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**One or Many: Using single particle microscopy to investigate perovskite quantum dot
surface chemistry**

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Abstract

One or Many: Using single particle microscopy to investigate perovskite quantum dot surface chemistry

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Since their initial discovery, colloidal quantum dots (QDs) have emerged as promising materials for a wide range of optoelectronic applications including Quantum Dot Light Emitting Diodes for display applications, solution-processible lasers, and photodetectors.

Perovskite quantum dots are a class of materials that are uniquely promising, due to their high photoluminescence quantum yield (PLQY), narrow ensemble linewidths and tunable bandgap. In particular, cesium lead halide nanocrystals have shown efficiency comparable to commercial Organic LEDs, and have even shown promise as quantum emitters, due to their high degree of coherent single photon emission relative to other colloidal quantum dots.

Remarkably, perovskite quantum dots achieve these desirable optoelectronic properties without an inorganic shell, which is required in II-VI or III-V colloidal quantum dots. Instead, perovskite nanocrystals have organic ligand shells as their surface termination. As a result, the properties of perovskite nanocrystals are highly dependent on the surface ligand identity. Despite this, efforts to systematically investigate the effect of ligand composition on single particle properties are in a nascent stage. To optimize the surface chemistry of perovskite quantum dots for single particle applications we need to gain a more systematic understanding of the role that surface ligand plays in photoluminescence blinking.

In the first project we investigate the effect of ligand binding equilibrium on photoluminescence blinking in cesium lead bromide quantum dots. Here we compared QDs capped with lecithin, a multidentate tightly binding ligand, to QDs capped with a binary ligand system of Oleic Acid and Oleylamine (OA/OAm). We find that lecithin acts to suppress blinking in CsPbBr₃ QDs. Under common experimental conditions lecithin-capped QDs are 7.5 times more likely to be non-blinking and spend 2.5 times longer in their most emissive state than OA/OAm QDs, despite having comparable ensemble PLQY post synthesis. We measure photoluminescence as a function of dilution and show via ligand re-addition that the differences between lecithin and OA/OAm capping emerge at low concentrations, because of differences in the ligand binding affinity. This work shows the importance of ligand binding affinity to single particle properties otherwise obfuscated by ensemble dynamics.

In the second project, we are investigating the effect of varying the ligand head group by comparing diquateryary amine (DC) and cationic ligand surface treatments, such as didodecylammonium bromide (DDAB) capped QDs to those capped by zwitterionic ligands, such as lecithin and recently reported primary amine zwitterionic (PEA-C₈C₁₂). These cation and

zwitterion-capped QDs show comparable ensemble properties, including near unity PLQY and narrow (<20nm fwhm) ensemble photoluminescence spectra. We further investigate the role of these ligand exchanges by investigating photoluminescence blinking and linewidth. We find that zwitterionic ligands reduce blinking and show narrower 4K linewidth compared to their cationic counterparts. We can rationalize these results by considering the geometry and ligand surface density. The cationic ligands have a lower number of ligands per QD and a more amorphous crystal habit compared to their zwitterionic counterparts. This suggest that zwitterionic ligands are a more favorable choice for ligand exchange reactions to improve single particle properties.

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Chapter 1: Introduction

1.1 Colloidal Quantum Dots

Colloidal quantum dots are nanometer sized particles that can be grown in solution, and that exhibit remarkable quantum confinement properties, such as size dependent emission energies, high color purity and high photoluminescence quantum yields.¹ These particles are composed of inorganic crystalline cores, capped with organic surface ligands that provide solubility in organic solvents.² Cadmium selenide (CdSe) quantum dots were the first quantum dot materials to successfully be grown in solution.³ Due to these desirable properties colloidal quantum dots have been employed in a wide range of optoelectronic applications including light emitting diodes (LEDs)⁵, solution processible lasers⁶, and bioimaging.⁷ Colloidal quantum dots have been so successful in LEDs that they are now integrated into commercial displays.

Since the initial discovery there has been an incredible amount of progress in the optimization of the quantum dots synthesis. Some of these improvements include decreased polydispersity, more benign reagents,⁸ and the development of core-shell heterostructures^{9,10} that improve materials photoluminescence quantum yield and stability.^{11–15} In fact, these developments have led to the synthesis of a wide range of colloidal materials beyond quantum dots.¹⁶ For the synthesis and initial discovery of quantum dots Louis Brus, Alexey Ekimov and Moungi Bawendi were awarded the 2023 Nobel Prize in Chemistry.

Since this initial discovery the scope of quantum dot materials has expanded dramatically from II-VI materials like CdSe to include III-V materials like indium phosphide, infrared emitters like lead sulfide, and more recently perovskite quantum dots. Perovskites have an ABX₃ structure,¹⁷ with A as a monovalent cation (for example cesium, or methylammonium) B as a divalent cation (like lead or tin), and the X site as a halide anion (commonly chloride, bromide, or iodide).

The synthesis of colloidal lead halide perovskite quantum dots via a hot injection method was originally reported in Protecescu et al.,¹⁸ resulting in highly emissive cesium lead halide quantum dots prepared by solubilizing metal precursors in a mixture of oleic acid and oleylamine. Protecescu observed that these materials also showed bandgap tunability via the

halide anion. Compared to conventional quantum dots lead halide perovskites exhibit weak quantum confinement, their emission energy is more insensitive to size¹⁹ and as such tuning halide content is a common strategy to change emission wavelength throughout the visible spectrum. Following these initial reports, lead halide perovskite quantum dots have achieved large absorption cross-sections,²⁰ near unity quantum yields,²¹ and narrow emission linewidths leading to high color purity throughout the visible spectrum.²²

Lead halide perovskite quantum dots can achieve narrow linewidths and high quantum yields as they are remarkably defect tolerant compared to typical semiconductors.²³ This defect tolerance originates from the electronic structure of lead halide perovskites. The band structure of lead halide perovskites is inverted relative to most semiconductors, with a p-orbital like conduction band and an s-like valence band.^{24,25} Typical defects sites in perovskite quantum dots, such as point defects are considered shallow, meaning they are energetically close to the band edge and do not have deleterious impacts on photoluminescence. However, as defect formation is a thermodynamically favorable process, perovskite QDs still require an organic ligand shell for both colloidal stability and surface defect passivation.^{26, 27}

Due to these remarkable optical properties lead halide perovskite quantum dots have been incorporated into a wide range of optoelectronic devices, including LEDs, which have shown external quantum efficiencies reaching up to 27% for green LEDs and to 25% for red-emitting compositions.²⁸ Improvements in LED device efficiencies have been realized by the optimization of quantum dot surface chemistry through a variety of strategies including short chain or aromatic ligands to optimize charge transport²⁹, bipolar shell resurfacing,³⁰ control of surface ligand density³¹ and improved surface passivation strategies.³²

This thesis seeks to understand the influence of surface chemistry on the photoluminescence properties of single CsPbBr₃ QDs. By using a combination of single particle microscopy and ensemble characterization we can gain insight into optimal ligand choice for improving single particle properties including photoluminescence blinking, linewidth, and photostability. Single particle microscopy serves as a valuable tool to capture the wide-ranging variations that can be observed in these materials, Figure 1.1 shows examples of the many particle to particle variations that can be captured with these techniques. Subsequent sections of this introduction describe recent developments in lead halide perovskite surface chemistry, the potential usage of lead halide perovskite quantum dots as single photon sources for quantum information science, the causes of spectral diffusion and photoluminescence blinking in colloidal quantum dots and mitigation strategies for time-dependent photoluminescence variations.

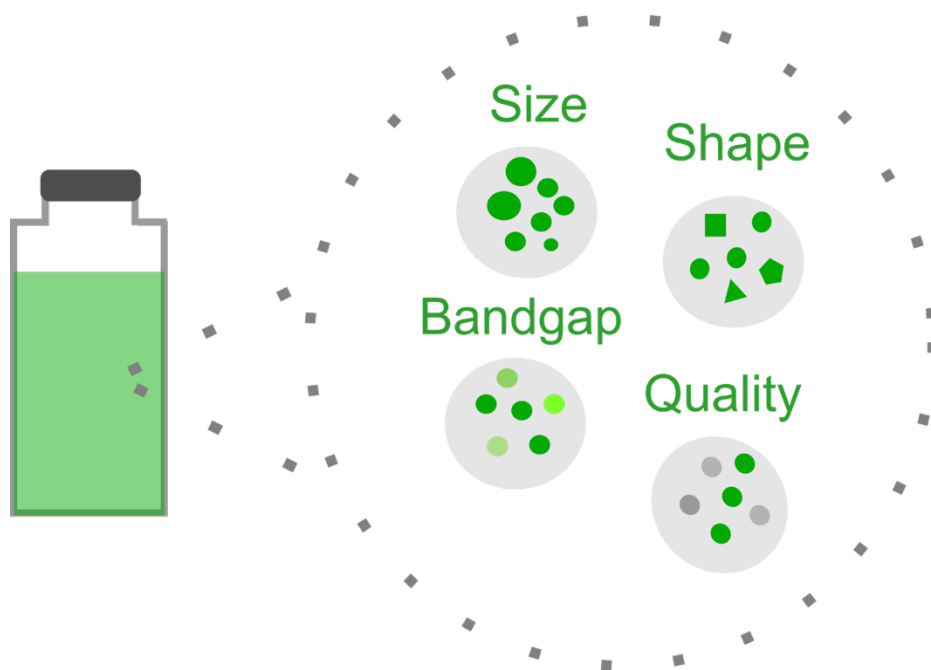


Figure 1.1 Scope of variation in quantum dots. Figure showing a graphical depiction of a solution of quantum dots. Within the ensemble individual quantum dots can show polydispersity in size, shape, bandgap, and in quality (referring to properties such as single particle linewidth, brightness or fluorescence intermittency, discussed in section 1.4)

1.2 Overview of Perovskite Surface Ligand Chemistry

Unlike their II-VI counterparts perovskite quantum dots have an ionic lattice.³³ As such it is more challenging to grow a high-quality inorganic shell on the surface of these materials.²⁴ There are ongoing synthetic efforts to realize high quality perovskite quantum dot heterostructures, with reports of shell composition using a range of materials including thin metal oxide coatings³⁴, ZnS³⁵ and bismuth.³⁶ In general, the quantum yield of these core-shell perovskite quantum dots lags behind their unshelled counterparts. Fortunately, unlike II-V or III-V quantum dots perovskite quantum dot can achieve high PLQYs without the need for shell heterostructures. For this reason, understanding the influence of surface ligand is paramount, as the photophysical properties in perovskite quantum dots depend strongly on ligand surface coverage and ligand identity. The large surface-area-to-volume ratio of quantum dots means that the surface, and its passivation by organic ligands, can dictate quantum dot properties.^{37–39}

Ligands play multiple roles for quantum dots; they modulate nucleation and growth,^{2,40} provide solubility in organic solvents, prevent degradation,⁴¹ control the nanocrystal shape,^{42–45} and affect the electronic structure via passivation of surface trap states.^{38,46} Organic surface ligands have two components, a head group that binds the quantum dot surface and a tail group that dictates solubility, typical tail groups are long-chain alkyl groups (e.g. C₁₂H₂₅) that yield nanocrystals soluble in apolar media such as hexanes or toluene.²

Perovskite quantum dots are typically synthesized with ligands with ionic head groups that occupy surface sites.⁴⁷ Most commonly this is achieved with a binary ligand system, usually an amine and an organic acid, which passivate A or X-site vacancies by substitution.^{43,47,48} Oleylamine (OAm) and oleic acid (OA) are frequently used to synthesize perovskite quantum dots because they are liquid at room temperature and can form oleylammonium halide, oleylammonium carboxylate, and lead oleate complexes which solubilize lead and cesium precursors commonly employed in quantum dot synthesis.⁴⁹

The binding of these complexes at the surface is complicated, with ligand-quantum dot, ligand-ligand, and ligand-solvent interactions playing a role in the binding affinity to the quantum dot surface. Additionally, for the typical oleic acid and oleylamine synthesis synthetic conditions⁴⁷ and acid base equilibria play key role in the affecting surface quality.^{50,51} The specific roles of oleic acid and oleylamine in the synthesis are the subject of some debate, with reports indicating that the ligand binding to the surface is highly dynamic and that oleic acid is the dominant surface ligand for high quality CsPbBr₃ quantum dots²⁰, but that the synthesis requires both oleic acid and oleylamine are to yield high PLQY perovskite quantum dots.⁴¹

Organic ligands have a specific binding affinity to the quantum dot surface, the larger the equilibrium constant, the more favorable the adsorption of the ligand to the surface.³⁸ This binding affinity can have a large impact on the photoluminescence properties of quantum dots leading to improvements in photoluminescence as the ligand binds the surface, or quenching if the specific ligand induces the formation of mid-gap trap states.^{52–54} Stronger binding ligands retain surface coverage upon dilution and are more robust to multiple antisolvent purification steps with polar solvents^{55,56} and retain higher quantum yields when processed into films.^{57,58} The energetics of ligand binding to the surface depends on a range of factors including ligand sterics, extent of surface coverage and solvent polarity.^{59,60} Poor ligand binding affinity is commonly invoked to rationalize poor colloidal stability (i.e. poor solubility and rapid material degradation) commonly observed with typically synthesized oleic acid/oleylamine capped quantum dots which has motivated the search for new ligands that can provide better long term stability and improved optical properties.³³

A more recent strategy for the synthesis of perovskite quantum dots entails the usage of multidentate zwitterionic ligands (which have multiple head groups that can bind the quantum dot surface), as an alternative to oleic acid/oleylamine.⁵⁵ Kreig et al. used commercially available sulfobetaines, phosphocholines and γ -amino acids, with positively and negatively charged functional groups as replacements for oleic acid/oleylamine.⁵⁵ They observed that the usage of ligands with multiple potential binding sites had a greater degree of colloidal stability and improved photoluminescence quantum yield after multiple antisolvent purification steps, which they ascribed to improvements in the surface binding affinity. Further work explored the usage of lecithin, a naturally occurring phospholipid with quaternary ammonium and phosphate head groups, as a zwitterionic ligand.⁶¹ Quantum dots capped by lecithin showed a remarkable colloidal stability, and were able to be isolated across a range of concentrations (400mg/mL to 4ng/mL). Researchers posited that this ligand displayed stronger ligand binding relative to oleic acid/oleylamine likely due to multisite binding. These predictions were corroborated in a recent report using a combination of molecular dynamics simulations and solid state nuclear magnetic resonance, showing that both positively and negatively charged head groups bind the surface of the quantum dot by replacing A and X sites within the lattice.⁶²

Additional synthetic strategies beyond hot injection have emerged that offer a greater degree of control over ligand chemistry by means of controlled growth followed by ligand exchange. A method reported by Akkermann and co-workers shows incredible promise for the facile synthesis of high quality perovskite quantum dots across a range of sizes.⁴² This synthesis achieves kinetic control and size-focused growth⁶³ through a slow growth mechanism.³⁶ leading to a narrower size distribution and consequently, a narrower ensemble FWHM. In this synthesis slow quantum dot growth (over the course of 30 minutes) is achieved through the usage of diisooctylphosphinic acid (DOPA)⁴² which coordinates cesium, and trioctylphosphine oxide (TOPO) which acts as a ligand coordinating the quantum dot surface.⁶⁴ Following this slow growth step the TOPO ligand is replaced via a ligand exchange with lecithin. This synthesis also produces quantum dots which a spheroidal crystal habit, likely facilitated by the lack of ammonium ligands during the synthesis.⁴² These quantum dots have increased quantum confinement and sharpened excitonic features relative to cubic QDs.³⁸ Due to this distinct combination of narrow size distribution and crystal geometry these materials have shown unique properties including halide exchange kinetics,³⁹ and crystal packing;⁴⁰ however, their single particle properties have not been systematically investigated.

Since the initial synthetic reports there have been a wide range of surface ligand candidates and post-synthesis passivation strategies to improve the issues with the dynamic ligand binding of oleic acid and oleylamine. Examples of these different ligands binding to the perovskite surface are shown in Figure 1.2. These strategies include efficient surface passivation with quaternary ammonium salts such as didodecyl ammonium bromide, which show unity PLQY via didodecyl ammonium replacement of oleic acid and oleylamine molecules on the quantum dot surface.^{43,65,66} Recently a large series of phospholipid zwitterionic ligands have been reported, which have shown improved surface coverage by means of a primary ammonium, which facilitates a greater degree of surface coverage.⁶² Additionally, bidentate cationic ligands based on quaternary ammonium functional groups have been reported and have been shown to have high ensemble PLQYs and record single particle linewidths.⁶⁷

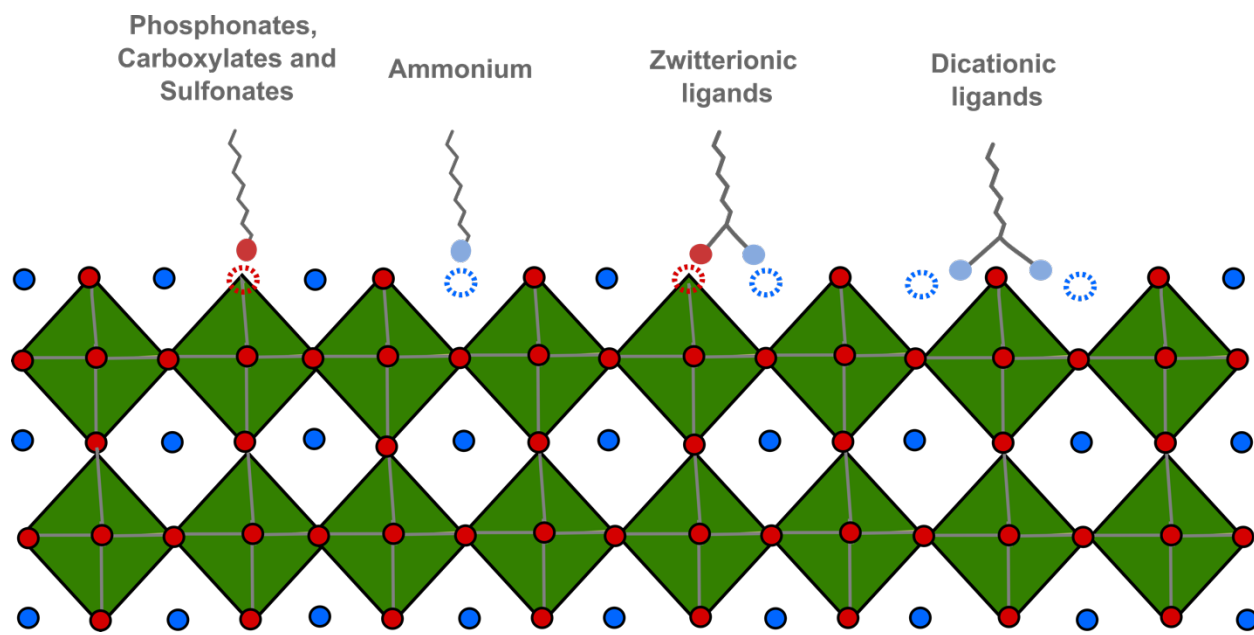


Figure 1.2 Overview of Ligand surface chemistry. The schematic depicts ligand head groups binding the perovskite surface including anionic ligands like phosphonates, carboxylates, and sulfonates, cationic ligands, which are typically ammonium, zwitterionic ligands such as lecithin or sulfobetaine, and finally dicationic with a diquatery ammonium head group.

This expansive library of ligand strategies (either via direct synthesis or ligand exchange post-synthesis) requires systematic investigation to better develop design rules.⁶⁸ Importantly, these investigations must be application specific, for example the best ligand for an electroluminescent device will not necessarily lead to the narrowest single particle linewidth. The following section (1.3) outlines the goals for harnessing perovskite quantum dots for quantum applications.

1.3 Perovskite Quantum Dots for Quantum Information Science

Single photon sources are an important bedrock of potential photonic quantum technology, they serve as the starting point for a quantum photonic chip.⁶⁹ Currently generation of quantum light is accomplished using probabilistic (non-deterministic) photon sources, such as spontaneous parametric down conversion, which can generate entangled photon pairs.⁷⁰ Two key challenges for employing nondeterministic sources are that these sources require complex optics, which are generally not scalable to a large number of sources and that the probabilistic nature of the source fails to provide photons on demand. These challenges with probabilistic sources have motivated the search for deterministic solid state single photon sources.⁷¹

Beyond their high performance in classical optoelectronics perovskite quantum dots have emerged as source of quantum light, most notably as highly coherent single photon emitters.⁷² A single colloidal quantum dot can act like a two-level-system that emits single photons. The process of single photon emission is shown in Figure 1.4. Upon photoexcitation a quantum dot forms an exciton, which can undergo radiative recombination. Before a second photon can be emitted the quantum dot must undergo a successive excitation and emission. In this way a colloidal quantum dot is a single photon source candidate similar to other atomic like systems^{71,73} including solid-state defects such as the nitrogen and silicon vacancy centers in diamond, hexagonal boron nitride,⁷⁴ two-dimensional transition metal dichalcogenides and single molecules.⁷⁵ Another possible single photon source are epitaxial quantum dots, which currently represent the ‘state of the art for single photon sources’.^{76,77} Unlike the previously mentioned defects or colloidal quantum dots, these materials are fabricated using molecular beam epitaxy methods, which creates issues with scalability, and consistency between emitters, despite near optimal performance for individual epitaxial quantum dots.⁷⁸ Single perovskite quantum dots are high pure single photon sources, even at room temperature, exhibiting second-order correlation functions close to 0, the value expected from a pure single photon source.^{79,80} The major advantage of colloidal materials for single photon sources is that they offer the prospect of truly scalable single photon sources via solution processability.⁸¹ Their solution processability is a unique advantage as it enables integration methods for deterministic positioning,^{82,83} like electrohydrodynamic ink-jet printing⁸⁴ which is scalable to larger number of emitters.

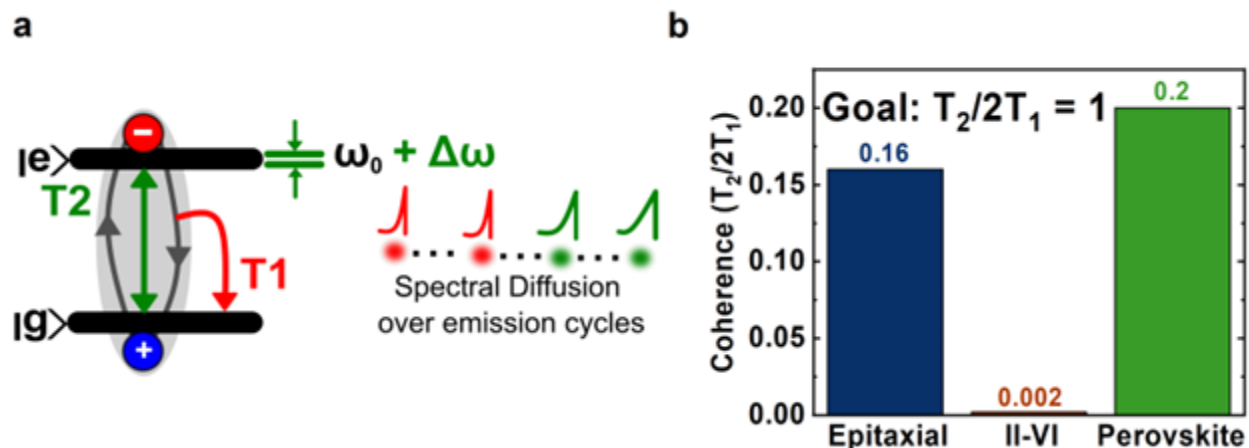


Figure 1.3 Comparison coherence for quantum dot light sources. **a)** schematic representation of relevant processes for determining coherence times. T_2 (green) is the dephasing time and T_1 (red) is the radiative lifetime. **b)** Comparison of reported coherence times for III-V epitaxial quantum dots,⁸⁵ II-VI core/shell CdSe quantum dots⁸⁶ and CsPbBr₃ perovskite quantum dots.⁸⁷

Recently, perovskite single photon sources have garnered a high level of interest relative to other colloidal materials due to their high coherence even in the absence of a nanophotonic cavity. To act as a source of quantum light a single photon source needs to be transform limited, meaning that these photons are quantum mechanically indistinguishable and can undergo entanglement. One way to quantify how close an emitter is to this limit is to compare the radiative lifetime of the emitter (T_1) to the dephasing time (T_2). In a transform limited system T_2 is equal to $2T_1$. Using Fourier-transform photon correlation spectroscopy, an interferometric technique, Utzat et al. measured the ratio of the coherence time to the radiative lifetime ($T_2/2T_1$), in CsPbBr₃ quantum dots and found ratios of 0.2.⁸⁷ Figure 1.4 compares this result to that of epitaxial quantum dots and II-VI quantum dots in the absence of an optical cavity. Remarkably, perovskite quantum dots show coherence times comparable to epitaxial quantum dots and two orders of magnitude greater than II-VI materials. Recent reports have even demonstrated the Hong-Ou-Mandel effect using CsPbBr₃ quantum dots.⁸⁸ Beyond these improved coherence times relative to other colloidal materials CsPbBr₃ quantum dots have also shown other desirable optical properties at low temperatures including reduced blinking⁸⁹ limited spectral wandering,⁸⁷ and fast radiative lifetimes (200 to 250ps).^{87,90} Amongst perovskite quantum dots the all inorganic CsPbBr₃ shows the most promise, as these materials have the narrowest linewidth due to reduced exciton-phonon coupling.⁹¹

Despite this promise, the optimization of perovskite surface chemistry for low temperature quantum applications is in a very early stage. An ideal single photon source will be scalable to large numbers of emitters, and provide indistinguishable photons.⁹² Even the highest quality perovskite quantum dots show evidence of photoluminescence blinking and spectral wandering.^{87,88} Comparatively, state of the art epitaxial quantum dots (which have undergone extensive optimization of fabrication and cavity design)⁷⁸ integrated into optical cavities show coherence of 0.93. Further studies are needed to improve the linewidth of perovskite quantum dots to match more established emitter systems.⁹³

There have been dramatic improvements in the deterministic positioning of colloidal quantum dots using patterning approaches and electrohydrodynamic ink jet printing methods, which can position quantum dots with 100nm precision.^{82–84} Further developments in dielectric and plasmonic cavity integration for colloidal materials have shown promise in improving the effect of cavities on the emission rate of colloidal materials (maximizing the Purcell Enhancement).⁸¹ Single particle line width also depends strongly on surface chemistry, particularly on the Pb/Br ratio at the surface.⁹⁴ Commonly CsPbBr₃ quantum dots show photoinstability and shrink in size upon dilution, which can result in increased photobleaching.^{94,95} In order to further improve the surface chemistry to minimize linewidths, photoluminescence blinking and material instability we need to gain further understanding of the link between specific ligand surface chemistry and single quantum dot properties.

The following section extensively describes the current understanding of spectral wandering and photoluminescence blinking, as minimizing these processes are of paramount in optimizing single perovskite quantum dots.

1.4 Quantum Dot Spectral Diffusion and Blinking

*Section (a) has been adapted from of “Hao A. Nguyen, Grant Dixon, Florence Y. Dou, **Shaun Gallagher**, Stephen Gibbs, Dylan M. Ladd, Emanuele Marino, Justin C. Ondry, James P. Shanahan, Eugenia S. Vasileiadou, Stephen Barlow, Daniel R. Gamelin, David S. Ginger, David M. Jonas, Mercouri G. Kanatzidis, Seth R. Marder, Daniel Morton, Christopher B. Murray, Jonathan S. Owen, Dmitri V. Talapin, Michael F. Toney, and Brandi M. Cossairt* Chem. Rev. 2023, 123, 12, 7890–7952. ⁶⁸ My contribution to this review article was writing the following included section on spectral diffusion and photoluminescence blinking.*

I. Spectral Diffusion: Overview

Measured over short times, the linewidths of some colloidal quantum dot emitters are already nearing the transform limit imposed by the radiative lifetime.⁹⁶ However, when measured over longer times, the emission peak position of almost all known quantum emitters drifts over time. This drift of the emission peak, known as *spectral diffusion*, can be an important contributor to the linewidth of colloidal emitters. Spectral diffusion is a ubiquitous phenomenon and is often easily observed at cryogenic temperatures where the various phonon broadening contributions from the emitter and its environment have been reduced. Indeed, spectral diffusion has been reported from single emitters in systems as diverse as diamond vacancies⁹⁷ epitaxially grown III-V quantum dots⁹⁸, single organic molecules, colloidal II-V quantum dots⁹⁹, and colloidal halide perovskite quantum dots⁹⁶. Within the subfield of colloidal materials, spectral diffusion has been reported in materials including nanorods¹⁰⁰ and nanoplatelets¹⁰¹ and dot-rod heterostructures¹⁰². In many of these systems, not only is the instantaneous emission energy changing with time, but the intensity (photoluminescence quantum yield) is as well. This intensity variation is known as fluorescence intermittency,¹⁰³ blinking,¹⁰⁴ or flickering,^{105,106} and is often coupled with spectral diffusion, as the non-radiative recombination rate and emission energy both fluctuate, sometimes due to related processes, as discussed below.

Given its ubiquity, spectral diffusion has been studied in systems such as II-VI colloidal quantum dots, and in III-V epitaxial quantum dots,^{107–109} and less well in newer materials systems like halide perovskite quantum dots.^{110,111} For single colloidal emitters, spectral diffusion

represents an important contribution to the total linewidth, especially at lower temperatures. Generally, spectral diffusion is less well studied than photoluminescence intermittency (i.e., blinking) in colloidal QDs, in part because of the drive to use colloidal QDs as fluorescent biological labels for single particle tracking. However, as interest develops in employing colloidal emitters in quantum information science, including their use as single photon sources and spin-qubits¹¹⁰, it is important to understand and minimize spectral diffusion, so that emitters may approach transform-limited linewidths needed for use as sources of coherent quantum light.

II. Causes of Spectral Diffusion Behavior in colloidal materials

One reason spectral diffusion is so common is that both the environment, and the emitter are fluctuating. Rearrangements of local bond geometries, dipole moments and, notably, charges all perturb the potential energy landscape of both the ground and excited states of a quantum emitter, leading to spectral shifts across many different timescales.^{112–114} While some of these rearrangements can be frozen out at low temperature,^{115–118} others are induced by the photoexcitation itself,¹¹⁹ and need to be understood and suppressed with different strategies.

Perhaps one of the most important sources of spectral diffusion and fluorescence intermittency (or blinking) in colloidal quantum dots is due to the photoinduced charge redistribution in the quantum dot, its surface, and the surrounding environment. Known from the epitaxial semiconductor quantum well literature,¹²⁰ Bawendi and co-workers explored this phenomenon in CdSe quantum dots,⁹ and explained spectral diffusion in terms of a Quantum Confined Stark Effect (QCSE). Importantly, they demonstrated, first, that applied electric fields could shift the photoluminescence of single CdSe emitters and, second, that the largest spectral jumps often accompany blinking-off and blinking-on events.¹¹ This correlation between blinking events and spectral diffusion is highly suggestive, since dark states are widely attributed to photoionization events,^{121–123} with the residual charge leading to a dark (non-emissive) dot via efficient Auger process.^{121–124} Further evidence in support of this mechanism was provided by direct confirmation of dot photoionization via electrostatic force microscopy,¹²⁵ and also by the observation that dots with wide-gap shells that prevent photoionization also tend to suppress blinking^{126–129} and reduce spectral diffusion.
130–132

Furthermore, in colloidal systems including CdSe, CdSe/ZnS, and CsPbBr₃, studies report that exciting a quantum dot far above the bandgap leads to increased spectral diffusion and blinking, presumably because the excess energy increases the chance of photoionization.^{119,133–135}

Within a photoionization model, we expect the surface of the dot to play a critical role. Not only is the surface (or a strained core/shell interface) a likely source of charge trapping, but the ligands themselves can play a role in charge localization. For instance, adsorption of a single quantum dot surface ligand can result in near complete quenching of a quantum dot fluorescence,¹³⁶ and we speculate that rearrangements in the organic ligand shell could be important. Indeed, Braam et al. used a simple model based on the Stark effect to calculate that the rearranging charges responsible for spectral diffusion reside either directly on the dot surface or in its ligand shell.¹³⁷ Using Photon Correlation Fourier Spectroscopy (PCFS) Beyler and co-workers were able to probe spectral diffusion dynamics across microsecond timescales inaccessible to grating spectroscopy. They observed variations in spectral diffusion rate and magnitude, which they rationalized as ligand rearrangement perturbing trapped carriers within the quantum dot.¹¹⁴ Other studies report that the magnitude of spectral diffusion is independent of polymer matrix, again suggesting that the quantum dot and its surface are essential variables.¹³⁸ Many other reports have implicated

surface chemistry in spectral diffusion. Early work by Empedocoles and co-workers compared organic-ligand-coated CdSe quantum dots with CdSe overcoated with ZnS.¹¹⁹ They reported that quantum dots coated only with organic ligands exhibited larger spectral shifts, confirming the importance of surface states in spectral diffusion. Trapped surface charges have also been reported to modulate the strength of the exciton-phonon coupling via the Fröhlich interaction, which emphasizes the importance on controlling surface chemistry in order to minimize the homogeneous linewidth both a short (sub-ns) times, as well as the longer times over which spectral diffusion is most important.¹³⁹

Finally, multi-exciton and Auger physics also play a role spectral diffusion in colloidal quantum dots. Although the exact threshold is system dependent, high intensity illumination, on the order of $\sim 20 \mu\text{J}/\text{cm}^2$ for single CdSe/ZnS quantum dots¹⁴⁰ (as often occurs in confocal systems trying to achieve high signal levels) can excite biexciton states, which, in addition to opening high-efficiency Auger decay pathways leading to charged dots,^{135,141} can also have spectrally distinct emission features.^{142,143} As a result quantum dots excited at higher excitation *intensities* also tend to exhibit more spectral diffusion and blinking^{133, 119}, as well as more complex spectral line shapes associated with the radiative decay of species such as biexcitons and trions.^{99,144,145}

III. Prospects for reducing diffusion and blinking

In some ways, the importance of charge fluctuations in controlling colloidal quantum dot spectral diffusion parallels the understanding of the importance of surface state charge fluctuations in the context of diamond vacancy emission, and suggests that improved understanding of interface and surface passivation in these materials could yield significant improvements in spectral diffusion, for instance through selection of materials systems – quantum dot emitters, shelling strategies, and host matrices – that help minimize spectral diffusion. For nitrogen vacancy centers great progress was made in reducing lifetime variation¹⁴⁶, spectral diffusion and fluorescence intermittency¹⁴⁷ in near-surface defects, improving the quality of shallow, implanted defect centers relative to naturally occurring vacancies by optimizing fabrication and implementation conditions.¹⁴⁸ For example, pulsed Optically Detected Magnetic Resonance (ODMR) measurements, which allow for estimation of NV center linewidth, the as fabricated NV centers demonstrated improved linewidths compared to previously reported values for defect centers.¹⁴⁹

In contrast, while much is known for colloidal materials, there is still much that is unknown. It remains an open question for instance, if the high dielectric constant of halide perovskites¹⁵⁰ and large polaron physics¹⁵¹ might contribute to making them more resistant to local environmental charge fluctuations (at least on slower timescales), or if shelling strategies reaching atomic precision with sufficient thickness can eliminate coupling to surface defects entirely, thereby suppressing the largest sources of spectral diffusion.

(A) Surface /Interface control for reducing blinking and spectral diffusion

As previously mentioned, growing wide-bandgap inorganic shells over colloidal quantum dots has been a subject of intense study, and is known to help suppress blinking, and, to a less-studied extent, spectral diffusion as well.¹²³ In early work, ZnS shells minimized spectral diffusion for CdSe, though large dot-dot variations in the effectiveness of this approach suggested that early shelling strategies yielded incomplete shell coverage or led to the incorporation of defects at the CdSe/ZnS interface.¹¹⁹ Later synthetic work improved the quality of core-shell interfaces by optimizing shell thickness and composition, resulting in quantum dots displaying suppressed

blinking, with 68% of quantum dots remaining bright for measurement times of 5 minutes with minimal blinking.¹²² Interestingly, the authors found that the non-blinking fraction depended strongly on the number of shell monolayers, highlighting the importance of optimizing thicker shells for achieving non-blinking quantum dots. Further improvements in ensemble Photoluminescence Quantum Yield (PLQY) and reductions in dot-to-dot inhomogeneity were achieved by optimizing the synthesis of Giant-Shells (>10 shell monolayers)¹²⁶, in this case the percentage of non-blinking quantum dots depends on both core diameter and the number of shell monolayers (Figure 3(b)).¹²⁶ In later work Ghosh et al. reported that the fraction of non-blinking Giant shells CdSe/ZnS dots synthesized via Successive Ionic Layer Adsorption and Reaction (SILAR) could be as high as 85% during 60 minutes of continuous observation.¹²⁷ Similar work in III-IV InP quantum dots corroborated the importance of the core-shell interfaces in those materials. Lee et al. investigated varying interface compositions of core-shell-shell InP/ZnSeS/ZnS dots, and attributed reduced blinking and spectral diffusion to strain reduction with gradient shells: a midshell composition of Se₇₅S₂₅ led to minimization of defects at the interface through reduced lattice strain, resulting in a decrease in overall PL linewidth (Figure 4(a)) compared to other gradient midshell compositions¹³²

(B) Cavity Control

Another promising, though less studied, strategy for mitigating spectral diffusion is the use of optical cavities or nanoscale plasmonic antenna to modulate the emissive properties of colloidal quantum dots. For a quantum emitter weakly coupled to a photonic cavity or antenna structure, the radiative decay rate is given by Fermi's Golden Rule:

(1)

$$\Gamma_{i \rightarrow f} = 2\pi\hbar \langle f | H' | i \rangle^2 \rho(E) \quad \Gamma_{i \rightarrow f} = 2\pi\hbar \langle f | H' | i \rangle^2 \rho(E)$$

Here, the intrinsic radiative decay rate,

$$\Gamma_{i \rightarrow f} \Gamma_{i \rightarrow f}$$

, is given by the transition matrix elements

$$\langle yf | H' | yi \rangle^2 \langle yf | H' | yi \rangle^2$$

where yi and yf represent the wavefunctions of the initial and final states (this same relationship determines the absorption coefficient). Importantly, the density of states term contains a contribution from the local photonic mode density (or local density of optical states LDOS $\rho(E)$),¹⁵² which quantifies the density of electromagnetic modes available at that point in space. Classic cavity structures like microcavities,¹⁵² waveguides,¹⁵³ and metasurfaces,¹⁵⁴ and plasmonic structures like metal nanoparticles,^{155–158} can all modify the local photonic mode density, enhancing (or suppressing) the radiative decay rate of an emitter.¹⁵⁹ Cavity coupling is frequently used with quantum emitters because enhancing the radiative decay rate, (reducing the population lifetime (T_1)) is advantageous when seeking to obtain a transform-limited linewidth. However, *we note that cavity coupling can also help reduce spectral diffusion and fluorescence blinking*: by increasing the radiative decay rate, light emission can more easily outcompete non-radiative processes such as photoionization events that contribute to spectral diffusion and blinking. Indeed, cavity integration has been shown to reduce spectral diffusion in epitaxial QDs, likely through radiative rate enhancement.^{158,160,161} The effects of cavity coupling the spectral diffusion of

colloidal emitters has been less well studied; however, Huang et al. reported that cavity integration suppressed spectral diffusion and reduced emitter linewidth for temperatures of up to 40K for perovskite nanoplatelets coupled to a quasi-2D cavity (Figure 4(b)).¹⁶² While there are fairly few studies of spectral diffusion of colloidal dots in cavities, we can infer the positive effects might be more general by examining the larger literature on the effect of cavity integration on the related problem of blinking statistics of colloidal emitters. For example, Novotny and co-workers found that a quantum dot emitter coupled to a plasmonic cavity emitter shows a slowed on to off state transition, resulting in a reduction in photoluminescence blinking relative to uncoupled quantum dots,¹⁵⁸. Similar results were demonstrated by Yuan et al., who coupled a CdSe/Cd_xZn_{1-x}S gradient shell quantum dot to a metallic mirror and observed 3.6-fold enhancement of the radiative lifetime as well as a reduction in the photoionization rate.¹⁶³ Given the rapid advances that have been made in nanophotonics, metasurfaces, and cavity integration, we speculate that working to maximize radiative rate enhancement could be fertile ground to explore in the quest to reduce spectral diffusion and blinking in colloidal materials. For instance, improvements in radiative rates by maximizing the Purcell Factor can be realized through novel cavity designs for colloidal materials integration¹⁶⁴ and by development of methods for nanoscale positioning and integration of solution-processable emitters.^{165,166}

(C) External Tuning

Finally, beyond surface chemistry and the integration of colloidal materials with nanophotonic cavities to control the environment, we propose it may also prove useful to develop mechanisms to tune emitters, which could conceivably be used to actively cancel residual spectral diffusion at longer timescales. As one possible strategy, one could use the Quantum Confined Stark Effect (QCSE) via an external applied electric field to tune the emitter to the cavity mode. Along these lines, Thomas et al. demonstrated that spectral diffusion can naturally bring an emitter into cavity resonance and thereby exhibit strong emitter/cavity coupling, an important proof of concept for applying external electric field to tune an emitter into cavity resonance.¹⁶⁷ It is possible that other effects could be used to tune the emission energy rapidly and dynamically, for example strain tuning of the emitter resonance, which was shown to shift the bandgap of a single perovskite Quantum Dot coupled to a gap-plasmon cavity.¹⁶⁸ In general, while active tuning approaches have not received significant attention for colloidal materials to date, we predict they will be of increasing interest as technologies for synthesizing high quality quantum dots and integrating them into cavity structures become more mature.

Overall, while spectral diffusion contributes to the broadening of spectral lines in a wide range of colloidal materials, we believe the field has not yet reached the ultimate limit of suppressing diffusion, and there exist both intrinsic chemical strategies, such as control over surface chemistry, as well as technological strategies, such as the use of cavities structures or active feedback to mitigate spectral diffusion in specific applications.

1.5 Single Quantum Dot Microscopy

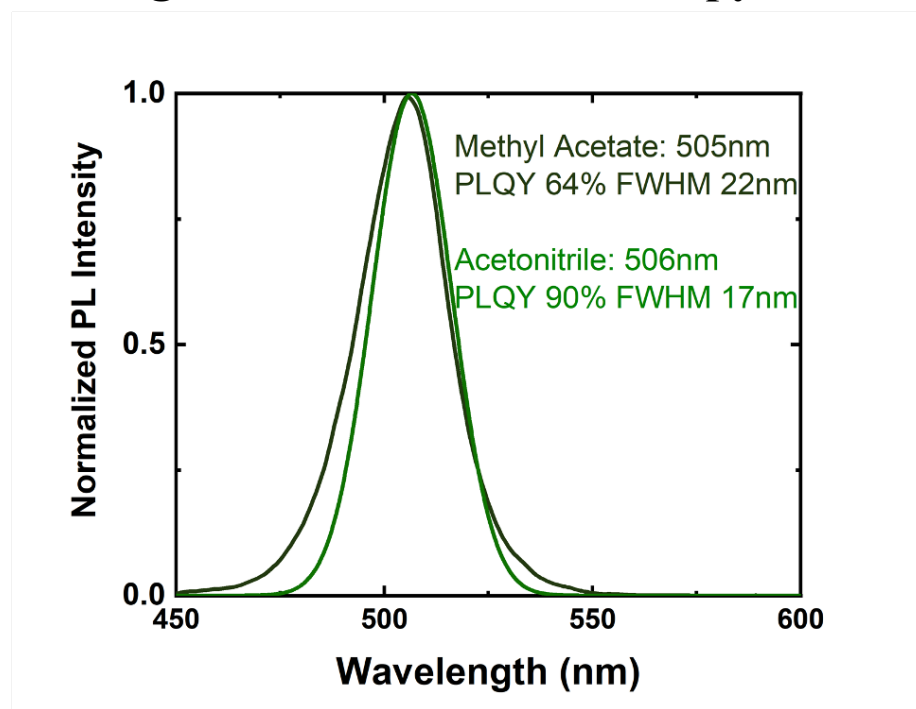


Figure 1.4 Comparing effects of antisolvent wash on CsPbBr₃ photoluminescence. Taken from unpublished data.

Single quantum dot spectroscopy typically employs a confocal microscope¹⁶⁹ to probe the optical properties of individual colloidal quantum dots in series. Samples for single particle microscopy are typically prepared by systematic dilution and spin-coating or drop-casting onto a substrate to achieve a sparsely packed quantum dot sample (typical dilutions >10,000-fold, ideal density <1 QD per micron).¹⁷⁰

One illustrative example regarding the benefits of single particle microscopy is shown in Figure 1.3(a) comparing two sets of quantum dots purified by the addition of two different antisolvent washes. The quantum dots purified by methyl acetate show a PLQY of 64% as compared to quantum dots purified by ethyl acetate, which show a PLQY of 90% and a FWHM of 17nm. When aiming to rationalize these data there are two extreme cases: first, that only 64% of methyl acetate quantum dots are emissive, the remaining 36% being dark in photoluminescence or second that all quantum dots emit light 64% of the time. In reality the true distribution lies between these two extremes. Improving the photophysical properties of these materials benefits from an improved understanding of single particle properties, such as linewidth, single photon purity.

