2:10:10 (see the supplementary material). Unlike all the other additives assessed here, the addition of the "PbI$_2$ solution" enabled the absorption and PL properties of the NC to be almost perfectly preserved after three wash cycles [Fig. 2(g)]. Further spectroscopic investigations into the "PbI$_2$ solution" washed NCs revealed that the PLQYs between the 1st and 3rd washing steps actually increased between 64% and 70%, respectively. With previous reports indicating a positive correlation between perovskite NC PLQY and halide content,[23] we have measured the iodide content of the NCs using Energy Dispersive X-ray (EDX, Fig. S4) spectroscopy. These measurements showed that the overall atomic percentage of the iodide gradually increased from 54% to 60% between the 1st and 3rd washes, confirming that a halide rich environment is indeed conducive for achieving a higher PLQY.

TEM was employed to further characterize the effect of the different additives during washing on the CsPbI$_3$ NC ensembles. As shown in Fig. 3(a), NCs washed a single time with neat IPA have a cubic structure with excellent monodispersity. Following a second washing step without any additives, the NCs were found to significantly coarsen and aggregate [Fig. 3(b)]. This is consistent with major ligand loss during this process. The extent of aggregation was reduced when different additives were used during the washing process [Figs. 3(c)–3(g)]; however, consistent with their optical measurements, the enhanced inhomogeneity of the NCs confirmed that none of the additives effectively stabilized the NCs. The use of the PbI$_2$ solution exhibited the most favorable washing conditions; the second wash [Fig. 3(h)] and the third wash (Fig. S5) yielded well-dispersed cubic NCs with a comparable size distribution (~11 nm) to the first wash. These TEM results demonstrate that the use of the PbI$_2$ solution during washing provides an advantageous chemical environment for the NCs, thus allowing for multiple washing cycles, while retaining their monodispersity. For

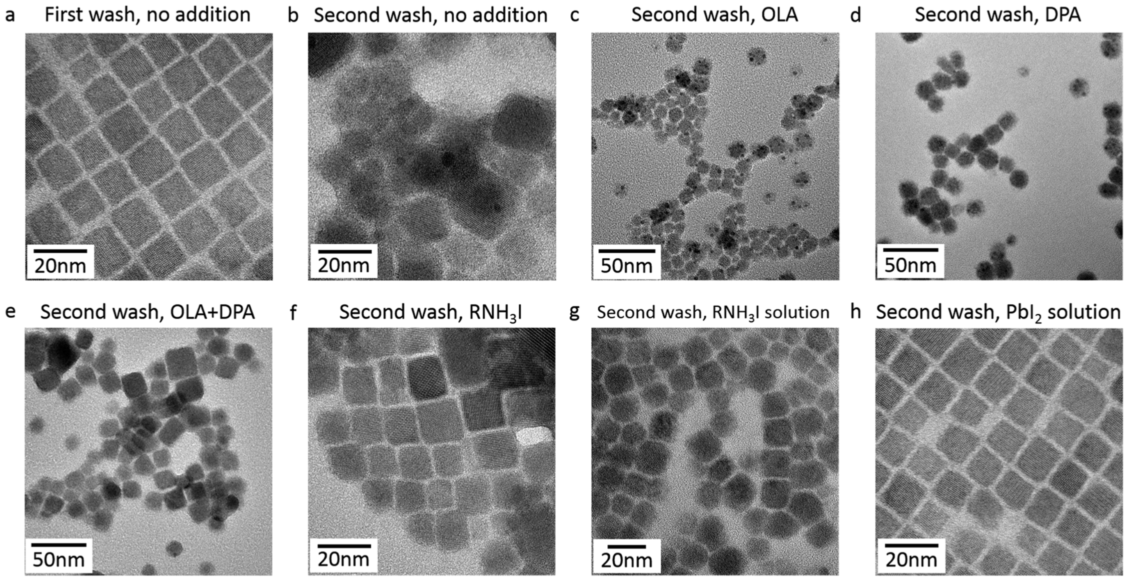

FIG. 3. TEM images for the $CsPbI_3$ NCs after various additions of washing additives during purification. (a) 1st wash, no additions, and 2nd wash with (b) no additions, (c) OLA, (d) DPA, (e) OLA+DPA, (f) RNH_3I, (g) RNH_3I solution, and (h) PbI_2 solution.

completeness, we also monitored the long term phase stability of the "PbI_2 solution" washed NCs with XRD. As shown in Fig. S6, a comparison of the XRD patterns between those freshly made and after storage for 20 days under ambient conditions exhibits identical diffraction patterns, with no δ-phase detected.

