Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand

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ABSTRACT: Attaining thermodynamic stability of colloids in a broad range of concentrations has long been a major thrust in the field of colloidal ligand-capped semiconductor nanocrystals (NCs). This challenge is particularly pressing for the novel NCs of cesium lead halide perovskites (CsPbX₃; X = Cl, Br) owing to their highly dynamic and labile surfaces. Herein, we demonstrate that soy lecithin, a mass-produced natural phospholipid, serves as a tightly binding surfacemapping ligand suited for a high-reaction yield synthesis of CsPbX₃ NCs (6–10 nm) and allowing for long-term retention of the colloidal and structural integrity of CsPbX₃ NCs in a broad range of concentrations—from a few ng/mL to >400 mg/mL (inorganic core mass). The high colloidal stability achieved with this long-chain zwitterionic ligand can be rationalized with the Alexander–De Gennes model that considers the increased particle–particle repulsion due to branched chains and ligand polydispersity. The versatility and immense practical utility of such colloids is showcased by the single NC spectroscopy on ultradilute samples and, conversely, by obtaining micrometer-thick, optically homogeneous dense NC films in a single spin-coating step from ultraconcentrated colloids.

INTRODUCTION

Colloidal nanocrystals (NCs) of lead halide perovskites (APbX₃; A = Cs, formamidinium; X = Cl, Br, I) are new semiconductor NCs which have both unique optical characteristics as well as specific challenges.1 Defect-tolerant photophysics,2 outstanding photoluminescence (PL) characteristics, narrow emitting bands, high quantum yields (QYs), spectral tunability, and facile synthesis make perovskite NCs appealing classical light sources (in LCD and LED displays),3 lasers,4 optical communication,5 scintillators6 as well as single-photon sources.7 Conversely, perovskite NCs are also pursued as promising light harvesters for solar cells8 and photodetectors.9,10 The surface state of semiconductor NCs has been the dominant factor defining the optical and electronic characteristics of individual NCs and their assemblies.10 The inorganic (NC core)—organic (ligands, solvents) interface is quintessential for the entire life cycle of a semiconductor NC—from its nucleation and growth to integration into devices.11 The surface chemistry of perovskite NCs has been shown to be vastly different from conventional semiconductor NCs, chiefly due to their ionic bonding and low lattice energy within the lead halide NC core (structural lability) and at the inorganic–organic interface.12 Most specific challenges are the susceptibility of the NC cores to water and many other solvents due to their finite solubility and the loose binding of the surface-capping ligands.13 These have been the major obstacles for studying, processing, and applications of perovskite NCs. For instance, rapid ligand desorption renders colloids unstable and eventually causes morphological degradation and coalescence of these NCs. Unsurprisingly, a rapid surge of reports is targeting these challenges by the judicious choice of the solvents, ligands, and other additives for the synthesis and isolation protocols.13a,b,14 Alternatively, NC films can be subjected to various surface stabilization and matrix-encapsulation strategies.7j,16

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The ideal ligand system is allowing for efficient synthesis and subsequent processing. Common solution-processing techniques—spin coating, inkjet printing, doctor blading, slot die coating, or screen printing—all require concentrated and stable colloids. Obtaining thick, optically homogeneous, and dense films of CsPbBr₃ and FAPbBr₃ NCs with high PL QYs is of paramount importance in quantum dot-color filter displays, wherein the emissive layer must be several micrometers thick in order to completely absorb the blue backlight to reach optimal luminance and a wide color gamut. On the other hand, highly dilute NC systems are required for engineering quantum light sources.⁷

In this study, we sought to devise an effective ligand system that allows retention of the colloidal state, structural integrity, and optical characteristics over a broad range of CsPbBr₃ NC concentrations. Using natural soy lecithin as a capping ligand (Figure 1a and 1b), we obtained concentrations of CsPbX₃ NCs exceeding 400 mg/mL (inorganic core mass/total volume of the colloid), i.e., approximately 30% by volume (Figure 1c). Furthermore, tight ligand binding allows attaining the colloidal state and maintaining NC integrity in a broad concentration range down to few ng/mL.