Figure 1.4 shows a schematic of a confocal microscope built in the Ginger Lab. The microscope is integrated into an Attodry800 Microscope optical cryostat, with an LT APO cryogenic objective. This microscope operates with piezostage scanning, which allows for sample movements with nm precision at room temperature and cryogenic temperatures. Optical signals can be routed to time correlated single photon counting hardware (Swabian TimeTagger), which can be used to localize bright single quantum dots by correlating avalanche photodiode

(APD) intensity to piezostage positions during a scan. Two APD detectors are mounted in a Hanbury-Brown-Twiss configuration, which can perform single photon purity measurements by measuring the second order correlation function, as well as measure time dependent changes in quantum dot emission (i.e. blinking.) Finally, an imaging spectrograph (Isoplan320 and Pixis400) enables single quantum dot spectroscopy, to investigate single particle linewidth.

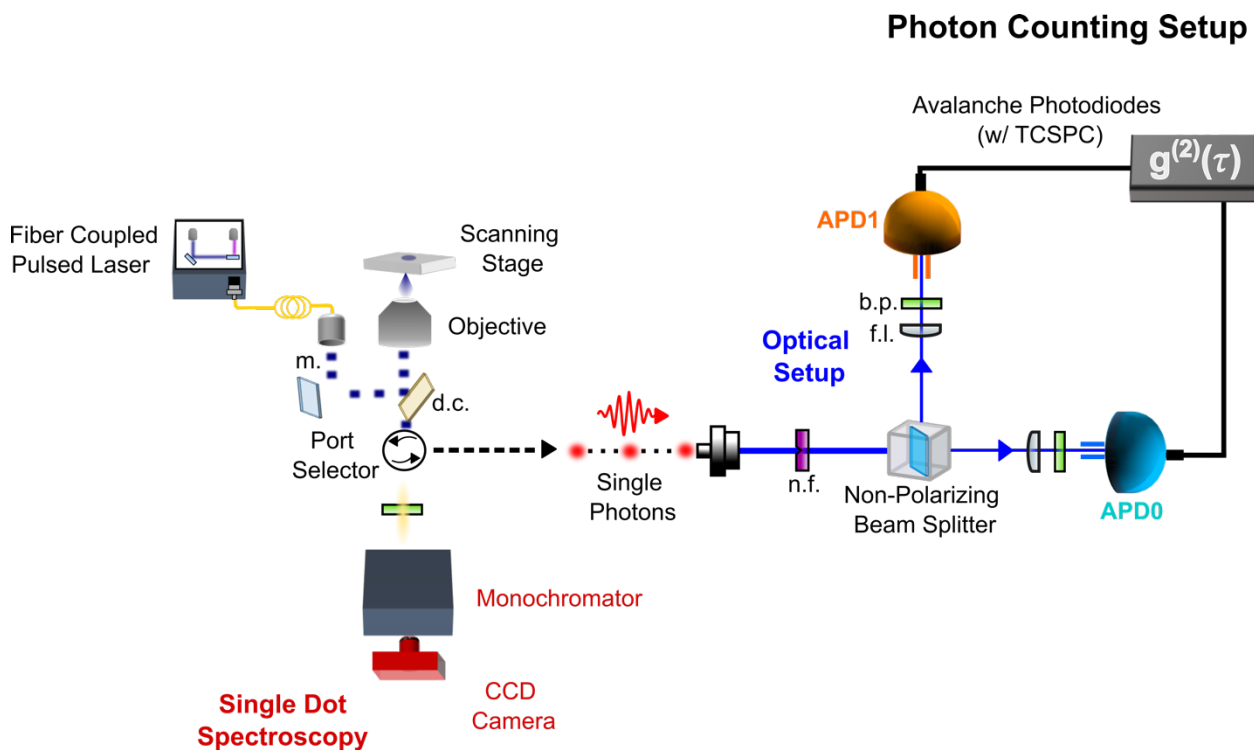


Figure 1.5 Schematic of confocal microscope for single quantum dot characterization.

1.6 Summary

This thesis aims to connect surface chemistry (ligand binding equilibrium and ligand head group) to single particle properties. By showing that strongly binding zwitterionic ligands reduce photoluminescence blinking (Chapters 3 and 4 respectively) we can guide the design of organic ligands to improve the properties of single perovskite quantum dots.

Chapter 2 discusses a collaborative project examining plasmon-exciton coupling in two-dimensional perovskite materials. By interfacing single silver nanoprisms with a polycrystalline thin film of butylammonium lead iodide we show strong coupling of the perovskite exciton to the silver nanoprism. We next investigate the effect of perovskite grain structure on the observed

scattering spectrum, finding that a Fano interference from scattering of perovskite grains contributes to the asymmetric line shape in the scattering spectrum.

Chapter 3 discusses the impact of ligand binding equilibrium on photoluminescence blinking in perovskite quantum dots. By comparing oleic acid and oleylamine capped quantum dots to those capped by lecithin, a bidentate zwitterionic ligand, we find that lecithin shows 7.5 times greater non-blinking behavior. We compare many quantum dots using widefield fluorescence microscopy, coupled with change point analysis. By incorporating concentration dependent experiments and density functional theory calculations we relate the observed disparity in blinking statistics to ligand binding energy. More strongly binding ligands like lecithin should be preferred for blinking reduction.

Chapter 4 is a publication draft investigating the effects of quantum dot ligand exchange on single particle properties. We compare the properties of zwitterionic ligands (lecithin and PEA-C₈C₁₂) to cationic ligands (dodecyl ammonium bromide, and a bidentate diquaternary ammonium ligand). We find that despite similar ensemble properties the quantum dots capped by zwitterionic ligands show narrower linewidth and reduced photoluminescence blinking.

References:

- (1) Owen, J.; Brus, L. Chemical Synthesis and Luminescence Applications of Colloidal Semiconductor Quantum Dots. *J Am Chem Soc* **2017**, *139* (32), 10939–10943. <https://doi.org/10.1021/jacs.7b05267>.
- (2) Calvin, J. J.; Brewer, A. S.; Alivisatos, A. P. The Role of Organic Ligand Shell Structures in Colloidal Nanocrystal Synthesis. *Nature Synthesis* **2022**, *1* (2), 127–137. <https://doi.org/10.1038/s44160-022-00025-4>.
- (3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites*; 1993; Vol. 115. <https://pubs.acs.org/sharingguidelines>.
- (4) Sacra, A.; Morris, D. J.; Murray, C. B.; Bawendi, M. G. Stark Spectroscopy of CdSe Nanocrystallites: The Significance of Transition Linewidths. *J Chem Phys* **1995**, *103* (13), 5236–5245. <https://doi.org/10.1063/1.470559>.
- (5) Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulović, V. Emergence of Colloidal Quantum-Dot Light-Emitting Technologies. *Nat Photonics* **2013**, *7* (1), 13–23. <https://doi.org/10.1038/nphoton.2012.328>.
- (6) Park, Y. S.; Roh, J.; Diroll, B. T.; Schaller, R. D.; Klimov, V. I. Colloidal Quantum Dot Lasers. *Nature Reviews Materials*. Nature Research May 1, 2021, pp 382–401. <https://doi.org/10.1038/s41578-020-00274-9>.

- (7) Kairdolf, B. A.; Smith, A. M.; Stokes, T. H.; Wang, M. D.; Young, A. N.; Nie, S. Semiconductor Quantum Dots for Bioimaging and Biodiagnostic Applications. *Annual Review of Analytical Chemistry* **2013**, 6, 143–162. <https://doi.org/10.1146/annurev-anchem-060908-155136>.
- (8) Talapin, D. V.; Lee, J. S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem Rev* **2010**, 110 (1), 389–458. <https://doi.org/10.1021/cr900137k>.
- (9) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility*; 1997. <https://pubs.acs.org/sharingguidelines>.
- (10) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, J. K. F.; Bawendi, M. G. *(CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites*; 1997. <https://pubs.acs.org/sharingguidelines>.
- (11) Ghosh, Y.; Mangum, B. D.; Casson, J. L.; Williams, D. J.; Htoon, H.; Hollingsworth, J. A. New Insights into the Complexities of Shell Growth and the Strong Influence of Particle Volume in Nonblinking “Giant” Core/Shell Nanocrystal Quantum Dots. *J Am Chem Soc* **2012**, 134 (23), 9634–9643. <https://doi.org/10.1021/ja212032q>.
- (12) Pal, B. N.; Ghosh, Y.; Brovelli, S.; Laocharoensuk, R.; Klimov, V. I.; Hollingsworth, J. A.; Htoon, H. “Giant” CdSe/CdS Core/Shell Nanocrystal Quantum Dots as Efficient Electroluminescent Materials: Strong Influence of Shell Thickness on Light-Emitting Diode Performance. *Nano Lett* **2012**, 12 (1), 331–336. <https://doi.org/10.1021/nl203620f>.
- (13) Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. “Giant” Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J Am Chem Soc* **2008**, 130 (15), 5026–5027. <https://doi.org/10.1021/ja711379k>.
- (14) Efros, A. L.; Nesbitt, D. J. Origin and Control of Blinking in Quantum Dots. *Nat Nanotechnol* **2016**, 11 (8), 661–671. <https://doi.org/10.1038/nnano.2016.140>.
- (15) Mahler, B.; Spinicelli, P.; Buil, S.; Quelin, X.; Hermier, J. P.; Dubertret, B. Towards Non-Blinking Colloidal Quantum Dots. *Nat Mater* **2008**, 7 (8), 659–664. <https://doi.org/10.1038/nmat2222>.
- (16) Manna, L. The Bright and Enlightening Science of Quantum Dots. *Nano Letters*. American Chemical Society November 8, 2023, pp 9673–9676. <https://doi.org/10.1021/acs.nanolett.3c03904>.
- (17) Akkerman, Q. A.; Manna, L. What Defines a Halide Perovskite? *ACS Energy Letters*. American Chemical Society February 14, 2020, pp 604–610. <https://doi.org/10.1021/acsenenergylett.0c00039>.

- (18) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
- (19) Swarnkar, A.; Chulliyil, R.; Ravi, V. K.; Irfanullah, M.; Chowdhury, A.; Nag, A. Colloidal CsPbBr_3 Perovskite Nanocrystals: Luminescence beyond Traditional Quantum Dots. *Angewandte Chemie - International Edition* **2015**, *54* (51), 15424–15428. <https://doi.org/10.1002/anie.201508276>.
- (20) De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, *10* (2), 2071–2081. <https://doi.org/10.1021/acsnano.5b06295>.
- (21) Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P. Essentially Trap-Free CsPbBr_3 Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J Am Chem Soc* **2017**, *139* (19), 6566–6569. <https://doi.org/10.1021/jacs.7b02817>.
- (22) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat Mater* **2018**, *17*, 394–405. <https://doi.org/10.1038/s41563-018-0018-4>.
- (23) Huang, H.; Bodnarchuk, M. I.; Kershaw, S. V.; Kovalenko, M. V.; Rogach, A. L. Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance. *ACS Energy Lett* **2017**, *2* (9), 2071–2083. <https://doi.org/10.1021/acsenergylett.7b00547>.
- (24) Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X. G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C. J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Mora-Seró, I.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Pérez-Prieto, J.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roeffaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Müller-Buschbaum, P.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15*, 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>.
- (25) Katan, C.; Mercier, N.; Even, J. Quantum and Dielectric Confinement Effects in Lower-Dimensional Hybrid Perovskite Semiconductors. *Chem Rev* **2019**, *acs.chemrev.8b00417*. <https://doi.org/10.1021/acs.chemrev.8b00417>.

- (26) Fiuza-Maneiro, N.; Sun, K.; López-Fernández, I.; Gómez-Graña, S.; Müller-Buschbaum, P.; Polavarapu, L. Ligand Chemistry of Inorganic Lead Halide Perovskite Nanocrystals. *ACS Energy Lett* **2023**, 1152–1191. <https://doi.org/10.1021/acsenenergylett.2c02363>.
- (27) Kang, J.; Wang, L. W. High Defect Tolerance in Lead Halide Perovskite CsPbBr₃. *Journal of Physical Chemistry Letters* **2017**, 8 (2), 489–493. <https://doi.org/10.1021/acs.jpcclett.6b02800>.
- (28) Han, T. H.; Jang, K. Y.; Dong, Y.; Friend, R. H.; Sargent, E. H.; Lee, T. W. A Roadmap for the Commercialization of Perovskite Light Emitters. *Nat Rev Mater* **2022**, 7 (10), 757–777. <https://doi.org/10.1038/s41578-022-00459-4>.
- (29) Vickers, E. T.; Graham, T. A.; Chowdhury, A. H.; Bahrami, B.; Dreskin, B. W.; Lindley, S.; Naghadeh, S. B.; Qiao, Q.; Zhang, J. Z. Improving Charge Carrier Delocalization in Perovskite Quantum Dots by Surface Passivation with Conductive Aromatic Ligands. *ACS Energy Lett* **2018**, 3 (12), 2931–2939. <https://doi.org/10.1021/acsenenergylett.8b01754>.
- (30) Dong, Y.; Wang, Y.; Yuan, F.; Johnston, A.; Liu, Y.; Ma, D.; Choi, M.; Chen, B.; Chekini, M.; Baek, S.; Sagar, L. K.; Fan, J.; Hou, Y.; Wu, M.; Lee, S.; Sun, B.; Hoogland, S.; Quintero-bermudez, R.; Ebe, H.; Todorovic, P.; Dinic, F.; Li, P.; Kung, H. T.; Saidaminov, M. I.; Kumacheva, E.; Spiecker, E.; Liao, L.; Voznyy, O.; Lu, Z.; Sargent, E. H. Bipolar-Shell Resurfacing Enables Blue LEDs Based on Strongly Confined Perovskite Quantum Dots. *Nat Nanotechnol* **2020**, 1–7. <https://doi.org/10.1038/s41565-020-0714-5>.
- (31) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Advanced Materials* **2017**, 29 (5). <https://doi.org/10.1002/adma.201603885>.
- (32) Hassan, Y.; Park, J. H.; Crawford, M. L.; Sadhanala, A.; Lee, J.; Sadighian, J. C.; Mosconi, E.; Shivanna, R.; Radicchi, E.; Jeong, M.; Yang, C.; Choi, H.; Park, S. H.; Song, M. H.; De Angelis, F.; Wong, C. Y.; Friend, R. H.; Lee, B. R.; Snaith, H. J. Ligand-Engineered Bandgap Stability in Mixed-Halide Perovskite LEDs. *Nature* **2021**, 591 (7848), 72–77. <https://doi.org/10.1038/s41586-021-03217-8>.
- (33) Shamsi, J.; Urban, A. S.; Imran, M.; Trizio, L. De; Manna, L. Metal Halide Perovskite Nanocrystals : Synthesis , Post-Synthesis Modi Fi Cations , and Their Optical Properties. *Chem Rev* **2018**. <https://doi.org/10.1021/acs.chemrev.8b00644>.
- (34) Guggisberg, D.; Yakunin, S.; Neff, C.; Aebli, M.; Günther, D.; Kovalenko, M. V.; Dirin, D. N. Colloidal CsPbX₃ Nanocrystals with Thin Metal Oxide Gel Coatings. *Chemistry of Materials* **2023**. <https://doi.org/10.1021/acs.chemmater.2c03562>.
- (35) Chen, K.; Liu, D.; Lu, W.; Zhuo, K.; Li, G. Surface and Interface Engineering for Highly Stable CsPbBr₃/ZnS Core/Shell Nanocrystals. *Inorg Chem* **2024**, 63 (4), 2247–2256. <https://doi.org/10.1021/acs.inorgchem.3c04210>.

- (36) Patra, A.; Jagadish, K.; Ravishankar, N.; Pradhan, N. Epitaxial Heterostructures of CsPbBr₃ Perovskite Nanocrystals with Post-Transition Metal Bismuth. *Nano Lett* **2024**, 24 (5), 1710–1716. <https://doi.org/10.1021/acs.nanolett.3c04513>.
- (37) De Roo, J. The Surface Chemistry of Colloidal Nanocrystals Capped by Organic Ligands. *Chemistry of Materials* **2023**. <https://doi.org/10.1021/acs.chemmater.3c00638>.
- (38) Peterson, M. D.; Cass, L. C.; Harris, R. D.; Edme, K.; Sung, K.; Weiss, E. A. The Role of Ligands in Determining the Exciton Relaxation Dynamics in Semiconductor Quantum Dots. *Annu Rev Phys Chem* **2014**, 65, 317–339. <https://doi.org/10.1146/annurev-physchem-040513-103649>.
- (39) Owen, J. The Coordination Chemistry of Nanocrystal Surfaces. *Science (1979)* **2015**, 347 (6222), 615–616. <https://doi.org/10.1126/science.1259924>.
- (40) Sadighian, J. C.; Wong, C. Y. Just Scratching the Surface: In Situ and Surface-Specific Characterization of Perovskite Nanocrystal Growth. *Journal of Physical Chemistry C* **2021**, 125 (38), 20772–20782. <https://doi.org/10.1021/acs.jpcc.1c06582>.
- (41) Kirakosyan, A.; Chinh, N. D.; Sihn, M. R.; Jeon, M. G.; Jeong, J. R.; Kim, D.; Jang, J. H.; Choi, J. Mechanistic Insight into Surface Defect Control in Perovskite Nanocrystals: Ligands Terminate the Valence Transition from Pb²⁺ to Metallic Pb⁰. *Journal of Physical Chemistry Letters* **2019**, 10 (15), 4222–4228. <https://doi.org/10.1021/acs.jpcllett.9b01587>.
- (42) Akkerman, Q. A.; Nguyen, T. P. T.; Boehme, S. C.; Montanarella, F.; Dirin, D. N.; Wechsler, P.; Beiglböck, F.; Rainò, G.; Erni, R.; Katan, C.; Even, J.; Kovalenko, M. V. Controlling the Nucleation and Growth Kinetics of Lead Halide Perovskite Quantum Dots. *Science (1979)* **2022**, 377 (6613), 1406–1412. <https://doi.org/10.1126/science.abq3616>.
- (43) Bodnarchuk, M. I.; Boehme, S. C.; Ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; Infante, I. Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Lett* **2019**, 4 (1), 63–74. <https://doi.org/10.1021/acsenenergylett.8b01669>.
- (44) Garai, A.; Behera, R. K.; Pradhan, N. Facet Chemistry and the Impact of Surface Ligands on the Photoluminescence of Different Polyhedral-Shaped CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry C* **2022**, 126 (39), 16759–16766. <https://doi.org/10.1021/acs.jpcc.2c05781>.
- (45) Pradhan, N. Why Do Perovskite Nanocrystals Form Nanocubes and How Can Their Facets Be Tuned? A Perspective from Synthetic Prospects. *ACS Energy Letters*. American Chemical Society January 8, 2021, pp 92–99. <https://doi.org/10.1021/acsenenergylett.0c02099>.

- (46) Li, J.; Gan, L.; Fang, Z.; He, H.; Ye, Z. Bright Tail States in Blue-Emitting Ultrasmall Perovskite Quantum Dots. *Journal of Physical Chemistry Letters* **2017**, 8 (24), 6002–6008. <https://doi.org/10.1021/acs.jpcllett.7b02786>.
- (47) De Trizio, L.; Infante, I.; Manna, L. Surface Chemistry of Lead Halide Perovskite Colloidal Nanocrystals. *Acc Chem Res* **2023**, 51, 1815–1825. <https://doi.org/10.1021/acs.accounts.3c00174>.
- (48) Ravi, V. K.; Santra, P. K.; Joshi, N.; Chugh, J.; Singh, S. K.; Rensmo, H.; Ghosh, P.; Nag, A. Origin of the Substitution Mechanism for the Binding of Organic Ligands on the Surface of CsPbBr₃ Perovskite Nanocubes. *Journal of Physical Chemistry Letters* **2017**, 8 (20), 4988–4994. <https://doi.org/10.1021/acs.jpcllett.7b02192>.
- (49) Zhang, Y.; Siegler, T. D.; Thomas, C. J.; Abney, M. K.; Shah, T.; De Gorostiza, A.; Greene, R. M.; Korgel, B. A. A “Tips and Tricks” Practical Guide to the Synthesis of Metal Halide Perovskite Nanocrystals. *Chemistry of Materials* **2020**, 32 (13), 5410–5423. <https://doi.org/10.1021/acs.chemmater.0c01735>.
- (50) Almeida, G.; Goldoni, L.; Akkerman, Q.; Dang, Z.; Khan, A. H.; Marras, S.; Moreels, I.; Manna, L. Role of Acid-Base Equilibria in the Size, Shape, and Phase Control of Cesium Lead Bromide Nanocrystals. *ACS Nano* **2018**, 12 (2), 1704–1711. <https://doi.org/10.1021/acs.nano.7b08357>.
- (51) Pan, A.; He, B.; Fan, X.; Liu, Z.; Urban, J. J.; Alivisatos, A. P.; He, L.; Liu, Y. Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr₃ Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors. *ACS Nano* **2016**, 10 (8), 7943–7954. <https://doi.org/10.1021/acs.nano.6b03863>.
- (52) Zhang, J. Z.; Geselbracht, M. J.; Ellis, A. B. *Binding of Fullerenes to Cadmium Sulfide and Cadmium Selenide Surfaces, Photoluminescence as a Probe of Strong, Lewis Acidity-Driven, Surface Adduct Formation*; 1993; Vol. 115. <https://pubs.acs.org/sharingguidelines>.
- (53) Munro, A. M.; Ginger, D. S. Photoluminescence Quenching of Single CdSe Nanocrystals by Ligand Adsorption. *Nano Lett* **2008**, 8 (8), 2585–2590. <https://doi.org/10.1021/nl801132t>.
- (54) Munro, A. M.; Plante, I. J. La; Ng, M. S.; Ginger, D. S. Quantitative Study of the Effects of Surface Ligand Concentration on CdSe Nanocrystal Photoluminescence. *Journal of Physical Chemistry C* **2007**, 111 (17), 6220–6227. <https://doi.org/10.1021/jp068733e>.
- (55) Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; Ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C. J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Lett* **2018**, 3 (3), 641–646. <https://doi.org/10.1021/acsenenergylett.8b00035>.

- (56) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *J Am Chem Soc* **2019**, *141* (50), 19839–19849. <https://doi.org/10.1021/jacs.9b09969>.
- (57) Manoli, A.; Papagiorgis, P.; Sergides, M.; Bernasconi, C.; Athanasiou, M.; Pozov, S.; Choulis, S. A.; Bodnarchuk, M. I.; Kovalenko, M. V.; Othonos, A.; Itskos, G. Surface Functionalization of CsPbBr₃ Nanocrystals for Photonic Applications. *ACS Appl Nano Mater* **2021**, *4* (5), 5084–5097. <https://doi.org/10.1021/acsanm.1c00558>.
- (58) Papagiorgis, P.; Sergides, M.; Manoli, A.; Athanasiou, M.; Bernasconi, C.; Galatopoulos, F.; Ioakeimidis, A.; Nicolaides, C.; Leontidis, E.; Trypiniotis, T.; Choulis, S.; Bodnarchuk, M. I.; Kovalenko, M. V.; Othonos, A.; Itskos, G. The Impact of Ligand Removal on the Optoelectronic Properties of Inorganic and Hybrid Lead Halide Perovskite Nanocrystal Films. *Adv Opt Mater* **2024**, *12* (3). <https://doi.org/10.1002/adom.202301501>.
- (59) Shen, Y.; Tan, R.; Gee, M. Y.; Greytak, A. B. Quantum Yield Regeneration: Influence of Neutral Ligand Binding on Photophysical Properties in Colloidal Core/Shell Quantum Dots. *ACS Nano* **2015**, *9* (3), 3345–3359. <https://doi.org/10.1021/acs.nano.5b00671>.
- (60) Greytak, A. B.; Abiodun, S. L.; Burrell, J. M.; Cook, E. N.; Jayaweera, N. P.; Islam, M. M.; Shaker, A. E. Thermodynamics of Nanocrystal-Ligand Binding through Isothermal Titration Calorimetry. *Chemical Communications* **2022**, *58* (94), 13037–13058. <https://doi.org/10.1039/d2cc05012a>.
- (61) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *J Am Chem Soc* **2019**, *141* (50), 19839–19849. <https://doi.org/10.1021/jacs.9b09969>.
- (62) Morad, V.; Stelmakh, A.; Svyrydenko, M.; Feld, L. G.; Boehme, S. C.; Aebli, M.; Affolter, J.; Kaul, C. J.; Schrenker, N. J.; Bals, S.; Sahin, Y.; Dirin, D. N.; Cherniukh, I.; Raino, G.; Baumketner, A.; Kovalenko, M. V. Designer Phospholipid Capping Ligands for Soft Metal Halide Nanocrystals. *Nature* **2023**, *625*, 542–548. <https://doi.org/10.1038/s41586-023-06932-6>.
- (63) Montanarella, F.; Akkerman, Q. A.; Bonatz, D.; van der Sluijs, M. M.; van der Bok, J. C.; Prins, P. T.; Aebli, M.; Mews, A.; Vanmaekelbergh, D.; Kovalenko, M. V. Growth and Self-Assembly of CsPbBr₃ Nanocrystals in the TOPO/PbBr₂ Synthesis as Seen with X-Ray Scattering. *Nano Lett* **2023**. <https://doi.org/10.1021/acs.nanolett.2c04532>.
- (64) Almeida, G.; Ashton, O. J.; Goldoni, L.; Maggioni, D.; Petralanda, U.; Mishra, N.; Akkerman, Q. A.; Infante, I.; Snaith, H. J.; Manna, L. The Phosphine Oxide Route toward Lead Halide

Perovskite Nanocrystals. *J Am Chem Soc* **2018**, *140* (44), 14878–14886.
<https://doi.org/10.1021/jacs.8b08978>.

- (65) Stelmakh, A.; Aebli, M.; Baumketner, A.; Kovalenko, M. V. On the Mechanism of Alkylammonium Ligands Binding to the Surface of CsPbBr₃ Nanocrystals. *Chemistry of Materials* **2021**, *33* (15), 5962–5973. <https://doi.org/10.1021/acs.chemmater.1c01081>.
- (66) Ding, Y.; Zhang, Z.; Toso, S.; Gushchina, I.; Trepalin, V.; Shi, K.; Peng, J. W.; Kuno, M. Mixed Ligand Passivation as the Origin of Near-Unity Emission Quantum Yields in CsPbBr₃ Nanocrystals. *J Am Chem Soc* **2023**. <https://doi.org/10.1021/jacs.2c13527>.
- (67) Ginterseder, M.; Sun, W.; Shcherbakov-Wu, W.; McIsaac, A. R.; Berkinsky, D. B.; Kaplan, A. E. K.; Wang, L.; Krajewska, C.; Šverko, T.; Perkinson, C. F.; Utzat, H.; Tisdale, W. A.; Van Voorhis, T.; Bawendi, M. G. Lead Halide Perovskite Nanocrystals with Low Inhomogeneous Broadening and High Coherent Fraction through Dicationic Ligand Engineering. *Nano Lett* **2023**, *23* (4), 1128–1134. <https://doi.org/10.1021/acs.nanolett.2c03354>.
- (68) Nguyen, H. A.; Dixon, G.; Dou, F. Y.; Gallagher, S.; Gibbs, S.; Ladd, D. M.; Marino, E.; Ondry, J. C.; Shanahan, J. P.; Vasileiadou, E. S.; Barlow, S.; Gamelin, D. R.; Ginger, D. S.; Jonas, D. M.; Kanatzidis, M. G.; Marder, S. R.; Morton, D.; Murray, C. B.; Owen, J. S.; Talapin, D. V.; Toney, M. F.; Cossairt, B. M. Design Rules for Obtaining Narrow Luminescence from Semiconductors Made in Solution. *Chem Rev* **2023**, *123* (12), 7890–7952.
<https://doi.org/10.1021/acs.chemrev.3c00097>.
- (69) Elshaari, A. W.; Pernice, W.; Srinivasan, K.; Benson, O.; Zwiller, V. Hybrid Integrated Quantum Photonic Circuits. *Nature Photonics*. Nature Research May 1, 2020, pp 285–298.
<https://doi.org/10.1038/s41566-020-0609-x>.
- (70) Zhang, C.; Huang, Y. F.; Liu, B. H.; Li, C. F.; Guo, G. C. Spontaneous Parametric Down-Conversion Sources for Multiphoton Experiments. *Advanced Quantum Technologies*. John Wiley and Sons Inc May 1, 2021. <https://doi.org/10.1002/qute.202000132>.
- (71) Buckley, S.; Rivoire, K.; Vučković, J. Engineered Quantum Dot Single-Photon Sources. **2012**.
<https://doi.org/10.1088/0034-4885/75/12/126503>.
- (72) Kagan, C. R.; Bassett, L. C.; Murray, C. B.; Thompson, S. M. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chem Rev* **2021**, *121* (5), 3186–3233.
<https://doi.org/10.1021/acs.chemrev.0c00831>.
- (73) Toth, M.; Aharonovich, I. Single Photon Sources in Atomically Thin Materials. *Annu Rev Phys Chem* **2019**, *70* (1), 123–142. <https://doi.org/10.1146/annurev-physchem-042018-052628>.
- (74) Caldwell, J. D.; Aharonovich, I.; Cassabois, G.; Edgar, J. H.; Gil, B.; Basov, D. N. Photonics with Hexagonal Boron Nitride. *Nat Rev Mater* **2019**, *4* (August). <https://doi.org/10.1038/s41578-019-0124-1>.

- (75) Toninelli, C.; Gerhardt, I.; Clark, A. S.; Reserbat-Plantey, A.; Götzinger, S.; Ristanović, Z.; Colautti, M.; Lombardi, P.; Major, K. D.; Deperasińska, I.; Pernice, W. H.; Koppens, F. H. L.; Kozankiewicz, B.; Gourdon, A.; Sandoghdar, V.; Orrit, M. Single Organic Molecules for Photonic Quantum Technologies. *Nat Mater* **2021**, *20* (12), 1615–1628. <https://doi.org/10.1038/s41563-021-00987-4>.
- (76) Juska, G.; Dimastrodonato, V.; Mereni, L. O.; Gocalinska, A.; Pelucchi, E. Towards Quantum-Dot Arrays of Entangled Photon Emitters. **2013**, *7* (July), 527–531. <https://doi.org/10.1038/nphoton.2013.128>.
- (77) Senellart, P.; Solomon, G.; White, A. High-Performance Semiconductor Quantum-Dot Single-Photon Sources. *Nature Nanotechnology*. Nature Publishing Group November 1, 2017, pp 1026–1039. <https://doi.org/10.1038/nnano.2017.218>.
- (78) Lodahl, P.; Mahmoodian, S.; Stobbe, S. Interfacing Single Photons and Single Quantum Dots with Photonic Nanostructures. *Rev Mod Phys* **2015**, *87* (2), 347–400. <https://doi.org/10.1103/RevModPhys.87.347>.
- (79) Zhu, C.; Marczak, M.; Feld, L.; Boehme, S. C.; Bernasconi, C.; Moskalenko, A.; Cherniukh, I.; Dirin, D.; Bodnarchuk, M. I.; Kovalenko, M. V.; Raino, G. Room-Temperature, Highly Pure Single-Photon Sources from All- Inorganic Lead Halide Perovskite Quantum Dots. *Nano Lett* **2022**, *22*, 3751–3760. <https://doi.org/10.1021/acs.nanolett.2c00756>.
- (80) Park, Y. S.; Guo, S.; Makarov, N. S.; Klimov, V. I. Room Temperature Single-Photon Emission from Individual Perovskite Quantum Dots. *ACS Nano* **2015**, *9* (10), 10386–10393. <https://doi.org/10.1021/acs.nano.5b04584>.
- (81) Chen, Y.; Sharp, D.; Saxena, A.; Nguyen, H.; Cossairt, B. M.; Majumdar, A. Integrated Quantum Nanophotonics with Solution-Processed Materials. *Adv Quantum Technol* **2022**, *5* (1), 1–22. <https://doi.org/10.1002/qute.202100078>.
- (82) Chen, Y.; Ryou, A.; Friedfeld, M. R.; Fryett, T.; Whitehead, J.; Cossairt, B. M.; Majumdar, A. Deterministic Positioning of Colloidal Quantum Dots on Silicon Nitride Nanobeam Cavities. *Nano Lett* **2018**, *18* (10), 6404–6410. <https://doi.org/10.1021/acs.nanolett.8b02764>.
- (83) Nguyen, H. A.; Sharp, D.; Fröch, J. E.; Cai, Y. Y.; Wu, S.; Monahan, M.; Munley, C.; Manna, A.; Majumdar, A.; Kagan, C. R.; Cossairt, B. M. Deterministic Quantum Light Arrays from Giant Silica-Shelled Quantum Dots. *ACS Appl Mater Interfaces* **2023**, *15* (3), 4294–4302. <https://doi.org/10.1021/acsami.2c18475>.
- (84) Cohen, T. A.; Sharp, D.; Kluherz, K. T.; Chen, Y.; Munley, C.; Anderson, R. T.; Swanson, C. J.; De Yoreo, J. J.; Luscombe, C. K.; Majumdar, A.; Gamelin, D. R.; Mackenzie, J. D. Direct Patterning of Perovskite Nanocrystals on Nanophotonic Cavities with Electrohydrodynamic Inkjet Printing. *Nano Lett* **2022**, *22*, 5681–5688. <https://doi.org/10.1021/acs.nanolett.2c00473>.

- (85) Kuhlmann, A. V.; Houel, J.; Ludwig, A.; Greuter, L.; Reuter, D.; Wieck, A. D.; Poggio, M.; Warburton, R. J. Charge Noise and Spin Noise in a Semiconductor Quantum Device. *Nat Phys* **2013**, *9* (9), 570–575. <https://doi.org/10.1038/nphys2688>.
- (86) Accanto, N.; Masia, F.; Moreels, I.; Hens, Z.; Langbein, W.; Borri, P. Engineering the Spin-Flip Limited Exciton Dephasing in Colloidal CdSe/CdS Quantum Dots. *ACS Nano* **2012**, *6* (6), 5227–5233. <https://doi.org/10.1021/nn300992a>.
- (87) Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberger, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science (1979)* **2018**, *360*, 1068–1072. <https://doi.org/10.1126/science.aau7392>.
- (88) Kaplan, A. E. K.; Krajewska, C. J.; Proppe, A. H.; Sun, W.; Sverko, T.; Berkinsky, D. B.; Utzat, H.; Bawendi, M. G. Hong–Ou–Mandel Interference in Colloidal CsPbBr₃ Perovskite Nanocrystals. *Nat Photonics* **2023**, *17*, 775–780. <https://doi.org/10.1038/s41566-023-01225-w>.
- (89) Rainò, G.; Nedelcu, G.; Protesescu, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Mahrt, R. F.; Stöferle, T. Single Cesium Lead Halide Perovskite Nanocrystals at Low Temperature: Fast Single-Photon Emission, Reduced Blinking, and Exciton Fine Structure. *ACS Nano* **2016**, *10* (2), 2485–2490. <https://doi.org/10.1021/acsnano.5b07328>.
- (90) Becker, M. A.; Vaxenburg, R.; Nedelcu, G.; Serce, P. C.; Shabaev, A.; Mehl, M. J.; Michopoulos, J. G.; Lambrakos, S. G.; Bernstein, N.; Lyons, J. L.; Stöferle, T.; Mahrt, R. F.; Kovalenko, M. V.; Norris, D. J.; Rainò, G.; Efros, A. L. Bright Triplet Excitons in Caesium Lead Halide Perovskites. *Nature* **2018**, *553* (7687), 189–193. <https://doi.org/10.1038/nature25147>.
- (91) Masada, S.; Yamada, T.; Tahara, H.; Hirori, H.; Saruyama, M.; Kawawaki, T.; Sato, R.; Teranishi, T.; Kanemitsu, Y. Effect of A-Site Cation on Photoluminescence Spectra of Single Lead Bromide Perovskite Nanocrystals. *Nano Lett* **2020**, *20* (5), 4022–4028. <https://doi.org/10.1021/acs.nanolett.0c01417>.
- (92) Couteau, C.; Barz, S.; Durt, T.; Gerrits, T.; Huwer, J.; Prevedel, R.; Rarity, J.; Shields, A.; Weihs, G. Applications of Single Photons to Quantum Communication and Computing. *Nature Reviews Physics* **2023**. <https://doi.org/10.1038/s42254-023-00583-2>.
- (93) He, Y. M.; He, Y.; Wei, Y. J.; Wu, D.; Atatüre, M.; Schneider, C.; Höfling, S.; Kamp, M.; Lu, C. Y.; Pan, J. W. On-Demand Semiconductor Single-Photon Source with near-Unity Indistinguishability. *Nat Nanotechnol* **2013**, *8* (3), 213–217. <https://doi.org/10.1038/nnano.2012.262>.
- (94) Rainò, G.; Yazdani, N.; Boehme, S. C.; Kober-Czerny, M.; Zhu, C.; Krieg, F.; Rossell, M. D.; Erni, R.; Wood, V.; Infante, I.; Kovalenko, M. V. Ultra-Narrow Room-Temperature Emission from Single CsPbBr₃ Perovskite Quantum Dots. *Nat Commun* **2022**, *13* (1). <https://doi.org/10.1038/s41467-022-30016-0>.

- (95) Rainò, G.; Landuyt, A.; Krieg, F.; Bernasconi, C.; Ochsenbein, S. T.; Dirin, D. N.; Bodnarchuk, M. I.; Kovalenko, M. V. Underestimated Effect of a Polymer Matrix on the Light Emission of Single CsPbBr₃ Nanocrystals. *Nano Lett* **2019**, *19* (6), 3648–3653. <https://doi.org/10.1021/acs.nanolett.9b00689>.
- (96) Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberger, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science (1979)* **2018**, *7392* (February), 1–9. <https://doi.org/10.1126/science.aau7392>.
- (97) Acosta, V. M.; Santori, C.; Faraon, A.; Huang, Z.; Fu, K. M. C.; Stacey, A.; Simpson, D. A.; Ganesan, K.; Tomljenovic-Hanic, S.; Greentree, A. D.; Prawer, S.; Beausoleil, R. G. Dynamic Stabilization of the Optical Resonances of Single Nitrogen-Vacancy Centers in Diamond. *Phys Rev Lett* **2012**, *108* (20), 6–11. <https://doi.org/10.1103/PhysRevLett.108.206401>.
- (98) Rice, J. H.; Robinson, J. W.; Jarjour, A.; Taylor, R. A.; Oliver, R. A.; Andrew, G.; Briggs, D.; Kappers, M. J.; Humphreys, C. J. Temporal Variation in Photoluminescence from Single InGaN Quantum Dots. *Appl Phys Lett* **2004**, *84* (20), 4110–4112. <https://doi.org/10.1063/1.1753653>.
- (99) Ibuki, H.; Ihara, T.; Kanemitsu, Y. Spectral Diffusion of Emissions of Excitons and Trions in Single CdSe/ZnS Nanocrystals: Charge Fluctuations in and around Nanocrystals. *Journal of Physical Chemistry C* **2016**, *120* (41), 23772–23779. <https://doi.org/10.1021/acs.jpcc.6b06220>.
- (100) Müller, J.; Lupton, J. M.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. Monitoring Surface Charge Movement in Single Elongated Semiconductor Nanocrystals. *Phys Rev Lett* **2004**, *93* (16), 2–5. <https://doi.org/10.1103/PhysRevLett.93.167402>.
- (101) Tessier, M. D.; Javaux, C.; Maksimovic, I.; Loriette, V.; Dubertret, B. Spectroscopy of Single CdSe Nanoplatelets. *ACS Nano* **2012**, *6* (8), 6751–6758. <https://doi.org/10.1021/nn3014855>.
- (102) Lohmann, S. H.; Harder, P.; Bourier, F.; Strelow, C.; Mews, A.; Kipp, T. Influence of Interface-Driven Strain on the Spectral Diffusion Properties of Core/Shell CdSe/CdS Dot/Rod Nanoparticles. *Journal of Physical Chemistry C* **2019**, *123* (8), 5099–5109. <https://doi.org/10.1021/acs.jpcc.8b12253>.
- (103) Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. “On”/“off” Fluorescence Intermittency of Single Semiconductor Quantum Dots. *Journal of Chemical Physics* **2001**, *115* (2), 1028–1040. <https://doi.org/10.1063/1.1377883>.
- (104) Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. Nonexponential “Blinking” Kinetics of Single CdSe Quantum Dots: A Universal Power Law Behavior. *J Chem Phys* **2000**, *112* (7), 3117–3120. <https://doi.org/10.1063/1.480896>.

- (105) Galland, C.; Ghosh, Y.; Steinbrück, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H. Two Types of Luminescence Blinking Revealed by Spectroelectrochemistry of Single Quantum Dots. *Nature* **2011**, 479 (7372), 203–207. <https://doi.org/10.1038/nature10569>.
- (106) Seth, S.; Ahmed, T.; Samanta, A. Photoluminescence Flickering and Blinking of Single CsPbBr₃ Perovskite Nanocrystals: Revealing Explicit Carrier Recombination Dynamics. *Journal of Physical Chemistry Letters* **2018**, 9 (24), 7007–7014. <https://doi.org/10.1021/acs.jpclett.8b02979>.
- (107) Cui, J.; Beyler, A. P.; Bischof, T. S.; Wilson, M. W. B.; Bawendi, M. G. Deconstructing the Photon Stream from Single Nanocrystals: From Binning to Correlation. *Chem Soc Rev* **2014**, 43 (4), 1287–1310. <https://doi.org/10.1039/c3cs60330j>.
- (108) Fernée, M. J.; Tamarat, P.; Lounis, B. Spectroscopy of Single Nanocrystals. *Chem Soc Rev* **2014**, 43 (4), 1311–1337. <https://doi.org/10.1039/c3cs60209e>.
- (109) Gómez, D. E.; Califano, M.; Mulvaney, P. Optical Properties of Single Semiconductor Nanocrystals. *Physical Chemistry Chemical Physics* **2006**, 8 (43), 4989–5011. <https://doi.org/10.1039/b607661k>.
- (110) Kagan, C. R.; Bassett, L. C.; Murray, C. B.; Thompson, S. M. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chem Rev* **2021**, 121 (5), 3186–3233. <https://doi.org/10.1021/acs.chemrev.0c00831>.
- (111) Cao, Z.; Hu, F.; Zhang, C.; Zhu, S.; Xiao, M.; Wang, X. Optical Studies of Semiconductor Perovskite Nanocrystals for Classical Optoelectronic Applications and Quantum Information Technologies : A Review. *Advanced Photonics* **2020**, 2 (5), 8–10. <https://doi.org/10.1117/1.AP.2.5.054001>.
- (112) Blanton, S. A.; Hines, M. A.; Guyot-Sionnest, P. Photoluminescence Wandering in Single CdSe Nanocrystals. *Appl Phys Lett* **1996**, 69 (25), 3905–3907. <https://doi.org/10.1063/1.117565>.
- (113) Brokmann, X.; Marshall, L. F.; Bawendi, M. G. Revealing Single Emitter Spectral Dynamics from Intensity Correlations in an Ensemble Fluorescence Spectrum. *Opt Express* **2009**, 17 (6), 4509. <https://doi.org/10.1364/oe.17.004509>.
- (114) Beyler, A. P.; Marshall, L. F.; Cui, J.; Brokmann, X.; Bawendi, M. G. Direct Observation of Rapid Discrete Spectral Dynamics in Single Colloidal Cdse-Cds Core-Shell Quantum Dots. *Phys Rev Lett* **2013**, 111 (17), 1–5. <https://doi.org/10.1103/PhysRevLett.111.177401>.
- (115) Fernée, M. J.; Littleton, B. N.; Cooper, S.; Rubinsztein-Dunlop, H.; Gómez, D. E.; Mulvaney, P. Acoustic Phonon Contributions to the Emission Spectrum of Single CdSe Nanocrystals. *Journal of Physical Chemistry C* **2008**, 112 (6), 1878–1884. <https://doi.org/10.1021/jp709939c>.
- (116) Fernée, M. J.; Sinito, C.; Mulvaney, P.; Tamarat, P.; Lounis, B. The Optical Phonon Spectrum of Cdse Colloidal Quantum Dots. *Physical Chemistry Chemical Physics* **2014**, 16 (32), 16957–16961. <https://doi.org/10.1039/c4cp02022g>.