We note that under these purification conditions the structural and optical properties of the NCs could be retained even after 10 washing steps (Fig. S7), suggesting that it is a robust approach to maintain the delicate equilibrium between surface bound and solution species. Furthermore, to demonstrate the generality of this washing process, we have applied the same washing protocol to both $CsPbCl_3$ and $CsPbBr_3$ NCs using analogous $PbCl_2$ and $PbBr_2$ solutions, respectively (Fig. S8). For $CsPbCl_3$, the absorption was preserved, albeit with a slight reduction in PL, while for $CsPbBr_3$ NCs, both the absorption and PL characteristics were retained. It is important to put the slight relative PL reduction for $CsPbCl_3$ into context because its absolute PLQY is very low (<4%) compared to both $CsPbBr_3$ and $CsPbI_3$ (>60%). As such, this represents a very minor change in absolute PLQY, which is consistent with bulk defects dominating the emissions processes in $CsPbCl_3$.[24]

To examine the versatility of this purification protocol, we have also washed the conventional OA-synthesized $CsPbX_3$ NCs with an analogous PbX_2 solution, albeit using OA instead of DPA, and using the widely accepted methyl-acetate as the antisolvent. As shown in Fig. S9, this approach appears favorable for retaining the absorption and luminescence of $CsPbBr_3$; however, this is not the case for both $CsPbCl_3$ and $CsPbI_3$ NCs, which show a progressive deterioration in optical properties and, for the latter, also resulting in poor phase stability (converting in 3 days). This difference between DPA and OA based washing solutions likely arises from the variation in the steric nature of these ligands, extent of surface passivation, acidity, and/or solubility of the resulting salts, although understanding the interplay between these is outside of this work's scope.

Given that an equilibrium must exist between surface bound and solution species, we probed the effective concentration limits of these washing additives to optimize the amount of PbI_2 solution required to retain the $CsPbI_3$ NC properties following purification. To do this, we first determined the NC concentration, [NC], using ICP-MS measurements and the average NCs size (see Table S2 for calculation). We then used the concentration of the NC after the 1st wash, $[NC_{1st\ wash}]$, and the corresponding absorption measurements to approximate the wavelength-dependent molar-extinction coefficient and absorption coefficient of our $CsPbI_3$ NCs, which is shown in Fig. S10. To further probe the interaction between the additives and the NC surfaces, we estimated the molarity of the total Cs^+ or Pb^{2+} ions at the NC surface, [Surface Ions], by calculating the relative percentage of these ions vs bulk (~30%, see the supplementary material). Using these concentration values, we then assessed the PLQY of NCs washed after 3 cycles with controlled amounts of PbI_2 solution added as a function of $[PbI_2]/[NC_{1st\ wash}]$ and $[PbI_2]$/[Surface Ions] [Fig. 4(a)]. The results show that when the $[PbI_2]/[NC_{1st\ wash}] < \sim 3000$ or $[PbI_2]$/[Surface Ions] < ~1.7, the NCs exhibit instability. The reduced absorption [Fig. 4(b)] at these low additive levels confirms the partial removal of NCs through either their aggregation or dissolution during the washing process. In contrast, at higher additive levels, a PLQY of 70% was stabilized and no further changes in absorption were observed. We note that in the typical synthesis crude solution, for which the $[NC] \sim 1.1 \times 10^{-6}$ M, the $[PbI_2]/[NC]$ is around 20 000. This is consistent with the first