### RESULTS AND DISCUSSION

Soy lecithin is an inexpensive, natural, zwitterionic phospholipid which contains a physiological mixture of saturated and unsaturated long hydrocarbon chains (total of five, Figure 1b), two per molecule. Hence, it can be viewed as a polydisperse ligand. The choice of lecithin was inspired, on one hand, by our earlier studies of other zwitterionic long-chain molecules as strongly binding ligands⁶ and, on the other hand, by insights from polymer physics. To achieve highly concentrated colloids the NC–NC repulsion—typically and in this study of purely steric nature—is needs to be maximized. Ligand-covered NC surfaces can be viewed as brush-like structures (Figure 1a). Details of modeling the ligand–ligand repulsion between two NC surfaces can be found in the SI, Table S1 and Figures S1 and S2. The repulsion between polymer brushes has been studied extensively by De Gennes¹⁹ and others.²⁰ The classical model considers these brushes as made up from stretched chains, permanently attached to an infinite, flat surface, which are valid assumptions for lecithin-covered CsPbBr₃ NCs due to static ligand binding (confirmed by NMR, see discussion later in the text) and their cuboidal shape. According to classical, self-consistent mean field theory the factors which increase the energy of repulsion and thus the energy barrier for aggregation are tight binding, long chains, high grafting density, and ligand chain polydispersity.²¹ Calculated energy of repulsion vs number of hydrocarbons reproduces the slope obtained in the logarithmic plot of the experimental saturation concentration vs number of hydrocarbons (Figure S3). We note that we have thus far ignored the effect of the ligand interpenetration (gain in enthalpy upon aggregation due to van der Waals ligand–ligand interaction) that counteracts the steric repulsion.

Interpenetration of ligands explains the lower solubility of stearyl-ASC18 compared to oleyl-ACS18 (Figure S3). Similar effects of the ligand steric has been observed on smaller, quasishpherical NCs (CdSe, Fe₂O₃, Ag, etc.).²³ For sufficiently long chains the overall impact of interdigitation on the system’s free energy will level off, as commonly observed with polymers.²⁴ In fact, both the experiment and the calculations agree on the grafting density and ligand-chain distribution as the factors able to boost the CsPbBr₃ NC–NC repulsion well beyond the impact of chain length. Soy lecithin is a natural ligand system that harnesses all three components (Figure 1c).

Our results on CsPbBr₃ NCs and recent work by others on CdSe NCs²⁵ point to a rather unexplored potential of ligand systems comprising the same headgroup and a mixture of different hydrocarbon tails.

Highly concentrated colloids of lecithin-covered CsPbBr₃ NCs retain a fully dispersed state without noticeable aggregation for at least 1 month, as can be readily seen by the Tindall effect (Figure S4) and confirmed by dynamic light scattering (DLS, Figures S5 and S6). They can be centrifuged at 29 500 rpm for 1 h without noticeable precipitation. At the other extreme, in very dilute solutions (Figure 2a and 2b, right), factors such as chain length become less important due to decreased collision probability. The tight binding of the ligand, however, gains a pivotal role as it counteracts dilution-favored desorption of the ligands (leading to NC degradation as well). The PL peak positions and PL QY values are retained upon deep dilution (Figure S7).

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**Figure 1.** (a) Schematic of a lecithin-ligand brush on a CsPbX₃ surface; h indicates the brush height. (b) Chemical structure of lecithin and statistical occurrence of side chains in soy lecithin. (c) Plot comparing the saturation concentration CsPbBr₃ NCs (ca. 7 nm) capped with different ligands: oleic acid (OA) and oleylamine (OLA), ASC8 [3-(N,N-dimethyloctylammonio)propanesulfonate] and its longer chain analogues (ASC12 and ASC18, having C12 and C18 carbon chains in place of octyl, see also an earlier study in ref 14k). The highest concentration of above 400 mg/mL (inorganic content per mL of toluene) is obtained with soy lecithin as a combined result of its higher chain length and natural lengths dispersity and, comparatively to all other studied ligands, higher grafting density (two vs one long chains per headgroup; i.e., 3.6 vs 2 tails/nm²). For comparison, ACS18-capped NCs exhibit a saturated concentration of ca. 90 mg/mL.
Soy-lecithin-capped CsPbX₃ NCs were obtained at 80–150 °C in a hot-injection synthesis (see details in SI) by adapting the methodology that we previously devised for synthetic zwitterionic molecules as capping ligands. In particular, Pb−oleate, Cs−oleate, and trioctylphosphine−halogen adduct (TOPBr₂, TOPCl₂) were used as precursors, whereas octadecene was employed as a solvent (effect of halide ratio Figure S8). The NCs crystallize into an orthorhombic perovskite lattice (Pbnm, Figure S9). NCs can be isolated by destabilizing the crude solution with acetone followed by centrifugation and redispersion in toluene. The synthesis yield can be ca. 70% (for a 150 °C, synthesis), which is about 800 mg from a 25 mL reaction scale. The loss is primarily due to incomplete precipitation at each stage. We note the practical