- (117) Strandell, D. P.; Kambhampati, P. The Temperature Dependence of the Photoluminescence of CsPbBr₃ Nanocrystals Reveals Phase Transitions and Homogeneous Linewidths. *Journal of Physical Chemistry C* **2021**, *125* (49), 27504–27508. <https://doi.org/10.1021/acs.jpcc.1c09501>.
- (118) Iaru, C. M.; Geuchies, J. J.; Koenraad, P. M.; Vanmaekelbergh, D.; Silov, A. Y. Strong Carrier-Phonon Coupling in Lead Halide Perovskite Nanocrystals. *ACS Nano* **2017**, *11* (11), 11024–11030. <https://doi.org/10.1021/acsnano.7b05033>.
- (119) Empedocles, S. A.; Bawendi, M. G. Influence of Spectral Diffusion on the Line Shapes of Single CdSe Nanocrystallite Quantum Dots. *Journal of Physical Chemistry B* **1999**, *103* (11), 1826–1830. <https://doi.org/10.1021/jp983305x>.
- (120) Bar-Joseph, I.; Klingshirn, C.; Miller, D. A. B.; Chemla, D. S.; Koren, U.; Miller, B. I. Quantum-Confined Stark Effect in InGaAs/InP Quantum Wells Grown by Organometallic Vapor Phase Epitaxy. *Appl Phys Lett* **1987**, *50* (15), 1010–1012. <https://doi.org/10.1063/1.97991>.
- (121) Cordones, A. A.; Leone, S. R. Mechanisms for Charge Trapping in Single Semiconductor Nanocrystals Probed by Fluorescence Blinking. *Chem Soc Rev* **2013**, *42* (8), 3209–3221. <https://doi.org/10.1039/c2cs35452g>.
- (122) Mahler, B.; Spinicelli, P.; Buil, S.; Quelin, X.; Hermier, J. P.; Dubertret, B. Towards Non-Blinking Colloidal Quantum Dots. *Nat Mater* **2008**, *7* (8), 659–664. <https://doi.org/10.1038/nmat2222>.
- (123) Efros, A. L.; Nesbitt, D. J. Origin and Control of Blinking in Quantum Dots. *Nat Nanotechnol* **2016**, *11* (8), 661–671. <https://doi.org/10.1038/nnano.2016.140>.
- (124) Galland, C.; Ghosh, Y.; Steinbrück, A.; Hollingsworth, J. A.; Htoon, H.; Klimov, V. I. Lifetime Blinking in Nonblinking Nanocrystal Quantum Dots. *Nat Commun* **2012**, *3* (May). <https://doi.org/10.1038/ncomms1916>.
- (125) Krauss, T. D.; Brus, L. E. Charge, Polarizability, and Photoionization of Single Semiconductor Nanocrystals. *Phys Rev Lett* **1999**, *83* (23), 4840–4843. <https://doi.org/10.1103/PhysRevLett.83.4840>.
- (126) Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. “Giant” Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J Am Chem Soc* **2008**, *130* (15), 5026–5027. <https://doi.org/10.1021/ja711379k>.
- (127) Ghosh, Y.; Mangum, B. D.; Casson, J. L.; Williams, D. J.; Htoon, H.; Hollingsworth, J. A. New Insights into the Complexities of Shell Growth and the Strong Influence of Particle Volume in Nonblinking “Giant” Core/Shell Nanocrystal Quantum Dots. *J Am Chem Soc* **2012**, *134* (23), 9634–9643. <https://doi.org/10.1021/ja212032q>.

- (128) Gao, F.; Bajwa, P.; Nguyen, A.; Heyes, C. D. Shell-Dependent Photoluminescence Studies Provide Mechanistic Insights into the Off-Grey-On Transitions of Blinking Quantum Dots. *ACS Nano* **2017**, *11* (3), 2905–2916. <https://doi.org/10.1021/acsnano.6b08040>.
- (129) Hohng, S.; Ha, T. Near-Complete Suppression of Quantum Dot Blinking in Ambient Conditions. *J Am Chem Soc* **2004**, *126* (5), 1324–1325. <https://doi.org/10.1021/ja039686w>.
- (130) Pal, B. N.; Ghosh, Y.; Brovelli, S.; Laocharoensuk, R.; Klimov, V. I.; Hollingsworth, J. A.; Htoon, H. “Giant” CdSe/CdS Core/Shell Nanocrystal Quantum Dots as Efficient Electroluminescent Materials: Strong Influence of Shell Thickness on Light-Emitting Diode Performance. *Nano Lett* **2012**, *12* (1), 331–336. <https://doi.org/10.1021/nl203620f>.
- (131) Lee, S. H.; Kim, Y.; Jang, H.; Min, J. H.; Oh, J.; Jang, E.; Kim, D. The Effects of Discrete and Gradient Mid-Shell Structures on the Photoluminescence of Single InP Quantum Dots. *Nanoscale* **2019**, *11* (48), 23251–23258. <https://doi.org/10.1039/c9nr06847c>.
- (132) Lee, Y.; Jo, D. Y.; Kim, T.; Jo, J. H.; Park, J.; Yang, H.; Kim, D. Effectual Interface and Defect Engineering for Auger Recombination Suppression in Bright InP/ZnSeS/ZnS Quantum Dots. *ACS Appl Mater Interfaces* **2022**, *14* (10), 12479–12487. <https://doi.org/10.1021/acsami.1c20088>.
- (133) Knappenberger, K. L.; Wong, D. B.; Romanyuk, Y. E.; Leone, S. R. Excitation Wavelength Dependence of Fluorescence Intermittency in CdSe/ZnS Core/Shell Quantum Dots. *Nano Lett* **2007**, *7* (12), 3869–3874. <https://doi.org/10.1021/nl0714740>.
- (134) Gibson, N. A.; Koscher, B. A.; Alivisatos, A. P.; Leone, S. R. Excitation Intensity Dependence of Photoluminescence Blinking in CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry C* **2018**, *122* (22), 12106–12113. <https://doi.org/10.1021/acs.jpcc.8b03206>.
- (135) Peterson, J. J.; Nesbitt, D. J. Modified Power Law Behavior in Quantum Dot Blinking: A Novel Role for Biexcitons and Auger Ionization. *Nano Lett* **2009**, *9* (1), 338–345. <https://doi.org/10.1021/nl803108p>.
- (136) Munro, A. M.; Plante, I. J. La; Ng, M. S.; Ginger, D. S. Quantitative Study of the Effects of Surface Ligand Concentration on CdSe Nanocrystal Photoluminescence. *Journal of Physical Chemistry C* **2007**, *111* (17), 6220–6227. <https://doi.org/10.1021/jp068733e>.
- (137) Braam, D.; Mölleken, A.; Prinz, G. M.; Notthoff, C.; Geller, M.; Lorke, A. Role of the Ligand Layer for Photoluminescence Spectral Diffusion of CdSe/ZnS Nanoparticles. *Phys Rev B Condens Matter Mater Phys* **2013**, *88* (12), 1–6. <https://doi.org/10.1103/PhysRevB.88.125302>.
- (138) Gómez, D. E.; Van Embden, J.; Mulvaney, P. Spectral Diffusion of Single Semiconductor Nanocrystals: The Influence of the Dielectric Environment. *Appl Phys Lett* **2006**, *88* (15), 1–4. <https://doi.org/10.1063/1.2193967>.

- (139) Gellen, T. A.; Lem, J.; Turner, D. B. Probing Homogeneous Line Broadening in CdSe Nanocrystals Using Multidimensional Electronic Spectroscopy. *Nano Lett* **2017**, *17* (5), 2809–2815. <https://doi.org/10.1021/acs.nanolett.6b05068>.
- (140) Fisher, B.; Caruge, J. M.; Zehnder, D.; Bawendi, M. Room-Temperature Ordered Photon Emission from Multiexciton States in Single CdSe Core-Shell Nanocrystals. *Phys Rev Lett* **2005**, *94* (8), 1–4. <https://doi.org/10.1103/PhysRevLett.94.087403>.
- (141) Yuan, G.; Gómez, D. E.; Kirkwood, N.; Boldt, K.; Mulvaney, P. Two Mechanisms Determine Quantum Dot Blinking. *ACS Nano* **2018**, *12* (4), 3397–3405. <https://doi.org/10.1021/acsnano.7b09052>.
- (142) Jha, P. P.; Guyot-Sionnest, P. Trion Decay in Colloidal Quantum Dots. *ACS Nano* **2009**, *3* (4), 1011–1015. <https://doi.org/10.1021/nn9001177>.
- (143) Daniel E. Gomez† Joel van Embden,† Paul Mulvaney,†, * Mark J. Fernee, ‡ and Halina Rubinsztein-Dunlop‡. Exciton-Trion Transitions in Single CdSe–CdS Core–Shell Nanocrystals. *ACS Nano* **2009**, *3* (8), 2281–2287.
- (144) Htoon, H.; Malko, A. V.; Bussian, D.; Vela, J.; Chen, Y.; Hollingsworth, J. A.; Klimov, V. I. Highly Emissive Multiexcitons in Steady-State Photoluminescence of Individual “Giant” CdSe/CdS Core/Shell Nanocrystals. *Nano Lett* **2010**, *10* (7), 2401–2407. <https://doi.org/10.1021/nl1004652>.
- (145) Mueller, S.; Lüttig, J.; Brenneis, L.; Oron, D.; Brixner, T. Observing Multiexciton Correlations in Colloidal Semiconductor Quantum Dots via Multiple-Quantum Two-Dimensional Fluorescence Spectroscopy . *ACS Nano* **2021**. <https://doi.org/10.1021/acsnano.0c09080>.
- (146) Tisler, J.; Balasubramanian, G.; Naydenov, B.; Kolesov, R.; Grotz, B.; Reuter, R.; Boudou, J. P.; Curmi, P. A.; Sennour, M.; Thorel, A.; Börsch, M.; Aulenbacher, K.; Erdmann, R.; Hemmer, P. R.; Jelezko, F.; Wrachtrup, J. Fluorescence and Spin Properties of Defects in Single Digit Nanodiamonds. *ACS Nano* **2009**, *3* (7), 1959–1965. <https://doi.org/10.1021/nn9003617>.
- (147) Bradac, C.; Gaebel, T.; Naidoo, N.; Sellars, M. J.; Twamley, J.; Brown, L. J.; Barnard, A. S.; Plakhotnik, T.; Zvyagin, A. V.; Rabeau, J. R. Observation and Control of Blinking Nitrogen-Vacancy Centres in Discrete Nanodiamonds. *Nat Nanotechnol* **2010**, *5* (5), 345–349. <https://doi.org/10.1038/nnano.2010.56>.
- (148) Wrachtrup, J.; Jelezko, F.; Grotz, B.; McGuinness, L. Nitrogen-Vacancy Centers Close to Surfaces. *MRS Bull* **2013**, *38* (2), 149–154. <https://doi.org/10.1557/mrs.2013.22>.
- (149) Ishikawa, T.; Fu, K. M. C.; Santori, C.; Acosta, V. M.; Beausoleil, R. G.; Watanabe, H.; Shikata, S.; Itoh, K. M. Optical and Spin Coherence Properties of Nitrogen-Vacancy Centers Placed in a 100 Nm Thick Isotopically Purified Diamond Layer. *Nano Lett* **2012**, *12* (4), 2083–2087. <https://doi.org/10.1021/nl300350r>.

- (150) De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, *10* (2), 2071–2081. <https://doi.org/10.1021/acsnano.5b06295>.
- (151) Eperon, G. E.; Jedlicka, E.; Ginger, D. S. Biexciton Auger Recombination Differs in Hybrid and Inorganic Halide Perovskite Quantum Dots. *Journal of Physical Chemistry Letters* **2018**, *9* (1), 104–109. <https://doi.org/10.1021/acs.jpclett.7b02805>.
- (152) Lodahl, P.; Mahmoodian, S.; Stobbe, S. Interfacing Single Photons and Single Quantum Dots with Photonic Nanostructures. *Rev Mod Phys* **2015**, *87* (2), 347–400. <https://doi.org/10.1103/RevModPhys.87.347>.
- (153) Brorson, S. D.; Yokoyama, H.; Ippen, E. P. Spontaneous Emission Rate Alteration in Optical Waveguide Structures. *IEEE J Quantum Electron* **1990**, *26* (9), 1492–1499. <https://doi.org/10.1109/3.102626>.
- (154) Li, A.; Singh, S.; Sievenpiper, D. Metasurfaces and Their Applications. *Nanophotonics* **2018**, *7* (6), 989–1011. <https://doi.org/10.1515/nanoph-2017-0120>.
- (155) Hugall, J. T.; Singh, A.; Van Hulst, N. F. Plasmonic Cavity Coupling. *ACS Photonics* **2018**, *5* (1), 43–53. <https://doi.org/10.1021/acsp Photonics.7b01139>.
- (156) Munechika, K.; Chen, Y.; Tillack, A. F.; Kulkarni, A. P.; Plante, I. J. La; Munro, A. M.; Ginger, D. S. Spectral Control of Plasmonic Emission Enhancement from Quantum Dots near Single Silver Nanoprisms. *Nano Lett* **2010**, *10* (7), 2598–2603. <https://doi.org/10.1021/nl101281a>.
- (157) Chen, Y.; Munechika, K.; Jen-La Plante, I.; Munro, A. M.; Skrabalak, S. E.; Xia, Y.; Ginger, D. S. Excitation Enhancement of CdSe Quantum Dots by Single Metal Nanoparticles. *Appl Phys Lett* **2008**, *93* (5), 1–4. <https://doi.org/10.1063/1.2956391>.
- (158) Bharadwaj, P.; Novotny, L. Robustness of Quantum Dot Power-Law Blinking. *Nano Lett* **2011**, *11* (5), 2137–2141. <https://doi.org/10.1021/nl200782v>.
- (159) Purcell, E. M. Spontaneous Emission Probabilities at Radio Frequencies. *Physical Review*. 1946, p 681.
- (160) Liu, X.; Nakajima, H.; Li, Y.; Odashima, S.; Suemune, I.; Kumano, H. Optical Control of Spectral Diffusion with Single InAs Quantum Dots in a Silver-Embedded Nanocone. *Opt Express* **2017**, *25* (7), 8073. <https://doi.org/10.1364/oe.25.008073>.
- (161) Lyasota, A.; Jarlov, C.; Rudra, A.; Dwir, B.; Kapon, E. Limiting the Spectral Diffusion of Nano-Scale Light Emitters Using the Purcell Effect in a Photonic-Confined Environment. *Sci Rep* **2019**, *9* (1), 1–9. <https://doi.org/10.1038/s41598-018-37677-2>.

- (162) Huang, Y.; Su, R.; Wang, Y.; Zhu, C.; Feng, J.; Zhao, J.; Liu, Z.; Xiong, Q. A Fano Cavity – Photon Interface for Directional Suppression of Spectral Diffusion of a Single Perovskite Nanoplatelet. **2022**. <https://doi.org/10.1021/acs.nanolett.2c03073>.
- (163) Yuan, G.; Gómez, D.; Kirkwood, N.; Mulvaney, P. Tuning Single Quantum Dot Emission with a Micromirror. *Nano Lett* **2018**, *18* (2), 1010–1017. <https://doi.org/10.1021/acs.nanolett.7b04482>.
- (164) Chen, Y.; Sharp, D.; Saxena, A.; Nguyen, H.; Cossairt, B. M.; Majumdar, A. Integrated Quantum Nanophotonics with Solution-Processed Materials. *Adv Quantum Technol* **2022**, *5* (1), 1–22. <https://doi.org/10.1002/qute.202100078>.
- (165) Kim, J.-H.; Aghaeimeibodi, S.; Carolan, J.; Englund, D.; Waks, E. Hybrid Integration Methods for On-Chip Quantum Photonics. *Optica* **2020**, *7* (4), 291. <https://doi.org/10.1364/optica.384118>.
- (166) Cohen, T. A.; Sharp, D.; Kluherz, K. T.; Chen, Y.; Munley, C.; Anderson, R. T.; Swanson, C. J.; De Yoreo, J. J.; Luscombe, C. K.; Majumdar, A.; Gamelin, D. R.; Mackenzie, J. D. Direct Patterning of Perovskite Nanocrystals on Nanophotonic Cavities with Electrohydrodynamic Inkjet Printing. *Nano Lett* **2022**. <https://doi.org/10.1021/acs.nanolett.2c00473>.
- (167) Le Thomas, N.; Schöps, O.; Woggon, U.; Artemyev, M. V.; Kazes, M.; Banin, U. Cavity QED with Semiconductor Nanocrystals. *Optics InfoBase Conference Papers* **2006**.
- (168) Lee, H.; Woo, J. Y.; Park, D. Y.; Jo, I.; Park, J.; Lee, Y.; Koo, Y.; Choi, J.; Kim, H.; Kim, Y. H.; Jeong, M. S.; Jeong, S.; Park, K. D. Tip-Induced Strain Engineering of a Single Metal Halide Perovskite Quantum Dot. *ACS Nano* **2021**, *15* (5), 9057–9064. <https://doi.org/10.1021/acs.nano.1c02182>.
- (169) Pawley, J. B. *Handbook of Biological Confocal Microscopy: Third Edition*; 2006. <https://doi.org/10.1007/978-0-387-45524-2>.
- (170) Empedocles, S.; Bawendi, M. Spectroscopy of Single CdSe Nanocrystallites. *Accounts of Chemical Research*. 1999, pp 389–396. <https://doi.org/10.1021/ar9501939>.

Chapter 2: Tuning Hybrid exciton–Photon Fano Resonances in Two-Dimensional Organic–Inorganic Perovskite Thin Films

Adapted from Muckel, Guye, **Gallagher** et al. *Nano Lett.* 2021, 21, 14, 6124–6131

My contributions to this work involved optimizing the perovskite film deposition conditions, performing some of the single particle dark field scattering measurements on glass and on the nanoprism on mirror gold film.

2.1 Overview:

As easy-to-grow quantum wells with narrow excitonic features at room temperature, two-dimensional (2D) Ruddleson–Popper perovskites are promising for realizing novel nanophotonic devices based on exciton–photon interactions. Here, we demonstrate a distinct hybrid exciton–photon Fano resonance in $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ thin films prepared via spin coating. Using a classical coupled-oscillator model and finite-difference time-domain simulations, we link the Fano interference to the coupling of the exciton with the Rayleigh-like scattering of the film microstructure. Combining colloidal plasmonic cavities with the 2D perovskite films, we demonstrate tuning of the Fano resonance. In combination with silver nanoparticles, the exciton–photon Fano interference couples to the in-plane plasmonic modes with indications of Rabi splitting. By creating a nanoparticle on mirror geometry, we address the out-of-plane excitonic component, reaching an intermediate coupling regime. These structures suggest possible photonic targets for biomolecular self-assembly applications.

2.2 Introduction:

Controlling light–matter interactions is crucial for the performance of optoelectronic devices. Because of their strong absorption^{1,2} and low trap densities,^{3,4} lead halide perovskites (LHPs) have gained significant attention as active materials in both photovoltaics and light-emitting diodes.^{5,6} LHPs can be synthesized with variable dimensionalities, displaying high oscillator strengths and large exciton binding energies.⁷ Ruddlesden–Popper perovskites,⁸ which self-assemble from solution as inorganic layers sandwiched between layers of intercalated alkylammonium cations, represent naturally grown quantum wells with large (>100 meV) exciton binding energies,⁹ high oscillator strengths (0.7 ± 0.1),¹⁰ and narrow line widths (52 meV fwhm)¹¹ at room temperature. With these characteristics, low-dimensional perovskites have emerged as a promising platform for the tailoring of light–matter interactions. Effects like lasing,^{12–14} enhanced absorption,¹⁵ increased spontaneous emission,^{16–19} and even Rabi splitting^{20–22}

have been demonstrated, which benefit both conventional optoelectronics,^{23–25} and may open the path to novel devices like polariton lasers,²⁶ quantum sensing or optical computation applications.^{27,28} Controlling distances in these systems is often of great importance, making them attractive targets for biomolecular self-assembly.^{29–32} Fano resonances are particularly intriguing due to their applications in sensing, switching, and slow light devices.^{33–37} A Fanoresonance^{34–37} is characterized by asymmetric spectral features and occurs due to the interference of a single, well-defined resonance with a continuum of states or another much broader mode. Originally developed to explain the asymmetric lineshapes in the atomic spectra of helium,³⁶ its theory has been adapted to describe the spectral response in a variety of systems,^{38–41} including coupling between excitons and plasmonic cavities.^{42–45} An interesting aspect of LHPs is that due to their high refractive index they can act as optically resonant nanophotonic structures on their own, rendering additional cavities unnecessary. Different implementations range from Mie, Fabry–Perot or whispering gallery mode resonances in single nanostructures^{46,47} to complex periodic structures such as photonic crystals,^{48–51} metasurfaces,^{52,53} or photonic microlasers.^{50,51} Recently, Franceschini et al. Showed ultrafast modulation of a Fano resonance in optically resonant microparticles made of bulklike CsPb(Br/Cl) 3.⁵⁴ However, the majority of resonant nanophotonic structures require complex synthetic strategies.²⁷

2.3 Results and Discussion:

Here, we study Fano resonances in 2D Ruddlesden–Popper butylammonium lead iodide ((C₄H₉NH₃)₂PbI₄, BAPI) perovskites skite thin films prepared via spin coating. Using microscopic dark-field scattering spectroscopy and finite-difference time-domain (FDTD) electrodynamics calculations, we find that the 2D excitonic transition, combined with a distinct grain-like microstructure, gives rise to a hybrid exciton–photon Fano interference. This Fano interference can be traced back to the coupling between the exciton and the scattering background caused by the dielectric material of the grain. Further, we investigated how this Fano resonance can be tuned by adding an additional plasmonic cavity. Near single silver nanoparticles, coupling with the exciton–photon Fano resonance of the 2D perovskites is observed, with indications of Rabi splitting in FDTD calculations. Using a particle-on-mirror geometry, we directly address the out-of-plane mode of the 2D perovskite exciton, achieving an intermediate coupling regime.

Figure 2.1a depicts an atomic force microscopy (AFM) image of the BAPI thin film prepared via spin coating, revealing its distinct microstructure. The 2D perovskite crystallizes in rectangular-shaped grains with thicknesses of about 10 to 25nm and lateral dimensions of 150 nm to 1 μ m (cf. Figure S1). Figure 2.1b shows the photoluminescence (PL) and absorbance spectra from typical BAPI films on glass at room temperature. The PL spectrum exhibits a distinct peak at 520 nm with a fullwidth at half-maximum (fwhm) of 17.5 nm (80 meV), consistent with previous reports for n = 1 BAPI.⁹ The absorption spectrum depicts an

excitonic peak at 512 nm and a steplike band onset around 535 nm, in good agreement with prior reports.⁹ These results are consistent with large exciton binding energies in the 2D perovskite of >400 meV.⁹

Scattering spectra on 2D perovskite films have not been commonly reported, although dark-field scattering is finding use as a probe of film degradation in 3D perovskites. shows the dark-field scattering spectrum obtained under white light excitation (see Supporting Information for normalization). Surprisingly, the scattering spectrum exhibits an asymmetric shape, with a peak at 524 nm and a sharp minimum at 496 nm. Notably, the maximum shifts and broadens compared to the excitonic feature in PL (see FigureS2). The asymmetric scattering line shape resembles that of a Fano resonance. ³⁶ A common way to identify a feature as a Fano interference is by fitting with the Fano equation. ^{37,56,57} However, due to the strong curvature of the continuous background in the region of the interference, such fit only captures the spectral shape in the immediate vicinity (cf. FigureS3). In order to correct for the curvature of the background, we utilize that a Fano interference can be described with a coupled oscillators model, where only the oscillator with the larger damping is driven. ^{37,58}

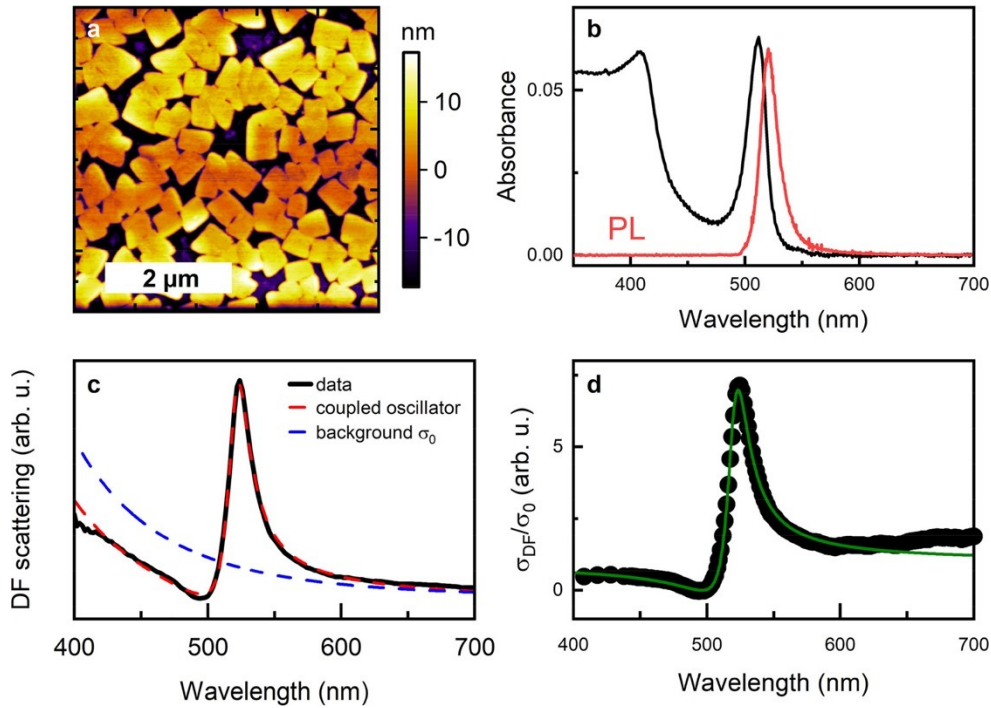


Figure 2.1. (a) Atomic force microscopy (AFM) image of a 2D perovskite thin films on glass. (b) Absorption and PL at 365 nm excitation of as-prepared 2D perovskite thin film on glass at room temperature. (c) Dark-field scattering spectrum of the 2D perovskite thin film at room temperature. The experimental data (black) is fit to a coupled-oscillator model (red dashed line). This allows isolating the contribution of the unperturbed scattering background (blue dashed line). (d) Normalized dark-field scattering spectrum. The experimental data is divided by

the scattering background σ_0 . The green line represents a fit to a normalized Fano formula ($E_0 = 2.386$ eV (519.7 nm), $\Gamma = 0.086$ eV, $q = -2.65$).

We describe the excitonic resonance as well as the background with two classical, dissipative harmonic oscillators, coupled by the rate following other work,^{59,60} the shape of the scattering spectrum is given by

$$\sigma_{scat} \propto \omega^4 \left| \frac{(\omega_{2D}^2 - \omega^2 - i\gamma_{2D}\omega)}{(\omega^2 - \omega_{2D}^2 + i\gamma_{2D}\omega)(\omega^2 - \omega_0^2 + i\gamma_0\omega) - \omega^2 g^2} \right|^2 \quad (1).$$

Here, ω_{2D} , γ_{2D} and ω_0 , γ_0 represent the resonance frequency and damping of the excitonic resonance and the broader back-ground, respectively. Figure 2.1c shows a fit of the scattering spectrum to the coupled oscillator model (red trace). On the basis of the fit of the coupled system ($g > 0$), the uncoupled continuous background σ_0 can be isolated mathematically (adjusting $g = 0$), as shown in blue in Figure 1c. Figure 1d shows the normalized scattering spectrum (experimental data divided by σ_0), which we fit with the normalized Fano equation. green line) to extract the Fano parameters ($\epsilon = \omega - \omega_0$, $\Gamma = \gamma_0$, with ω_0 and Γ describing the resonance frequency and width).

$$\frac{\sigma_{scat}}{\sigma_0} = \left| \frac{q + \epsilon}{\epsilon + i} \right|^2 \quad (2)$$

The scattering data are well described by eq 2, with $q = -2.65 \pm 0.3$, providing strong evidence that the optical feature observed in the scattering of BAPI thin film represent Fano resonance.

Next, we investigate the broad scattering background causing Fano interference. In bulklike CsPb(Br/Cl)₃ perovskite microcrystals, Fano interferences have been reported due to the coupling between the excitonic transition and Mie resonances supported by the microscopic structure of the material.^{54,61} However, these structures have significantly larger dimensions (>100 nm) in all three directions. To test whether the interference is related to the grain like micro-structure of the samples, we measured the material's full dielectric function using ellipsometry and then performed FDTD simulations.

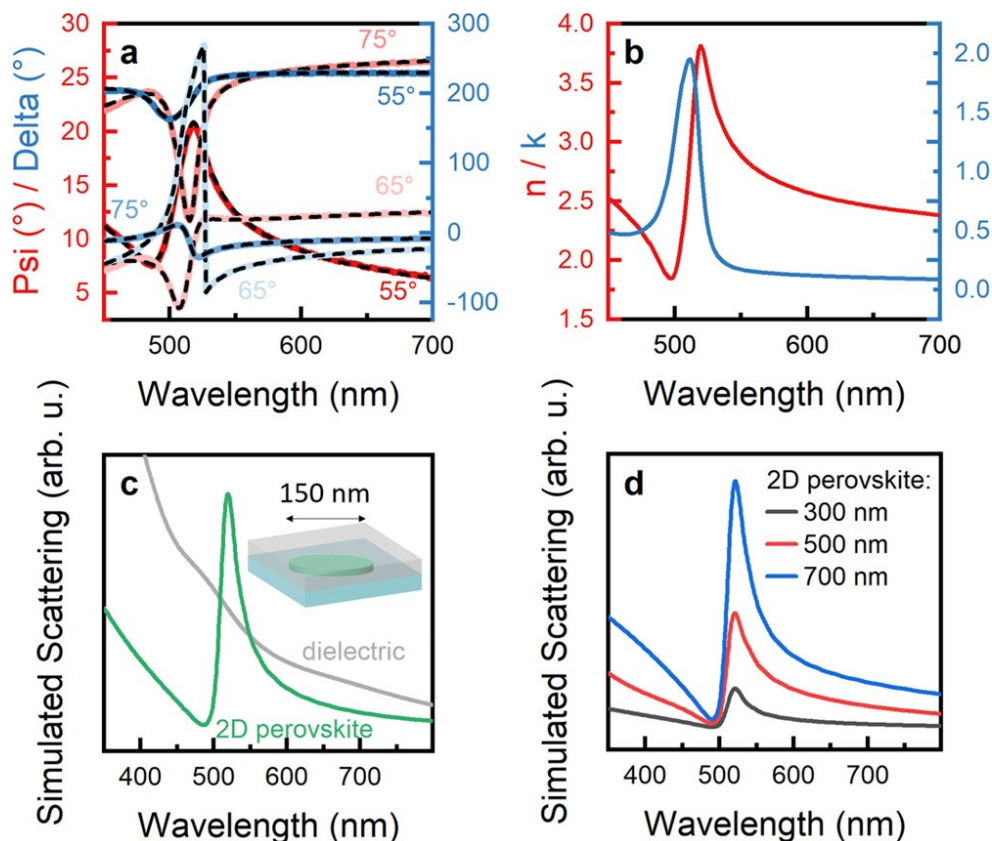


Figure 2.2 (a) Spectroscopic ellipsometry data and globally fitted model (dashed lines) for different incident angles of the light (55°, 65°, and 75°), measured on a BAPI thin film on glass at room temperature. (b) Refractive index and extinction coefficient of the 2D perovskite, as extracted from the ellipsometry measurements. (c) Simulated scattering spectrum (green line) assuming a cylindrical 2D perovskite grain. The gray line represents the scattering of a dielectric disk with the same dimensions and a constant refractive index of 2.15, providing a reference for BAPI without the excitonic resonance. The inset depicts a schematic of the FDTD model used for the simulations. The perovskite grains are modeled as a cylinder with a thickness of 20 nm and a diameter of 150 nm embedded in a matrix of PMMA (refractive index of 1.4) on a glass substrate. (d) Simulated scattering spectra for 2D perovskite grains with a thickness of 20 nm and different diameters of 300, 500, and 700 nm, all embedded in PMMA.

Figure 2.2a shows the spectroscopic ellipsometry measurements of a 2D perovskite thin film. These traces were simultaneously fit with the transmission measurements (see Figure S4) to extract the complex dielectric function, shown in Figure 2.2b. We then performed FDTD simulations assuming a 20 nm thick 2D perovskite layer located on top of a glass substrate embedded in a poly(methylmethacrylate) (PMMA) layer (see Supporting Information). Modeling the 2D perovskite as a continuous layer results in negligible scattering (see Figure S5). However, modeling the grain like microstructure as a thin 2D perovskite cylinder with a diameter of ~150 nm and a thickness of 20 nm (Figure 2.2c), produces a close-match to the experimental dark-field

spectrum (Figure 2.1b). In addition, we reproduce the bare scattering stemming from a dielectric grain with a constant refractive index of 2.15 (baseline for the BAPI n value), shown in gray in Figure 2.2c. The spectrum resembles the mathematically deconvoluted background in Figure 1c. On the basis of these simulations, we conclude that the observed Fano interference occurs due to the coupling between the excitonic transition and the scattering caused by the film microstructure and is best described as a hybrid photon–exciton Fano resonance. Note that no external cavity besides the perovskite grain itself is involved in the formation of the Fano resonance here in contrast to previous works about Fano resonances in perovskite materials coupled to plasmonic cavities.^{62,63}

Figure 2.2d depicts simulated scattering cross sections of BAPI grains with different diameters between 300 and 700 nm. The scattering amplitude scales with the grain size, while the spectral shape is conserved (grains with diameters >40 nm behave consistently, see Figure S5b). These trends are in good agreement with our experimental results, which show no deviation in the spectral shape between grains from 150 nm to 1 μ m sizes. This result indicates that the observed hybrid Fano resonance is not influenced by small changes in layer morphology, as regularly occur with LHPs synthesized via spin coating. In a broader context, this hybrid exciton–photon Fano resonance related to the excitonic transition can be expected in the scattering spectrum of any 2D film which exhibits geometric structures causing Rayleigh scattering. This situation is the case in many 2D LHP samples prepared via spin coating. Next, we investigate how the hybrid exciton–photon Fano resonance can be addressed by coupling to plasmonic nanocavities. We synthesized silver nanoparticles (AgNP), predominantly nanoprisms, truncated prisms, and some nanodisks, in the size range of 15–50 nm exhibiting plasmon resonances centered around 480–520 nm following literature procedures (see Figure S6 for ensemble extinction and electron microscopy images).^{64,65}

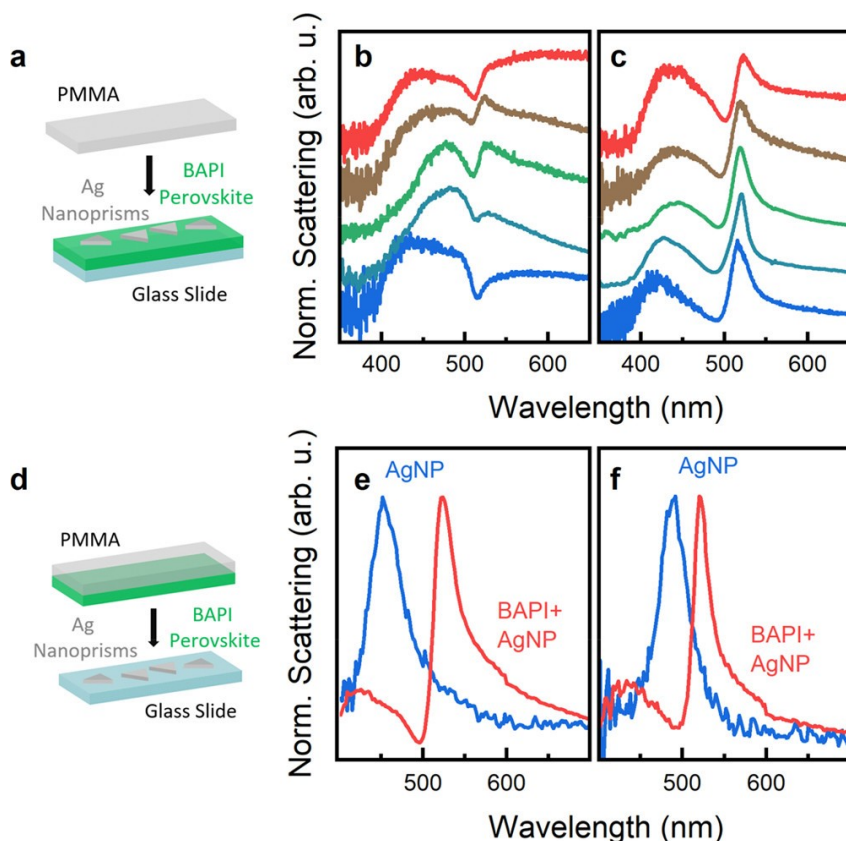


Figure 2.3. (a) Schematic illustration of the sample architecture for the coupled nanoparticle-perovskite system. (b,c) Dark-field scattering spectra of individual nanoparticles coupled to 2D perovskites. (d) Schematic illustrating the sample stacking for the inverted nanoparticle-perovskite system. (e,f) Single AgNP dark-field scattering spectra of two different individual AgNP on glass without (blue) and after covering with a 2D perovskite layer (red) and PMMA.

We transferred the AgNPs from aqueous solution to hexane⁶⁶ and subsequently spin coated them on top of the BAPI, followed by the PMMA top layer (cf. Figure 2.3a). We adjusted the particle density on the film, allowing spectroscopic measurements of individual AgNPs. Figure 2.3b,c shows dark-field scattering spectra typical of individual nanoparticles coupled to the BAPI film. All spectra exhibit two maxima and a minimum between 490 and 515 nm, correlated with the BAPI excitonic transition/hybrid Fano resonance. The single-particle spectra are corrected for the surrounding BAPI background (see Supporting Information). Figure 2.3b depicts representative spectra typical of about half the particles with relatively high dark-field scattering intensity and a large total width of the spectrum (>150 nm/700 meV fwhm), where the reduction in the scattering amplitude at the excitonic position amounts for less than 50% of the maximum value. The spectral minima are between 510 and 516 nm. The asymmetric spectral shape identifies these spectra as Fano dips, indicative of an intermediate coupling regime. We hypothesize that these spectra are associated with larger particles with less defined

geometries or potentially small agglomerates. The other half of the particles exhibit more distinct dips in the spectrum reaching the baseline, as depicted in Figure 2.3c. These spectra exhibit a distinct maximum at around 520 nm, which seems to be related to the BAPI exciton-Fano resonance. The high energy maxima are found to shift between different spectra, while the minima are located between 494 and 502 nm. To eliminate the possibility that those spectra are superpositions of uncoupled BAPI with resonance peaks of AgNPs, we fabricated samples with inverted geometry (Figure 2.3d), allowing us to compare the dark-field scattering of specific individual AgNPs as bare particles on glass and coupled to the BAPI. Figure 3e,f depicts dark-field scattering of two individual AgNPs before (blue) and after deposition of the BAPI layer (red). The spectra of bare particles depict line widths of 209 and 211 meV, consistent with single particles. The spectra of the coupled system resemble those assorted in Figure 3c, deviating from a simple superposition (cf. Figure S7).

To gain more insight into the nature of the coupling, we conducted FDTD simulations of the coupled system (see Figure 2.4). While a splitting in scattering can arise in both regimes, a Fano interaction or a Rabi splitting, mode splitting in the absorption signal is usually taken to unambiguously indicate strong coupling.^{67–69} As absorption on single particles is difficult to obtain, simulated absorption has often been used to distinguish between intermediate and strong coupling for a specific emitter-cavity combination.^{70–74} Here, we model the AgNPs as nanodisks using the Palik optical constants for Ag⁷⁵ to give a lower estimate of the coupling strength as compared to nanoprisms with electric field enhancement at the edges. First, we analyzed the coupling between the BAPI exciton and the AgNPs, neglecting the microstructure of the 2D perovskite by modeling the BAPI as a continued layer.

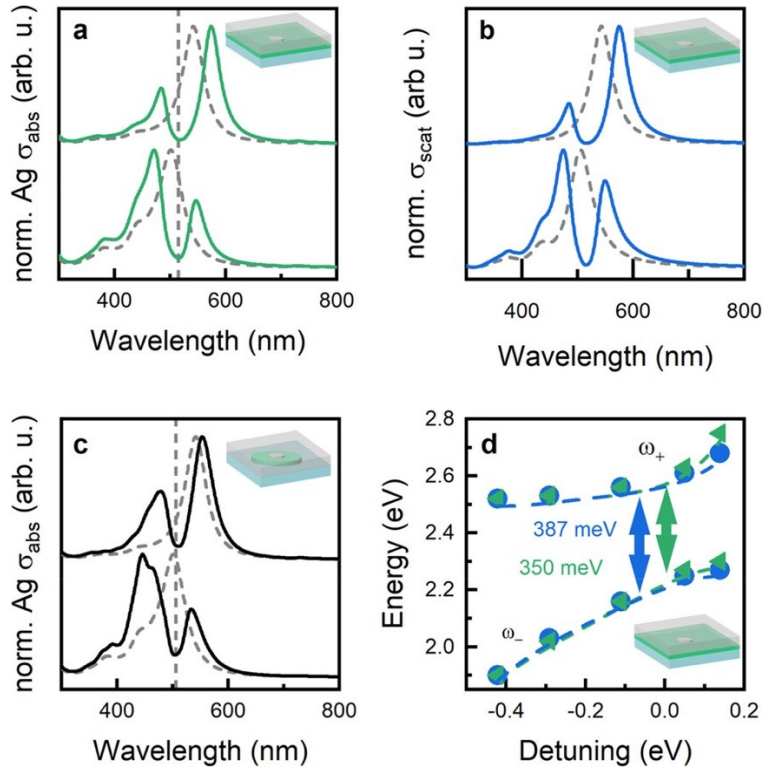


Figure 2.4. (a) Simulated absorption caused by the Ag nanodisks within the AgNP–2D perovskite system: Ag nanodisks with different sizes (30 nm and 40 nm from bottom to top) placed on a uniform layer of 2D perovskite embedded in PMMA. (b) Simulated scattering spectra of the AgNP–2D perovskite systems. Gray spectra in (a,b) depict the scattering or absorption spectra, respectively, of the uncoupled Ag nanodisks embedded in a dielectric material with refractive index of 1.4 on glass. (c) Isolated AgNP absorption of Ag nanodisks with a 20 nm (bottom) and 30 nm (top) diameter on top of a 150 nm diameter BAPI grain placed on glass and embedded in PMMA. Simulations in b,c are compared to experimental data from Figure 3 in Figure S11. (d) Detuning plot extracted from the maxima in the scattering and absorption spectra of Ag nanodisks with different sizes (panels a and among others), placed on a uniform layer of 2D perovskite embedded in PMMA (see panels a,b). The detuning value is determined as the difference between the medium peak position of the scattering of uncoupled AgNP and the energetic position of the dip in the scattering of coupled particles (2.401 eV). Dashed lines are guides to the eye.

Figure 2.4a,b depicts the scattering of the combined system as well as the absorption of the AgNP coupled to the BAPI for AgNPs of different sizes. The spectra of the uncoupled AgNPs embedded in a dielectric of $n = 1.4$ on glass are shown as reference in gray. For all particle sizes, the spectra of the coupled system display a splitting with a minimum at around 513 nm/515 nm for absorption and scattering, respectively. We thus conclude that those AgNPs with high scattering amplitude directly couple to the exciton of the 2D perovskite. Next, we include the microstructure in our simulation. The total scattering spectra of the coupled system become

dominated by the spectral features of the BAPI exciton–photon Fano resonance, with shoulders indicating the contribution of the plasmonic particles(see Figure S8b). It resembles the raw experimental data well, as obtained prior to the subtraction of the BAPI background(see Figure S8). Figure 2.4c depicts the simulated absorption spectra of the AgNP coupled to BAPI grain, revealing a splitting with a profound dip shifted to 506 nm, roughly coinciding with the position observed in experimental scattering spectra with lower intensities (Figure 2.3c,e,f). This result suggests that the spectra in Figure 2.3c,e,f evidence coupling between the AgNP and the hybrid exciton–photon Fano resonance. It indicates that strongly scattering particles directly couple with the excitonic emitter, while for particles with smaller scattering cross sections and less intense scattering the scattering due to the microstructure dominates the lineshape. To estimate the coupling regime in the system, we extracted the spectral positions of the two maxima in the simulated scattering (blue) and absorption (green) spectra for AgNPs of different sizes, revealing a splitting of $\Omega = 387 \text{ meV}/350 \text{ meV}$. This value exceeds the mean line width of the AgNPs measured in single particle spectra of $\gamma_P = 202 \pm 11 \text{ meV}$ as well as the line width of the 2D perovskite ($\gamma_{2D} = 55 \pm 11 \text{ meV}$ among all fits in this work), fulfilling the requirements for strong coupling $\Omega > \gamma_P, \gamma_{2D}$. Together with the observed splitting in the simulated absorption spectra (Figure 2.4a,c), this value of the Rabi splitting indicates, at least in our simulations, the BAPI is strongly coupled to AgNPs. Although strong coupling is not the main focus of the present study, these results nevertheless indicate that Rabi splitting between the hybrid exciton–photon Fano resonance and the AgNP plasmon is likely occurring in this system with realistic sample properties, although final experimental evidence, for example, through photoluminescence splitting, cannot be observed here due to the strong signal of the surrounding BAPI.