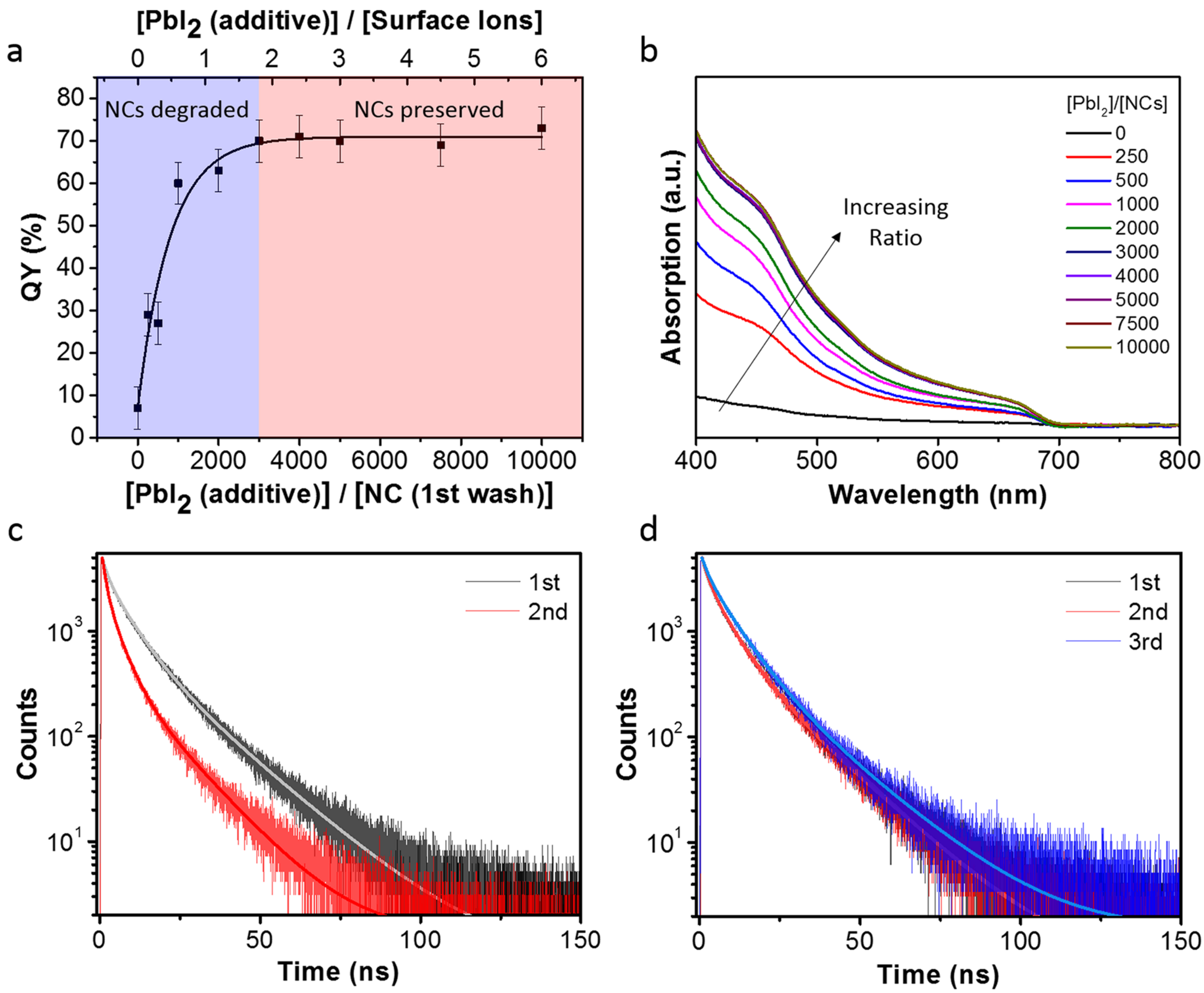

FIG. 4. Correlation between (a) the PLQY and (b) the absorption change of NCs after the 3rd wash against different molar ratios of added PbI$_2$ in the "PbI$_2$ wash solution" and the concentration of the NCs after the 1st wash. Time resolved photoluminescence (TRPL) measurements and the fitting curves for CsPbI$_3$ NCs after (c) the 1st and 2nd washing steps with no additional additives and (d) after the 1st, 2nd, and 3rd washing steps with the PbI$_2$ solution.

wash always yielding high quality NC dispersions that retain their optical properties.

We further tracked the impact of the washing process on the optical properties of the NCs by conducting time-resolved PL (TRPL) measurements (fitting details are in Table S3). For cycles featuring no additives during washing [Fig. 4(c)], the average lifetime significantly decreased between the 1st and 2nd washing steps from 6.7 ns to 3.0 ns. After the 3rd wash, the degradation of NCs was extremely fast under the required dilution preventing effective TRPL measurements. In contrast, but consistent with the slight increase in PLQY, processing using an optimal $[\mathrm{PbI_2}]/[\mathrm{NC_{1st\ wash}}] = 30\,000$, yielded similar PL lifetimes after the 1st, 2nd, and 3rd wash [Fig. 4(d)] of 5.8, 6.0, and 7.5 ns, respectively. These results confirm that washing with neat IPA yields an increase in nonradiative trap states, while employing the PbI$_2$ solution acts to preserve the NC bulk and surface properties.