Figure 2. (a and b) Vials containing lecithin-covered ∼8 nm CsPbBr₃ NCs at various concentrations (indicated on the figure) under day light and UV light, respectively. (c) Typical absorption spectra (gray, as synthesized; black, fraction 8) and emission spectrum (green, fraction 8). (d) high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image, (e) HR-TEM image, and (f) high-resolution HAADF-STEM image of CsPbBr₃ NCs from fraction 8 obtained by size fractioning; full size-selected series is given in Figure 3a and 3b as well as Figures S15 and S16.
utility of perovskite NCs is often handicapped by the low synthesis yields caused by the losses at the isolation and purification stages, not by the initial precursor-to-NC conversion. For instance, 90% of NCs are typically lost in conventional OA/OLA synthesis due to the desorption of OA/OLA coating and NC aggregation. With zwitterionic ligands, on the contrary, up to 80% of NCs can be obtained in the form of well-purified colloids. In this regard, lecithin is a similarly efficient ligand yet with its own specifics caused by drastically enhanced colloidal stabilization. For instance, running the synthesis at the concentrations of reagents commensurate with conventional OA/OLA synthesis (i.e., five times lower than we report here) yields colloids that are hard to destabilize by acetone.

Lecithin-capped NCs fully retain their spectral characteristics after intense purification by repetitive precipitation with diverse nonsolvents under ambient conditions and after prolonged storage (Figure S10). We note that all results presented in this work are obtained for samples that were at least several weeks old. Efficient ligand binding and ligand retention upon isolation is directly confirmed by NMR spectroscopy and thermal gravimetric analysis (TGA). The $^1$H and $^{31}$P NMR spectra of lecithin-covered NCs show severe line broadening compared to lecithin reference spectra and spectra of decomposed NCs (Figures S11 and S12). Decomposition of NCs was conducted by mixing a concentrated colloid with $d_6$-DMSO. A plausible reason for the line broadening is the increase of the ligand’s rotational correlation time due to association with the NCs. Association of the ligand molecules with each other into micelles, an alternative cause for the reduced molecular tumbling and hence line broadening, can be excluded based on analytical ultracentrifugation (AUC) measurements, as discussed later in the text. Diffusion-ordered NMR spectroscopy (DOSY) shows an increase of the ligand’s diffusion coefficient by a factor of 10 when associated with the NCs (Figure S13). This is in agreement with values previously seen with other zwitterionic ligands (see ref 14k and Table S2). The NC size received from DOSY, assuming tight binding of the ligands, is commensurate with NC sizes determined by TEM or DLS (Table S2). The combination of these arguments suggests the absence of free organic solutes. With the TGA weight loss of ca. 25% (at 300 °C, Figure S14), one can estimate ligand surface densities of ca. 1.8 nm$^{-2}$. This value is close to that obtained with single-chain zwitterionic ligands such as ASC18 (ca. 2.0
nm$^{12,145}$), suggesting that bulkier lecithin molecules do not suffer from much increased sterical encumbrance at the NC surface.

The typical absorption spectrum for CsPbBr$_3$ NCs synthesized at 130 °C is shown in Figure 2c (gray line). Such colloids are characterized by the standard size deviation of ca. 20%. For obtaining practical quantities of narrowly dispersed NCs (size distribution below 10%) we employed a so-called size-selective precipitation technique, extensively used in the past for conventional semiconductor NCs (InP, CdSe, CdTe). Size fractioning is conducted by the gradual destabilization of a colloid with a nonsolvent and collection of each fraction by centrifugation. High concentrations and stable surface capping are imperative for an overall practicality of this approach. So-obtained NCs exhibit better-resolved excitonic features in the absorption spectra, as follows from Figure 2c (black curve), showing fraction 8 in this specific case, comprising 16 wt % of the initial ensemble. Electron microscopy reveals a uniform cuboid shape, mean NC size of ~9 nm, and confirms monodispersity of these NCs (ca. 9.9% of size distribution). Monodisperse NC colloids with a mean NC size precisely adjustable in the range of 6–10 nm can be obtained by combining the effect of the synthesis temperature (higher for larger sizes) and size-selective precipitation (Figures S15 and S16, Table S3). For smaller NCs (<8 nm), which fall into strong and intermediate quantum confinement regimes, the benefits of size selection on the sharpening of absorption spectra and narrowing PL lines are most pronounced. At larger sizes, PL bands are already limited by the homogeneous line width, as can be seen from the spectral indistinguishability of fractions 1–8 (Figure 3b). Absorbance spectra often are less subjected to homogeneous broadening and hence render a better estimate for the spectral polydispersity of the colloids (Figure 3a).