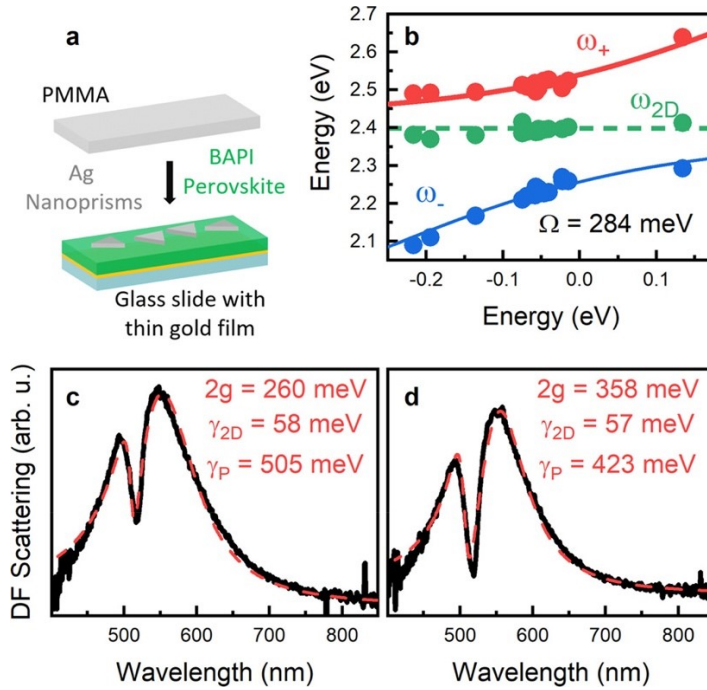


Figure 2.5. (a) Schematic illustrating the sample architecture for the AgNP-on-mirror system. (b) Energetic position of the lower maximum (ω^-), upper maximum (ω^+), and dip (ω_{2D}) in the spectra of individual AgNP-on-mirror. The red and blue line represent fits to a Jaynes-Cummings model. (c,d) Single particle dark-field spectra of individual AgNP-on-mirror cavities. Red dashed lines depict coupled oscillator fits to the data.

Finally, we turn to explore the out-of-plane mode of the excitonic transition by modifying our sample geometry using a particle-on-mirror design,⁷⁶ evaporating a chromium/gold layer prior to spin coating of the BAPI (cf. Figure 2.5a). In this architecture, the out-of-plane plasmon mode in the nanoparticle couples with mirror charges induced in the gold film, giving rise to a vertically coupled plasmon mode. In contrast to III–V or II–V quantum wells, transitions with out-of-plane polarization are not forbidden in 2D halide perovskite materials. While the main extinction peak for silver AgNPs is defined by the in-plane dipole resonance mode,⁷⁷ the dominant resonances in particle-on-mirror geometries are known to stem from out-of-plane modes.⁷⁶ Using unpolarized white light as the dark-field excitation source, we are able to excite modes polarized in both directions.⁷⁶ Compared to the bare AgNP, the AgNP-on-mirror cavities exhibit broader resonance peaks in single particle dark-field scattering, which are slightly shifted to the red (cf. Figure S9). In combination with the BAPI 2D perovskite, the spectra exhibit a pronounced peak splitting with a spectral dip around 515 nm; compare Figure 2.5c,d. As the scattering of the AgNP-on-mirror plasmonic system is significantly more intense than the BAPI scattering, we expect the cavities to couple directly to the exciton. Indeed, the observed spectra can be well described with a two-oscillator model (red dashed lines in Figure 2.5c,d) with one oscillator representing the excitonic transition of 2D perovskite (ω_{2D}, γ_{2D}) and the other the plasmonic resonance (ω_p, γ_p , replacing ω_0, γ_0 in Equation 1). Fits to 14 different single particle dark-field spectra reveal a mean coupling strength $\Omega = 2g$ of 327 ± 56 meV. Figure 2.5b depicts the spectral position of the two maxima ($\omega_{\pm}$) as well as the minimum, which relates to the spectral position of the BAPI excitonic transition (ω_{2D}), for the different spectra in relation to the detuning $\delta = \omega_p - \omega_{2D}$ (ω_p is calculated based on the knowledge of ω_{2D} , ω^+ and ω^-).⁷⁸ To extract the coupling strength, the spectral positions of the upper and lower branch of two coupled oscillators can be described within the quantum mechanical Jaynes-Cummings model (provided $\gamma_{2D} \ll \Omega$): (3) [Equation] We fit the experimental data in Figure 2.5b to obtain a coupling strength of 284 meV, in fair agreement with the value estimated by fitting the spectra directly. Although the coupling strength is in the same order of magnitude as the estimated coupling strength for the in-plane mode of the bare AgNPs, the system remains in the intermediate coupling regime due to the increased line width of the AgNP-on-mirror plasmonic cavity (mean value among the two-oscillator fits accounts for $\gamma_p = 472 \pm 92$ meV). This characterizes the spectral feature observed in the spectra of AgNP-on-mirror cavities coupled to BAPI as intermediate coupling rather than Rabi splitting.

2.4 Conclusion:

In conclusion, we have characterized scattering resonances in 2D halide perovskite films, both in isolation and when coupled to plasmonic cavities. This work not only confirms the potential of 2D perovskite quantum wells as excitonic materials in resonant nanophotonics but also underlines the importance of accounting for the film microstructure when considering 2D perovskites for photonic or optoelectronic applications. We show that the coupling between the scattering generated by the grainlike structure of the BAPI and the strongly bound excitonic transition gives rise to a pronounced exciton–photon Fano resonance, which can alter the light–matter interactions drastically. In combination with plasmonic cavities, we demonstrate tuning of this resonance. The comparison between different emitter-cavity systems indicates that the impact of the microstructure-related Fano interference depends on the optical cross-section of the coupled cavity resonator. Even though our findings were obtained on sample specifically designed to exhibit a high degree of microscopic inhomogeneity, they have broader importance for the usage of 2D perovskites coupled to cavities in general. The 2D perovskite layers of any thickness prepared via spin coating crystallize in grains with boundaries which inherently cause scattering, therefore the excitonic features cannot be fully decoupled from the structural optical properties. Thus, the impact of the microstructure on the optical properties of coupled 2D-perovskite-emitter-cavity systems need to be considered.

2.5 References:

- 1) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. *Nat. Photonics* 2014, 8 (7), 506–514.
- (2) Sun, S.; Salim, T.; Mathews, N.; Duchamp, M.; Boothroyd, C.; Xing, G.; Sum, T. C.; Lam, Y. M. The Origin of High Efficiency in Low-Temperature Solution-Processable Bilayer Organometal Halide Hybrid Solar Cells. *Energy Environ. Sci.* 2014, 7 (1), 399–407.
- (3) Stranks, S. D.; Burlakov, V. M.; Leijtens, T.; Ball, J. M.; Goriely, A.; Snaith, H. J. Recombination Kinetics in Organic-Inorganic Perovskites: Excitons, Free Charge, and Subgap States. *Phys. Rev. Appl.* 2014, 2 (3), 034007.
- (4) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M. Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. *Science* 2015, 347 (6221), 519–522.
- (5) Ji, K.; Anaya, M.; Abfalterer, A.; Stranks, S. D. Halide Perovskite Light-Emitting Diode Technologies. *Adv. Opt. Mater.* 2021, 9, 2002128.

- (6) Li, J.; Duan, J.; Yang, X.; Duan, Y.; Yang, P.; Tang, Q. Review on Recent Progress of Lead-Free Halide Perovskites in Optoelectronic Applications. *Nano Energy* 2021, 80, 105526.
- (7) Katan, C.; Mercier, N.; Even, J. Quantum and Dielectric Confinement Effects in Lower-Dimensional Hybrid Perovskite Semiconductors. *Chem. Rev.* 2019, 119 (5), 3140–3192.
- (8) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden-Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chem. Mater.* 2016, 28 (8), 2852–2867.
- (9) Blancon, J.-C.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Pedesseau, L.; Katan, C.; Kepenekian, M.; Soe, C. M. M.; Appavoo, K.; Sfeir, M. Y.; Tretiak, S.; Ajayan, P. M.; Kanatzidis, M. G.; Even, J.; Crochet, J. J.; Mohite, A. D. Extremely Efficient Internal Exciton Dissociation through Edge States in Layered 2D Perovskites. *Science* 2017, 355(6331), 1288–1292.
- (10) Straus, D. B.; Kagan, C. R. Electrons, Excitons, and Phonons in Two-Dimensional Hybrid Perovskites: Connecting Structural, Optical, and Electronic Properties. *J. Phys. Chem. Lett.* 2018, 9 (6), 1434–1447.
- (11) Fieramosca, A.; De Marco, L.; Passoni, M.; Polimeno, L.; Rizzo, A.; Rosa, B. L. T.; Cruciani, G.; Dominici, L.; De Giorgi, M.; Gigli, G.; Andreani, L. C.; Gerace, D.; Ballarini, D.; Sanvitto, D. Tunable Out-of-Plane Excitons in 2D Single-Crystal Perovskites. *ACS Photonics* 2018, 5 (10), 4179–4185.
- (12) Zhang, Q.; Su, R.; Du, W.; Liu, X.; Zhao, L.; Ha, S. T.; Xiong, Q. Advances in Small Perovskite-Based Lasers. *Small Methods* 2017, 1(9), 1700163.
- (13) Schlaus, A. P.; Spencer, M. S.; Zhu, X.-Y. Light–Matter Interaction and Lasing in Lead Halide Perovskites. *Acc. Chem. Res.* 2019, 52 (10), 2950–2959.
- (14) Park, K.; Lee, J. W.; Kim, J. D.; Han, N. S.; Jang, D. M.; Jeong, S.; Park, J.; Song, J. K. Light–Matter Interactions in Cesium Lead Halide Perovskite Nanowire Lasers. *J. Phys. Chem. Lett.* 2016, 7 (18), 3703–3710. [Nano Letters pubs.acs.org/NanoLett](https://pubs.acs.org/NanoLett)
[Letter https://doi.org/10.1021/acs.nanolett.1c01504](https://doi.org/10.1021/acs.nanolett.1c01504) *Nano Lett.* 2021, 21, 6124–6131
- (15) Carretero-Palacios, S.; Calvo, M. E.; Míguez, H. Absorption Enhancement in Organic-Inorganic Halide Perovskite Films with Embedded Plasmonic Gold Nanoparticles. *J. Phys. Chem. C* 2015, 119(32), 18635–18640.
- (16) Li, H.; He, F.; Ji, C.; Zhu, W.; Xu, Y.; Zhang, W.; Meng, X.; Fang, X.; Ding, T. Purcell-Enhanced Spontaneous Emission from Perovskite Quantum Dots Coupled to Plasmonic Crystal. *J. Phys. Chem. C* 2019, 123 (41), 25359–25365.
- (17) Adl, H. P.; Gorji, S.; Habil, M. K.; Suárez, I.; Chirvony, V. S.; Gualdrón-Reyes, A. F.; Mora-Seró, I.; Valencia, L. M.; de la Mata, M.; Hernández-Saz, J.; Molina, S. I.; Zapata-Rodríguez, C. J.; Martínez-Pastor, J. P. Purcell Enhancement and Wavelength Shift of

Emitted Light by CsPbI₃ Perovskite Nanocrystals Coupled to Hyperbolic Metamaterials. *ACS Photonics* 2020, 7 (11), 3152–3160.

(18) Adamo, G.; Swaha Krishnamoorthy, H. N.; Cortecchia, D.; Chaudhary, B.; Nalla, V.; Zheludev, N. I.; Soci, C. Metamaterial Enhancement of Metal-Halide Perovskite Luminescence. *Nano Lett.* 2020, 20, 7906.

(19) Yang, Z.; Pelton, M.; Bodnarchuk, M. I.; Kovalenko, M. V.; Waks, E. Spontaneous Emission Enhancement of Colloidal Perovskite Nanocrystals by a Photonic Crystal Cavity. *Appl. Phys. Lett.* 2017, 111(22), 221104.

(20) Zhang, X.; Shi, H.; Dai, H.; Zhang, X.; Sun, X. W.; Zhang, Z. Exciton-Polariton Properties in Planar Microcavity of Millimeter-Sized Two-Dimensional Perovskite Sheet. *ACS Appl. Mater. Interfaces* 2020, 12 (4), 5081–5089.

(21) Du, W.; Zhang, S.; Zhang, Q.; Liu, X. Recent Progress of Strong Exciton–Photon Coupling in Lead Halide Perovskites. *Adv. Mater.* 2019, 31 (45), 1804894.

(22) Fieramosca, A.; Polimeno, L.; Ardizzone, V.; De Marco, L.; Pugliese, M.; Maiorano, V.; De Giorgi, M.; Dominici, L.; Gigli, G.; Gerace, D.; Ballarini, D.; Sanvitto, D. Two-Dimensional Hybrid Perovskites Sustaining Strong Polariton Interactions at Room Temperature. *Sci. Adv.* 2019, 5 (5), eaav9967.

(23) Shen, T.; Siontas, S.; Pacifici, D. Plasmon-Enhanced Thin-Film Perovskite Solar Cells. *J. Phys. Chem. C* 2018, 122 (41), 23691–23697.

(24) Li, Y.-F.; Kou, Z.-L.; Feng, J.; Sun, H.-B. Plasmon-Enhanced Organic and Perovskite Solar Cells with Metal Nanoparticles. *Nanophotonics* 2020, 9 (10), 3111–3133.

(25) Gu, L.; Wen, K.; Peng, Q.; Huang, W.; Wang, J. Surface-Plasmon-Enhanced Perovskite Light-Emitting Diodes. *Small* 2020, 16(30), 2001861.

(26) Su, R.; Diederichs, C.; Wang, J.; Liew, T. C. H.; Zhao, J.; Liu, S.; Xu, W.; Chen, Z.; Xiong, Q. Room-Temperature Polariton Lasing in All-Inorganic Perovskite Nanoplatelets. *Nano Lett.* 2017, 17 (6), 3982–3988.

(27) Makarov, S.; Furasova, A.; Tiguntseva, E.; Hemmetter, A.; Berestennikov, A.; Pushkarev, A.; Zakhidov, A.; Kivshar, Y. Halide-Perovskite Resonant Nanophotonics. *Adv. Opt. Mater.* 2019, 7 (1), 1800784.

(28) Su, R.; Ghosh, S.; Wang, J.; Liu, S.; Diederichs, C.; Liew, T. C. H.; Xiong, Q. Observation of Exciton Polariton Condensation in a Perovskite Lattice at Room Temperature. *Nat. Phys.* 2020, 16 (3), 301–306.

(29) Pyles, H.; Zhang, S.; De Yoreo, J. J.; Baker, D. Controlling Protein Assembly on Inorganic Crystals through Designed Protein Interfaces. *Nature* 2019, 571 (7764), 251–256.

- (30) Zhao, Y.; Xu, C. DNA-Based Plasmonic Heterogeneous Nanostructures: Building, Optical Responses, and Bioapplications. *Adv. Mater.* 2020, 32 (41), 1907880.
- (31) Chen, Y.; Munechika, K.; Ginger, D. S. Dependence of Fluorescence Intensity on the Spectral Overlap between Fluorophores and Plasmon Resonant Single Silver Nanoparticles. *Nano Lett.* 2007, 7(3), 690–696.
- (32) Chen, J. I. L.; Chen, Y.; Ginger, D. S. Plasmonic Nanoparticle Dimers for Optical Sensing of DNA in Complex Media. *J. Am. Chem. Soc.* 2010, 132 (28), 9600–9601.
- (33) Wang, B.; Yu, P.; Wang, W.; Zhang, X.; Kuo, H. C.; Xu, H.; Wang, Z. M. High-Q Plasmonic Resonances: Fundamentals and Applications. *Adv. Opt. Mater.* 2021, 9, 2001520.
- (34) Miroshnichenko, A. E.; Flach, S.; Kivshar, Y. S. Fano Resonances in Nanoscale Structures. *Rev. Mod. Phys.* 2010, 82 (3), 2257–2298.
- (35) Bekele, D.; Yu, Y.; Yvind, K.; Mork, J. In-Plane Photonic Crystal Devices Using Fano Resonances. *Laser Photonics Rev.* 2019, 13(12), 1900054.
- (36) Fano, U. Effects of Configuration Interaction on Intensities and Phase Shifts. *Phys. Rev.* 1961, 124 (6), 1866–1878.
- (37) Limonov, M. F.; Rybin, M. V.; Poddubny, A. N.; Kivshar, Y. S. Fano Resonances in Photonics. *Nat. Photonics* 2017, 11 (9), 543–554.
- (38) Pelton, M.; Storm, S. D.; Leng, H. Strong Coupling of Emitters to Single Plasmonic Nanoparticles: Exciton-Induced Transparency and Rabi Splitting. *Nanoscale* 2019, 11 (31), 14540–14552.
- (39) Liu, N.; Liedl, T. DNA-Assembled Advanced Plasmonic Architectures. *Chem. Rev.* 2018, 118 (6), 3032–3053.
- (40) Thakkar, N.; Rea, M. T.; Smith, K. C.; Heylman, K. D.; Quillin, S. C.; Knapper, K. A.; Horak, E. H.; Masiello, D. J.; Goldsmith, R. H. Sculpting Fano Resonances to Control Photonic-Plasmonic Hybridization. *Nano Lett.* 2017, 17 (11), 6927–6934.
- (41) Pan, F.; Smith, K. C.; Nguyen, H. L.; Knapper, K. A.; Masiello, D. J.; Goldsmith, R. H. Elucidating Energy Pathways through Simultaneous Measurement of Absorption and Transmission in a Coupled Plasmonic-Photonic Cavity. *Nano Lett.* 2020, 20 (1), 50–58.
- (42) Luk'yanchuk, B.; Zheludev, N. I.; Maier, S. A.; Halas, N. J.; Nordlander, P.; Giessen, H.; Chong, C. T. The Fano Resonance in Plasmonic Nanostructures and Metamaterials. *Nat. Mater.* 2010, 9(9), 707–715.
- (43) Sugawara, Y.; Kelf, T. A.; Baumberg, J. J.; Abdelsalam, M. E.; Bartlett, P. N. Strong Coupling between Localized Plasmons and Organic Excitons in Metal Nanovoids. *Phys. Rev. Lett.* 2006, 97 (26), 266808.

- (44) Sonnefraud, Y.; Verellen, N.; Sobhani, H.; Vandenbosch, G. A.E.; Moshchalkov, V. V.; Van Dorpe, P.; Nordlander, P.; Maier, S. A. Experimental Realization of Subradiant, Superradiant, and Fano Resonances in Ring/Disk Plasmonic Nanocavities. *ACS Nano* 2010, 4(3), 1664–1670.
- (45) Liu, W.; Lee, B.; Naylor, C. H.; Ee, H.-S.; Park, J.; Johnson, A.T. C.; Agarwal, R. Strong Exciton-Plasmon Coupling in MoS₂ Coupled with Plasmonic Lattice. *Nano Lett.* 2016, 16 (2), 1262–1269.
- (46) Shang, Q.; Zhang, S.; Liu, Z.; Chen, J.; Yang, P.; Li, C.; Li, W.; Zhang, Y.; Xiong, Q.; Liu, X.; Zhang, Q. Surface Plasmon Enhanced Strong Exciton–Photon Coupling in Hybrid Inorganic–Organic Perovskite Nanowires. *Nano Lett.* 2018, 18 (6), 3335–3343.
- (47) Zhang, S.; Shang, Q.; Du, W.; Shi, J.; Wu, Z.; Mi, Y.; Chen, J.; Liu, F.; Li, Y.; Liu, M.; Zhang, Q.; Liu, X. Strong exciton–photon Coupling in Hybrid Inorganic–Organic Perovskite Micro/Nanowires. *Adv. Opt. Mater.* 2018, 6 (2), 1701032.
- (48) Schünemann, S.; Brittman, S.; Chen, K.; Garnett, E. C.; Tüysüz, H. Halide Perovskite 3D Photonic Crystals for Distributed Feedback Lasers. *ACS Photonics* 2017, 4 (10), 2522–2528.
- (49) Hou, S.; Xie, A.; Xie, Z.; Tobing, L. Y. M.; Zhou, J.; Tjahjana, L.; Yu, J.; Hettiarachchi, C.; Zhang, D.; Dang, C.; Teo, E. H. T.; Birowosuto, M. D.; Wang, H. Concurrent Inhibition and Redistribution of Spontaneous Emission from All Inorganic Perovskite Photonic Crystals. *ACS Photonics* 2019, 6 (6), 1331–1337.
- (50) Huang, C.; Zhang, C.; Xiao, S.; Wang, Y.; Fan, Y.; Liu, Y.; Zhang, N.; Qu, G.; Ji, H.; Han, J.; Ge, L.; Kivshar, Y.; Song, Q. Ultrafast Control of Vortex Microlasers. *Science* 2020, 367 (6481), 1018–1021.
- (51) Sun, W.; Liu, Y.; Qu, G.; Fan, Y.; Dai, W.; Wang, Y.; Song, Q.; Han, J.; Xiao, S. Lead Halide Perovskite Vortex Microlasers. *Nat. Commun.* 2020, 11 (1), 4862 DOI: 10.1038/s41467-020-18669-1.
- (52) Fan, Y.; Wang, Y.; Zhang, N.; Sun, W.; Gao, Y.; Qiu, C.; Song, Q.; Xiao, S. Resonance-Enhanced Three-Photon Luminescence via Lead Nano Letters pubs.acs.org/NanoLett Letter <https://doi.org/10.1021/acs.nanolett.1c01504> *Nano Lett.* 2021, 21, 6124–6131 10.1021/acs.nanolett.1c01504 Halide Perovskite Metasurfaces for Optical Encoding. *Nat. Commun.* 2019, 10, 1–8.
- (53) Li, Z.; Smalley, J. S. T.; Haroldson, R.; Lin, D.; Hawkins, R.; Gharajeh, A.; Moon, J.; Hou, J.; Zhang, C.; Hu, W.; Zakhidov, A.; Gu, Q. Active Perovskite Hyperbolic Metasurface. *ACS Photonics* 2020, 7(7), 1754–1761.
- (54) Franceschini, P.; Carletti, L.; Pushkarev, A. P.; Preda, F.; Perri, A.; Tognazzi, A.; Ronchi, A.; Ferrini, G.; Pagliara, S.; Banfi, F.; Polli, D.; Cerullo, G.; De Angelis, C.; Makarov, S. V.;

- Giannetti, C. Tuning the Ultrafast Response of Fano Resonances in Halide Perovskite Nanoparticles. *ACS Nano* 2020, 14 (10), 13602–13610.
- (55) Stoddard, R. J.; Dunlap-Shohl, W. A.; Qiao, H.; Meng, Y.; Kau, W. F.; Hillhouse, H. W. Forecasting the Decay of Hybrid Perovskite Performance Using Optical Transmittance or Reflected Dark-Field Imaging. *ACS Energy Lett.* 2020, 5 (3), 946–954.
- (56) Schwarz, L.; Cartarius, H.; Wunner, G.; Heiss, W. D.; Main, J. Fano Resonances in Scattering: An Alternative Perspective. *Eur. Phys. J. D* 2015, 69 (8), 1–4.
- (57) Rybin, M. V.; Khanikaev, A. B.; Inoue, M.; Samusev, K. B.; Steel, M. J.; Yushin, G.; Limonov, M. F. Fano Resonance between Mie and Bragg Scattering in Photonic Crystals. *Phys. Rev. Lett.* 2009, 103(2), 1–4.
- (58) Thakkar, N.; Rea, M. T.; Smith, K. C.; Heylman, K. D.; Quillin, S. C.; Knapper, K. A.; Horak, E. H.; Masiello, D. J.; Goldsmith, R. H. Sculpting Fano Resonances To Control Photonic-Plasmonic Hybridization. *Nano Lett.* 2017, 17 (11), 6927–6934.
- (59) Wu, X.; Gray, S. K.; Pelton, M. Quantum-Dot-Induced Transparency in a Nanoscale Plasmonic Resonator. *Opt. Express* 2010, 18 (23), 23633.
- (60) Zengin, G.; Johansson, G.; Johansson, P.; Antosiewicz, T. J.; Käll, M.; Shegai, T. Approaching the Strong Coupling Limit in Single Plasmonic Nanorods Interacting with J-Aggregates. *Sci. Rep.* 2013, 3(1), 3074.
- (61) Tiguntseva, E. Y.; Baranov, D. G.; Pushkarev, A. P.; Munkhbat, B.; Komissarenko, F.; Franckevičius, M.; Zakhidov, A. A.; Shegai, T.; Kivshar, Y. S.; Makarov, S. V. Tunable Hybrid Fano Resonances in Halide Perovskite Nanoparticles. *Nano Lett.* 2018, 18 (9), 5522–5529.
- (62) Cai, C.; Bi, G.; Xu, T. Fano Resonance in the CsPbBr₃ Nanocrystal/Ag Nanostructure through the Exciton-Plasmon Coupling. *Appl. Phys. Lett.* 2019, 115 (16), 161602.
- (63) Chen, J.; Zhang, Q.; Shi, J.; Zhang, S.; Du, W.; Mi, Y.; Shang, Q.; Liu, P.; Sui, X.; Wu, X.; Wang, R.; Peng, B.; Zhong, H.; Xing, G.; Qiu, X.; Sum, T. C.; Liu, X. Room Temperature Continuous-Wave Excited Biexciton Emission in Perovskite Nanoplatelets via Plasmonic Nonlinear Fano Resonance. *Commun. Phys.* 2019, 2 (1), 80.
- (64) Xue, C.; Mirkin, C. A. PH-Switchable Silver Nanoprism Growth Pathways. *Angew. Chem., Int. Ed.* 2007, 46 (12), 2036–2038.
- (65) Jin, R.; Charles Cao, Y.; Hao, E.; Métraux, G. S.; Schatz, G. C.; Mirkin, C. A. Controlling Anisotropic Nanoparticle Growth through Plasmon Excitation. *Nature* 2003, 425 (6957), 487–490.

- (66) Kulkarni, A. P.; Munechika, K.; Noone, K. M.; Smith, J. M.; Ginger, D. S. Phase Transfer of Large Anisotropic Plasmon Resonant Silver Nanoparticles from Aqueous to Organic Solution. *Langmuir* 2009, 25 (14), 7932–7939.
- (67) Antosiewicz, T. J.; Apell, S. P.; Shegai, T. Plasmon-Exciton Interactions in a Core-Shell Geometry: From Enhanced Absorption to Strong Coupling. *ACS Photonics* 2014, 1 (5), 454–463.
- (68) Houdré, R. Early Stages of Continuous Wave Experiments on Cavity-Polaritons. *Phys. Status Solidi B* 2005, 242 (11), 2167–2196.
- (69) Luo, Y.; Zhao, J. Plasmon-Exciton Interaction in Colloidally Fabricated Metal Nanoparticle-Quantum Emitter Nanostructures. *Nano Res.* 2019, 12 (9), 2164–2171.
- (70) Wen, J.; Wang, H.; Wang, W.; Deng, Z.; Zhuang, C.; Zhang, Y.; Liu, F.; She, J.; Chen, J.; Chen, H.; Deng, S.; Xu, N. Room-Temperature Strong Light–Matter Interaction with Active Control in Single Plasmonic Nanorod Coupled with Two-Dimensional Atomic Crystals. *Nano Lett.* 2017, 17 (8), 4689–4697.
- (71) Stührenberg, M.; Munkhbat, B.; Baranov, D. G.; Cuadra, J.; Yankovich, A. B.; Antosiewicz, T. J.; Olsson, E.; Shegai, T. Strong light–matter Coupling between Plasmons in Individual Gold Bi-Pyramids and Excitons in Mono- and Multilayer WSe₂. *Nano Lett.* 2018, 18 (9), 5938–5945.
- (72) Geisler, M.; Cui, X.; Wang, J.; Rindzevicius, T.; Gammelgaard, L.; Jessen, B. S.; Gonçalves, P. A. D.; Todisco, F.; Bøggild, P.; Boisen, A.; Wubs, M.; Mortensen, N. A.; Xiao, S.; Stenger, N. Single-Crystalline Gold Nanodisks on WS₂ Mono- and Multilayers for Strong Coupling at Room Temperature. *ACS Photonics* 2019, 6 (4), 994–1001.
- (73) Wang, H.; Wen, J.; Wang, W.; Xu, N.; Liu, P.; Yan, J.; Chen, H.; Deng, S. Resonance Coupling in Heterostructures Composed of Silicon Nanosphere and Monolayer WS₂: A Magnetic-Dipole-Mediated Energy Transfer Process. *ACS Nano* 2019, 13 (2), 1739–1750.
- (74) Munkhbat, B.; Baranov, D. G.; Bisht, A.; Hoque, M. A.; Karpiak, B.; Dash, S. P.; Shegai, T. Electrical Control of Hybrid Monolayer Tungsten Disulfide-Plasmonic Nanoantenna Light–Matter States at Cryogenic and Room Temperatures. *ACS Nano* 2020, 14 (1), 1196–1206.
- (75) Handbook of Optical Constants of Solids; Palik, E. D., Ed.; Elsevier, 1985. (76) Li, G.-C.; Zhang, Q.; Maier, S. A.; Lei, D. Plasmonic Particle-on-Film Nanocavities: A Versatile Platform for Plasmon-Enhanced Spectroscopy and Photochemistry. *Nanophotonics* 2018, 7 (12), 1865–1889.
- (77) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. Photoinduced Conversion of Silver Nanospheres to Nanoprisms. *Science* 2001, 294 (5548), 1901–1903.
- (78) Chikkaraddy, R.; De Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J. Single-Molecule Strong Coupling at Room Temperature in Plasmonic Nanocavities. *Nature* 2016, 535 (7610), 127–130.

Chapter 3: Ligand Equilibrium Influences Photoluminescence Blinking in CsPbBr₃: A Change Point Analysis of Widefield Imaging Data

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My contributions on this project include implementing the widefield fluorescence blinking setup, parts of the quantum dot synthesis and characterization (focused on Oleic Acid/ Oleyl Amine synthesis and performing the concentration dependent photoluminescence and photoluminescence lifetime measurements.

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3.1 Overview:

Photoluminescence intermittency remains one of the biggest challenges to realizing perovskite quantum dots (QDs) as scalable single photon emitters. We compare CsPbBr₃ QDs capped with different ligands, lecithin, and a combination of oleic acid and oleylamine, to elucidate the role of surface chemistry on photoluminescence intermittency. We employ widefield photoluminescence microscopy, sampling the blinking behavior of hundreds of QDs. Using change point analysis, we achieve the robust classification of blinking trajectories, and we analyze representative distributions from large numbers of QDs ($N_{\text{lecithin}} = 1308$, $N_{\text{oleic acid/oleylamine}} = 1317$). We find that lecithin suppresses blinking in CsPbBr₃ QDs compared to oleic acid/oleylamine. Under common experimental conditions, lecithin-capped QDs are 7.5 times more likely to be non-blinking and spend 2.5 times longer in their most emissive state, despite both QDs having nearly identical solution photoluminescence quantum yields. We measure photoluminescence as a function of dilution and show that the differences between lecithin and oleic acid/oleylamine capping emerge at low concentrations during preparation for single particle experiments. From experiment and first principles calculations, we attribute the differences in lecithin and oleic acid/oleylamine performance to differences in their ligand binding equilibria. Consistent with our experimental data, density functional theory calculations suggest a stronger binding affinity of lecithin to the QD surface compared to oleic acid/oleylamine, implying a reduced likelihood of ligand desorption during dilution. These results suggest that using more tightly binding ligands is a necessity for

surface passivation and consequently, blinking reduction in perovskite QDs used for single particle and quantum light experiments.

3.2 Introduction:

Inorganic cesium lead bromide (CsPbBr_3) perovskite quantum dots (QDs) are promising solution-processable materials for a wide range of optoelectronic applications.¹ These materials exhibit high (>90%) photoluminescence quantum yields (PLQY),² narrow ensemble photoluminescence linewidths,³ and emission spectra that can be tuned throughout the visible region.⁴ These properties have motivated increased efforts to use perovskite QDs as the active layer in devices such as light-emitting diodes (QLEDs),⁵ photovoltaics,⁶ and even X-ray detectors.⁷ More recently, their high degree of quantum coherence has positioned CsPbBr_3 QDs as leading candidates for next-generation quantum light sources - scalable, coherent single photon emitters⁸⁻¹¹

Successful single photon emitters must demonstrate a high degree of single photon purity, have long coherence times, and be deterministically positioned within nanophotonic cavities.¹² Undesirable characteristics for single emitter candidates include photobleaching, particle heterogeneity, spectral diffusion, and photoluminescence intermittency.¹² Prior reports for CsPbBr_3 QDs have shown high single photon purity,^{13,14} quantum interference between sequential photons,¹⁵ and progress towards deterministic cavity positioning.¹⁶⁻¹⁸ However, as even the highest quality perovskite QDs currently exhibit photoluminescence intermittency and spectral diffusion, events which have been linked in other quantum dot systems;^{12,19} these challenges must be overcome to further improve these systems and reduce their photoluminescence linewidth.^{8,20,21}

Quantum-confined materials possess high surface-area-to-volume ratios, meaning their properties are heavily influenced by their surfaces as has been extensively explored for II-VI quantum dots.²²⁻²⁷ Improving CsPbBr_3 single photon emitters requires a more fundamental understanding and optimization of their surface chemistry.^{12,28} CsPbBr_3 QDs are often described as defect tolerant and can achieve narrow linewidths and high PLQYs without the use of a core-shell heterostructure (as in II-VI or III-VI QDs). However as defect formation is still a thermodynamically favorable process, CsPbBr_3 QDs require an organic ligand shell for both colloidal stability and surface defect passivation.^{29,30} Due to the highly ionic bonding character of CsPbBr_3 QDs, many popular ligand systems contain both positive and negative charges, either in the form of zwitterions or monodentate ligand pairs.^{31,32} The identity of this ligand layer plays a major role in modulating the properties of CsPbBr_3 QDs, including PLQY,³³ linewidth,³⁴ device performance,³⁵⁻³⁹ and colloidal stability.^{31,32}

Sustained synthetic efforts have identified several promising ligand species for CsPbBr_3 QDs. These include monodentate ligand pairs, like oleic acid/oleylamine⁴⁰, quaternary amines, like didodecyldimethylammonium bromide^{41,42} and multi-dentate ligands, such as sulfobetaine,⁴³ lecithin,⁴⁴ diquaternary amines,³⁴ and phosphonic acids.^{45,46} Despite ligands resulting in

measurably different ensemble properties, including long-term colloidal stability,⁴⁴ and surface-defect induced electronic traps³⁷ there has been a lack of emphasis on understanding how these ligands affect the properties of single QDs. While some multi-dentate ligands display improved ensemble linewidths and near unity PLQY,^{43,44} results from device integration are mixed,³⁸ underscoring the need for application-specific investigations, particularly at the single-particle level.

One way to probe the effects of surface chemistry on the optical properties of individual QDs is through monitoring their photoluminescence intermittency, or blinking.^{47,48} Like other single photon emitters,¹² CsPbBr₃ QDs exhibit time-dependent variations in photoluminescence intensity at the single emitter level.⁴⁹ This variation in photoluminescence intensity arises from fluctuations in the non-radiative decay rates.⁴⁹ Prior studies of blinking in perovskite QDs have focused on understanding and passivating defects – through temperature-dependent measurements⁵⁰, and in-situ halide treatments.⁵¹ However, relatively few studies have examined how varying the surface ligand chemistry of CsPbBr₃ QDs affects their blinking behavior.

Here we study the blinking dynamics of CsPbBr₃ QDs prepared via two different synthetic routes that result in dots passivated with two different ligands, a typical oleic acid/oleylamine based hot injection resulting in oleic acid/oleylamine-capped dots, and a recently reported room-temperature slow growth synthesis, leading to lecithin-capped dots via ligand exchange.⁵² We utilize widefield photoluminescence microscopy and implement an automated particle selection and unique change point analysis algorithm adapted to the noise profile of scientific cameras. This approach allows for significantly improved throughput and more robust sampling of the QD distributions. We find that, while both syntheses produce QDs with comparable PLQYs as synthesized, the lecithin-capped dots show dramatically reduced blinking when prepared and studied at the single particle level. We show that this difference primarily arises from the difference in ligand capping, and, despite similar ensemble characteristics, lecithin passivation leads to a dramatic decrease in blinking, seen through an improved ON percent distribution, a larger ON/OFF ratio, and a larger non-blinking fraction. We reconcile the apparent discrepancy between the ensemble photoluminescence properties and those of single dots by showing that the oleic acid/oleylamine dots suffer from significant degradation of their photoluminescence properties upon dilution to appropriate concentrations for single particle experiments. We present experimental evidence and theoretical analysis using density functional theory (DFT) calculations that rationalize these differences in terms of the ligand binding affinity, with lecithin showing significantly stronger binding to the QD surface compared to oleic acid/oleylamine.

3.3 Results and Discussion:

We synthesized CsPbBr₃ QDs using one of two different methods from the literature to produce QDs with either oleic acid/oleylamine⁴⁰ or lecithin⁵² as surface ligands (Figure 3.1a). Figures 3.1c and 3.1d show the UV-Vis absorption and photoluminescence spectra for representative synthetic batches of oleic acid/oleylamine-capped, and lecithin-capped dots, respectively. We find that the two ligand compositions impart similar ensemble properties to the QDs. The band-edge absorbance onset is nearly identical for both sets of QDs. However, lecithin-capped QDs show distinctly sharper excitonic features due to their spheroidal shape. The lecithin dots exhibit an emission at 506 nm with a FWHM of 19 nm, while the photoluminescence of oleic acid/oleylamine-capped QDs is slightly broader, as expected from the hot-injection synthesis, with an emission maximum at 509 nm and a 24 nm FWHM (Figures 1c and 1d). The lecithin-capped QDs batches tend to have slightly higher PLQY ($95 \pm 2\%$ compared to $90 \pm 5\%$) but shorter lifetimes (4.43 ± 0.04 ns vs 4.95 ± 0.02 ns) than oleic acid/oleylamine-capped QDs (Figure 3.1b-d). The shorter lifetime is qualitatively consistent with predictions for a spherical crystal habit, which was predicted to have faster recombination due to difference in dielectric confinement and asymmetry of the photon's electric field between spherical and cubic QDs at comparable sizes.⁵³ Interestingly, the spheroidal lecithin-capped QDs also show a low-energy tail in the photoluminescence lineshape, consistent with prior reports.^{52,54} From the absorption band edge,⁵⁵ the oleic acid/oleylamine-capped QDs are determined to be 9.5 ± 2.7 nm, comparable in size to our 9.7 ± 1.5 nm lecithin-capped QDs, which were measured via TEM (Figure S1).

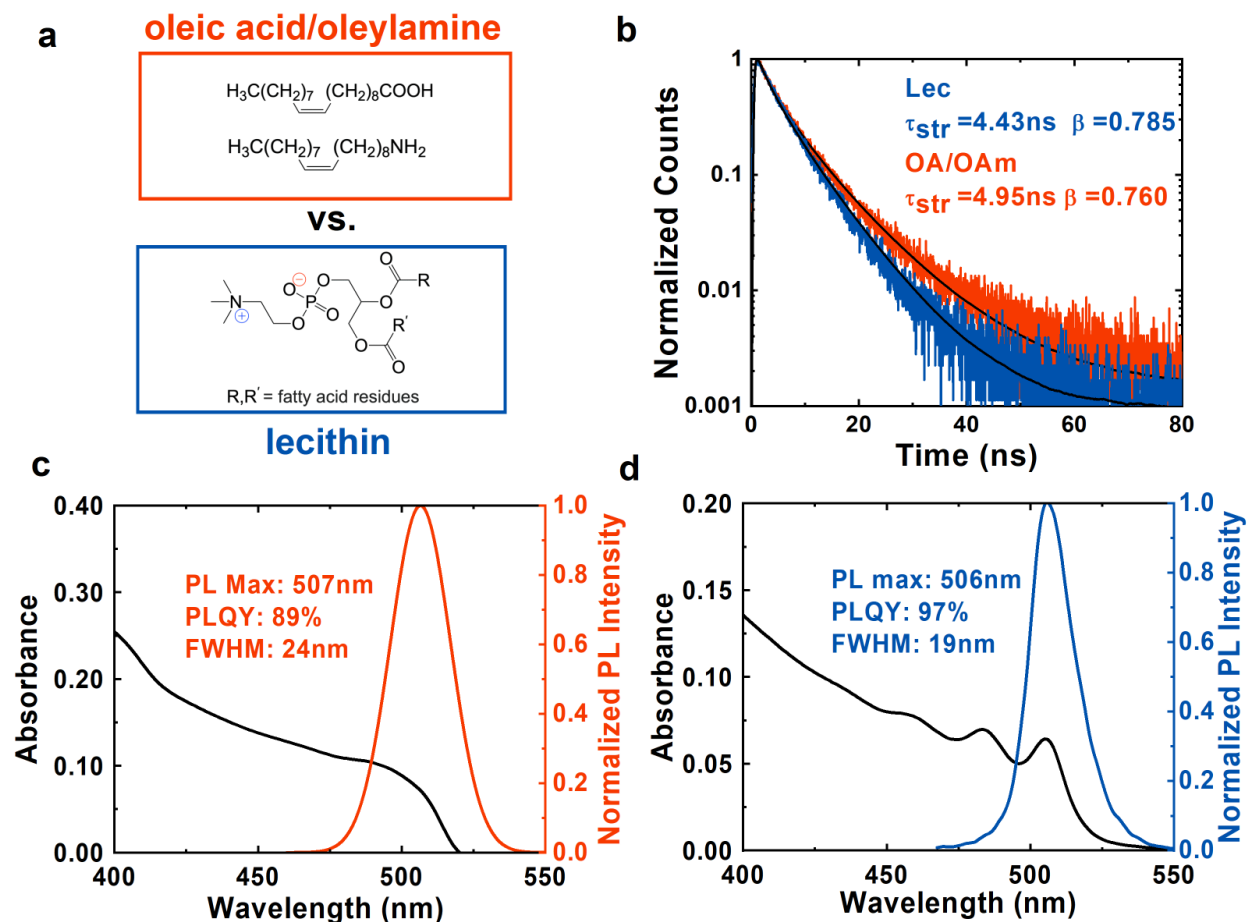


Figure 3.1. Ensemble characterization of lecithin and oleylamine/oleic acid capped QDs: **a)** Chemical structures of zwitterionic lecithin (blue) and the monodentate ligand pair oleic acid (OA) and oleylamine (OAm) (red). **b)** Ensemble lifetimes of oleic acid/oleylamine-capped and lecithin-capped CsPbBr₃ QDs fit to a stretch exponential function (Equation 1) **c)** Ensemble solution characterization of oleic acid/oleylamine-capped CsPbBr₃ QDs **d)** Ensemble solution characterization lecithin-capped CsPbBr₃ QDs.

Studies of QD blinking statistics are commonly limited by two factors: the quantity of observed QDs and the analysis method.^{56,57} Using confocal microscopy, blinking traces must be collected in series; limiting typical sample distributions to tens of QDs.⁵⁸ Instead, we collect blinking traces in parallel using widefield photoluminescence microscopy, allowing rapid collection of thousands of blinking traces.⁵⁹ Perovskite QDs also display complex blinking statistics, including multi-level dynamics, beyond simple two-level ON/OFF dynamics.⁶⁰ A data set of this size and complexity requires an automated, robust analysis method to extract accurate statistics. We satisfy this requirement through change point analysis (CPA) adapted to the noise profile of scientific cameras.^{61–63} This combination of widefield imaging and CPA provides more representative sampling than previously possible, enabling a more accurate description of intermittency in these systems.

Figure 3.2 provides an overview of our analysis method on a representative image sequence of lecithin-capped CsPbBr₃ QDs. After the collection of a widefield image sequence, our analysis method works to extract the time series describing each QD's behavior and completes an unbiased classification of the photoluminescence trajectory. Figure 3.2a shows the mean intensity image of a widefield image sequence. Single QDs (shown circled in red and labeled with a white number) are identified by an automated particle picking algorithm, designed to select small bright spots from a dark background.⁶⁴ Figure 3.2b shows the time series behavior of representative QDs (2, 6, and 11) extracted from the same widefield image sequence as Figure 2a. We generate these time series by intensity averaging the central pixels of selected QDs at each image in the sequence. Figures 3.2c and 3.2d show the photoluminescence trajectories identified for QD 2 (2-level) and QD 6 (3-level) respectively. We use change point analysis^{61,62}, which applies Bayesian statistics to find the photoluminescence trajectory which best describes a time series and to assign states to the photoluminescence vs. time trajectories. The methods section contains additional details about the analysis. Figure S2 shows representative trajectories from the oleic acid/oleylamine-capped quantum dots.