Having shown that the use of PbI$_2$ solution effectively preserves the optical properties and nanostructure of the CsPbI$_3$ NCs over multiple washing cycles, we further investigated the surface chemistry of the NCs with NMR spectroscopy. First, as the presence of ODE creates difficulties in characterizing OLA species,[17] we monitored its removal by performing ^{1}H-NMR spectroscopy on NC dispersions after the 1st, 2nd, and 3rd washing cycles with the PbI$_2$ solution at a $[\mathrm{PbI_2}]/[\mathrm{NC_{1st\ wash}}]$ of 30 000 (Fig. S11 and full spectra in Figs. S12–S14). The distinct NMR resonance peaks of the terminal alkene group of ODE located at 5.0 and 5.8 ppm remain after the

1st wash but become negligible after the 3rd wash, indicating the successful removal of ODE. Meanwhile, the presence of OLA was confirmed by the broad peak at 5.5 ppm (denoted as * in Fig. S11), arising from its alkene resonance.[25] The average binding affinity of the oleylamine/oleylammonium species was measured with diffusion ordered NMR spectroscopy (DOSY), and diffusion coefficients of 524 and 345 $\mu m^2 s^{-1}$ were obtained for the species contained in solutions of NCs washed once and three times, respectively. As a comparison, the diffusion coefficient for free oleylamine was measured as 1068 $\mu m^2 s^{-1}$. Meanwhile, using the Stokes-Einstein equation and considering NCs with a tightly bound oleylamine shell of an overall diameter of ~12 nm, we calculated the nominal diffusion coefficient to be only 49 $\mu m^2 s^{-1}$ (see the supplementary material). As the experimentally obtained diffusion coefficient is the weighted average between the tightly bound and free species, the decrease in diffusion coefficient demonstrates that after multiple washes the portion of OLA which is free is reduced.[26] For completeness, we have also calculated the effective total ligand density of the 1st and 3rd washed samples to be 4.6 nm^{-2} and 2.9 nm^{-2}, respectively (see the supplementary material for details). This effective decrease in ligand density supports the notion of a lower concentration of free ligands within the 3rd washed sample, reaching a value that is consistent with those reported for $CsPbBr_3$.[17]

The above analyses highlight the sensitivity of $CsPbI_3$ nanocrystals to their purification conditions. We consolidate these results in Fig. 5 by schematically depicting the effect of the different additives investigated here on the NC dispersion. Evidently, in the crude solution of $CsPbI_3$ NCs, free OLA, DPA, their conjugates, alkyl ammonium iodide, and DPA-lead complexes act to stabilize the NC surface. We have shown that unless all of these chemical species are introduced into the washing solution, and at a sufficient concentration, the NCs tend to lose their surface capping ligands, causing them to dissolve, aggregate, or transform into the δ-phase. This indicates that a complicated equilibrium involving ligands, lead ions, and iodide species must exist between the surface and solution, and only by preserving its balance, can the optical and structural properties of the NCs be maintained. This purification approach has been extended across the $CsPbX_3$ NC family, demonstrating its generalized and facile nature for the production of high quality and high purity perovskite NC inks. Achieving this dispersion state is essential to carrying out reliable fundamental studies of perovskite NC structure-property relations and, ultimately, their integration into high-efficiency and reproducible optoelectronic devices.

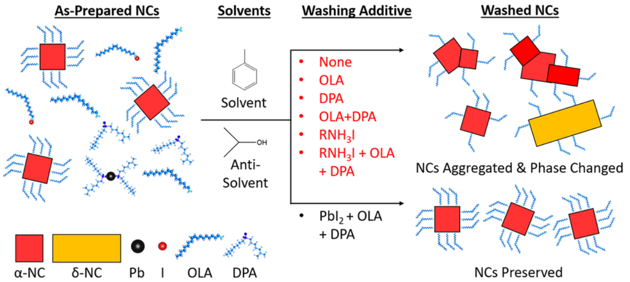

FIG. 5. Schematic illustration of how different additives used for purifying α-$CsPbI_3$ NCs from within a toluene solvent and IPA antisolvent mixture affect the nanocrystal dispersion.

See the supplementary material for experimental methods of the synthesis, purification procedure, characterization techniques, additional tables, photos, and data of UV-vis absorption and PL spectra, TEM, EDX, ICP, NMR, XRD, etc. (PDF).

This work was funded by the Australian Research Council funded Center of Excellence in Exciton Science (Grant No. CE170100026). We thank the staff in the Monash Centre of Electron Microscopy, Monash X-ray platform, and CSIRO NMR and ICP facility for their support.

The authors declare no competing financial interests.

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[26] Unfortunately, as other OLA containing species, such as OLA-DPA ion pairs, are also present in solution in unknown quantities, it is not possible to quantitatively determine the ratio of free vs bound ligand species in solution.