The size distribution of the size-selected fractions (for the same 130 °C synthesis) has been further quantified with two very distinct techniques which can probe the NCs in their native colloidal state: analytical ultracentrifugation (AUC) and small-angle X-ray scattering (SAXS). The results for fractions 6–9 are presented in Table 1 and compared to TEM data (Figure S17).

**Table 1. NC Edge Lengths (in nm) Determined by Various Methods**

| fraction | TEM    | AUC    | SAXS |
|----------|--------|--------|------|
| 6        | 10.4 ± 0.99 | 10.3   |      |
| 7        | 10.5 ± 1.2  | 9.9    |      |
| 8        | 8.9 ± 0.89  | 8.7    | 7.9 × 9.1 × 9.1, σ = 6.5%, average 8.7 |
| 9        | 8.75 ± 0.87 | 8.0    | 7.2 × 8.2 × 8.3, σ = 6.6%, average 7.9 |

We employed AUC sedimentation velocity (SV) measurement for its capability in determining solvodynamic parameters of the NCs in their original dispersion. In an AUC-SV experiment, the dispersion in a cell is spun at a constant speed, causing a net sedimenting movement of the NCs toward the bottom of the cell. The concentration of the nanocrystals is monitored along the cell as time progresses. Absorbance or interference optics can be utilized (Figure 3c). The evolution of the absorbance signal with space and time depends on the sedimentation of the species that absorb at a given wavelength. The evolution of the interference pattern is sensitive to all species present because their sedimentation causes a change in the refractive index of the dispersion. In our AUC-SV experiments we recorded both absorbance and interference simultaneously. A sample composed solely of NCs should have the same distribution of sedimentation coefficients derived from absorbance and interference AUC; any difference would be an indication of optically inactive species in solution (i.e., impurities). The distribution of sedimentation coefficients C(s), which is determined by the particle size, shape, and density, is obtained by numerically fitting the Lamm’s solution to the AUC radial profiles (Figures S18–20). We ran AUC on multiple fractions of the NCs. We found that for all fractions the distribution results from absorbance (550 nm) data and interference data were essentially the same (Figure S20), indicating that the particles have a high degree of purity. Representative distributions of the sedimentation coefficients are shown in Figure 3d (and others are in Figure S20). These plots clearly show that each fraction contains NCs of rather narrow size distribution and that fractionation improved size distribution.

In order to better explain the working principle of AUC we can take the example of a NCs-containing sample. The centrifugal forces that act on the NCs determine the movement of the absorbance boundary that is related to the NCs sedimentation coefficient that is proportional to their solvodynamic size. As the experiment progresses, the natural diffusion of the NCs tends to broaden the absorbance boundary whose thickness is effectively infinitely sharp at time zero and progressively can evolve to be sizable. Such evolution of the boundary is used to determine either the particle’s density (assuming spherical shape) or the particle’s frictional coefficient (a parameter related to the shape of the NCs, assuming a known density). In the analysis of the NCs described here we assume a frictional coefficient of a cube (f/f₀ = 1.05); this allowed us to calculate the density for the NCs. As explained in ref 30a, the simultaneous knowledge of the NCs solvodynamic radius (from the sedimentation coefficient) and the overall particle density allowed us to calculate the size of the inorganic core of the NCs. Overall, the core sizes found in AUC agree quantitatively with the edge lengths retrieved from HR-TEM and SAXS (see Table 1). In addition, we can also conclude that the samples are free from known impurities for these NCs (such as CsPbBr$_3$Br$_2$ and CsPbBr$_{3.5}$Br$_{0.5}$, delaminated Ruddlesdon–Popper phases, organic micelles, etc.) as AUC at 500 nm leads to identical results to AUC at 335 nm or AUC run in interference mode. Any of the impurities named above would have led to additional contributions to the AUC distributions.

Colloids of NCs with less than 10% polydispersity are highly suited for analysis with small angle X-ray scattering (SAXS). Size- and shape-dependent scattering features can thus be identified and interpreted, as we illustrate here for toluene solutions of lecithin-capped CsPbBr$_3$ NCs (fractions 8 and 9 from 130 °C synthesis). Colloids were filled in a flow cell capillary, followed by the SAXS measurements at a synchrotron source (see SI section 4.5 for details). After applying intensity and background corrections, the scattering traces all showed clear features of form factor scattering and were hence compared to analytical models. Additionally, the shape was reconstructed using SASHEL, a model-free Monte Carlo 3D fitting algorithm, which operates without prior assumptions. The results of both methods are shown in Figures 4 and S21 for the NCs of fractions 8 and 9, respectively.