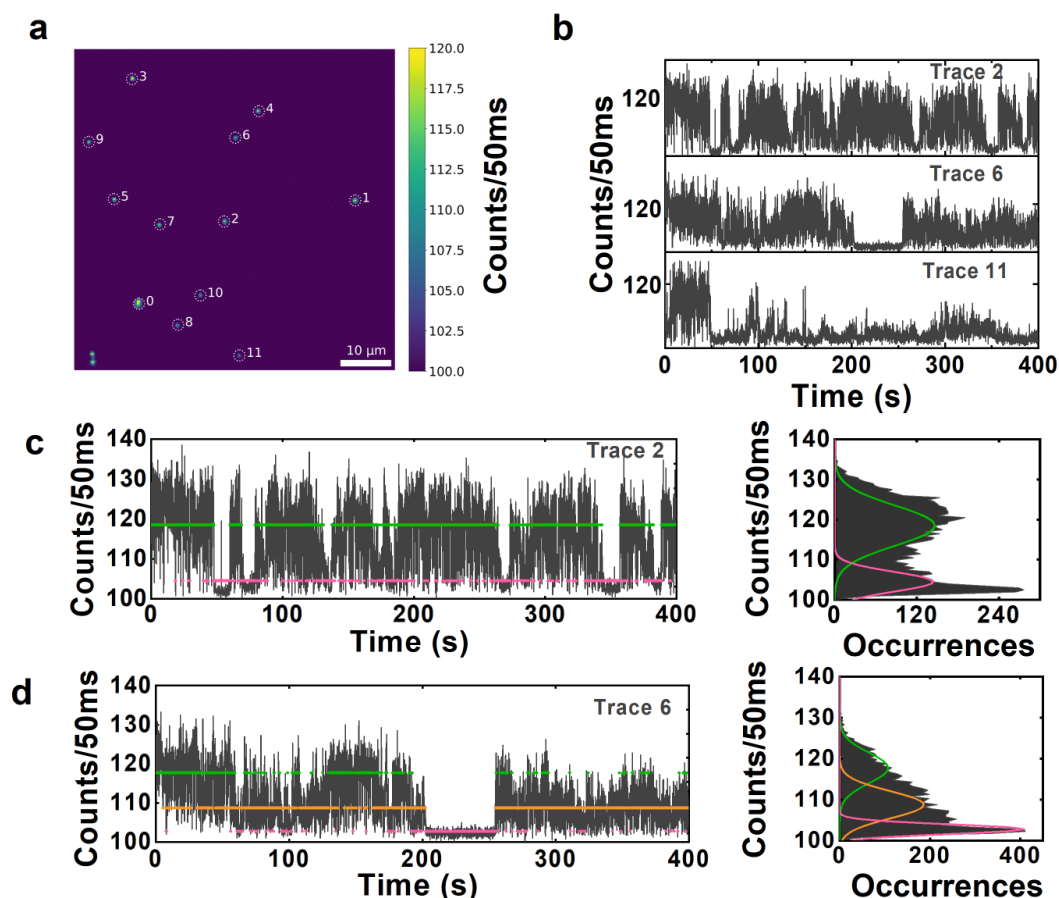


Figure 3.2. Workflow of widefield photoluminescence microscopy measurements. a) Automated particle selection results; particle selections are plotted on the mean intensity image in the sequence. For clarity, we show results from

a small region of the overall image. Red circles labeled with a white number indicate quantum dot locations. **b)** Photoluminescence time series extracted from the selected regions in 2a corresponding to identified QDs 2, 6 and 11. **c)** CPA fitting of the time series from QD 2 (a). CPA finds that this time series is best described by a photoluminescence trajectory containing two average intensity levels (pink and green). **d)** CPA fitting of the time series from QD 6 (a). CPA finds that this time series is best described by a photoluminescence trajectory containing three average intensity levels (pink, orange and green).

To classify the blinking dynamics of lecithin-capped QD samples systematically, we analyzed the dynamics of five separate synthetic batches of comparable quality (Table S1 and Figure S3) to control for batch-to-batch variation, which can often serve as a confounding variable.⁶⁵ Figures S4 and S5 explore the statistics for these five synthetic batches in more detail. The blinking statistics of lecithin-capped QDs we report in the main text of this paper are aggregated from the blinking behavior of all five batches.

We focus on four key metrics to compare blinking statistics: the non-blinking fraction, the ON percentage, the number of CPA levels in each trajectory, and the weighted ON/OFF ratio. We define the non-blinking fraction as all the QDs which are in their highest intensity level for greater than 95% of the observation time, consistent with previously reported widefield blinking studies.⁴⁸ The ON percentage quantifies how long we observed each QD in its highest intensity level state during the observation window. The weighted ON/OFF ratio quantifies, given an infinite observation time frame, how much more likely a QD is to be in its most emissive intensity level. Further details explaining how we calculate these statistics from our CPA results are in the supporting information. Here, we compare the blinking statistics across five different synthetic batches of lecithin-capped QDs (1308 QDs in total), to an oleic acid/oleylamine synthetic batch (1317 QDs in total). Additional comparisons between other synthetic batches of lecithin-capped and oleic acid/oleylamine-capped QDs are shown in Figure S6.

Surprisingly, despite similar ensemble properties, at the single particle level, we observe disparate blinking behaviors from the two QD compositions. Figure 3.3b shows a similar distribution of identified CPA levels between the two compositions. Nevertheless, at the single particle level lecithin-capped QDs significantly outperform those capped by oleic acid/oleylamine. Lecithin-capped QDs exhibit a larger non-blinking fraction (0.15 vs 0.02, Figure 3.3a), higher average ON percentage (68% vs 30%, Figure 3.3c), and a larger weighted ON/OFF ratio (3.1 vs 0.73, Figure 3d); all metrics are consistent with dramatic reductions in their blinking. Additional metrics comparing blinking in lecithin-capped and oleic acid/oleylamine-capped CsPbBr₃ QDs are shown in Figure S7. At face value, this result seems surprising – after all, the ensemble is the sum of the individual single particles, yet the single particle data differ dramatically.

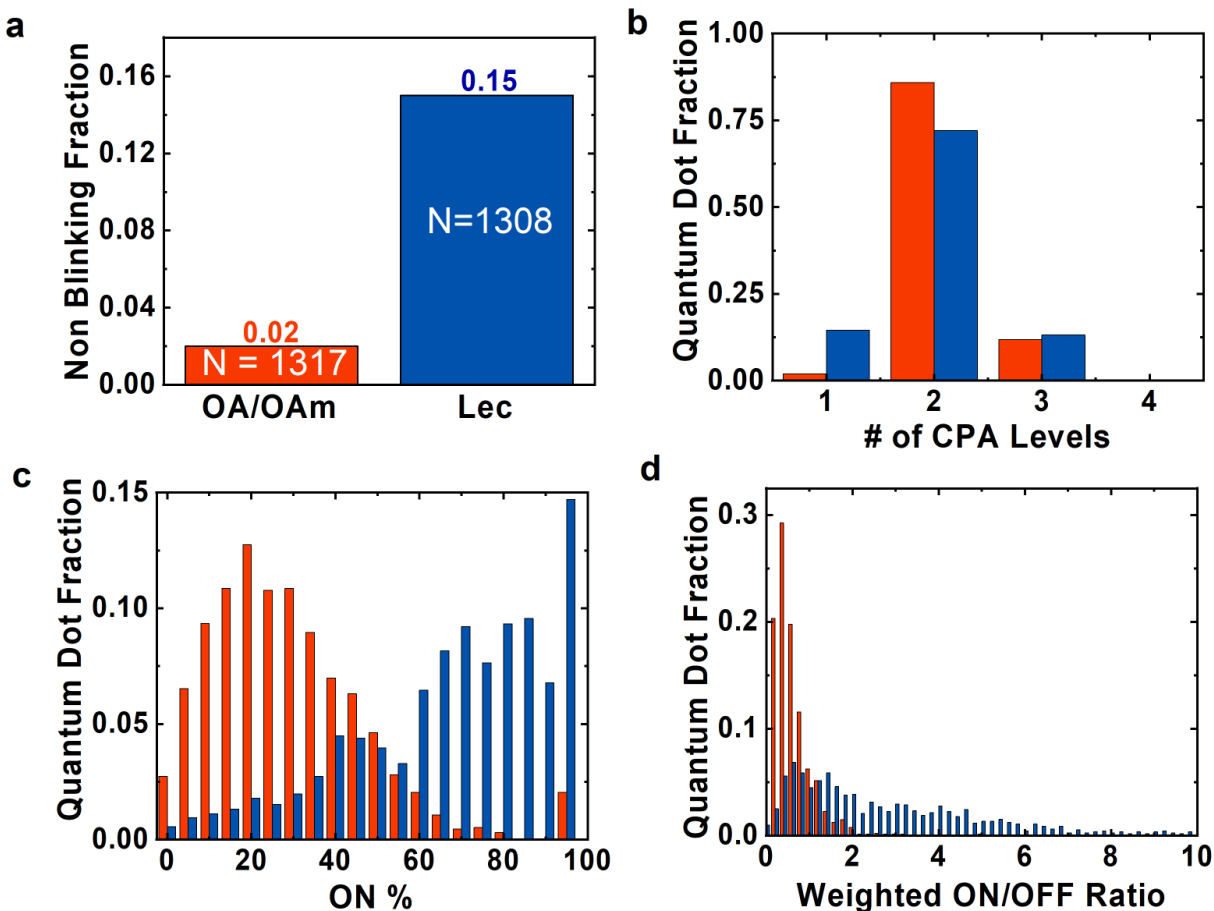


Figure 3.3. Comparison of blinking statistics between oleic acid/oleylamine-capped (OA/OAm, red) and lecithin-capped (Lec, blue) CsPbBr₃. **a)** The non-blinking fraction (>95% ON). **b)** The distribution of the number of intensity levels fit by CPA across all studied QDs. **c)** Distribution of the ON percentages for all QDs. **d)** The weighted ON/OFF ratio distribution.

To better understand these contrasting blinking distributions, we turn to concentration dependent photoluminescence and time-resolved photoluminescence (TRPL) studies. First, we use TRPL for a comparative estimate of surface quality based on lifetime duration. At the QD concentration used to acquire our ensemble PLQY data the oleic acid/oleylamine-capped QDs have an average lifetime of 4.95 ± 0.02 ns and a stretching exponent of $\beta = 0.779 \pm 0.001$ (Figure 3.4a). After diluting the QD sample to the concentration used to prepare single particle samples, we find that the average lifetime has decreased to 2.08 ± 0.03 ns with a stretching exponent of $\beta = 0.455 \pm 0.002$ (Figure 3.4a). The observed decrease in average lifetime and stretching exponent indicates that the surface passivation and sample homogeneity have worsened during the dilution process.⁶⁶ In contrast, Figure 3.4b shows the average lifetime for lecithin-capped QDs remains essentially constant during the dilution process (4.43 ± 0.04 ns vs 4.50 ± 0.08 ns). Additional concentration dependent lifetimes for oleic acid/oleylamine-capped and lecithin-capped QDs are shown in Figures S8 and S9.

We next turn to concentration-dependent photoluminescence studies for a more quantitative understanding of the changes in surface passivation inferred from the TRPL data. If the PLQY of a material remains constant with dilution, the integrated photoluminescence intensity should scale linearly with concentration. A sub-linear trend would indicate a loss of PLQY with dilution. This fact allows integrated photoluminescence intensity to serve as a proxy for PLQY at concentrations too dilute to be directly measured in the integrating sphere. Figure 4c plots the photoluminescence intensity versus concentration for both the lecithin-capped and oleic acid/oleylamine-capped QDs. For the lecithin-capped dots, we observe a linear relationship between the photoluminescence intensity and concentration over three orders of magnitude in concentration, spanning from typical measurement concentrations for solution PLQY to a concentration range below that used in our single QD microscopy experiments. In contrast, Figure 3.4c shows that the integrated photoluminescence intensity for the oleic acid/oleylamine-capped QDs is linear at higher concentrations, but falls off rapidly as the concentration decreases. This additional decrease in intensity is consistent with the change in the non-radiative recombination dynamics we deduce from the TRPL shown in Figure 3.4a. Approximately midway between the PLQY concentration (indicated with a green square) and the single QD microscopy concentration (indicated with a green circle), oleic acid/oleylamine-capped QDs see a significant decrease in integrated photoluminescence intensity, which we interpret as a decrease in PLQY due to ligand desorption.

Previous studies on a range of QDs have attributed photoluminescence decreases during washing to an equilibrium between the ligand bound to the QD surface and free-ligand in solution which shifts to favor free-ligand during dilution or antisolvent washing.⁴¹ As the concentration of unbound ligand decreases during dilution, the equilibrium shifts, and monodentate ligands like oleic acid and oleylamine are likely to detach from perovskite QDs in two ways – as a neutral ligand pair (OAm-OA) or as ligand-ion pairs (OA-Cs⁺ and OAm⁺-Br⁻) which leave behind additional vacancies.³¹ As the ligands desorb from the surface, the number of surface traps increases which can explain both the sub-linear photoluminescence trend and increased blinking observed in oleic acid/oleylamine-capped QDs. These single particle results are consistent with prior reports of decreased PLQY in halide perovskite QDs at low concentrations.⁶⁷

To test whether ligand desorption might cause the observed non-linear decrease in quantum dot emission with decreasing concentration, we investigate the effect of the adding back additional ligand to dilute solutions of oleic acid/oleylamine-capped QDs. Figure 4d plots the photoluminescence intensity of a dilute solution oleic acid/oleylamine-capped QDs as a function of excess ligand addition. The solution's photoluminescence intensity increases after adding small amounts of oleylamine or lecithin, resulting in a maximum 120% increase in photoluminescence intensity. The photoluminescence recovery associated with the addition of other ligands is shown in Figure S10.

Taken together the results above suggest that the increased blinking behavior in the oleic acid/oleylamine-capped QDs stems from ligand loss with dilution. We speculate that the lack of

full photoluminescence recovery (which is expected to be approximately 220% according to the trend line) after excess ligand addition might indicate that ligand loss in oleic acid/oleylamine-capped CsPbBr₃ contributes to the irreversible degradation of a fraction of these QDs. These results are consistent with widefield photoluminescence images of lecithin-capped and oleic acid/oleylamine-capped samples prepared at the same concentration indicating that a smaller fraction of oleic acid/oleylamine capped QDs remain emissive after dilution (Figure S11).

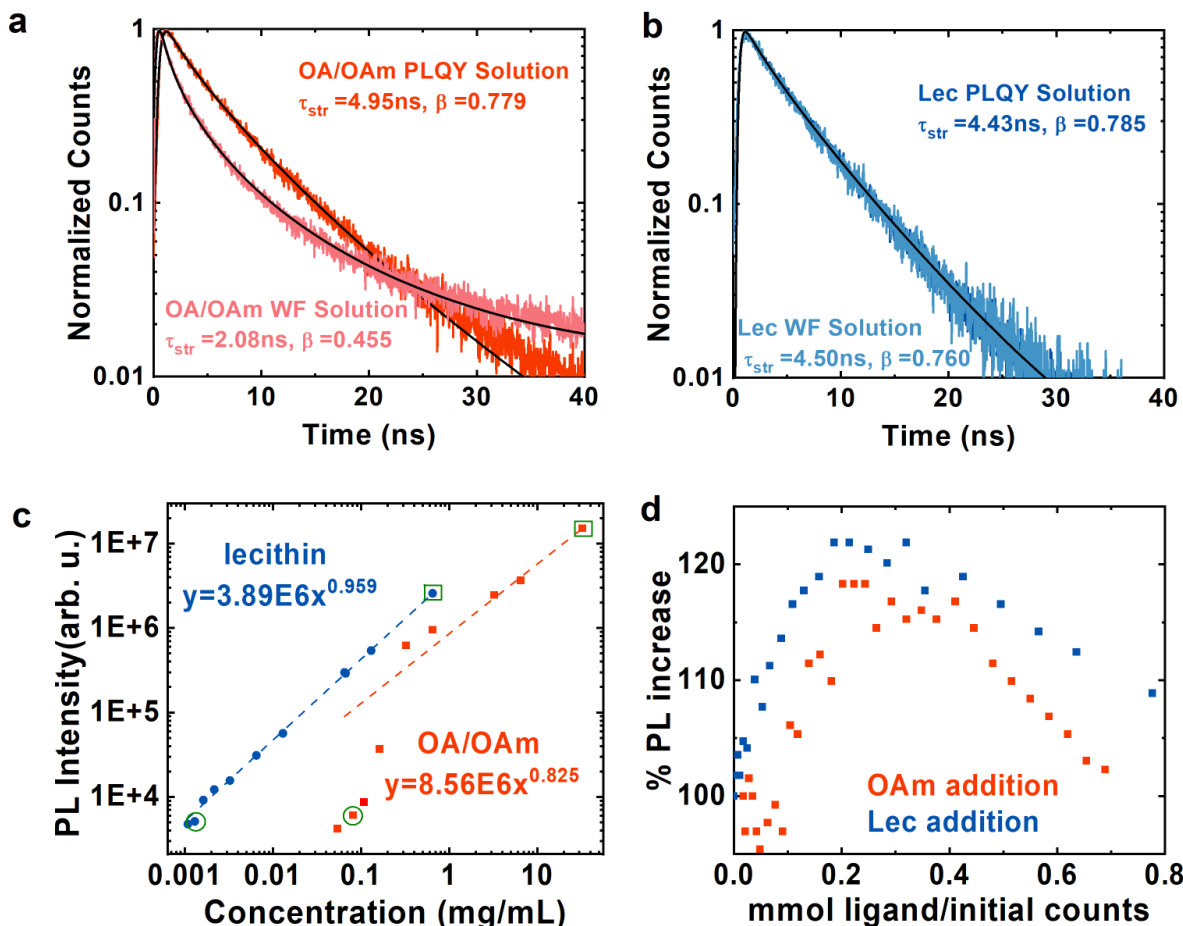


Figure 3.4. Rationalizing reduced blinking in lecithin-capped QDs. **a)** Concentration dependent TRPL for oleic acid/oleylamine-CsPbBr₃ at the PLQY concentration (green box in (c)) and widefield (WF) concentration (green circle in (c)). **b)** Concentration dependent TRPL for lecithin-capped CsPbBr₃ at the PLQY concentration (green box in (c)) and widefield concentration (green circle in (c)). **c)** Concentration dependent photoluminescence intensity for oleic acid/oleylamine (OA/OAm, red) and lecithin (blue) capped QDs. Intensity vs. concentration values are fit to a power law (a power law exponent of 1 indicates a linear relationship). The experimental concentrations for PLQY and widefield photoluminescence blinking measurements on both compositions are indicated with green box and a green circle, respectively. **d)** Photoluminescence increase resulting from the addition of oleylamine (OAm) and lecithin (Lec) to a widefield concentration solution (green circle in (c)) of oleic acid/oleylamine-capped CsPbBr₃ QDs.

To rationalize the differences in blinking behavior between oleic acid/oleylamine- and lecithin-capped QDs, we study the quantum dot electronic structure and compute the binding energies of the capping ligands to the surface of the QDs. To begin, we calculated the density of

states for the pristine and the defective (containing v_{Br} or v_{Cs}) slabs of CsPbBr_3 , shown in Figure S12. We performed DFT-PBE calculations considering spin orbit coupling effects, which are known to strongly influence the position of band edges in lead halide perovskites.⁶⁸ We calculated the band gaps of the pristine slab as well as v_{Br} and v_{Cs} containing slabs of CsPbBr_3 to be 1.4 eV, 1.17 eV and 1.0 eV, respectively. Figures S12b and S12c depict near gap states due to the presence of surface vacancies (v_{Br} and v_{Cs}) that are known potential recombination centers,⁶⁹ and the band gap closure that stems from them compared to the pristine slab (Figure S12a). We posit that the origin of the difference in blinking behavior between lecithin- and oleic acid/oleylamine- capped QDs lies in the ability of the ligands to passivate these defects. To this end, we investigated the potential difference in surface binding energy between lecithin and oleic acid/oleylamine using first principles studies.

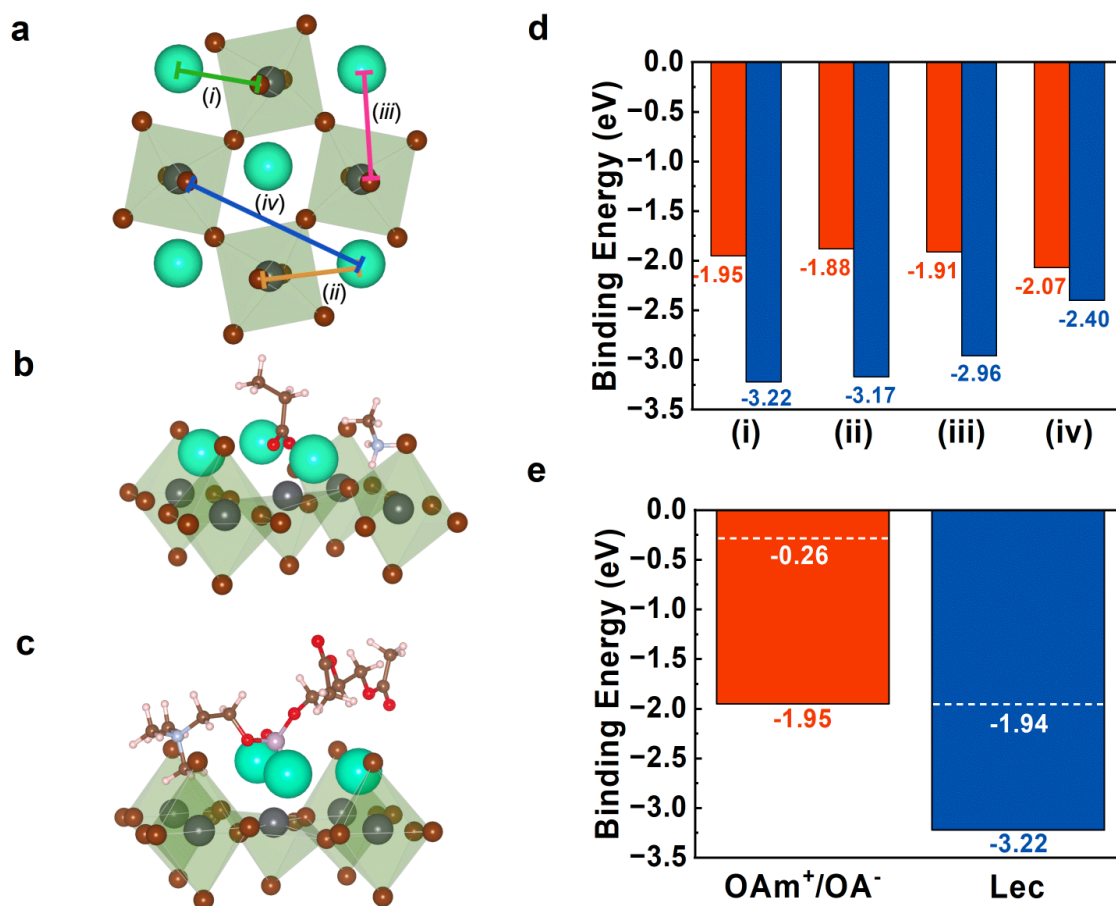


Figure 3.5. Calculated binding energies for binary monodentate ligand system oleic acid/oleylamine (OAm^+/OA^-) and bidentate lecithin (Lec) a) Top view of the PBE-relaxed lattice of orthorhombic CsPbBr_3 (8.19 Å, 8.54 Å, 11.99 Å) and different types of vacancy pairs studied here marked as *i*, *ii*, *iii* and *iv* **b)** PBE+D3-relaxed CsPbBr_3 slab with a type *i* vacancy pair passivated by oleic acid/oleylamine **c)** PBE+D3-relaxed CsPbBr_3 slab with a type *i* vacancy pair passivated by lecithin **d)** Calculated binding energies in eV for CsPbBr_3 slabs containing v_{Cs} and v_{Br} passivated by oleic acid/oleylamine (red) and lecithin (blue), at PBE+D3 level of theory. **e)** Vacancy pair type *i*

binding energy for both lecithin and oleic acid/oleylamine with binding energy in the presence of solvent represented by white dashed lines.

We conducted a comparative study on the passivation of $V'_{Cs}-V\bullet_{Br}$ vacancy pairs by oleic acid/oleylamine and lecithin ligands. Figure 3.5a shows the orthorhombic phase of $CsPbBr_3$ and different types of the adjacent (types *i*, *ii* and *iii*) and non-adjacent (type *iv*) vacancy pairs used in our calculations. Figures 3.5b and 3.5c depict the monodentate ligand pair and the bidentate ligand binding the QD surface and passivating an adjacent surface vacancy pair. As we do not expect the long alkyl tails of the ligands to participate in surface binding, we use simplified forms of the ligands (methylamine, propionic acid and truncated lecithin, Figure S13 for computational purposes). Given the dynamic equilibrium between the charged and neutral ligands in the solution, we studied surface defect passivation for both cases. Between charged and neutral ligands, we found that OAm^+/OA^- passivating an adjacent vacancy pair is the most stable configuration and that the neutral ligand pair could only passivate a non-adjacent vacancy pair and exhibits a lower binding affinity (-1.07 eV) than that of the charged ligands (-1.95 eV). Additionally, our calculations revealed that the neutral ligand pair binding the defective surface in the presence of solvent is relatively thermodynamically unfavorable (Table S2). Figure 5d shows the binding energies calculated at the DFT level for lecithin and OAm^+/OA^- (-3.22 eV and -1.95 eV, respectively), when passivating the vacancy pairs. Figure 3.5d and Table S3 summarize the binding energies calculated for the different vacancy pair types and show that for both adjacent and non-adjacent vacancies, lecithin binds the QD surface more strongly than OAm^+/OA^- . However, for non-adjacent vacancies, the relative binding energy of OAm^+/OA^- increases while the lecithin binding energy decreases. For both ligands we rationalize this difference by considering the larger distance between the non-adjacent vacancies (3.7-5.0 Å vs 8.5 Å). For OAm^+/OA^- , the larger distance between the two vacancies results in a weaker intermolecular interaction and a subsequent higher affinity for the QD surface. Lecithin, as a bidentate ligand, demonstrates a preference for passivating adjacent vacancy pairs. Our theoretical findings suggest that lecithin binds more strongly to the QD surface, which aligns qualitatively with experiments. However, the magnitudes of calculated binding energies do not reproduce the observed ligand equilibrium shifting to unbound ligands over the experimental concentrations. Such observed difference led us to consider the impact of solvents that appear critical in representing the experimental conditions.

Since experiments indicate that the dilution effects on ligand binding equilibria should be significant, we further refined the binding energies by including solvation effects (Figure S14). As shown in Figure 5e, the net change in the binding energy due to solvation effects is remarkable for both ligands in the representative case of a type *i* vacancy pair. The calculated binding energy of -0.26 eV for OAm^+/OA^- suggests a high likelihood of ligand desorption which we speculate to be the root cause of the observed difference in the blinking behavior between oleic acid/oleylamine- and lecithin-capped $CsPbBr_3$ QDs. However, the binding energy of lecithin remains significantly large (more negative) upon solvation and can explain the observed reduction in blinking. Notably,

the binding energy for OAm^+/OA^- calculated *via* DFT (-0.26 eV) is in good agreement with the analogous binding energy estimated from Figure 3.4c (-0.34 eV). We ascribe the remaining discrepancies between the calculated and experimental binding energies to the absence of entropy and finite-temperature effects in our calculations, the inherent challenges in accurately modelling solvation effects, and the limitations in the assumptions behind the experimental analysis (see supporting information). The supporting information contains a detailed explanation of solvation effects calculations, equilibrium constants and binding energies summarized in Table S4.

Conclusion

We use widefield photoluminescence microscopy and CPA to analyze the blinking statistics of 2,600 QDs to compare the effect of bidentate and monodentate ligands on photoluminescence intermittency in CsPbBr_3 . We show that, despite similar ensemble properties, using lecithin as a capping ligand results in QDs with a non-blinking fraction 7.5 times larger than that of the oleic acid/oleylamine ligand pair. This difference in performance is explained through a ligand binding equilibrium where oleic acid and oleylamine desorb during serial dilutions, degrading the surface. This ligand binding model is supported by two key sets of findings. First, concentration dependent photoluminescence measurements, which expose a non-linear relationship between oleic acid/oleylamine photoluminescence intensity and concentration. Second, theoretical investigation and binding energy calculations at the DFT level highlight striking differences in solvated-binding energy between lecithin and OAm^+/OA^- . This blinking suppression highlights the promise of these lecithin capped CsPbBr_3 QDs as scalable single photon emitters.

We also demonstrate the promising capabilities of widefield photoluminescence microscopy paired with CPA. Together, these two techniques facilitate rapid, representative sampling of QD blinking statistics, allowing more accurate determinations of QD behavior and its connections to surface chemistry. This method can compare blinking through the number of intensity levels, the non-blinking fraction, the percent of time spent in the most intense state, the expected dwell time in an ON state, the expected dwell time in an OFF state and the weighted ON/OFF ratio. The variety of statistics available from this analysis method, combined with the larger sample size available *via* widefield microscopy allow us to determine representative blinking statistics of a sample more accurately, enabling deeper and more accurate investigations of the role QD surface chemistry plays in blinking.

While we address the difference in blinking caused by using oleic acid/oleylamine and lecithin as ligands, it is also possible that the spheroidal shape of these QDs influences their blinking as well. Though we have demonstrated, through several control experiments, the significant impact ligand binding has on photoluminescence blinking, it is still possible that the spheroidal shape of these QDs contributes to their better stability. Given the interest in these materials for such a wide range of applications and their impressive non-blinking characteristics,

a more detailed understanding of how the spherical crystal habit affects trap density and the ligand-binding equilibrium could prove valuable. Future work is needed to explore this relationship. The differences in blinking behavior observed here also lead naturally to the exploration of other ligands used to passivate CsPbBr₃, including alternative zwitterions,⁷⁰ dications,³⁴ and tightly binding monodentate ligands.²⁹

High throughput of widefield imaging, combined with the robust nature of CPA, permits detailed analysis of larger sample sizes of QDs. As we have demonstrated, the choice of surface ligand is vital to ensure that the QDs maintain their properties at the low concentrations required for both single particle characterization and nanophotonic cavity integration. The experimental techniques discussed here pave the way for systematic investigations into the root causes of photoluminescence intermittency in QDs.

Methods

Chemicals

Cesium carbonate (Cs₂CO₃, 99.9% metals basis), octadecene (ODE, 90%), oleic acid (OA, ≥ 99%), oleylamine (OAm, 70%), diisooctylphosphinic acid (DOPA, 90%), trioctylphosphine oxide (TOPO, 99%), hexanes (anhydrous 95%), hexanes (≥ 95%), polystyrene (PS, MW 280,000), toluene (anhydrous 99.8%), octane (anhydrous ≥ 99%), acetone (90%), isopropyl alcohol (IPA, 90%) and acetonitrile (ACN, anhydrous 99.8%) were purchased from Millipore Sigma. Lecithin (90%) and lead (II) bromide (PbBr₂, 99.998% metals basis) were purchased from Alfa Aesar. ODE and OAm were degassed by freeze-pump-thaw method and stored in a glovebox at 0°C. Cs₂CO₃ was dried in a vacuum oven at 120°C for 8 hours and stored in a glovebox. All other chemicals were used as received.

Synthesis of oleic acid/oleylamine-capped CsPbBr₃ QDs

Oleic acid/oleylamine-capped CsPbBr₃ were synthesized according to Protesescu et al.⁴⁰ and washed with ACN according to Zhang et al.³³ After washing, the resulting QDs were dissolved in 2 mL anhydrous hexanes, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Synthesis of Lecithin-Capped CsPbBr₃ QDs

The precursor solutions for lecithin-capped CsPbBr₃ were prepared according to Akkerman et al.⁵² The QDs were synthesized under ambient conditions in 6 mL hexanes with 160 μL of 0.04 M PbBr₂-TOPO, 320 μL of 0.2 M TOPO, 80 μL of 0.02 M Cs-DOPA. After 30 minutes of stirring at room temperature 80 μL of 0.13 M lecithin was added to the reaction. The QDs were subsequently washed by adding acetone in a 3:1 v:v ratio and centrifuged at 10,000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was dissolved in 2 mL anhydrous hexanes, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Ensemble Characterization

Absorbance spectra of the QD solutions were performed using a Perkin-Elmer Lambda 950 UV/Vis/NIR Spectrometer with a range of 400-700 nm with an integration time of 0.5 s.

Steady-state photoluminescence spectra were acquired using Perkin-Elmer Fluorescence Spectrometer LS 55. Spectra were collected using an excitation wavelength of 405 nm. The emission bandwidth was kept at 3 nm and dwell time at 0.2 s.

Time resolved photoluminescence measurements at 405 nm excitation were acquired using a commercial PicoQuant FluorTime 100 system with LDH-405 laser diode, a 405 nm picosecond pulsed diode laser. The repetition rate is controlled by an external trigger input from a PicoHarp PDL 800-B laser driver and was set to 5 MHz. A photomultiplier tube (PMT) detector was used in TCSPC mode with an instrumental response function (IRF) of approximately 400 ps. The instrument response function (IRF) was measured via laser scatter from a solution of colloidal silica (LUDOX). Concentration dependent photoluminescence was collected on the same instrument with a laser repetition rate of 50 MHz. TRPL lifetime analysis was performed using a custom Python IRF-deconvolution package. Lifetimes were fit using a stretch exponential decay (Equation 1).⁶⁶

$$I(t) = A \exp(-t/\tau_k) + C/t = A \exp(-t/\tau_k) + C \quad (1)$$

Where A is the pre-exponential factor, τ_k is the lifetime of the decay, C is the background of the measurement and β is the distribution of decay rates. τ_{str} , the average lifetime of a stretch exponential, is calculated according to Equation 2 where Γ is the gamma function.⁶⁶

$$\tau_{str} = \tau_k \beta \Gamma(1/\beta) \quad \tau_{str} = \tau_k \beta \Gamma(1/\beta) \quad (2)$$

The series of QD solutions prepared for TRPL and concentration dependent TRPL are described in Table S5.

Photoluminescence quantum yield measurements (PLQY) were performed on a commercial integrating sphere system (Hamamatsu Photonics K.K). PLQY values are determined using a white light source (Hamamatsu Mercury Xenon Lamp) and a monochromator for wavelength selection (405 nm) as the excitation source to illuminate the samples in an integrating sphere (Hamamatsu Photonics K.K). The optical density of samples was kept below 0.1 at the excitation wavelength to minimize reabsorption effects. Spectral correction was performed using a calibrated white light source (Ocean Insight HL-3P-INT-CAL) to correct for the responsivity of the detector. PLQY was calculated using the following formula:

$$PLQY = \frac{I_{em, sample} - I_{em, blank}}{I_{ex, sample} - I_{ex, blank}} \times 100 \quad PLQY = \frac{I_{em, sample} - I_{em, blank}}{I_{ex, sample} - I_{ex, blank}} \times 100 \quad (3)$$

Where $I_{em, sample}$ and $I_{em, blank}$ are the integrated area under the curve in the emission region (450-600 nm) of the sample and the neat hexane blank, respectively. The $I_{ex, sample}$ and $I_{ex, blank}$ are the

integrated area under the curve in the excitation region (395-415 nm) of the sample and the neat hexane blank respectively.

Widefield Microscopy Sample Preparation

Low fluorescence glass coverslips (VistaVision #1.5 22x22 mm, VWR) were cleaned through a sequential sonication of 10 minutes in soap solution, de-ionized water (x2), acetone and IPA. Each side of the coverslips were ozone cleaned for 23 minutes before spin coating.

Low concentration QD solutions were prepared in 5 wt% PS in toluene via serial dilutions. For oleic acid/oleylamine-capped QDs 2 μ L of stock QD solution were added to 2 mL of PS-toluene (solution A_{oleic acid/oleylamine}). 200 μ L of solution A_{oleic acid/oleylamine} were added to 2 mL of PS-toluene (solution B_{oleic acid/oleylamine}). For lecithin-capped QDs 1 μ L of stock QD solution were added to 2 mL of PS-toluene (solution A_{lec}). 100 μ L of solution A_{lec} were added to 2 mL of PS-toluene (solution B_{lec}). 100 μ L of solution B_{lec} were added to 2 mL of PS-toluene (solution C_{lec}). Single QDs films were prepared via spin coating solution B_{oleic acid/oleylamine} (60 μ L) or solution C_{lec} (60 μ L) onto the cleaned coverslips at 2,000 rpm for 40 seconds. The films were stored in a glovebox until measurement.

Widefield Microscopy

Widefield microscopy measurements were performed on a Nikon TE2000 inverted optical microscope using a CFI Super Fluor 40x Oil immersion objective (NA = 1.3), with Olympus F immersion oil. The illumination source was a 415 nm LED (SOLIS-415C, Thor Labs) at a power density of 9 mW/cm². The following filters were used for the measurement: ET510/80m (Chroma), FF01-424/SP-25 (Semrock) and ZT442rdc (Chroma) mounted in Chroma Laser TIRF for Nikon TE2000/T filter cube. Videos of the sample photoluminescence in time were collected on a Prime 95B (Photometrics) camera for 6 minutes and 40 seconds (8000 total images) with an integration time of 50 ms per image. Individual QD blinking traces were extracted from the videos using a custom-built Python package for selecting bright objects from a dark background.⁶⁴ Briefly, individual quantum dots were selected using the Laplacian of Gaussian method to automatically identify bright single particles from the mean image. The image coordinates of these identified particles were used to extract the relevant single particle time traces from the image sequence for further analysis. The efficacy of particle identification was assessed by constricting the microscope field of view to rule out false positive selections (Figure S15).

Analysis of Blinking Traces Using Change Point Analysis

We used a version of Change Point Analysis (CPA) adapted for a Gaussian-distributed time series. Our home-built Python CPA package is based on the equations published by Yang et al.⁶² A more detailed explanation of our CPA package can be found in the supporting information – including a confusion matrix quantifying the performance of our CPA package on synthetically generated blinking data (Figure S16) and a detailed breakdown of how we extract our main

blinking statistics from CPA fit traces. Our particle selection and CPA code is publicly available at: <https://github.com/GingerLabUW/Widefield-CPA>.

Computational Methods

To investigate the passivation of different types of adjacent and non-adjacent vacancies, nonstoichiometric Cs-terminated slabs with a vacuum of ~ 15 Å were constructed from 2x1, 1x2, and 2x2 replications (corresponding to vacancy-pair types i-ii, iii and iv, respectively) of the PBE-relaxed conventional lattice of orthorhombic CsPbBr₃ (8.19 Å, 8.54 Å, 11.99 Å), shown in Figure 5a. DFT calculations were performed using the Quantum Espresso suite of codes,⁷¹ whereby energetically minimized atomic structures were obtained using the Perdew–Burke–Ernzerhof (PBE) formulation.⁷² Ultrasoft pseudopotentials were used to describe the interaction between the valence electrons and the ionic cores. Kohn–Sham orbitals were expanded in a plane wave basis set with a kinetic-energy cutoff of 60 Ry and a density cutoff of 420 Ry. Van der Waals interactions were considered by applying the empirical D3 dispersion correction scheme of Grimme.⁷³ Band gaps and partial density of states were calculated with PBE⁷², including spin-orbit coupling (SOC) effect,⁶⁸ that is known to strongly influence the position of band edges in lead-containing halide perovskites. Although PBE+SOC is not expected to reproduce the experimental gap of this material, we applied SOC to ensure that the band edges and the trap states near them were captured properly. An explicit solvent model was employed to simulate solvation effects, providing a more realistic representation that, unlike implicit models, includes direct and specific interactions between the solvent and solute. A detailed explanation of these calculations can be found in the supporting information.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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References

- (1) Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X. G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C. J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Mora-Seró, I.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Pérez-Prieto, J.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roeffaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Müller-Buschbaum, P.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15*, 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>.
- (2) Xian-gang Wu; Honglei Ji; Xiaolin Yan; and Haizheng Zhong. Industry Outlook of Perovskite Quantum Dots for Display Applications. *Nat Nanotechnol* **2022**, *17* (8), 811–813. <https://doi.org/10.1038/s41565-022-01147-8>.
- (3) Han, T. H.; Jang, K. Y.; Dong, Y.; Friend, R. H.; Sargent, E. H.; Lee, T. W. A Roadmap for the Commercialization of Perovskite Light Emitters. *Nat Rev Mater* **2022**, *7* (10), 757–777. <https://doi.org/10.1038/s41578-022-00459-4>.
- (4) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat Mater* **2018**, *17*, 394–405. <https://doi.org/10.1038/s41563-018-0018-4>.
- (5) Kim, Y. H.; Kim, S.; Kakekhani, A.; Park, J.; Park, J.; Lee, Y. H.; Xu, H.; Nagane, S.; Wexler, R. B.; Kim, D. H.; Jo, S. H.; Martínez-Sarti, L.; Tan, P.; Sadhanala, A.; Park, G. S.; Kim, Y. W.; Hu, B.; Bolink, H. J.; Yoo, S.; Friend, R. H.; Rappe, A. M.; Lee, T. W. Comprehensive Defect Suppression in Perovskite Nanocrystals for High-Efficiency Light-Emitting Diodes. *Nat Photonics* **2021**, *15*, 148–155. <https://doi.org/10.1038/s41566-020-00732-4>.
- (6) Akkerman, Q. A.; Gandini, M.; Di Stasio, F.; Rastogi, P.; Palazon, F.; Bertoni, G.; Ball, J. M.; Prato, M.; Petrozza, A.; Manna, L. Strongly Emissive Perovskite Nanocrystal Inks for High-Voltage Solar Cells. *Nat Energy* **2017**, *2* (2). <https://doi.org/10.1038/nenergy.2016.194>.

- (7) Lu, L.; Sun, M.; Wu, T.; Lu, Q.; Chen, B.; Huang, B. All-Inorganic Perovskite Nanocrystals: Next-Generation Scintillation Materials for High-Resolution X-Ray Imaging. *Nanoscale Adv* **2022**, 4 (3), 680–696. <https://doi.org/10.1039/d1na00815c>.
- (8) Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberger, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science (1979)* **2018**, 7392, 1068–1072. <https://doi.org/10.1126/science.aau7392>.
- (9) Ricci, F.; Marougail, V.; Varnavski, O.; Wu, Y.; Padgaonkar, S.; Irgen-Giorgio, S.; Weiss, E. A.; Goodson, T. Enhanced Exciton Quantum Coherence in Single CsPbBr₃ Perovskite Quantum Dots Using Femtosecond Two-Photon Near-Field Scanning Optical Microscopy. *ACS Nano* **2021**. <https://doi.org/10.1021/acsnano.1c01615>.
- (10) Kagan, C. R.; Bassett, L. C.; Murray, C. B.; Thompson, S. M. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chem Rev* **2021**, 121 (5), 3186–3233. <https://doi.org/10.1021/acs.chemrev.0c00831>.
- (11) Rainò, G.; Becker, M. A.; Bodnarchuk, M. I.; Mahrt, R. F.; Kovalenko, M. V.; Stöferle, T. Superfluorescence from Lead Halide Perovskite Quantum Dot Superlattices. *Nature* **2018**, 563 (7733), 671–675. <https://doi.org/10.1038/s41586-018-0683-0>.
- (12) Nguyen, H. A.; Dixon, G.; Dou, F. Y.; Gallagher, S.; Gibbs, S.; Ladd, D. M.; Marino, E.; Ondry, J. C.; Shanahan, J. P.; Vasileiadou, E. S.; Barlow, S.; Gamelin, D. R.; Ginger, D. S.; Jonas, D. M.; Kanatzidis, M. G.; Marder, S. R.; Morton, D.; Murray, C. B.; Owen, J. S.; Talapin, D. V.; Toney, M. F.; Cossairt, B. M. Design Rules for Obtaining Narrow Luminescence from Semiconductors Made in Solution. *Chem Rev* **2023**, 123 (12), 7890–7952. <https://doi.org/10.1021/acs.chemrev.3c00097>.
- (13) Zhu, C.; Marczak, M.; Feld, L.; Boehme, S. C.; Bernasconi, C.; Moskalenko, A.; Cherniukh, I.; Dirin, D.; Bodnarchuk, M. I.; Kovalenko, M. V.; Raino, G. Room-Temperature, Highly Pure Single-Photon Sources from All-Inorganic Lead Halide Perovskite Quantum Dots. *Nano Lett* **2022**, 22, 3751–3760. <https://doi.org/10.1021/acs.nanolett.2c00756>.
- (14) Boehme, S. C.; Bodnarchuk, M. I.; Burian, M.; Bertolotti, F.; Cherniukh, I.; Bernasconi, C.; Zhu, C.; Erni, R.; Amenitsch, H.; Naumenko, D.; Andrusiv, H.; Semkiv, N.; John, R. A.; Baldwin, A.; Galkowski, K.; Masciocchi, N.; Stranks, S. D.; Rainò, G.; Guagliardi, A.; Kovalenko, M. V. Strongly Confined CsPbBr₃ Quantum Dots as Quantum Emitters and Building Blocks for Rhombic Superlattices. *ACS Nano* **2023**. <https://doi.org/10.1021/acsnano.2c07677>.
- (15) Kaplan, A. E. K.; Krajewska, C. J.; Proppe, A. H.; Sun, W.; Sverko, T.; Berkinsky, D. B.; Utzat, H.; Bawendi, M. G. Hong–Ou–Mandel Interference in Colloidal CsPbBr₃ Perovskite Nanocrystals. *Nat Photonics* **2023**, 17, 775–780. <https://doi.org/10.1038/s41566-023-01225-w>.

- (16) Chen, Y.; Ryou, A.; Friedfeld, M. R.; Fryett, T.; Whitehead, J.; Cossairt, B. M.; Majumdar, A. Deterministic Positioning of Colloidal Quantum Dots on Silicon Nitride Nanobeam Cavities. *Nano Lett* **2018**, *18* (10), 6404–6410. <https://doi.org/10.1021/acs.nanolett.8b02764>.
- (17) Cohen, T. A.; Sharp, D.; Kluherz, K. T.; Chen, Y.; Munley, C.; Anderson, R. T.; Swanson, C. J.; De Yoreo, J. J.; Luscombe, C. K.; Majumdar, A.; Gamelin, D. R.; Mackenzie, J. D. Direct Patterning of Perovskite Nanocrystals on Nanophotonic Cavities with Electrohydrodynamic Inkjet Printing. *Nano Lett* **2022**, *22*, 5681–5688. <https://doi.org/10.1021/acs.nanolett.2c00473>.
- (18) Nguyen, H. A.; Sharp, D.; Fröch, J. E.; Cai, Y. Y.; Wu, S.; Monahan, M.; Munley, C.; Manna, A.; Majumdar, A.; Kagan, C. R.; Cossairt, B. M. Deterministic Quantum Light Arrays from Giant Silica-Shelled Quantum Dots. *ACS Appl Mater Interfaces* **2023**, *15* (3), 4294–4302. <https://doi.org/10.1021/acsami.2c18475>.
- (19) Neuhauser, R. G.; Shimizu, K. T.; Woo, W. K.; Empedocles, S. A.; Bawendi, M. G. Correlation between Fluorescence Intermittency and Spectral Diffusion in Single Semiconductor Quantum Dots. *Phys Rev Lett* **2000**, *85* (15), 3301–3304. <https://doi.org/10.1103/PhysRevLett.85.3301>.
- (20) Rainoì, G.; Nedelcu, G.; Protesescu, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Mahrt, R. F.; Stöferle, T. Single Cesium Lead Halide Perovskite Nanocrystals at Low Temperature: Fast Single-Photon Emission, Reduced Blinking, and Exciton Fine Structure. *ACS Nano* **2016**, *10* (2), 2485–2490. <https://doi.org/10.1021/acsnano.5b07328>.
- (21) Rainò, G.; Yazdani, N.; Boehme, S. C.; Kober-Czerny, M.; Zhu, C.; Krieg, F.; Rossell, M. D.; Erni, R.; Wood, V.; Infante, I.; Kovalenko, M. V. Ultra-Narrow Room-Temperature Emission from Single CsPbBr₃ Perovskite Quantum Dots. *Nat Commun* **2022**, *13* (1). <https://doi.org/10.1038/s41467-022-30016-0>.
- (22) Munro, A. M.; Plante, I. J. La; Ng, M. S.; Ginger, D. S. Quantitative Study of the Effects of Surface Ligand Concentration on CdSe Nanocrystal Photoluminescence. *Journal of Physical Chemistry C* **2007**, *111* (17), 6220–6227. <https://doi.org/10.1021/jp068733e>.
- (23) Munro, A. M.; Ginger, D. S. Photoluminescence Quenching of Single CdSe Nanocrystals by Ligand Adsorption. *Nano Lett* **2008**, *8* (8), 2585–2590. <https://doi.org/10.1021/nl801132t>.
- (24) Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. “Giant” Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J Am Chem Soc* **2008**, *130* (15), 5026–5027. <https://doi.org/10.1021/ja711379k>.
- (25) Pal, B. N.; Ghosh, Y.; Brovelli, S.; Laocharoensuk, R.; Klimov, V. I.; Hollingsworth, J. A.; Htoon, H. “Giant” CdSe/CdS Core/Shell Nanocrystal Quantum Dots as Efficient Electroluminescent Materials: Strong Influence of Shell Thickness on Light-Emitting Diode Performance. *Nano Lett* **2012**, *12* (1), 331–336. <https://doi.org/10.1021/nl203620f>.

- (26) Ghosh, Y.; Mangum, B. D.; Casson, J. L.; Williams, D. J.; Htoon, H.; Hollingsworth, J. A. New Insights into the Complexities of Shell Growth and the Strong Influence of Particle Volume in Nonblinking “Giant” Core/Shell Nanocrystal Quantum Dots. *J Am Chem Soc* **2012**, *134* (23), 9634–9643. <https://doi.org/10.1021/ja212032q>.
- (27) Peterson, M. D.; Cass, L. C.; Harris, R. D.; Edme, K.; Sung, K.; Weiss, E. A. The Role of Ligands in Determining the Exciton Relaxation Dynamics in Semiconductor Quantum Dots. *Annu Rev Phys Chem* **2014**, *65*, 317–339. <https://doi.org/10.1146/annurev-physchem-040513-103649>.
- (28) Sadighian, J. C.; Wong, C. Y. Just Scratching the Surface: In Situ and Surface-Specific Characterization of Perovskite Nanocrystal Growth. *Journal of Physical Chemistry C* **2021**, *125* (38), 20772–20782. <https://doi.org/10.1021/acs.jpcc.1c06582>.
- (29) Fiuza-Maneiro, N.; Sun, K.; López-Fernández, I.; Gómez-Graña, S.; Müller-Buschbaum, P.; Polavarapu, L. Ligand Chemistry of Inorganic Lead Halide Perovskite Nanocrystals. *ACS Energy Lett* **2023**, 1152–1191. <https://doi.org/10.1021/acsenerylett.2c02363>.
- (30) Kang, J.; Wang, L. W. High Defect Tolerance in Lead Halide Perovskite CsPbBr₃. *Journal of Physical Chemistry Letters* **2017**, *8* (2), 489–493. <https://doi.org/10.1021/acs.jpclett.6b02800>.
- (31) De Trizio, L.; Infante, I.; Manna, L. Surface Chemistry of Lead Halide Perovskite Colloidal Nanocrystals. *Acc Chem Res* **2023**, *51*, 1815–1825. <https://doi.org/10.1021/acs.accounts.3c00174>.
- (32) Almeida, G.; Goldoni, L.; Akkerman, Q.; Dang, Z.; Khan, A. H.; Marras, S.; Moreels, I.; Manna, L. Role of Acid-Base Equilibria in the Size, Shape, and Phase Control of Cesium Lead Bromide Nanocrystals. *ACS Nano* **2018**, *12* (2), 1704–1711. <https://doi.org/10.1021/acsnano.7b08357>.
- (33) Zhang, Y.; Siegler, T. D.; Thomas, C. J.; Abney, M. K.; Shah, T.; De Gorostiza, A.; Greene, R. M.; Korgel, B. A. A “Tips and Tricks” Practical Guide to the Synthesis of Metal Halide Perovskite Nanocrystals. *Chemistry of Materials* **2020**, *32* (13), 5410–5423. <https://doi.org/10.1021/acs.chemmater.0c01735>.
- (34) Ginterseder, M.; Sun, W.; Shcherbakov-Wu, W.; McIsaac, A. R.; Berkinsky, D. B.; Kaplan, A. E. K.; Wang, L.; Krajewska, C.; Šverko, T.; Perkinson, C. F.; Utzat, H.; Tisdale, W. A.; Van Voorhis, T.; Bawendi, M. G. Lead Halide Perovskite Nanocrystals with Low Inhomogeneous Broadening and High Coherent Fraction through Dicationic Ligand Engineering. *Nano Lett* **2023**. <https://doi.org/10.1021/acs.nanolett.2c03354>.
- (35) Ye, J.; Li, Z.; Kubicki, D. J.; Zhang, Y.; Dai, L.; Otero-Mart, C.; Reus, M. A.; Arul, R.; Dudipala, K. R.; Andaji-garmaroudi, Z.; Huang, Y.; Li, Z.; Chen, Z.; Mu, P.; Yip, H.; Stranks, S. D.; Grey, C. P.; Baumberg, J. J.; Greenham, N. C.; Polavarapu, L.; Rao, A.; Hoye, R. L. Z. Elucidating the Role of Antisolvents on the Surface Chemistry and Optoelectronic Properties of

CsPbBr₃I_{3-x}. *J Am Chem Soc* **2022**, *144* (27), 12102–12115.

<https://doi.org/10.1021/jacs.2c02631>.

- (36) Mir, W. J.; Alamoudi, A.; Yin, J.; Yarov, K. E.; Maity, P.; Naphade, R.; Shao, B.; Wang, J.; Lintangpradipito, M. N.; Nematulloev, S.; Emwas, A. H.; Genovese, A.; Mohammed, O. F.; Bakr, O. M. Lecithin Capping Ligands Enable Ultrastable Perovskite-Phase CsPbI₃ Quantum Dots for Rec. 2020 Bright-Red Light-Emitting Diodes. *J Am Chem Soc* **2022**, *144* (29), 13302–13310. <https://doi.org/10.1021/jacs.2c04637>.
- (37) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Advanced Materials* **2017**, *29* (5). <https://doi.org/10.1002/adma.201603885>.
- (38) Manoli, A.; Papagiorgis, P.; Sergides, M.; Bernasconi, C.; Athanasiou, M.; Pozov, S.; Choulis, S. A.; Bodnarchuk, M. I.; Kovalenko, M. V.; Othonos, A.; Itskos, G. Surface Functionalization of CsPbBr₃ Nanocrystals for Photonic Applications. *ACS Appl Nano Mater* **2021**, *4* (5), 5084–5097. <https://doi.org/10.1021/acsanm.1c00558>.
- (39) Hassan, Y.; Park, J. H.; Crawford, M. L.; Sadhanala, A.; Lee, J.; Sadighian, J. C.; Mosconi, E.; Shivanna, R.; Radicchi, E.; Jeong, M.; Yang, C.; Choi, H.; Park, S. H.; Song, M. H.; De Angelis, F.; Wong, C. Y.; Friend, R. H.; Lee, B. R.; Snaith, H. J. Ligand-Engineered Bandgap Stability in Mixed-Halide Perovskite LEDs. *Nature* **2021**, *591* (7848), 72–77. <https://doi.org/10.1038/s41586-021-03217-8>.
- (40) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
- (41) Bodnarchuk, M. I.; Boehme, S. C.; Ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; Infante, I. Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Lett* **2019**, *4* (1), 63–74. <https://doi.org/10.1021/acsenergylett.8b01669>.
- (42) Boehme, S. C.; Bodnarchuk, M. I.; Burian, M.; Bertolotti, F.; Cherniukh, I.; Bernasconi, C.; Zhu, C.; Erni, R.; Amenitsch, H.; Naumenko, D.; Andrusiv, H.; Semkiv, N.; John, R. A.; Baldwin, A.; Galkowski, K.; Masciocchi, N.; Stranks, S. D.; Rainò, G.; Guagliardi, A.; Kovalenko, M. V. Strongly Confined CsPbBr₃ Quantum Dots as Quantum Emitters and Building Blocks for Rhombic Superlattices. *ACS Nano* **2023**, *17* (3), 2089–2100. <https://doi.org/10.1021/acsnano.2c07677>.

- (43) Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; Ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C. J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Lett* **2018**, *3* (3), 641–646. <https://doi.org/10.1021/acsenergylett.8b00035>.
- (44) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *J Am Chem Soc* **2019**, *141* (50), 19839–19849. <https://doi.org/10.1021/jacs.9b09969>.
- (45) Zhang, B.; Goldoni, L.; Zito, J.; Dang, Z.; Almeida, G.; Zaccaria, F.; De Wit, J.; Infante, I.; De Trizio, L.; Manna, L. Alkyl Phosphonic Acids Deliver CsPbBr₃ Nanocrystals with High Photoluminescence Quantum Yield and Truncated Octahedron Shape. *Chemistry of Materials* **2019**, *31* (21), 9140–9147. <https://doi.org/10.1021/acs.chemmater.9b03529>.
- (46) Zhang, B.; Goldoni, L.; Lambruschini, C.; Moni, L.; Imran, M.; Pianetti, A.; Pinchetti, V.; Brovelli, S.; De Trizio, L.; Manna, L. Stable and Size Tunable CsPbBr₃ Nanocrystals Synthesized with Oleylphosphonic Acid. *Nano Lett* **2020**, *20* (12), 8847–8853. <https://doi.org/10.1021/acs.nanolett.0c03833>.
- (47) Efros, A. L.; Nesbitt, D. J. Origin and Control of Blinking in Quantum Dots. *Nat Nanotechnol* **2016**, *11* (8), 661–671. <https://doi.org/10.1038/nnano.2016.140>.
- (48) Mahler, B.; Spinicelli, P.; Buil, S.; Quelin, X.; Hermier, J. P.; Dubertret, B. Towards Non-Blinking Colloidal Quantum Dots. *Nat Mater* **2008**, *7* (8), 659–664. <https://doi.org/10.1038/nmat2222>.
- (49) Frantsuzov, P. A.; Volkán-Kacsó, S.; Jankó, B. Universality of the Fluorescence Intermittency in Nanoscale Systems: Experiment and Theory. *Nano Lett* **2013**, *13* (2), 402–408. <https://doi.org/10.1021/nl3035674>.
- (50) Gerhard, M.; Louis, B.; Camacho, R.; Merdasa, A.; Li, J.; Kiligaridis, A.; Dobrovolsky, A.; Hofkens, J.; Scheblykin, I. G. Microscopic Insight into Non-Radiative Decay in Perovskite Semiconductors from Temperature-Dependent Luminescence Blinking. *Nat Commun* **2019**, *10* (1). <https://doi.org/10.1038/s41467-019-09640-w>.
- (51) Biju, V.; Chouhan, L.; Ito, S.; Thomas, E. M.; Takano, Y.; Ghimire, S.; Miyasaka, H. Real-Time Blinking Suppression of Perovskite Quantum Dots by Halide Vacancy Filling. *ACS Nano* **2021**, *15* (2), 2831–2838. <https://doi.org/10.1021/acsnano.0c08802>.
- (52) Akkerman, Q. A.; Nguyen, T. P. T.; Boehme, S. C.; Montanarella, F.; Dirin, D. N.; Wechsler, P.; Beiglböck, F.; Rainò, G.; Erni, R.; Katan, C.; Even, J.; Kovalenko, M. V. Controlling the

- Nucleation and Growth Kinetics of Lead Halide Perovskite Quantum Dots. *Science* (1979) **2022**, 377 (6613), 1406–1412. <https://doi.org/10.1126/science.abq3616>.
- (53) Becker, M. A.; Vaxenburg, R.; Nedelcu, G.; Sercel, P. C.; Shabaev, A.; Mehl, M. J.; Michopoulos, J. G.; Lambrakos, S. G.; Bernstein, N.; Lyons, J. L.; Stöferle, T.; Mahrt, R. F.; Kovalenko, M. V.; Norris, D. J.; Rainò, G.; Efros, A. L. Bright Triplet Excitons in Caesium Lead Halide Perovskites. *Nature* **2018**, 553 (7687), 189–193. <https://doi.org/10.1038/nature25147>.
- (54) Barfüßer, A.; Rieger, S.; Dey, A.; Tosun, A.; Akkerman, Q. A.; Debnath, T.; Feldmann, J. Confined Excitons in Spherical-Like Halide Perovskite Quantum Dots. *Nano Lett* **2022**, 22, 8810–8817. <https://doi.org/10.1021/acs.nanolett.2c02223>.
- (55) Maes, J.; Balcaen, L.; Drijvers, E.; Zhao, Q.; De Roo, J.; Vantomme, A.; Vanhaecke, F.; Geiregat, P.; Hens, Z. Light Absorption Coefficient of CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry Letters* **2018**, 9 (11), 3093–3097. <https://doi.org/10.1021/acs.jpcclett.8b01065>.
- (56) Sun, Y.; Zhao, J. Unconventional Blinking Characteristics of Single Quantum Dots Revealed by Timing Analyses. *Journal of Physical Chemistry C* **2021**, 125 (2), 1171–1179. <https://doi.org/10.1021/acs.jpcc.0c09721>.
- (57) Crouch, C. H.; Sauter, O.; Wu, X.; Purcell, R.; Querner, C.; Drndic, M.; Pelton, M. Facts and Artifacts in the Blinking Statistics of Semiconductor Nanocrystals. *Nano Lett* **2010**, 10 (5), 1692–1698. <https://doi.org/10.1021/nl100030e>.
- (58) Fernée, M. J.; Tamarat, P.; Lounis, B. Spectroscopy of Single Nanocrystals. *Chem Soc Rev* **2014**, 43 (4), 1311–1337. <https://doi.org/10.1039/c3cs60209e>.
- (59) Cordones, A. A.; Leone, S. R. Mechanisms for Charge Trapping in Single Semiconductor Nanocrystals Probed by Fluorescence Blinking. *Chem Soc Rev* **2013**, 42 (8), 3209–3221. <https://doi.org/10.1039/c2cs35452g>.
- (60) Palstra, I. M.; de Buy Wenniger, I. M.; Patra, B. K.; Garnett, E. C.; Koenderink, A. F. Intermittency of CsPbBr₃ Perovskite Quantum Dots Analyzed by an Unbiased Statistical Analysis (). *Journal of Physical Chemistry C* **2021**, 125 (22), 12061–12072. <https://doi.org/10.1021/acs.jpcc.1c01671>.
- (61) Watkins, L. P.; Yang, H. Detection of Intensity Change Points in Time-Resolved Single-Molecule Measurements. *Journal of Physical Chemistry B* **2005**, 109 (1), 617–628. <https://doi.org/10.1021/jp0467548>.
- (62) Li, H.; Yang, H. Statistical Learning of Discrete States in Time Series. *Journal of Physical Chemistry B* **2019**, 123 (3), 689–701. <https://doi.org/10.1021/acs.jpcc.8b10561>.
- (63) Pálmai, M.; Beckwith, J. S.; Emerson, N. T.; Zhao, T.; Kim, E. B.; Yin, S.; Parajuli, P.; Tomczak, K.; Wang, K.; Sapkota, B.; Tien, M.; Jiang, N.; Klie, R. F.; Yang, H.; Snee, P. T.

Parabolic Potential Surfaces Localize Charge Carriers in Nonblinking Long-Lifetime “Giant” Colloidal Quantum Dots. *Nano Lett* **2022**, 22, 9470–9476.
<https://doi.org/10.1021/acs.nanolett.2c03563>.

- (64) Yaman, M. Y.; Kalinin, S. V.; Guye, K. N.; Ginger, D. S.; Ziatdinov, M. Learning and Predicting Photonic Responses of Plasmonic Nanoparticle Assemblies via Dual Variational Autoencoders. *Small* **2023**, 19 (25). <https://doi.org/10.1002/smll.202205893>.
- (65) Cui, J.; Beyler, A. P.; Marshall, L. F.; Chen, O.; Harris, D. K.; Wanger, D. D.; Brokmann, X.; Bawendi, M. G. Direct Probe of Spectral Inhomogeneity Reveals Synthetic Tunability of Single-Nanocrystal Spectral Linewidths. *Nat Chem* **2013**, 5 (7), 602–606.
<https://doi.org/10.1038/nchem.1654>.
- (66) Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S. Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. *ACS Energy Lett* **2022**, 7 (12), 4265–4273.
<https://doi.org/10.1021/acsenergylett.2c01998>.
- (67) Nenon, D. P.; Pressler, K.; Kang, J.; Koscher, B. A.; Olshansky, J. H.; Osowiecki, W. T.; Koc, M. A.; Wang, L. W.; Alivisatos, A. P. Design Principles for Trap-Free CsPbX₃ Nanocrystals: Enumerating and Eliminating Surface Halide Vacancies with Softer Lewis Bases. *J Am Chem Soc* **2018**, 140 (50), 17760–17772. <https://doi.org/10.1021/jacs.8b11035>.
- (68) Even, J.; Pedesseau, L.; Jancu, J. M.; Katan, C. Importance of Spin-Orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. *Journal of Physical Chemistry Letters* **2013**, 4 (17), 2999–3005. <https://doi.org/10.1021/jz401532q>.
- (69) Li, W.; Sun, Y. Y.; Li, L.; Zhou, Z.; Tang, J.; Prezhdov, O. V. Control of Charge Recombination in Perovskites by Oxidation State of Halide Vacancy. *J Am Chem Soc* **2018**, 140 (46), 15753–15763. <https://doi.org/10.1021/jacs.8b08448>.
- (70) Morad, V.; Stelmakh, A.; Svyrydenko, M.; Feld, L. G.; Boehme, S. C.; Aebli, M.; Affolter, J.; Kaul, C. J.; Schrenker, N. J.; Bals, S.; Sahin, Y.; Dirin, D. N.; Cherniukh, I.; Raino, G.; Baumketner, A.; Kovalenko, M. V. Designer Phospholipid Capping Ligands for Soft Metal Halide Nanocrystals. *Nature* **2023**, 625, 542–548. <https://doi.org/10.1038/s41586-023-06932-6>.
- (71) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; De Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum

Simulations of Materials. *Journal of Physics Condensed Matter* **2009**, 21 (39).

<https://doi.org/10.1088/0953-8984/21/39/395502>.

(72) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Generalized Gradient Approximation Made Simple*; 1996.

(73) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J Comput Chem* **2006**, 27 (15), 1787–1799.

<https://doi.org/10.1002/jcc.20495>.

Chapter 4: Influence of Ligand Exchange on single particle properties of CsPbBr₃ Quantum Dots

This chapter has been adapted from an in-preparation manuscript.

Influence of Ligand Exchange on Single Particle Properties of CsPbBr₃ Quantum Dots

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4.1 Overview

Improving the properties of perovskite quantum dots (QDs) for single photon emitter and quantum light applications requires a systematic understanding of the influence of ligand surface chemistry on single particle properties including linewidth, and photoluminescence blinking. Here we investigate the influence of ligand exchange on both the optical and structural properties of single quantum dots. We examine photoluminescence blinking using a widefield fluorescence microscope with ligand-exchanged quantum dots. We find the zwitterionic ligands lecithin and phosphoethanolamine (PEA-C₈C₁₂) reduce blinking compared to dodecylammonium bromide (DDAB) and a bidentate dicationic quaternary ammonium bromide (DC) ligands which have mono and bi-dentate cationic head groups respectively. The champion PEA-C₈C₁₂ shows a non-blinking fraction of 0.21, compared to 0.01 for the cationic capped quantum dots. We further investigate the effect of ligand capping on low temperature linewidth. We find that quantum dots capped with PEA-C₈C₁₂ show narrower ensemble linewidth at 3.6 K as compared to lecithin, DDAB and DC-capped QDs. Finally, we probe single particle linewidths and show that zwitterionic PEA-C₈C₁₂ and lecithin outperform the cationic surface ligands for ligand-exchanged samples, having a narrower average single particle linewidth (24 meV for lecithin and 18 meV PEA-C₈C₁₂ compared to 39 meV for and 42 meV for DDAB capped QDs) over long integration times. We rationalize these findings by quantifying ligand surface coverage using nuclear magnetic resonance (NMR), observing that QDs capped

by zwitterions have higher ligand surface coverage (~ 6.4 and 7.5 ligands/nm²), consistent with their superior performance at the single particle level. These linewidth and blinking results show that zwitterionic ligands are a preferable design strategy for reducing photoluminescence blinking and improving single particle linewidths.

4.2 Introduction:

Lead halide perovskite quantum dots have emerged as promising materials for optoelectronic applications.^{1,2} Among these materials inorganic cesium lead bromide (CsPbBr₃) quantum dots have shown promising light emission properties including near-unity photoluminescence quantum yields (PLQYs),³ narrow ensemble linewidths and emission spectra that can be tuned throughout the visible spectrum via halide exchange.⁴ These materials have been employed in a range of optoelectronic applications including light emitting diodes (LEDs),^{5,6} lasing, and photovoltaics.⁷ Recently, CsPbBr₃ quantum dots have emerged as promising candidates⁸ for quantum information science, showing potential as single spin-photon interfaces⁹ and single photon emitters.¹⁰

Single photon sources are the core building block for the development of on-chip quantum photonics.¹¹ Colloidal quantum dots can act as sources of single photons, like other solid-state emitters including nitrogen vacancy centers, epitaxial quantum dots^{12–14} and two-dimensional materials.¹⁵ Among these materials, lead halide perovskites are of particular interest due to a high degree of single photon purity^{10,16} and high degree of coherence at cryogenic temperatures¹⁷ with a fringe visibility of up to 52% in the first report of quantum interference in single perovskite quantum dots.¹⁸ These promising results have ignited interest in the usage of perovskite quantum dots as scalable^{19,20} sources of quantum light.²¹ Despite rapid progress thus far, several significant challenges exist to realizing the promise of perovskite quantum dots as scalable single photon sources including photoluminescence intermittency, spectral diffusion, linewidths larger than the transform limit, and photobleaching.^{8,22}

Improving the single particle properties of perovskite quantum dots requires further understanding and optimization of their surface ligand chemistry. Due to large surface to volume ratios, the photoluminescence properties of quantum dots are significantly influenced by surface defects. Unlike II-VI and III-V semiconductor quantum dots, lead halide perovskites are highly defect tolerant, and do not require core-shell heterostructures to achieve high quantum yield.²³ Despite this defect tolerance, perovskite quantum dots are not defect-free and require organic ligands to passivate the surface.²⁴ Organic ligands play multiple roles for perovskite quantum dots: they modulate nucleation and growth,^{25,26} provide solubility in organic solvents, prevent degradation,²⁷ control morphology,^{28–31} and influence electronic structure through passivation of surface traps.^{32,33}

Perhaps the most employed ligand scheme in perovskite quantum dots is a binary mixture of oleic acid and oleylamine.^{33,24} Oleic acid and oleylamine (oleate and oleylammonium) bind dynamically to the quantum dot leading to poor long-term colloidal stability,³⁴ and the formation of defects upon dilution.³⁵ This dynamic binding leads to a range of deleterious phenomena, including ion migration in devices,³⁶ and increased photoluminescence blinking at the single particle level.³⁷ These issues have led to wide-ranging investigations into alternative ligands for improving the properties of these materials.^{25,38}

Current ligand design approaches focus on replacing oleic acid and oleylamine with either zwitterionic or quaternary ammonium-based ligands. Common zwitterionic ligands including sulfobetaine,³⁴ lecithin³⁹ and phosphoethanolamine (PEA-C₈C₁₂),⁴⁰ show improved colloidal stability via multidentate A and X-site binding, and are employed in a range of low temperature quantum-light experiments.^{17,18} Alternatively, quaternary-ammonium-based ligands, like didodecyldimethyl ammonium bromide (DDAB), bind to A-site vacancies,²⁹ and show promise as low-temperature emitters in superlattices.⁴¹ Additionally, bidentate quaternary ammonium-based ligands demonstrate high ensemble PLQYs and record narrow single particle linewidths.⁴² Understanding the optimal ligand strategies (i.e. zwitterionic vs cationic head groups) will optimize perovskite single photon sources by reducing single particle linewidth and photoluminescence blinking. Ligand identity and surface coverage have been directly linked to narrowing linewidths,^{43–46} and reducing blinking,³⁷ however, systematic investigation into the role of ligands on single quantum dot properties are still in a nascent stage compared to investigations into the effect of surface chemistry on LED device performance.^{36,47–49}

Here we report the effect of ligand exchange on the optical properties of CsPbBr₃ quantum dots prepared via a room temperature slow growth mechanism.²⁸ We prepare quantum dots capped by the zwitterionic ligands, lecithin and PEA-C₈C₁₂, and compare their properties to a bidentate dicationic quaternary ammonium bromide ligand (DC) and monodentate (DDAB) cationic ligands. At the ensemble level, all quantum dots show high photoluminescence quantum yield, narrow room temperature linewidths, and minimal (< 20 meV) Stokes shifts. However, at the single particle level, we find that quantum dots capped by zwitterions show reduced photoluminescence blinking and narrower single particle linewidths compared to dots capped by their cationic counterparts. We rationalize these results by quantifying ligand surface coverage via NMR spectroscopy, finding that zwitterionic ligands have a higher ligand density on the quantum dot surface.

4.3 Results and Discussion

Figure 1(a) shows a schematic of the ligand exchange reaction. Initially, trioctylphosphine oxide (TOPO) capped-quantum dots are produced via a slow-growth mechanism,⁵⁰ which undergo ligand exchange treatment with the selected capping ligand,²⁸ and are subsequently isolated via antisolvent wash. Figure 1(b) shows the chemical structures of capping ligands investigated in this study, we compare zwitterionic ligands, including lecithin, a soy-derivative with quaternary ammonium and phosphonic acid head groups (royal blue) and PEA-C₈C₁₂ a recently reported zwitterionic ligand,⁴⁰ which has a primary ammonium and a phosphonate head groups (cyan), to cationic ligands, first to a bidentate diquaternary ammonium bromide ligand (DC, green)⁴² and didodecyldimethylammonium bromide, (DDAB, orange) a monodentate quaternary ammonium.^{29,41}

After the synthesis and isolation procedures (described in the Supporting Information), we compare representative ensemble optical properties of these quantum dots with varying ligand capping. Figure 1(c) shows the ensemble absorbance spectra, all these quantum dots show excitonic transitions consistent with this spherical slow-growth synthesis.^{28,51} Figure 1(d) shows the ensemble solution photoluminescence spectra for these quantum dots, all surface ligands show similar ensemble full width at half maxima (f) 80meV, 70meV, 80meV, 80meV respectively, and near unity quantum yields (ranging from 100% for PEA-C₈C₁₂ to 95% for DDAB capped QDs). Additionally, these quantum dots show an asymmetric

photoluminescence line shape, with an elongated red-tail, consistent with previous reports of quantum dots synthesized by this slow growth method,^{28,37,51} likely originating from emissive trap states, observed in quantum dots prepared via the slow-growth method.⁵² Given the similar ensemble optical properties, we regard these quantum dots as similar at the ensemble level.

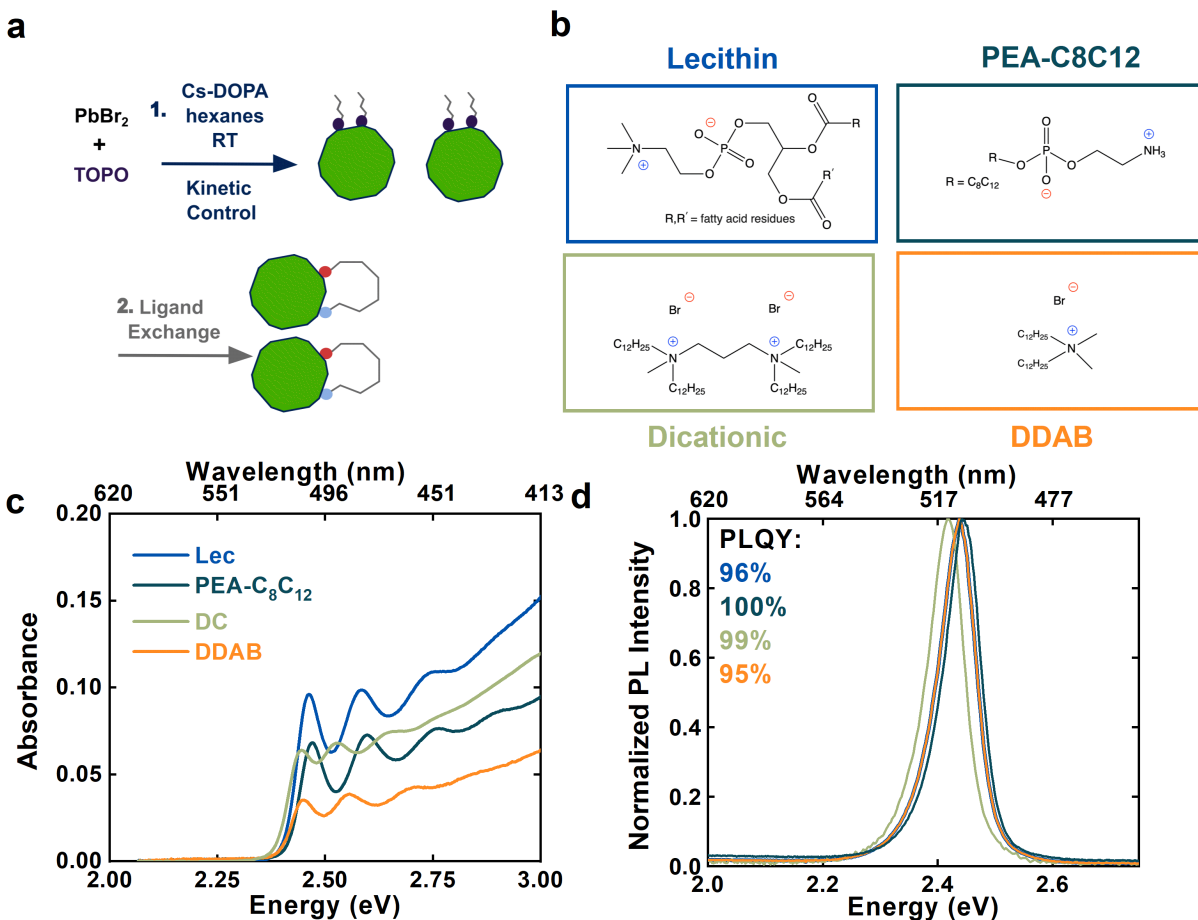


Figure 1: Overview of ligand exchange and ensemble optical properties. **a**) Schematic of ligand exchange **b**) of zwitterionic lecithin (royal blue), PEA-C₈C₁₂ (cyan), DC (green), and DDAB (orange). **c**) Solution ensemble absorbance and **d**) photoluminescence, photoluminescence quantum yield values are inset.

To understand the effect of the ligand exchange on the structure of these quantum dots we turn to small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) to characterize the size and shape of the QDs post-ligand exchange. From SAXS, we determine mean QD size and size polydispersity following a Schulz distribution. For each sample, we prescribe a particle morphology and fit this form factor model to the SAXS pattern (Fig. S4).^{53,54} The supporting information contains additional discussion on scattering data reduction and fitting procedures. Figure 2(a) shows the quantum dot size distributions showing that these quantum dots are range in diameter, with averages sizes and fwhm of 8.5 ± 0.7 nm for lecithin, 6.5 ± 0.5 nm for PEA-C₈C₁₂, 9.0 ± 1.3 nm for DC, and 8.7 ± 0.7 nm. We note that the PEA-C₈C₁₂ capped QDs are best described by a cubic model, in contrast to the others, which are best

described by polydisperse spheres. To further understand the effect of the ligand exchange on quantum dot shape, we turn to TEM. Figure 2 shows representative TEM images of the ligand-exchanged quantum dots. While the lecithin-capped QDs are spheroidal (Figure 2b), the PEA-C₈C₁₂-capped QDs (Figure 2c) show a more cuboidal shape. The facets and narrow size distribution of the PEA-C₈C₁₂-capped QDs lead to ordered packing of the nanocrystals. The long-range order in nanocrystal packing is illustrated by the sharp peaks in the inset FFT. In contrast, the QDs capped by DC (Figure 2d) and DDAB (Figure 2e) show a greater degree of polydispersity with respect to size and shape, with the DC-capped QDs showing a more cuboidal shape and those capped by DDAB showing a more spheroidal shape. The shape of these QDs can be described more quantitatively using circularity.⁵⁵ Circularity is a descriptor of shape, with spheroidal particles having higher values of circularity while cuboidal particles have lower values of circularity. These results are shown in Figure S2, with lecithin capped QDs having the highest degree of circularity (more-spheroidal, 0.55) and the PEA-C₈C₁₂ with the least (more-cuboidal, 0.33), consistent with prior reports of rhombicuboctahedral⁴⁰ and cubic geometries.⁴⁰ We note that some of the images show dark areas, consistent with damage during electron beam irradiation.⁵⁶ Dark areas appear most frequently in cation-capped QDs, less so in zwitterion-capped QDs, and least of all in PEA-C₈C₁₂-capped QDs. Since we prepared these quantum dots from the same synthetic method, followed by a ligand exchange process, we conclude that shape variations arise as a consequence of the ligand exchange treatment. We next seek to understand the effect of the ligand exchange on the single quantum dot properties.

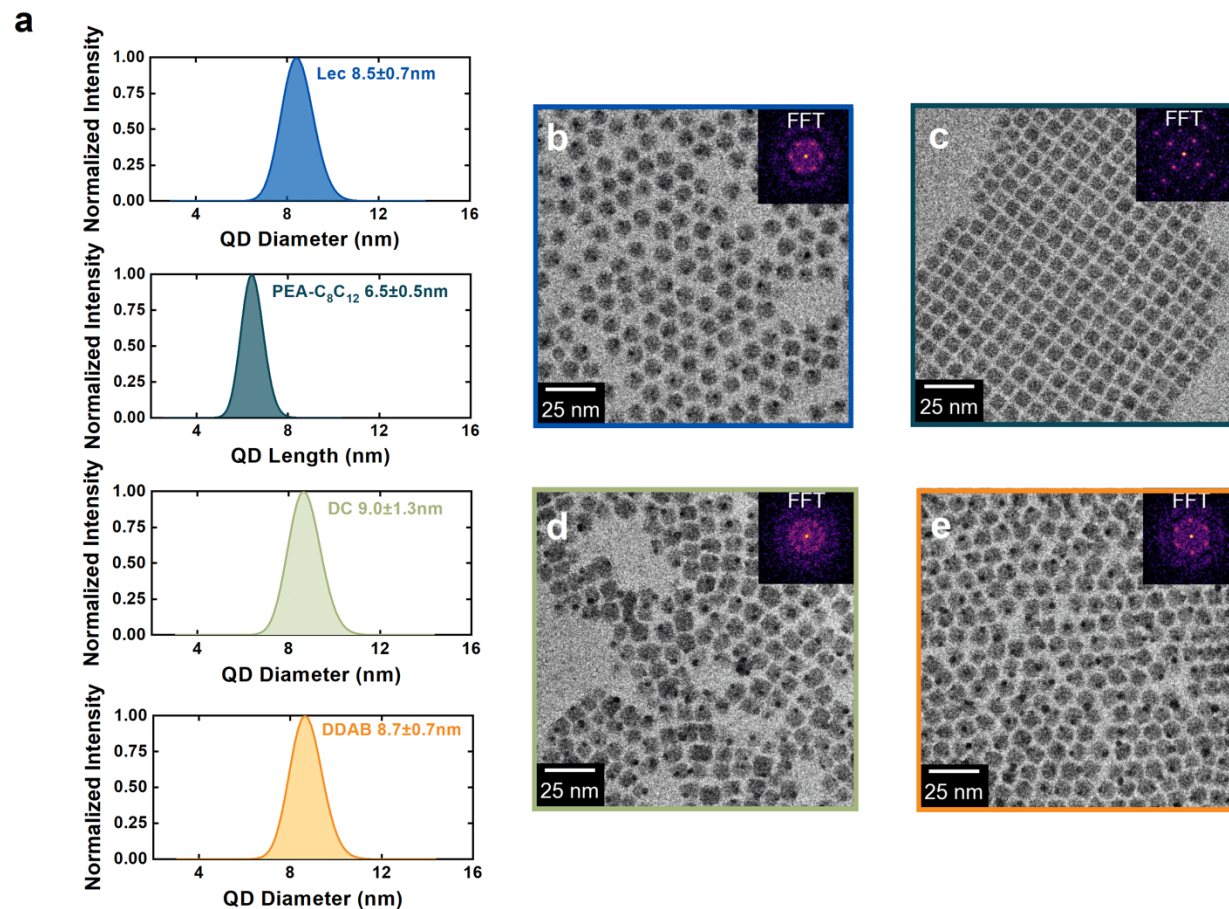


Figure 2: Quantum dot structural characterization **a)** Quantum dot sizing (diameter or cube side length) via small angle x-ray scattering (SAXS) for lecithin (blue), PEA-C₈C₁₂(cyan), DC (green) and DDAB (orange). **b-d)** Transmission electron microscopy (TEM) of quantum dots capped by lecithin (b), PEA-C₈C₁₂ (c), DC (d) and DDAB (e). The inset figure shows the fast Fourier transform (FFT) of the images.

After characterizing the ensemble properties and structure of these quantum dots, we investigate single quantum dot blinking and linewidths to understand how ligand exchange has altered their properties at the single particle level. To understand the effect of the ligand exchange on photoluminescence blinking in these quantum dots we use a previously reported wide field measurement coupled to a sCMOS camera.³⁷ This approach allows for rapid, representative sampling of large number of quantum dots. We analyze blinking trajectories using change point analysis, which allows for systematic and unbiased classification of fluorescence intensity levels.⁵⁷ We employ four metrics to compare blinking statistics for each surface ligand: the non-blinking fraction, the ON percentage, the number of intensity levels in each trajectory identified by change point analysis, and the weighted ON/OFF ratio. We define the non-blinking fraction as the percentage of QDs in their highest intensity level for greater than 95% of the measurement.⁴⁸ The ON percentage quantifies how long each QD remains in its highest intensity level state during the observation window. The weighted ON/OFF ratio quantifies, given an infinitely long observation time frame, how likely a QD is to be in its most emissive state. The Supporting Information includes further details explaining how we calculate these statistics. Figure S5 shows additional blinking metrics including ON and OFF time distributions and particle intensities.

Surprisingly, despite similar ensemble solution properties, we observe distinct blinking behaviors when comparing our zwitterionic and cationic ligands. Lecithin and PEA-C₈C₁₂-capped QDs significantly outperform those capped by DC and DDAB. Zwitterionic-exchanged QDs exhibit a larger non-blinking fraction (0.14 and 0.21 vs 0.01 for cationic QDs, Figure 3a), higher average ON percentages (60% and 64% vs. 44% and 48%, Figure S5), and a larger weighted ON/OFF ratio (1.5 and 2.5 vs 0.86 and 0.93, Figure 3c); all these metrics are consistent with reduced blinking in the QDs ligand-exchanged with zwitterionic ligands. Additional metrics comparing blinking for zwitterion- and cation-capped CsPbBr₃ QDs are shown in Figure S3. These blinking results are consistent with prior reports of PEA-C₈C₁₂ having reduced blinking compared to lecithin capped QDs,⁴⁰ and to prior reports of reduced blinking in perovskite quantum dots with aziridinium occupying the A-site.⁵⁸

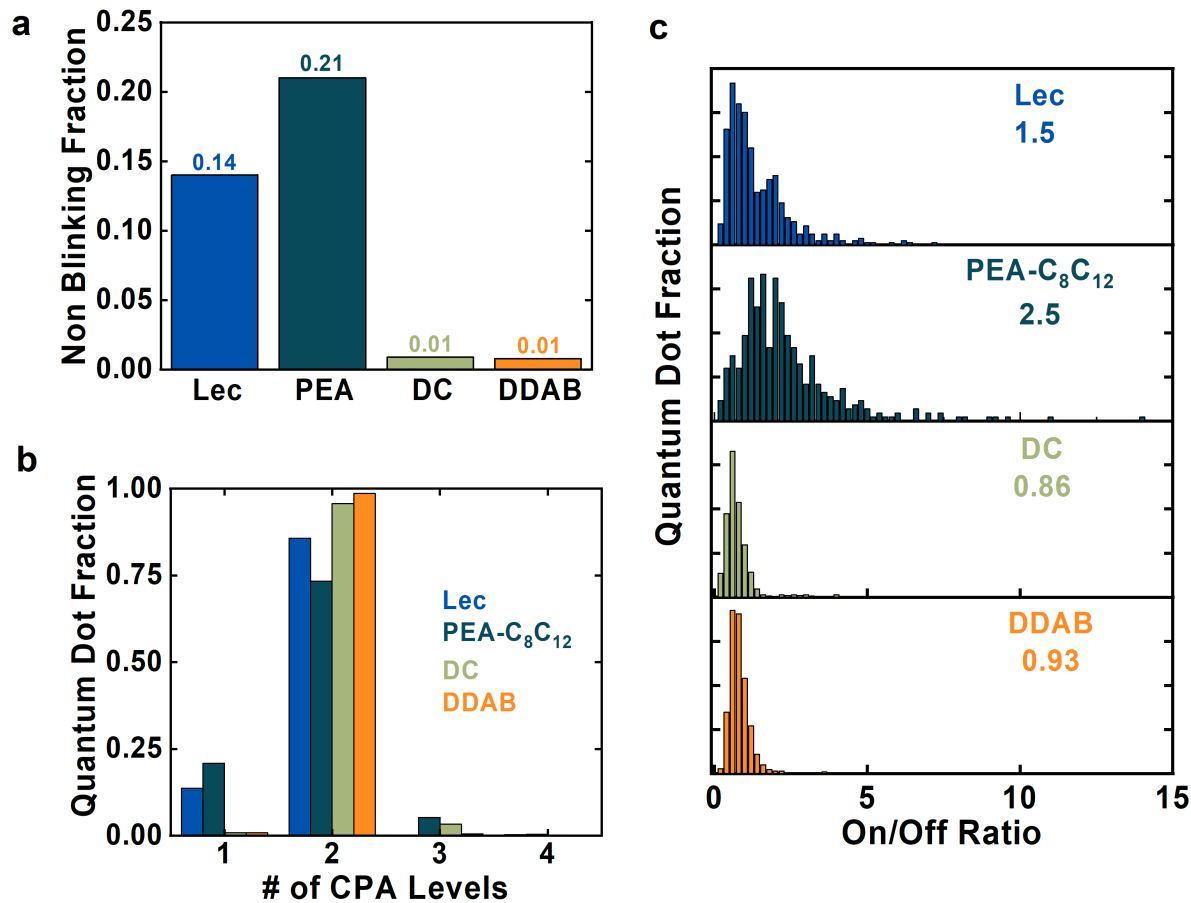


Figure 3: Effect of ligand exchange on photoluminescence blinking. **a)** The non-blinking fraction ($>95\%$ ON). **b)** The distribution of the number of intensity levels fit by change point across all studied QD ($N_{\text{Lec}} = 611$, $N_{\text{PEA-C}_8\text{C}_{12}} = 508$, $N_{\text{DC}} = 772$, $N_{\text{DDAB}} = 717$). **c)** The time and frequency weighted ON/OFF ratio distribution.