In the analytical model, an oblate cuboid with dimensions 7.99 × 9.27 × 9.27 nm (i.e., aspect ratio of 0.86) and 6.43% relative polydispersity was found to most closely represent the NCs of fraction 8. Alternative models such as monodisperse
cuboids and cubes with 9.4% relative polydispersity did not reproduce the measured scattering traces as closely, as can be seen from the residuals in Figure 4a. Full reconstruction yielded a cuboidal NC shape of $7.9 \times 9.1 \times 9.3$ nm for NCs of fraction 8 (Figures 4b).

Retention of colloidal, structural, and optical integrity over a broad concentration range of CsPbX$_3$ NCs, i.e., from 400 mg/mL down to few ng/mL, will have diverse practical implications. In the following, we showcase two instances of immense practical utility of ultraconcentrated as well as ultradilute colloids of CsPbX$_3$ NCs.
Highly concentrated colloids can be used as inks for one-step deposition of thick, smooth, optically clear films by spin coating. The thickness of the film can be readily adjusted by the concentration of the colloid to above 1 μm while maintaining a roughness of just 1.5 nm (Figure 5a–d, Figures S22 and S23). Previously, micrometer-thick perovskite NC films were obtained mostly by stepwise deposition with intermittent consolidation steps or by filling of a scaffold structure. The experimental thickness vs concentration dependence—while linear in ASC18-covered NCs (black)—can be approximated with a square root law for lecithin-covered NCs (green), although an increase with the power of 1/3 would be generally expected. This deviation can be rationalized by the variation of solution properties such as viscosity, vapor pressure, or contact angle at high volumetric loadings, which are critical to the spin-coating process. In particular, higher viscosity leads to thicker films. Importantly, these films exhibit excellent optical clarity, indicative of their aggregation-free deposition and high PL QYs of ca. 30% at all thicknesses. Such thick films may find applications in the next-generation displays with NC films serving as both light filters and emitters or as scintillators for detecting X-rays and gamma-rays.

Ultradilute colloids are also in great demand. For example, dilution to the ng/mL level is necessary for obtaining sparsely distributed NCs upon deposition and solvent evaporation. In particular, dilutions which result in the average NC-to-NC separation by several micrometers are ideally suited for single NC spectroscopy with typical microphotoluminescence setups. As discussed above, labile ligand shells rapidly lead to the loss of colloidal state and NC aggregation upon such severe dilution due to ligand desorption. We therefore tested the durability of lecithin-capped CsPbBr$_3$ NCs for obtaining single-photon emission at room temperature (Figure 5e and 5f), moreover, by conducting all steps under ambient conditions. Despite the presence of PL blinking as usually reported for these NCs, the PL is stable for several tens of seconds and without significant PL blue shift (typical for perovskite NCs). Second-order correlation measurements attest single-photon emission with the characteristic antibunching behavior and a good single-photon purity ($g^2(0) \approx 0.2$), further confirming a non-aggregated, intact state of these NCs.

**CONCLUSIONS**

We found that soy lecithin—an inexpensive, natural, mass-produced zwitterionic phospholipid—makes for an effective capping ligand for the synthesis of colloidal CsPbX$_3$ NCs. Most importantly, it imparts high colloidal stability in a broad range of NC concentrations (from few ng/mL to above 400 mg/mL). Tight ligand binding, high grafting density, long chains, and ligand polydispersity are the key contributors of the effectiveness of this ligand. High synthesis yield and robustness of the colloids allow for facile size fractioning of the colloids, yielding practical quantities of monodisperse NCs with mean particle size tunable in the range of 6–10 nm. The size, shape, and size distribution of so-obtained NCs have been thoroughly examined with TEM, SAXS, and AUC techniques. In particular, the shape of these NCs have been confirmed to be oblate cuboids with a small aspect ratio of ca. 0.86.

An immense practical utility of such ultraconcentrated and ultradilute colloids has been illustrated by two showcase experiments. First, we have shown a one-step deposition of thick (up to 1.5 μm) NC films by spin coating. Such films exhibit excellent optical clarity while retaining bright fluorescence. Second, such colloids are also versatile inks for obtaining highly dilute NC systems as required for single-dot spectroscopy. Single-photon emission with pronounced photon antibunching has thus been readily observed.

**ASSOCIATED CONTENT**

† Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b09969. Experimental methods and supplementary figures (PDF)

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**Notes**
The authors declare no competing financial interest.

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