After observing differences in the room temperature photoluminescence blinking, we turn our attention to photoluminescence linewidths. We focus on the low temperature linewidths (3.6 K) as this is most relevant to quantum applications, such as single photon emission.²² To understand the influence of ligand exchange on linewidth we perform single particle spectroscopy. Figure 4(a) shows representative single particle spectra for varying ligand capping, while Figure 4(b) shows the PL peak fwhm distribution. QDs capped by lecithin and PEA-C₈C₁₂ show narrower average linewidths of $24 \text{ meV} \pm 4 \text{ meV}$ for lecithin and $18 \text{ meV} \pm 4 \text{ meV}$ PEA-C₈C₁₂ compared to $39 \text{ meV} \pm 4 \text{ meV}$ for and $42 \text{ meV} \pm 2 \text{ meV}$ for DDAB capped QDs. Critically, the QDs capped by zwitterionic ligands show narrower single particle linewidths despite being smaller than their cationic counterparts (Figure 2(a)). Linewidth in perovskite QDs is strongly correlated to size,⁴³ with smaller QDs having broader linewidths, attributed to increased exciton-phonon coupling in smaller QDs. Their narrower PL linewidth despite their smaller size suggests that the zwitterionic ligands facilitate narrower single particle linewidths.⁵⁹ One possible explanation for these narrower linewidths is reduced spectral diffusion events,⁶⁰ which have been correlated to photoluminescence blinking. This mechanism is consistent with our observed blinking results in Figure 3, where zwitterionic capped lecithin and PEA-C₈C₁₂ have a reduced non blinking fraction and improved ON-

OFF ratio compared to QDs capped by cationic ligands. A low temperature single quantum dot spectra of a PEA-C₈C₁₂ shows appreciable spectral diffusion (Figure S5), suggesting that spectral diffusion may contribute to the observed linewidth differences at 3.6 K.

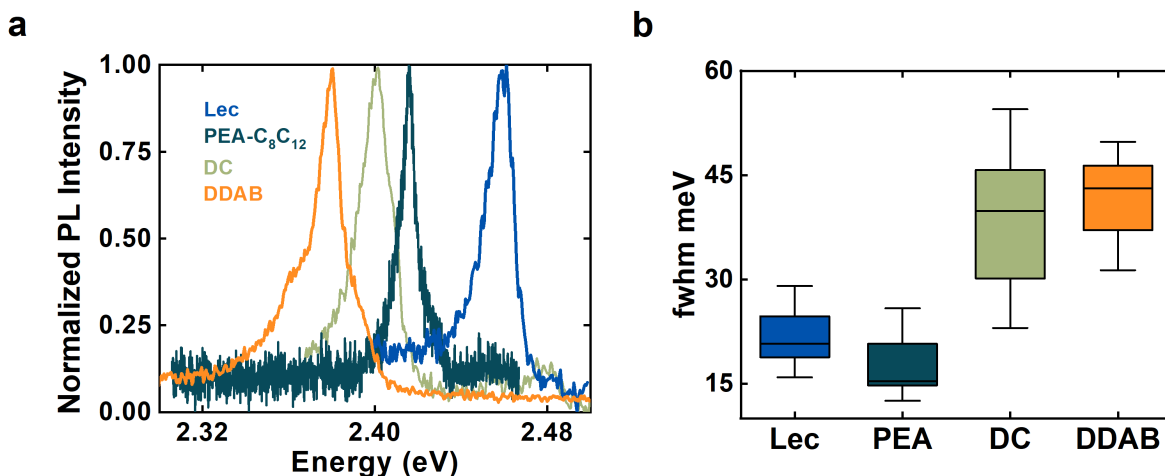


Figure 4: Ligand exchange and low temperature single particle linewidth. a) Representative single quantum dot spectra measured at 3.6 K b) PL max vs. fwhm extracted from single particle spectra.

Next, we aim to further understand the beneficial role of the zwitterionic ligand exchange in improving single particle properties by investigating ligand surface coverage. To understand the ligand surface coverage quantitatively we turn to NMR to characterize the number of ligands per QD for each ligand shell. First, we calculate the quantum dot concentration using an absorbance measurement (shown in Figure S6).⁶¹ Then, we digest representative synthetic batches of QDs using deuterated dimethylsulfoxide (DMSO)³⁴ and compare the integrated signal intensity of recovered free ligand to an internal standard (mesitylene). NMR spectra from this process are shown in Figures S7-S10. We then compare the recovered mmols of ligand to the QD concentration, with QD concentration extracted from an absorbance measurement, to calculate the number of ligands per quantum dot and corresponding ligand surface density, using the quantum dot surface area, which affords us a shape independent measure of ligand surface coverage. Figure 5(a) shows that the zwitterionic ligands have significantly higher ligand surface density (as well as ligands per QD, shown in the Supporting Information): 6.5 ± 1.6 ligands/nm² for lecithin and 7.4 ± 1.9 ligands/nm² for PEA, as compared to 0.9 ± 0.2 ligands/nm² for DC and 2.1 ± 0.5 ligands/nm² DDAB respectively). Consistent with other reports we find that PEA-C₈C₁₂ has higher coverage than zwitterionic ligands with tertiary amines (i.e. lecithin).⁴⁰ Notably, we find that the surface density of zwitterionic ligand in our samples (6.5 ± 1.6 and 7.4 ± 1.9 ligands/nm² for PEA) are comparable with literature values for zwitterion (sulfobetaine) capped QDs of 4.9 ligands/nm².⁶⁰ Additionally, consistent with the findings of Morad et al.,⁴⁰ we find that PEA has the highest surface coverage – likely due to the primary ammonium. We find that surface ligand density is strongly correlated to single particle performance, with the high coverage zwitterionic ligand outperforming the low coverage cationic ligands. Additional information on these calculations is contained in the Supporting Information, including error estimates from the ligand mass estimation in Figure S12, showing a high degree of correlation between NMR calculated mass and ligand mass (slope = 1.03, $R^2 = 0.99$) and additional metrics including mmol ligand and ligands per QD

and shown in Tables S3 and S4. These results showing improved ligand coverage on the quantum dot surface are consistent with previous literature reporting that zwitterionic ligands have a strong affinity to the perovskite quantum dot surface.^{34,37} We propose that this higher surface ligand density allows for better single particle performance by better protecting the surface from harmful processes such as extreme dilution and prolonged exposure to high excitation powers ($>1\mu\text{J}/\text{cm}^2$).^{37,40}

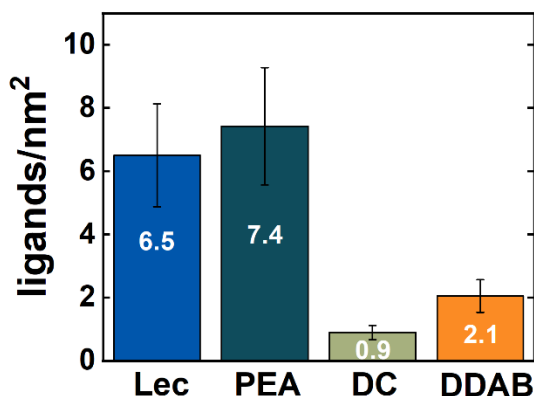


Figure 5: Rationalizing single particle performance. Ligand surface density, reported in ligands per nm², obtained from NMR characterization of recovered ligand from digested quantum dots. The Supporting Information describes the error propagation of NMR quantitation (Figure S11), and sizing errors used to generate the error bar.

4.5 Conclusion:

Here we observe significant differences in single particle properties between quantum dots we have subjected to ligand exchange with zwitterionic ligands, compared to those we have ligand exchanged with bidentate (DC) and monodentate cationic ligands (DDAB). This difference suggests that ligand exchange reactions employing zwitterionic ligands are preferable for applications involving single perovskite quantum dots. We find that QDs capped with zwitterionic ligands show narrower average low temperature single particle linewidths and reduced photoluminescence blinking.

We understand these results by investigating ligand surface coverage. Our results show that the better performing lecithin and PEA-C₈C₁₂ have a higher ligand surface density than their cationic counterparts, suggesting that ligand surface coverage affects the improvements in single particle performance following ligand exchange. This result is consistent with prior reports of zwitterion-capped ligands having increased binding affinity to the surface facilitated by multiple binding sites.⁴⁰ While we observe variations in quantum dot shape occur following exchange with the varying quantum dot ligands, we observe that zwitterion-capped quantum dots have improved performance across single particle metrics (reduced PL blinking and narrower PL fwhm), for both spheroidal and cuboidal crystal habits. While we acknowledge that shape variations may be an underlying contributor our observed differences, the measurements of ligand density suggest that large differences in ligand surface coverage correlate with improved single particle performance for both cuboidal (PEA-C₈C₁₂) and spheroidal QDs (lecithin) capped by zwitterionic ligands. Furthermore, these single-particle properties such as linewidth, improve *despite*

shape changes (such as decreasing dot size) that should lead to worse outcomes based on shape change alone.

Our results suggest that zwitterionic ligands are attractive as surface capping ligands in ligand exchanges for single perovskite quantum dots, both for blinking reduction and narrowing linewidth. Based on these conclusions, we propose further investigations should explore additional strategies which can provide multi-site binding to perovskite quantum dots including multi-zwitterionic ligands, extended hydrogen bonding and van der Waals interactions⁶² and polymer ligands.⁶³ To better understand how crystal habit affects linewidth and coherence in perovskite quantum dots more detailed surface characterization and single particle studies are needed to further correlate specific quantum dot crystal habits and surface terminations to changes in single particle linewidths and in exciton-phonon coupling. Some prior work has correlated quantum dot shape to increased biexciton formation,⁶⁴ and reduced Auger-Meitner recombination,⁶⁵ but further investigation into ligand surface coverage and the role of geometry can disentangle the role of electronic structure, surface coverage and quantum dot geometry.

Supporting Information

Additional experimental details, synthesis methods, and characterization.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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References:

- (1) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat Mater* **2018**, *17*, 394–405. <https://doi.org/10.1038/s41563-018-0018-4>.
- (2) Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X. G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C. J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Mora-Seró, I.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Pérez-Prieto, J.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roefsaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Müller-Buschbaum, P.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoyer, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15*, 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>.
- (3) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
- (4) Akkerman, Q. A.; D’Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. *J Am Chem Soc* **2015**, *137* (32), 10276–10281. <https://doi.org/10.1021/jacs.5b05602>.
- (5) Sutherland, B. R.; Sargent, E. H. Perovskite Photonic Sources. *Nat Photonics* **2016**, *10* (5), 295–302. <https://doi.org/10.1038/nphoton.2016.62>.
- (6) Han, T. H.; Jang, K. Y.; Dong, Y.; Friend, R. H.; Sargent, E. H.; Lee, T. W. A Roadmap for the Commercialization of Perovskite Light Emitters. *Nat Rev Mater* **2022**, *7* (10), 757–777. <https://doi.org/10.1038/s41578-022-00459-4>.
- (7) Akkerman, Q. A.; Gandini, M.; Di Stasio, F.; Rastogi, P.; Palazon, F.; Bertoni, G.; Ball, J. M.; Prato, M.; Petrozza, A.; Manna, L. Strongly Emissive Perovskite Nanocrystal Inks for High-Voltage Solar Cells. *Nat Energy* **2017**, *2* (2). <https://doi.org/10.1038/nenergy.2016.194>.
- (8) Kagan, C. R.; Bassett, L. C.; Murray, C. B.; Thompson, S. M. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chem Rev* **2021**, *121* (5), 3186–3233. <https://doi.org/10.1021/acs.chemrev.0c00831>.
- (9) Strohmair, S.; Dey, A.; Tong, Y.; Polavarapu, L.; Bohn, B. J.; Feldmann, J. Spin Polarization Dynamics of Free Charge Carriers in CsPbI₃ Nanocrystals. *Nano Lett* **2020**, *20* (7), 4724–4730. <https://doi.org/10.1021/acs.nanolett.9b05325>.

- (10) Park, Y. S.; Guo, S.; Makarov, N. S.; Klimov, V. I. Room Temperature Single-Photon Emission from Individual Perovskite Quantum Dots. *ACS Nano* **2015**, *9* (10), 10386–10393. <https://doi.org/10.1021/acsnano.5b04584>.
- (11) Elshaari, A. W.; Pernice, W.; Srinivasan, K.; Benson, O.; Zwiller, V. Hybrid Integrated Quantum Photonic Circuits. *Nature Photonics*. Nature Research May 1, 2020, pp 285–298. <https://doi.org/10.1038/s41566-020-0609-x>.
- (12) Senellart, P.; Solomon, G.; White, A. High-Performance Semiconductor Quantum-Dot Single-Photon Sources. *Nature Nanotechnology*. Nature Publishing Group November 1, 2017, pp 1026–1039. <https://doi.org/10.1038/nnano.2017.218>.
- (13) Wang, H.; He, Y.-M.; Chung, T.-H.; Hu, H.; Yu, Y.; Chen, S.; Ding, X.; Chen, M.-C.; Qin, J.; Yang, X.; Liu, R.-Z.; Duan, Z.-C.; Li, J.-P.; Gerhardt, S.; Winkler, K.; Jurkat, J.; Wang, L.-J.; Gregersen, N.; Huo, Y.-H.; Dai, Q.; Yu, S.; Höfling, S.; Lu, C.-Y.; Pan, J.-W. Towards Optimal Single-Photon Sources from Polarized Microcavities. *Nat Photonics* **2019**. <https://doi.org/10.1038/s41566-019-0494-3>.
- (14) Buckley, S.; Rivoire, K.; Vu, J. Engineered Quantum Dot Single-Photon Sources. **2012**. <https://doi.org/10.1088/0034-4885/75/12/126503>.
- (15) Toth, M.; Aharonovich, I. Single Photon Sources in Atomically Thin Materials. *Annu Rev Phys Chem* **2019**, *70* (1), 123–142. <https://doi.org/10.1146/annurev-physchem-042018-052628>.
- (16) Raino, G.; Nedelcu, G.; Protesescu, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Mahrt, R. F.; Stöferle, T. Single Cesium Lead Halide Perovskite Nanocrystals at Low Temperature: Fast Single-Photon Emission, Reduced Blinking, and Exciton Fine Structure. *ACS Nano* **2016**, *10* (2), 2485–2490. <https://doi.org/10.1021/acsnano.5b07328>.
- (17) Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberg, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science (1979)* **2018**, *7392*, 1068–1072. <https://doi.org/10.1126/science.aau7392>.
- (18) Kaplan, A. E. K.; Krajewska, C. J.; Proppe, A. H.; Sun, W.; Sverko, T.; Berkinsky, D. B.; Utzat, H.; Bawendi, M. G. Hong–Ou–Mandel Interference in Colloidal CsPbBr₃ Perovskite Nanocrystals. *Nat Photonics* **2023**, *17*, 775–780. <https://doi.org/10.1038/s41566-023-01225-w>.
- (19) Guymon, G. G.; Sharp, D.; Cohen, T. A.; Gibbs, S. L.; Manna, A.; Tzanetopoulos, E.; Gamelin, D. R.; Majumdar, A.; MacKenzie, J. D. Electrohydrodynamic Printing-Based Heterointegration of Quantum Dots on Suspended Nanophotonic Cavities. *Adv Mater Technol* **2024**, *9* (10). <https://doi.org/10.1002/admt.202301921>.
- (20) Chen, Y.; Sharp, D.; Saxena, A.; Nguyen, H.; Cossairt, B. M.; Majumdar, A. Integrated Quantum Nanophotonics with Solution-Processed Materials. *Adv Quantum Technol* **2022**, *5* (1), 1–22. <https://doi.org/10.1002/qute.202100078>.
- (21) Zhu, J.; Li, Y.; Lin, X.; Han, Y.; Wu, K. Coherent Phenomena and Dynamics of Lead Halide Perovskite Nanocrystals for Quantum Information Technologies. *Nat Mater* **2024**. <https://doi.org/10.1038/s41563-024-01922-z>.

- (22) Nguyen, H. A.; Dixon, G.; Dou, F. Y.; Gallagher, S.; Gibbs, S.; Ladd, D. M.; Marino, E.; Ondry, J. C.; Shanahan, J. P.; Vasileiadou, E. S.; Barlow, S.; Gamelin, D. R.; Ginger, D. S.; Jonas, D. M.; Kanatzidis, M. G.; Marder, S. R.; Morton, D.; Murray, C. B.; Owen, J. S.; Talapin, D. V.; Toney, M. F.; Cossairt, B. M. Design Rules for Obtaining Narrow Luminescence from Semiconductors Made in Solution. *Chem Rev* **2023**, *123* (12), 7890–7952. <https://doi.org/10.1021/acs.chemrev.3c00097>.
- (23) Hollingsworth, J. A. Heterostructuring Nanocrystal Quantum Dots toward Intentional Suppression of Blinking and Auger Recombination. *Chemistry of Materials*. April 23, 2013, pp 1318–1331. <https://doi.org/10.1021/cm304161d>.
- (24) De Trizio, L.; Infante, I.; Manna, L. Surface Chemistry of Lead Halide Perovskite Colloidal Nanocrystals. *Acc Chem Res* **2023**, *51*, 1815–1825. <https://doi.org/10.1021/acs.accounts.3c00174>.
- (25) Sadighian, J. C.; Wong, C. Y. Just Scratching the Surface: In Situ and Surface-Specific Characterization of Perovskite Nanocrystal Growth. *Journal of Physical Chemistry C* **2021**, *125* (38), 20772–20782. <https://doi.org/10.1021/acs.jpcc.1c06582>.
- (26) Calvin, J. J.; Brewer, A. S.; Alivisatos, A. P. The Role of Organic Ligand Shell Structures in Colloidal Nanocrystal Synthesis. *Nature Synthesis* **2022**, *1* (2), 127–137. <https://doi.org/10.1038/s44160-022-00025-4>.
- (27) Kirakosyan, A.; Chinh, N. D.; Sihn, M. R.; Jeon, M. G.; Jeong, J. R.; Kim, D.; Jang, J. H.; Choi, J. Mechanistic Insight into Surface Defect Control in Perovskite Nanocrystals: Ligands Terminate the Valence Transition from Pb²⁺ to Metallic Pb⁰. *Journal of Physical Chemistry Letters* **2019**, *10* (15), 4222–4228. <https://doi.org/10.1021/acs.jpclett.9b01587>.
- (28) Akkerman, Q. A.; Nguyen, T. P. T.; Boehme, S. C.; Montanarella, F.; Dirin, D. N.; Wechsler, P.; Beiglböck, F.; Rainò, G.; Erni, R.; Katan, C.; Even, J.; Kovalenko, M. V. Controlling the Nucleation and Growth Kinetics of Lead Halide Perovskite Quantum Dots. *Science (1979)* **2022**, *377* (6613), 1406–1412. <https://doi.org/10.1126/science.abq3616>.
- (29) Bodnarchuk, M. I.; Boehme, S. C.; Ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; Infante, I. Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Lett* **2019**, *4* (1), 63–74. <https://doi.org/10.1021/acsenerylett.8b01669>.
- (30) Garai, A.; Behera, R. K.; Pradhan, N. Facet Chemistry and the Impact of Surface Ligands on the Photoluminescence of Different Polyhedral-Shaped CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry C* **2022**, *126* (39), 16759–16766. <https://doi.org/10.1021/acs.jpcc.2c05781>.
- (31) Pradhan, N. Why Do Perovskite Nanocrystals Form Nanocubes and How Can Their Facets Be Tuned? A Perspective from Synthetic Prospects. *ACS Energy Letters*. American Chemical Society January 8, 2021, pp 92–99. <https://doi.org/10.1021/acsenerylett.0c02099>.
- (32) Peterson, M. D.; Cass, L. C.; Harris, R. D.; Edme, K.; Sung, K.; Weiss, E. A. The Role of Ligands in Determining the Exciton Relaxation Dynamics in Semiconductor Quantum Dots. *Annu Rev Phys Chem* **2014**, *65*, 317–339. <https://doi.org/10.1146/annurev-physchem-040513-103649>.

- (33) Li, J.; Gan, L.; Fang, Z.; He, H.; Ye, Z. Bright Tail States in Blue-Emitting Ultrasmall Perovskite Quantum Dots. *Journal of Physical Chemistry Letters* **2017**, *8* (24), 6002–6008. <https://doi.org/10.1021/acs.jpclett.7b02786>.
- (34) Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; Ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C. J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Lett* **2018**, *3* (3), 641–646. <https://doi.org/10.1021/acsenergylett.8b00035>.
- (35) Nenon, D. P.; Pressler, K.; Kang, J.; Koscher, B. A.; Olshansky, J. H.; Osowiecki, W. T.; Koc, M. A.; Wang, L. W.; Alivisatos, A. P. Design Principles for Trap-Free CsPbX₃ Nanocrystals: Enumerating and Eliminating Surface Halide Vacancies with Softer Lewis Bases. *J Am Chem Soc* **2018**, *140* (50), 17760–17772. <https://doi.org/10.1021/jacs.8b11035>.
- (36) Ye, J.; Li, Z.; Kubicki, D. J.; Zhang, Y.; Dai, L.; Otero-mart, C.; Reus, M. A.; Arul, R.; Dudipala, K. R.; Andaji-garmaroudi, Z.; Huang, Y.; Li, Z.; Chen, Z.; Mu, P.; Yip, H.; Stranks, S. D.; Grey, C. P.; Baumberg, J. J.; Greenham, N. C.; Polavarapu, L.; Rao, A.; Hoye, R. L. Z. Elucidating the Role of Antisolvents on the Surface Chemistry and Optoelectronic Properties of CsPbBr₃I_{3-x}. *J Am Chem Soc* **2022**, *144* (27), 12102–12115. <https://doi.org/10.1021/jacs.2c02631>.
- (37) Gallagher, S.; Kline, J.; Jahanbakhshi, F.; Sadighian, J. C.; Lyons, I.; Shen, G.; Hammel, B. F.; Yazdi, S.; Dukovic, G.; Rappe, A. M.; Ginger, D. S. Ligand Equilibrium Influences Photoluminescence Blinking in CsPbBr₃: A Change Point Analysis of Widefield Imaging Data. *ACS Nano* **2024**, *18* (29), 19208–19219. <https://doi.org/10.1021/acsnano.4c04968>.
- (38) Fiuza-Maneiro, N.; Sun, K.; López-Fernández, I.; Gómez-Graña, S.; Müller-Buschbaum, P.; Polavarapu, L. Ligand Chemistry of Inorganic Lead Halide Perovskite Nanocrystals. *ACS Energy Lett* **2023**, 1152–1191. <https://doi.org/10.1021/acsenergylett.2c02363>.
- (39) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *J Am Chem Soc* **2019**, *141* (50), 19839–19849. <https://doi.org/10.1021/jacs.9b09969>.
- (40) Morad, V.; Stelmakh, A.; Svyrydenko, M.; Feld, L. G.; Boehme, S. C.; Aebli, M.; Affolter, J.; Kaul, C. J.; Schrenker, N. J.; Bals, S.; Sahin, Y.; Dirin, D. N.; Cherniukh, I.; Raino, G.; Baumketner, A.; Kovalenko, M. V. Designer Phospholipid Capping Ligands for Soft Metal Halide Nanocrystals. *Nature* **2023**, *625*, 542–548. <https://doi.org/10.1038/s41586-023-06932-6>.
- (41) Boehme, S. C.; Bodnarchuk, M. I.; Burian, M.; Bertolotti, F.; Cherniukh, I.; Bernasconi, C.; Zhu, C.; Erni, R.; Amenitsch, H.; Naumenko, D.; Andrusiv, H.; Semkiv, N.; John, R. A.; Baldwin, A.; Galkowski, K.; Masciocchi, N.; Stranks, S. D.; Rainò, G.; Guagliardi, A.; Kovalenko, M. V. Strongly Confined CsPbBr₃ Quantum Dots as Quantum Emitters and Building Blocks for Rhombic Superlattices. *ACS Nano* **2023**, *17* (3), 2089–2100. <https://doi.org/10.1021/acsnano.2c07677>.
- (42) Ginterseder, M.; Sun, W.; Shcherbakov-Wu, W.; McIsaac, A. R.; Berkinsky, D. B.; Kaplan, A. E. K.; Wang, L.; Krajewska, C.; Šverko, T.; Perkinson, C. F.; Utzat, H.; Tisdale, W. A.; Van Voorhis, T.;

- Bawendi, M. G. Lead Halide Perovskite Nanocrystals with Low Inhomogeneous Broadening and High Coherent Fraction through Dicationic Ligand Engineering. *Nano Lett* **2023**, *23* (4), 1128–1134. <https://doi.org/10.1021/acs.nanolett.2c03354>.
- (43) Yazdani, N.; Volk, S.; Yarema, O.; Yarema, M.; Wood, V. Size, Ligand, and Defect-Dependent Electron-Phonon Coupling in Chalcogenide and Perovskite Nanocrystals and Its Impact on Luminescence Line Widths. *ACS Photonics* **2020**, *7* (5), 1088–1095. <https://doi.org/10.1021/acsphotonics.0c00034>.
- (44) Ryu, J.; Park, S. D.; Baranov, D.; Rreza, I.; Owen, J. S.; Jonas, D. M. *Relations between Absorption, Emission, and Excited State Chemical Potentials from Nanocrystal 2D Spectra*; 2021; Vol. 7. <https://www.science.org>.
- (45) Manoli, A.; Papagiorgis, P.; Sergides, M.; Bernasconi, C.; Athanasiou, M.; Pozov, S.; Choulis, S. A.; Bodnarchuk, M. I.; Kovalenko, M. V.; Othonos, A.; Itskos, G. Surface Functionalization of CsPbBr₃ Nanocrystals for Photonic Applications. *ACS Appl Nano Mater* **2021**, *4* (5), 5084–5097. <https://doi.org/10.1021/acsanm.1c00558>.
- (46) Rainò, G.; Yazdani, N.; Boehme, S. C.; Kober-Czerny, M.; Zhu, C.; Krieg, F.; Rossell, M. D.; Erni, R.; Wood, V.; Infante, I.; Kovalenko, M. V. Ultra-Narrow Room-Temperature Emission from Single CsPbBr₃ Perovskite Quantum Dots. *Nat Commun* **2022**, *13* (1), 1–8. <https://doi.org/10.1038/s41467-022-30016-0>.
- (47) Hassan, Y.; Park, J. H.; Crawford, M. L.; Sadhanala, A.; Lee, J.; Sadighian, J. C.; Mosconi, E.; Shivanna, R.; Radicchi, E.; Jeong, M.; Yang, C.; Choi, H.; Park, S. H.; Song, M. H.; De Angelis, F.; Wong, C. Y.; Friend, R. H.; Lee, B. R.; Snaith, H. J. Ligand-Engineered Bandgap Stability in Mixed-Halide Perovskite LEDs. *Nature* **2021**, *591* (7848), 72–77. <https://doi.org/10.1038/s41586-021-03217-8>.
- (48) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Advanced Materials* **2017**, *29* (5). <https://doi.org/10.1002/adma.201603885>.
- (49) Dai, J.; Roshan, H.; De Franco, M.; Goldoni, L.; De Boni, F.; Xi, J.; Yuan, F.; Dong, H.; Wu, Z.; Di Stasio, F.; Manna, L. Partial Ligand Stripping from CsPbBr₃ Nanocrystals Improves Their Performance in Light-Emitting Diodes. *ACS Appl Mater Interfaces* **2024**, *16* (9), 11627–11636. <https://doi.org/10.1021/acsami.3c15201>.
- (50) Montanarella, F.; Akkerman, Q. A.; Bonatz, D.; van der Sluijs, M. M.; van der Bok, J. C.; Prins, P. T.; Aebli, M.; Mews, A.; Vanmaekelbergh, D.; Kovalenko, M. V. Growth and Self-Assembly of CsPbBr₃ Nanocrystals in the TOPO/PbBr₂ Synthesis as Seen with X-Ray Scattering. *Nano Lett* **2023**. <https://doi.org/10.1021/acs.nanolett.2c04532>.
- (51) Barfüßer, A.; Rieger, S.; Dey, A.; Tosun, A.; Akkerman, Q. A.; Debnath, T.; Feldmann, J. Confined Excitons in Spherical-Like Halide Perovskite Quantum Dots. *Nano Lett* **2022**, *22*, 8810–8817. <https://doi.org/10.1021/acs.nanolett.2c02223>.
- (52) Kline, J.; Gallagher, S.; Hammel, B. F.; Mathew, R.; Ladd, D. M.; Westbrook, R. J. E.; Pryor, J. N.; Toney, M. F.; Pelton, M.; Yazdi, S.; Dukovic, G.; Ginger, D. S. Emissive Traps Lead to Asymmetric

Photoluminescence Line Shape in Spheroidal CsPbBr₃ Quantum Dots. *Nano Lett* **2025**.

<https://doi.org/10.1021/acs.nanolett.4c04995>.

- (53) Maes, J.; Castro, N.; De Nolf, K.; Walravens, W.; Abécassis, B.; Hens, Z. Size and Concentration Determination of Colloidal Nanocrystals by Small-Angle x-Ray Scattering. *Chemistry of Materials* **2018**, *30* (12), 3952–3962. <https://doi.org/10.1021/acs.chemmater.8b00903>.
- (54) Li, T.; Senesi, A. J.; Lee, B. Small Angle X-Ray Scattering for Nanoparticle Research. *Chemical Reviews*. American Chemical Society September 28, 2016, pp 11128–11180. <https://doi.org/10.1021/acs.chemrev.5b00690>.
- (55) Nguyen, H. A.; Hammel, B. F.; Sharp, D.; Kline, J.; Schwartz, G.; Harvey, S.; Nishiwaki, E.; Sandeno, S. F.; Ginger, D. S.; Majumdar, A.; Yazdi, S.; Dukovic, G.; Cossairt, B. M. Colossal Core/Shell CdSe/CdS Quantum Dot Emitters. *ACS Nano* **2024**, *18* (31), 20726–20739. <https://doi.org/10.1021/acsnano.4c06961>.
- (56) Deng, Y. H. Perovskite Decomposition and Missing Crystal Planes in HRTEM. *Nature*. Nature Research June 10, 2021, pp E6–E7. <https://doi.org/10.1038/s41586-021-03423-4>.
- (57) Watkins, L. P.; Yang, H. Detection of Intensity Change Points in Time-Resolved Single-Molecule Measurements. *Journal of Physical Chemistry B* **2005**, *109* (1), 617–628. <https://doi.org/10.1021/jp0467548>.
- (58) Bodnarchuk, M. I.; Feld, L. G.; Zhu, C.; Boehme, S. C.; Bertolotti, F.; Avaro, J.; Aebli, M.; Mir, S. H.; Masciocchi, N.; Erni, R.; Chakraborty, S.; Guagliardi, A.; Rainò, G.; Kovalenko, M. V. Colloidal Aziridinium Lead Bromide Quantum Dots. *ACS Nano* **2024**. <https://doi.org/10.1021/acsnano.3c11579>.
- (59) Zhu, C.; Feld, L. G.; Svyrydenko, M.; Cherniukh, I.; Dirin, D. N.; Bodnarchuk, M. I.; Wood, V.; Yazdani, N.; Boehme, S. C.; Kovalenko, M. V.; Rainò, G. Quantifying the Size-Dependent Exciton-Phonon Coupling Strength in Single Lead-Halide Perovskite Quantum Dots. *Advanced Optical Materials*. John Wiley and Sons Inc March 14, 2024. <https://doi.org/10.1002/adom.202301534>.
- (60) Neuhauser, R. G.; Shimizu, K. T.; Woo, W. K.; Empedocles, S. A.; Bawendi, M. G. Correlation between Fluorescence Intermittency and Spectral Diffusion in Single Semiconductor Quantum Dots. *Phys Rev Lett* **2000**, *85* (15), 3301–3304. <https://doi.org/10.1103/PhysRevLett.85.3301>.
- (61) Maes, J.; Balcaen, L.; Drijvers, E.; Zhao, Q.; De Roo, J.; Vantomme, A.; Vanhaecke, F.; Geiregat, P.; Hens, Z. Light Absorption Coefficient of CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry Letters* **2018**, *9* (11), 3093–3097. <https://doi.org/10.1021/acs.jpclett.8b01065>.
- (62) Kim, D. H.; Woo, S. J.; Huelmo, C. P.; Park, M. H.; Schankler, A. M.; Dai, Z.; Heo, J. M.; Kim, S.; Reuveni, G.; Kang, S.; Kim, J. S.; Yun, H. J.; Park, J.; Park, J.; Yaffe, O.; Rappe, A. M.; Lee, T. W. Surface-Binding Molecular Multipods Strengthen the Halide Perovskite Lattice and Boost Luminescence. *Nat Commun* **2024**, *15* (1). <https://doi.org/10.1038/s41467-024-49751-7>.
- (63) Tsai, C. H.; Shen, N.; Mi, C.; Bu, J.; Dong, Y.; Xu, W. Designed Polymer Ligands for Perovskite Quantum Dots and Their Block Copolymer Nanocomposites. *Adv Opt Mater* **2024**, *12* (13). <https://doi.org/10.1002/adom.202302731>.

- (64) Titus, T.; Vishnu, E. K.; Garai, A.; Dutta, S. K.; Sandeep, K.; Shelke, A.; Ajithkumar, T. G.; Shaji, A.; Pradhan, N.; Thomas, K. G. Biexciton Emission in CsPbBr₃ Nanocrystals: Polar Facet Matters. *Nano Lett* **2024**. <https://doi.org/10.1021/acs.nanolett.4c01186>.
- (65) Bera, S. K.; Bera, S.; Shrivastava, M.; Pradhan, N.; Adarsh, K. V. Facet Engineering for Amplified Spontaneous Emission in Metal Halide Perovskite Nanocrystals. *Nano Lett* **2022**. <https://doi.org/10.1021/acs.nanolett.2c02982>.

Appendix A: Supporting Information for Chapter 2

Methods

Synthesis of AgNP. Silver nanoprisms were synthesized by slightly modifying the process as previously described. 1,2 All glassware and stir bars were cleaned beforehand with aqua regia (3:1 v:v HCl:HNO₃) and rinsed thoroughly with Milli-Q purified water (18.2 MΩ/cm). All reagents were purchased from Millipore Sigma. In a 250 mL round bottom flask, 95 mL of water, 2 mL of 5 mM AgNO₃, and 1 mL of 30 mM sodium citrate were combined. The flask was wrapped in foil and placed in ice. The solution was purged with N₂ and stirred with a magnetic stirrer for 1 hour. At this time, 1 mL of 50 mM NaBH₄, freshly prepared in cold water, was injected into the reaction solution under rigorous stirring, yielding a transparent, pale yellow solution indicating the formation of silver seeds. The solution was then allowed to equilibrate for 5 minutes. 400 μL of the 50 mM NaBH₄ solution was then slowly added to the solution over six minutes. In a separate vial, 1 mL of 5 mM bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP) was combined with 500 μL of the 50 mM NaBH₄ solution. 15 minutes after the first borohydride injection, the BSPP/NaBH₄ solution was slowly added to the reaction solution over 5 minutes. The seed solution was then allowed to age in the dark for 15 hours in an

ice bath without stirring. At this time, if the extinction peak of the precursor solution was 393-394 nm, the pH of the solution was adjusted to 11.0, monitored with a LabQuest 2 pH electrode. The spherical silver particles were then photochemically converted to flattened nanoprisms by placing the solution under a 470 nm or 505 nm LED for smaller and larger prisms, respectively. Samples were exposed to the LED until no significant change to the plasmon resonance was observed. During this time, the solution changed from bright yellow to orange or purple, respectively. Sample preparation.

Single crystals of $n=1$ BAPI were prepared using methods previously published in literature.³ A solution at a concentration of 10 mg/ml DMF of single crystal $n=1$ BAPI was prepared in a glovebox before spin coating. The as-synthesized silver nanoparticles were diluted to an optical density of ~ 1 and extracted into hexanes using sodium oleate in a protocol previously published.⁴ The hexane dispersion was then further diluted by 100-fold to prepare a solution for spin-coating. A solution of PMMA was prepared at a concentration of 30 mg/ml in chlorobenzene in a glovebox. The solution was then heated with vigorous stirring at 80°C until the PMMA was dissolved. Samples were prepared on glass substrates by successively spin-coating the $n=1$ BAPI, the nanoprism dispersion, and then the PMMA protecting layer at 2000 rpm for 40s. All spin coating steps were performed in a glovebox integrated SAWATEC SM-150 Spin Coater. For the inverted architecture the AgNP were³ transferred on a glass substrate functionalized with 3-aminopropyltriethoxysilane (APTES). For the functionalization, the glass substrates were sonicated in a mixture of methanol, 2-propanol and acetone (1:1:1) and plasma treated for 1 min. Then the substrates were heated to 100°C and exposed to an APTES atmosphere by placing them next to an open vial with APTES under reduced pressure within a vacuum oven. The substrates were rinsed with ethanol and dried. To deposit the AgNP, the initial AgNP in hexanes were diluted by a factor of 5-8 and drop-casted on the substrates. The substrate was rinsed with water and dried with nitrogen. Further layers (BAPI and PMMA) were deposited as described above.

Optical characterization.

The darkfield scattering spectra were either taken with a Hyperspectral Microscope from Photon etc. or a Nikon TE-2000 inverted microscope. The Nikon is equipped with a transmitted dark field condenser and a 50x objective (Nikon Plan RT, NA 0.7) in combination with a 1.5x lens for a total of 75x magnification. A standard tungsten halogen lamp is used for transmitted light darkfield illumination. Spectra are obtained with a portable charge coupled device spectrometer (USB2000, Ocean Optics) coupled through a 100 μm fiber optical cable, which acts as an aperture restricting the area where the light is collected to a spot of ~ 1.3 μm diameter. All spectra are corrected for the intensity of the excitation lamp by normalizing the scattering spectra with a lamp spectrum, which was obtained as the scattering spectrum of a strongly and homogeneously scattering sample (piece of kimwipe or roughened glass substrate). To obtain the darkfield scattering spectrum of a single AgNP (with dimension < 100 nm) coupled to BAPI, we subtracted a spectrum of the bare BAPI to correct for the BAPI background within the spot

diameter, measured right next to the AgNP (compare Figure S8). The hyperspectral microscope is equipped with a dark field condenser and a standard tungsten halogen lamp for transmitted light dark field excitation. The hyperspectral microscope creates cubes containing spatial and spectral information. All cubes are corrected for electrical background noise, rectified regarding the wavelength, and corrected for lateral dilatation. The cubes are corrected for variations in excitation intensity by normalization with a lamp spectrum (obtained on a roughened glass substrate). As the pixel size of the camera used for the hyperspectral images is smaller than the optical spatial resolution, the scattering of single AgNP can be separated from the BAPI background by choice of pixels to be integrated to obtain a spectrum. Photoluminescence spectra were taken with the Nikon TE-2000 inverted microscope using the same objective and detector, and a 365 nm light emitting diode as excitation source. UV/VIS and extinction spectra were taken with a Perkin Elmer Lambda 950 UV-VIS/NIR or an Agilent 8453. Ellipsometry measurements and extraction of the complex dielectric function of the BAPI perovskite material. Ellipsometry measurements on a BAPI thin film on glass at room temperature were conducted on a Woolam M-2000 in reflection at angles of 55°, 65° and 75° as well as in transmission. To extract the n and k values, the experimental data were modeled using the software 4 Complete EASE. The BAPI layer was placed on top of a glass substrate (determined from a bare glass substrate as $k < 10^{-6}$ and $1.533 < n < 1.548$ between 450 nm and 700 nm) and described within the EMA (effective medium approximation, with 10% void) using two Lorentz oscillators. The complex dielectric function $\epsilon_{\text{Lorentz}}$ of a Lorentz oscillator is given by: $\epsilon_{\text{Lorentz}} = \frac{Amp \cdot Br \cdot En}{En^2 - E - i \cdot E \cdot Br}$, wherein E denotes the energy of the electromagnetic wave, Amp describes the amplitude, En the energetic position of the oscillator and Br approximates the FWHM⁵. All data (reflection and transmission) were simultaneously fit, obtaining an mean squared error of 3.343. The fits are depicted in Figure S4a) and b) and Figure 2b) as dashed black lines. The fit parameter for the Lorentz oscillators can be found in Table S1. While oscillator #1 is related to the excitonic transition of the BAPI 2D perovskite, the second oscillator describes the influence of the band-onset. The extracted n and k values are depicted in Figure S4c and Figure 2c.

Structural characterization.

Atomic force microscopy (AFM) topography images were taken with an Asylum MFP-3D in tapping mode, using a 300 kHz tip. A FEI Sirion was used to obtain scanning electron microscopy images. FDTD simulations. To investigate the BAPI exciton-photon Fano resonance and estimate the coupling strength between the AgNP and the BAPI 2D films, we conduct 3-dimensional finitedifference time-domain (FDTD) calculations using a commercial software (Lumerical Solutions, Inc. FDTD solver, version 8.18). The coupled structure is modeled as a silver nanodisk (14 nm thickness with diameters between 20 and 40 nm) on top of the BAPI film, which is placed on top of an infinite glass substrate. The AgNP is covered with an infinite PMMA layer (constant $n=1.4$). The simulations of bare BAPI in Figure 2 were obtained omitting the AgNP. The BAPI was either modeled as an infinite film of 20 nm thickness (compare

schematic in Figure 4), or as a disk with 20 nm thickness and various diameters (see schematic in Figure 4d), with a gap of 1 nm between the BAPI and the AgNP to represent the capping ligand layer. The dielectric function of the silver was modeled using the Palik (0 – 2 μm) Ag model⁶, and the glass substrates was described as the Palik SiO₂ model. The BAPI dielectric function extracted via ellipsometry measurements was implemented in the simulation with a single Lorentzian (see Figure S4). The system was illuminated with a broadband total-field scattered-field light source. Scattering and absorption cross sections are calculated by placing frequency-domain field and power monitors outside and inside the source, respectively. The absorption of the AgNP within the coupled system is isolated with a monitor surrounding only the particle. 5 Figure S1. Topography images acquired using atomic force microscopy of three different regions on the same sample, highlighting the variations in grain size. Figure S2. Comparison between darkfield scattering and PL at 365 nm excitation of typical BAPI thin films on glass at room temperature. The scattering peak is redshifted (16 meV) and broadened (18 meV) compared to the PL feature, ruling out the possibility that the feature is caused by crosstalk from PL in the darkfield scattering spectrum. 6 Figure S3. Fano fit to the dark field scattering spectrum of the BAPI 2D perovskite thin film. The red dashed line represents a Fano fit of the photon-exciton Fano resonance using the fundamental Fano profile⁷ $\sigma_{\text{scat}} \propto (\epsilon + q)^2 / \epsilon^2 + 1$. Herein q is the Fano parameter describing the line shape asymmetry and ϵ is the dimensionless reduced energy ($\epsilon = (w - w_0) / \Gamma$, with w_0 and Γ describing the resonance frequency and width). The fitting parameter are $E_0 = 2.3901 \text{ eV}$, $\Gamma = 0.0765 \text{ eV}$ and $q = -2.73$. Figure S4. Extraction of BAPI 2D perovskite complex dielectric function. a) and b) depict the ellipsometry measurements in reflection (a) and transmission (b) geometry of a BAPI thin film on glass, taken with a Woolam M-2000. To extract the n and k values, the experimental data are modeled using the software Complete EASE (see Methods for details). Fits are shown as black dashed lines. c) n and k values extracted from the fits. The dashed black lines indicate how the two parts of the dielectric function are described within Lumerical for the FDTD simulations.

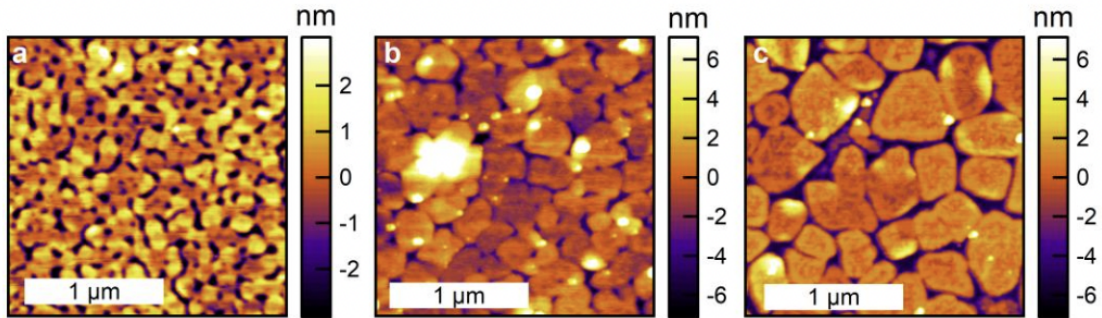


Figure S1. Topography images acquired using atomic force microscopy of three different regions on the same sample, highlighting the variations in grain size.

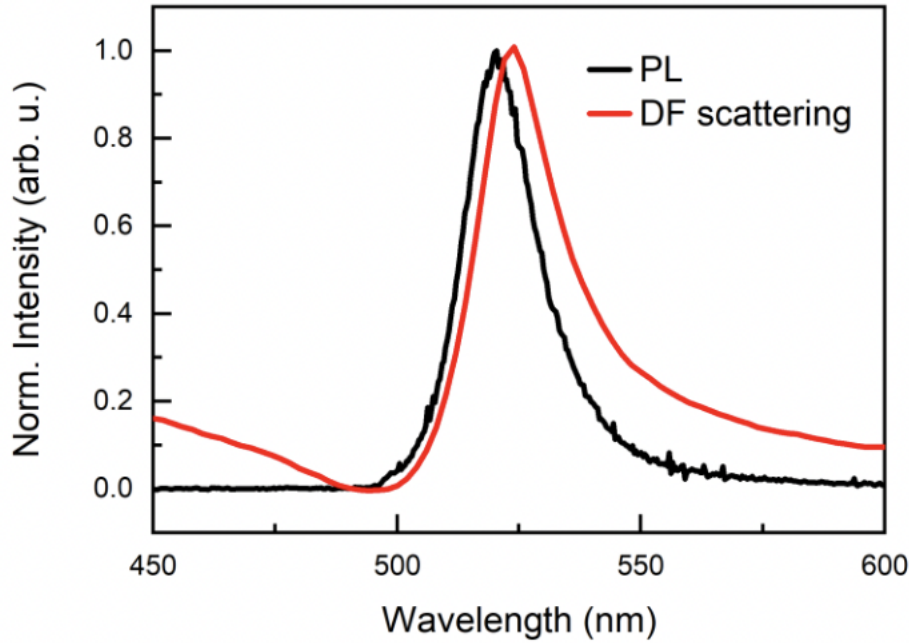


Figure S2. Comparison between darkfield scattering and PL at 365 nm excitation of typical BAPI thin films on glass at room temperature. The scattering peak is redshifted (16 meV) and broadened (18 meV) compared to the PL feature, ruling out the possibility that the feature is caused by crosstalk from PL in the darkfield scattering spectrum.

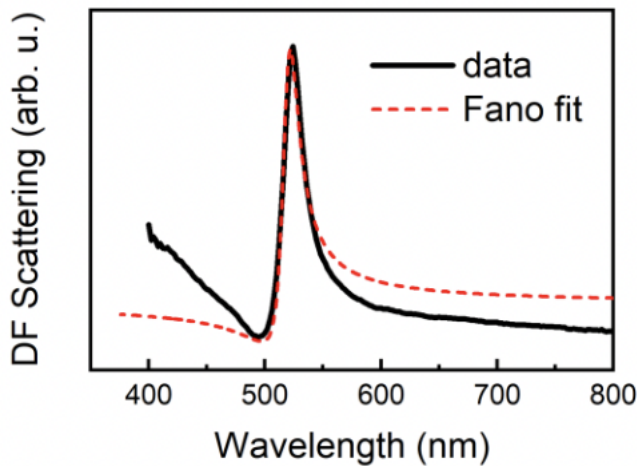


Figure S3. Fano fit to the dark field scattering spectrum of the BAPI 2D perovskite thin film. The red dashed line represents a Fano fit of the photon-exciton Fano resonance using the fundamental Fano profile $\sigma_{\text{scat}} \propto (\epsilon + q)^2 / (\epsilon^2 + 1)$. Herein q is the Fano parameter describing the line shape asymmetry and ϵ is the dimensionless reduced energy ($\epsilon = (w - w_0) / \Gamma/2$, with w_0

and Γ describing the resonance frequency and width). The fitting parameters are $E0 = 2.3901$ eV, $\Gamma = 0.0765$ eV and $q = -2.73$.

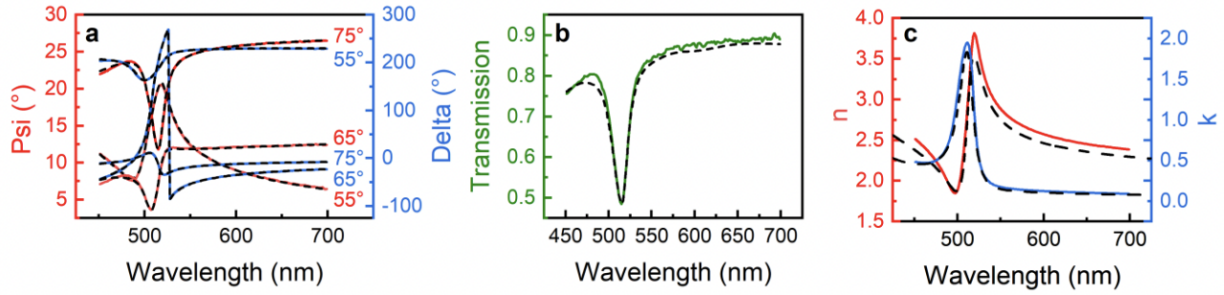


Figure S4. Extraction of BAPI 2D perovskite complex dielectric function. a) and b) depict the ellipsometry measurements in reflection (a) and transmission (b) geometry of a BAPI thin film on glass, taken with a Woolam M-2000. To extract the n and k values, the experimental data are modeled using the software Complete EASE (see Methods for details). Fits are shown as black dashed lines. c) n and k values extracted from the fits. The dashed black lines indicate how the two parts of the dielectric function are described within Lumerical for the FDTD simulations.

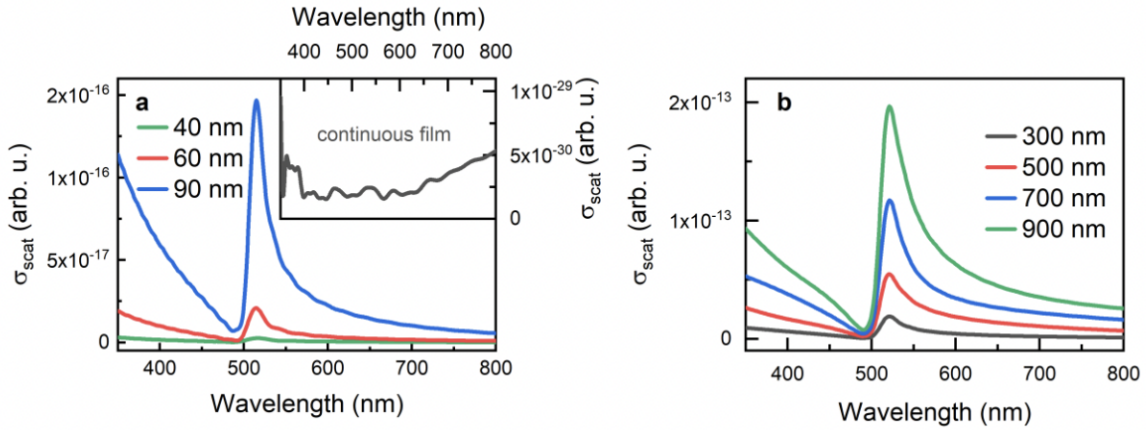


Figure S5. FDTD simulations of the scattering cross section of 2D BAPI nano disks with 20 nm thickness and different diameters of a) 40 nm - 90 nm and b) 300 nm - 900 nm). The inset in a) depicts the scattering of an infinitely continuous BAPI film.

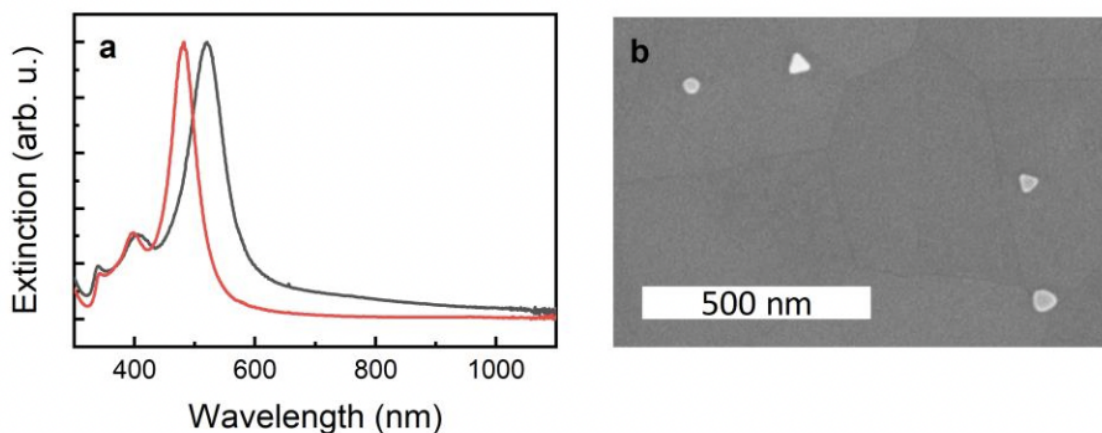


Figure S6. Silver nanoparticle. a) Normalized extinction spectra of two different batches of AgNP in aqueous solution. B) SEM images of AgNP transferred to a glass substrate with a thin layer of indium thin oxide (Glass/ITO/AgNP).

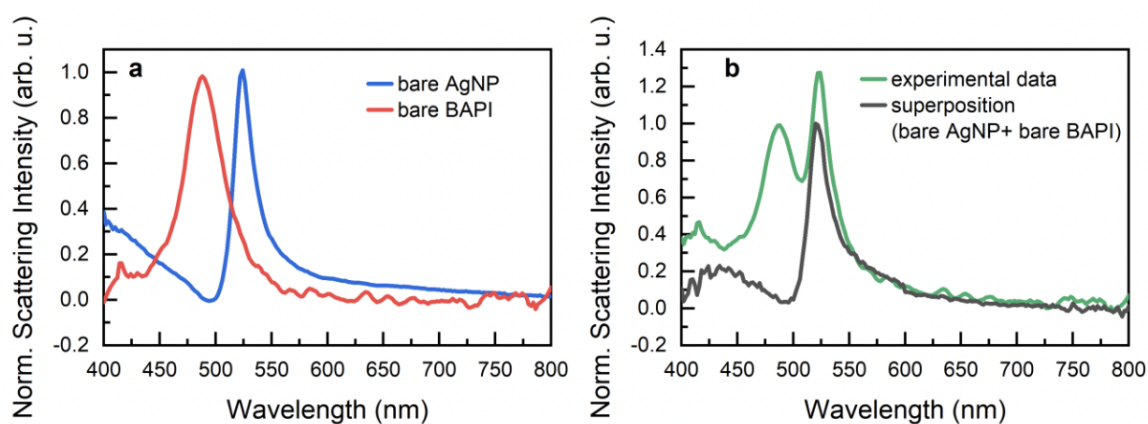


Figure S7. a) Spectrum of a bare single particle AgNP (red) and the bare BAPI scattering spectrum (blue). B) Comparison between the spectrum of the same single AgNP after spin coating of the BAPI film and a mathematical superposition of the two spectra shown in a).

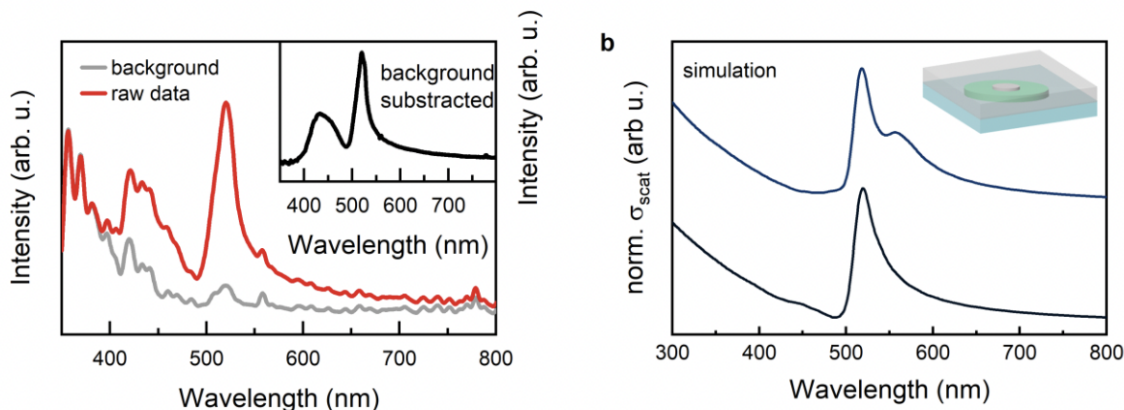


Figure S8. Extraction of a single particle DF scattering spectrum for an AgNP coupled to BAPI 2D perovskite with the Nikon TE-2000 setup. a) and b) Spectra of two different AgNP before background correction (red) compared to the BAPI background (grey), measured right next to the AgNP. All spectra are already corrected for the excitation light intensity, i.e., divided by the lamp spectrum. The insets depict the DF scattering spectrum corrected for the background, obtained as the difference between on-particle and background spectrum. Note that a lot of the noise in the raw spectrum is due to inhomogeneities in the pixel dark noise, which cancel out upon subtraction.

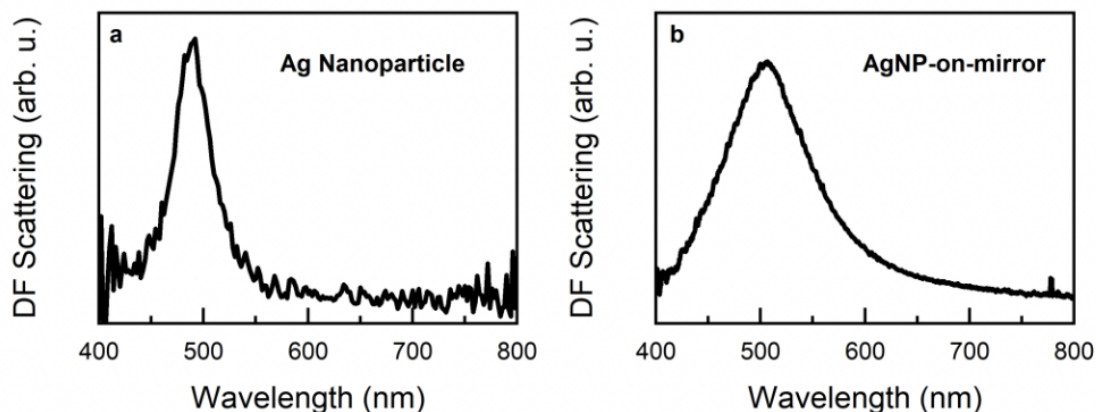


Figure S9. Single particle DF scattering of a) an isolated AgNP on glass and b) an AgNP-on mirror cavity. In b), the gold film and the particle are separated by a thin PMMA layer to replace the BAPI film to obtain a reference spectrum.

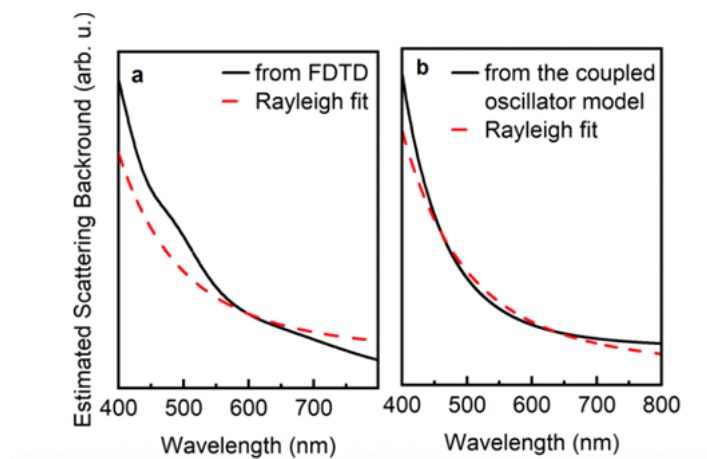


Figure S10. Fits to the scattering background signal estimated via a) FDTD or b) the coupled oscillator model with a Rayleigh scattering ($\propto c_1 \cdot \lambda^4 + c_2$, with c_1 and c_2 being fitting constants).

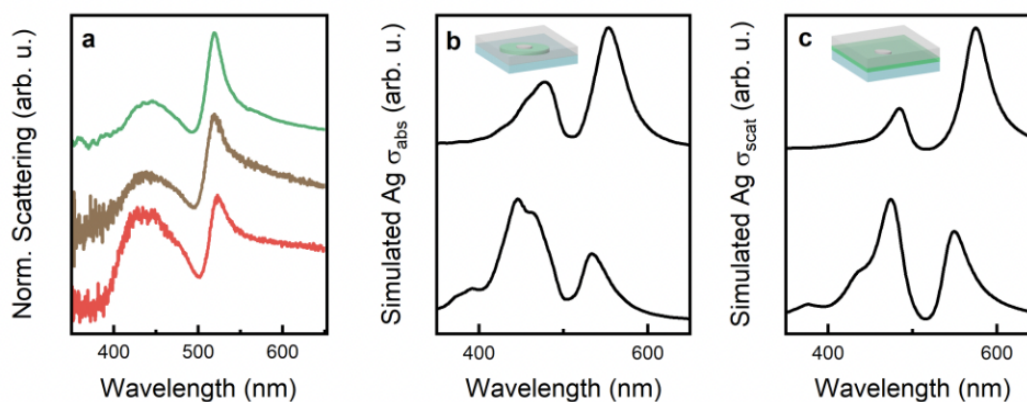


Figure S11. Side-by-side comparison between the experimental data, the simulated absorption of the AgNP coupled to the BAPI grains (Figure 4c) and the scattering of the AgNP coupled to the BAPI film (Figure 4b).

Parameter	Lorentz Oscillator #1	Lorentz Oscillator #2
<i>Amp</i>	42.5 ± 1.3	21.36 ± 0.33
<i>En</i>	$2.393 \pm 0.0014 \text{ eV}$	$3.322 \pm 0.0072 \text{ eV}$
<i>Bn</i>	$0.0489 \pm 0.00086 \text{ eV}$	$0.6826 \pm 0.010 \text{ eV}$

Table S1 Fitting parameter for the Lorentz oscillators used to describe the complex dielectric function of the BAPI film.

- (1) Xue, C.; Mirkin, C. A. PH-Switchable Silver Nanoprism Growth Pathways. *Angew. Chemie Int. Ed.* 2007, 46 (12), 2036–2038.
- (2) Jin, R.; Charles Cao, Y.; Hao, E.; Métraux, G. S.; Schatz, G. C.; Mirkin, C. A. Controlling Anisotropic Nanoparticle Growth through Plasmon Excitation. *Nature* 2003, 425 (6957), 487–490.
- 3) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden–Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chem. Mater.* 2016, 28 (8), 2852–2867.
- (4) Kulkarni, A. P.; Munechika, K.; Noone, K. M.; Smith, J. M.; Ginger, D. S. Phase Transfer of Large Anisotropic Plasmon Resonant Silver Nanoparticles from Aqueous 11 to Organic Solution. *Langmuir* 2009, 25 (14), 7932–7939.
- (5) CompleteEASE TM Data Analysis Manual; J. A. Woolam Co., Inc., 2011.
- (6) Handbook of Optical Constants of Solids; Palik, E. D., Ed.; Elsevier, 1985.
- (7) Fano, U. Effects of Configuration Interaction on Intensities and Phase Shifts. *Phys. Rev.* 1961, 124 (6), 1866–1878.

Appendix B: Supporting Information for Chapter 3

Ligand Equilibrium Influences Photoluminescence Blinking in CsPbBr₃: A Change Point Analysis of Widefield Imaging Data

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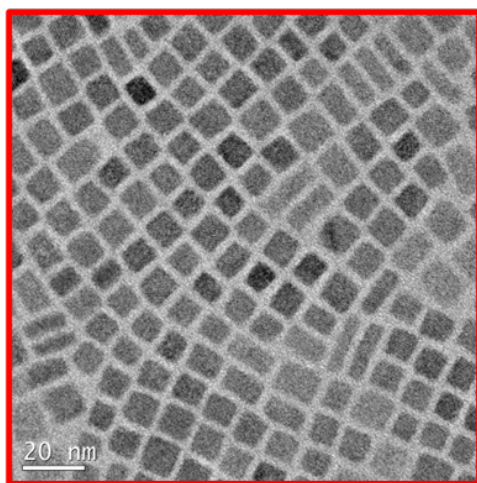
[†]These authors contributed equally to this work

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a



b

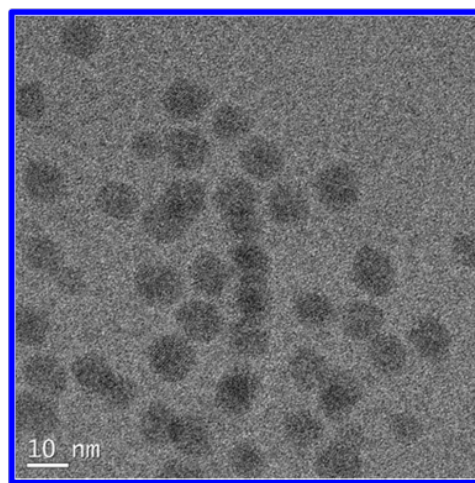


Figure S1. TEM of a) OA/OAm-capped quantum dots showing a cubic crystal habit and b) lecithin-capped quantum dots showing a spherical crystal habit

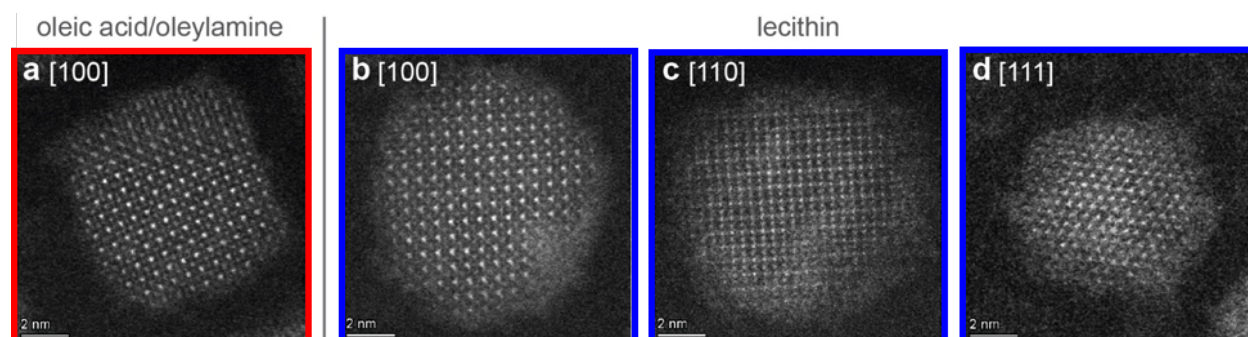


Figure S2. HAADF-STEM images of CsPbBr₃ capped with a) OA/OAM and b-d) lecithin ligands. The cuboidal morphology of the OA/OAM-capped QDs leads to preferential orientation down the [100] direction. At high resolution the rhombicuboctahedral morphology of the “spherical” lecithin-capped QDs allows for orientation down the b) [100], c) [110], and d) [111] directions.

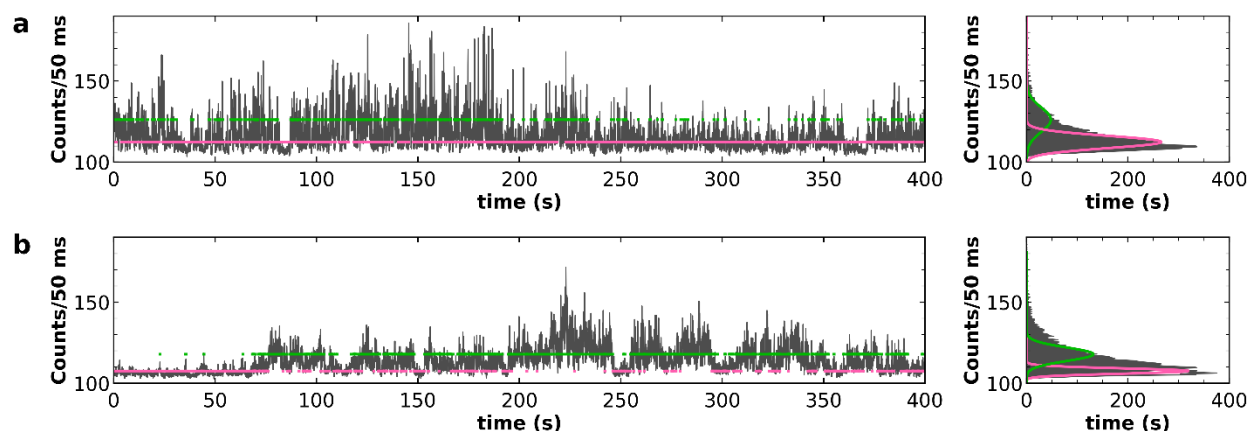


Figure S3. Randomly selected example blinking traces from OA/OAM-QDs showing the CPA identified intensity trajectories. Both traces have been fit to two average intensity-levels (pink and green).

Table S1. Ensemble characteristics of the five lecithin synthetic batches used in this study

	Absorption Band Edge (nm)	PL Maximum (nm)	PL Linewidth (nm)	PLQY (%)
LEC 1	503	505	19	97
LEC 2	505	508	19	97
LEC 3	505	507	17	98
LEC 4	507	509	16	94
LEC 5	507	508	18	93

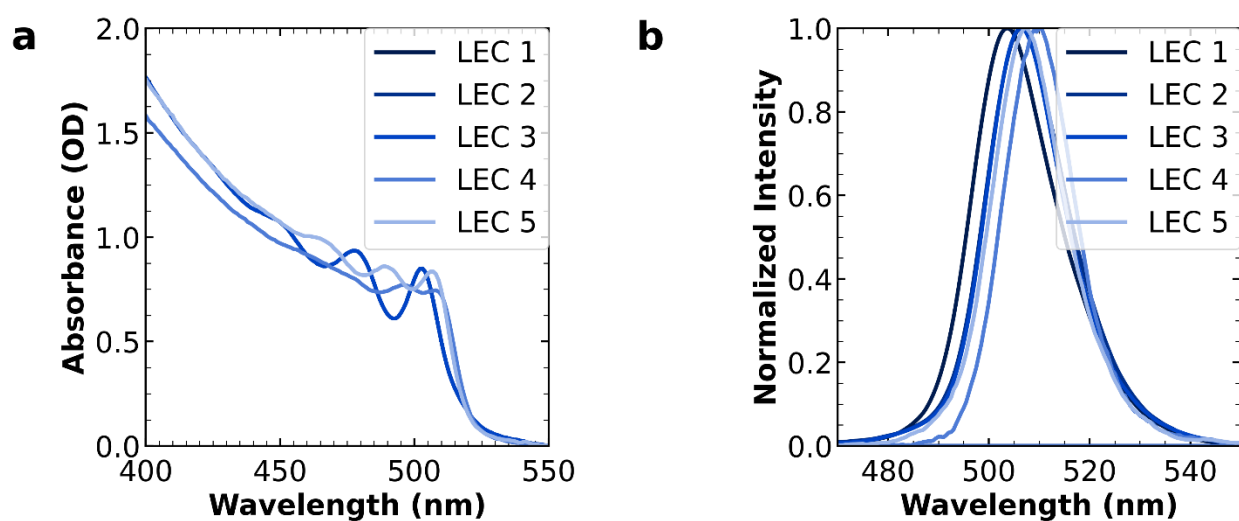


Figure S4. a) absorption spectra of the five lecithin synthetic batches used in this study b) PL of five lecithin synthetic batches used in this study

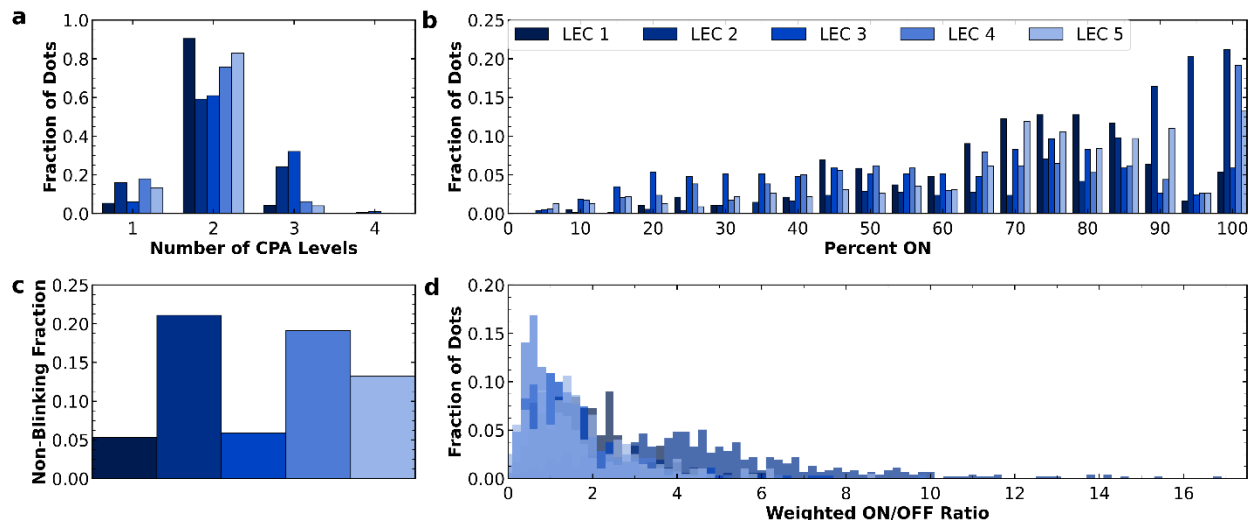


Figure S5. Comparisons of blinking behavior between the five lecithin synthetic batches across our four major blinking metrics. These statistics are comprised of 188, 553, 374, 340 and 227 QDs for batches 1-5 respectively a) number of intensity levels fit to each blinking trace by CPA. The average CPA levels are 2.0 ± 0.3 , 2.1 ± 0.6 , 2.2 ± 0.6 , 1.9 ± 0.5 and 1.9 ± 0.4 for batches 1-5 respectively b) percent of the trace duration that each QD spends ON. The average ON percentages are $66 \pm 17\%$, $77 \pm 20\%$, $53 \pm 24\%$, $56 \pm 23\%$ and $64 \pm 22\%$ for batches 1-5 respectively c) non-blinking fraction of QDs in each batch, 0.053, 0.22, 0.059, 0.19 and 0.13 for batches 1-5 respectively and d) the weighted ratio of expected time spent ON to expected time spent OFF

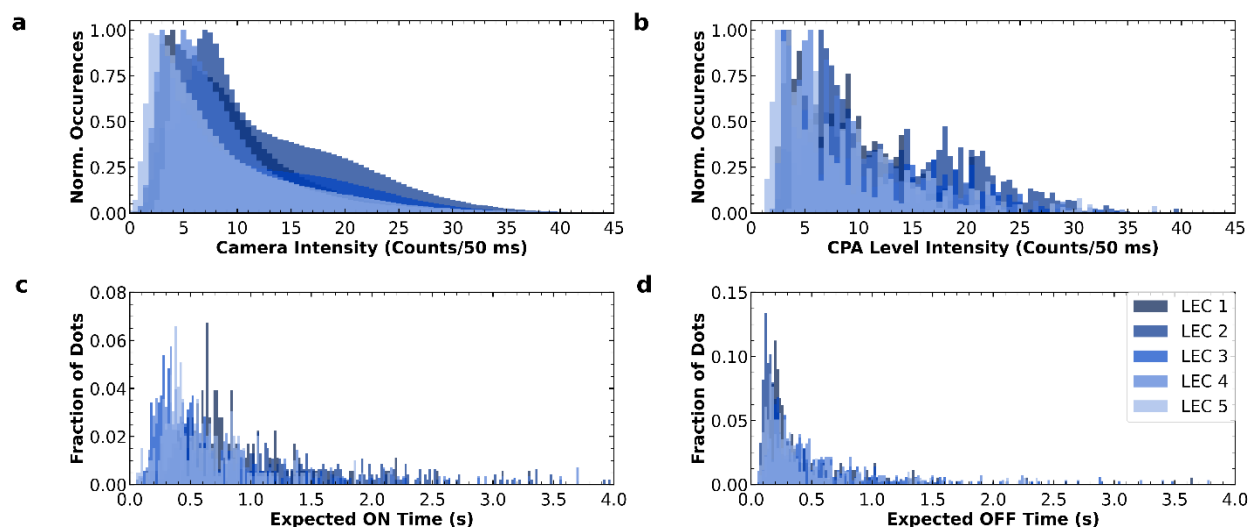


Figure S6. Comparison of blinking behavior between the five lecithin synthetic batches across four additional metrics a) distribution of intensities in the blinking traces according to the camera b) distribution of intensities in the blinking traces according to the CPA fits

c) distribution of the expected ON times from power-law dynamics and d) distribution of the expected OFF times from power-law dynamics.

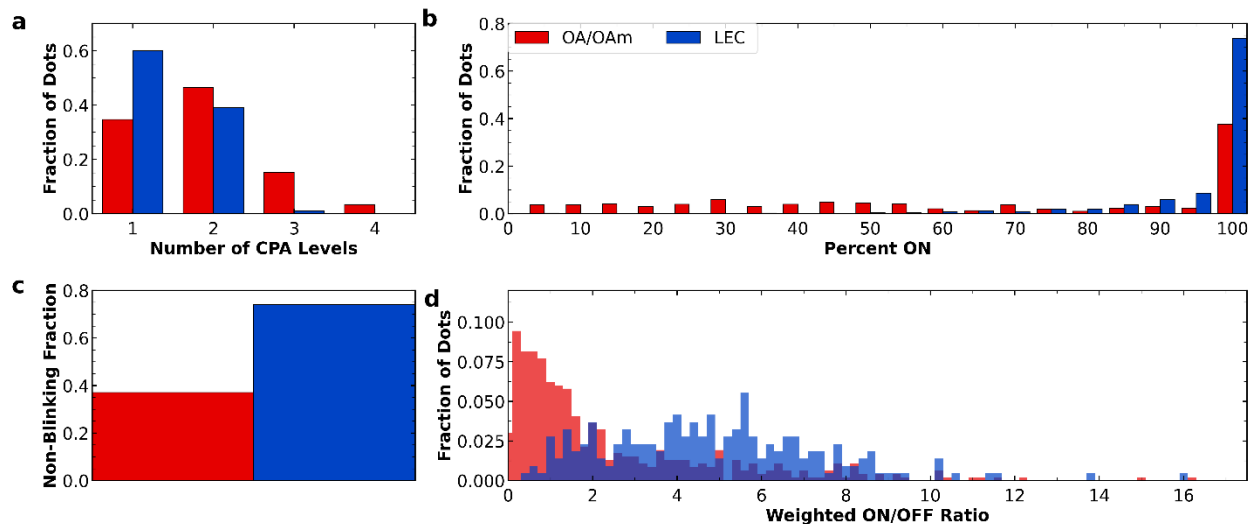


Figure S7. Comparisons of blinking behavior between two additional OA/OAm and lecithin synthetic batches across our four major blinking metrics. These data were obtained at an integration time of 200 ms using a 100x NA 0.95 objective. These statistics are comprised of 716 OA/OAm QDs and 543 lecithin QDs. a) number of intensity levels fit to each blinking trace by CPA. The average CPA levels are 1.8 ± 0.8 and 1.4 ± 0.5 for OA/OAm and lecithin respectively b) percent of the trace duration that each QD spends ON. The average ON percentages are $44 \pm 28\%$ and $87 \pm 13\%$ for OA/OAm and lecithin respectively c) non-blinking fraction of QDs in each batch, 0.38 and 0.73 for OA/OAm and lecithin respectively and d) the weighted ratio of time spent ON to time spent OFF

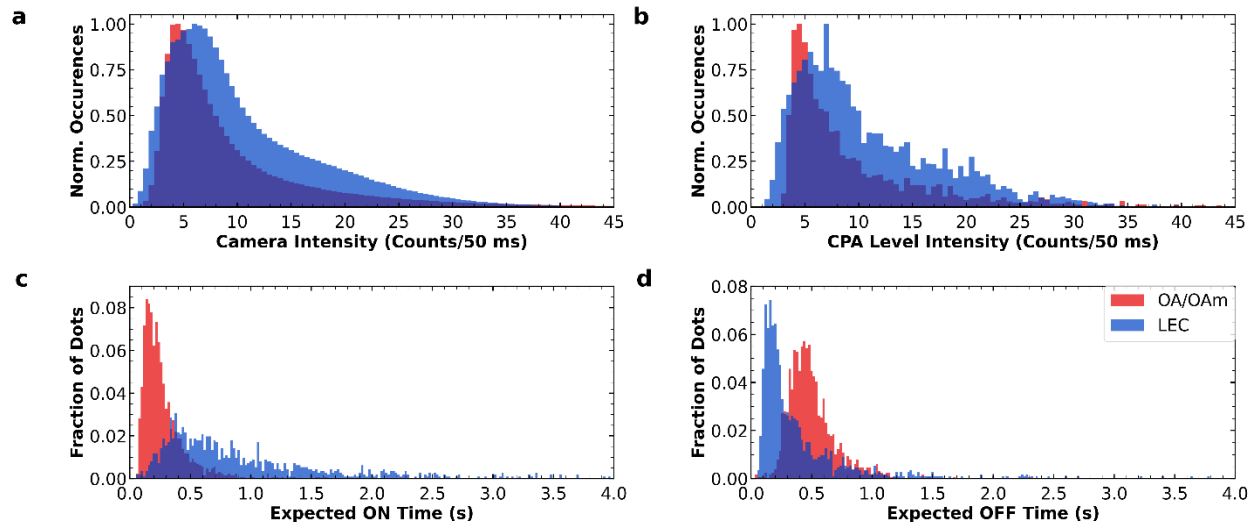


Figure S8. Comparison of blinking behavior between the OA/OAm- and lecithin- capped QDs across four additional metrics a) distribution of intensities in the blinking traces according to the camera b) distribution of intensities in the blinking traces according to the CPA fits c) distribution of the expected ON times from power-law dynamics and d) distribution of the expected OFF times from power-law dynamics.

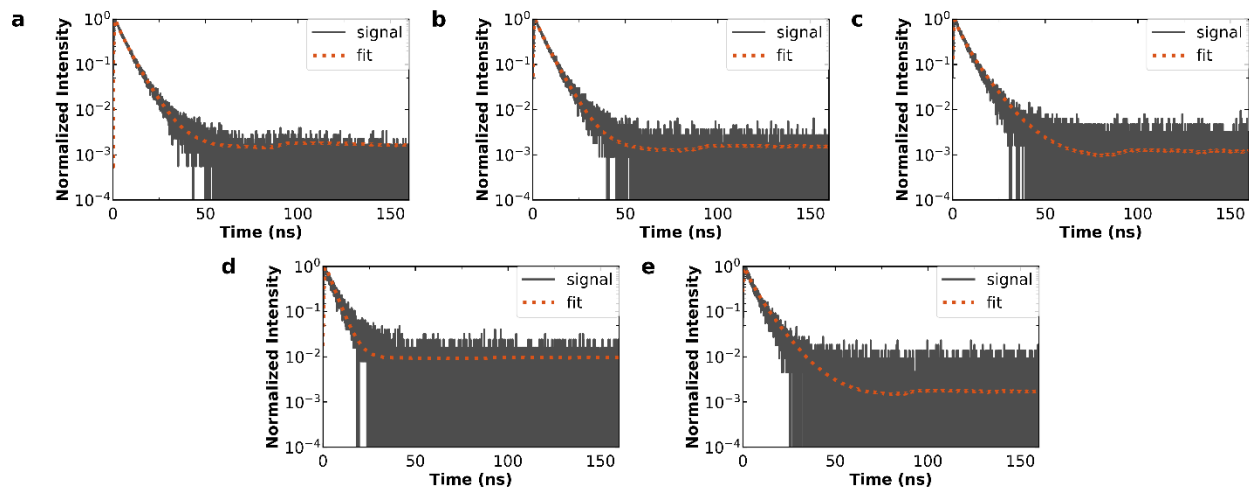


Figure S9. TRPL stretch-exponential fits (eq S2) for LEC 1 QDs as a function of concentration (see Table S1) a) solution 1: $\tau_{str} = 4.43$ ns, $\beta = 0.78$, $R^2 = 0.994$ b) solution 2: $\tau_{str} = 4.71$ ns, $\beta = 0.87$, $R^2 = 0.998$ c) solution 3: $\tau_{str} = 4.52$ ns, $\beta = 0.74$, $R^2 = 0.985$ d) solution 4: $\tau_{str} = 4.90$ ns, $\beta = 0.78$, $R^2 = 0.960$ and e) solution 9: $\tau_{str} = 4.50$ ns, $\beta = 0.76$, $R^2 = 0.982$

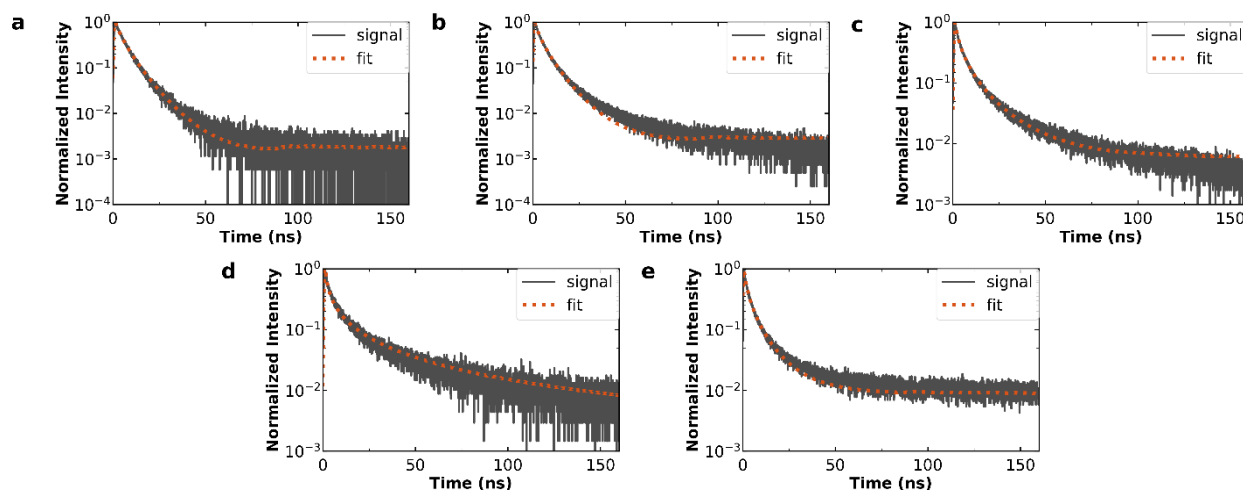


Figure S10. TRPL stretch-exponential fits (eq S2) for OA/OAm QDs as a function of concentration (see Table S1) a) solution 1: $\tau_{str} = 4.95$ ns, $\beta = 0.78$, $R^2 = 0.998$ b) solution 2: $\tau_{str} = 4.08$ ns, $\beta = 0.67$, $R^2 = 0.985$ c) solution 3: $\tau_{str} = 2.81$ ns, $\beta = 0.45$, $R^2 = 0.993$ d) solution 4: $\tau_{str} = 2.51$ ns, $\beta = 0.43$, $R^2 = 0.980$ and e) solution 9: $\tau_{str} = 2.08$ ns, $\beta = 0.45$, $R^2 = 0.992$

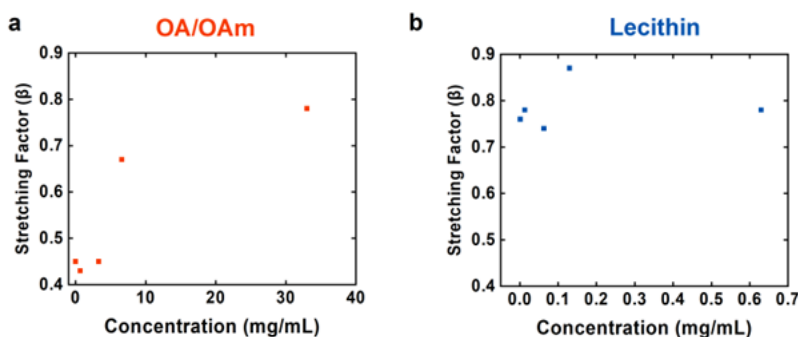


Figure S11. Comparison of stretch exponential beta-factors for concentration dependent lifetime data for a) OA/OAm- and b) lecithin- capped QDs. Beta-factors are taken from the lifetime fits shown in Figures S8 and S9 respectively.

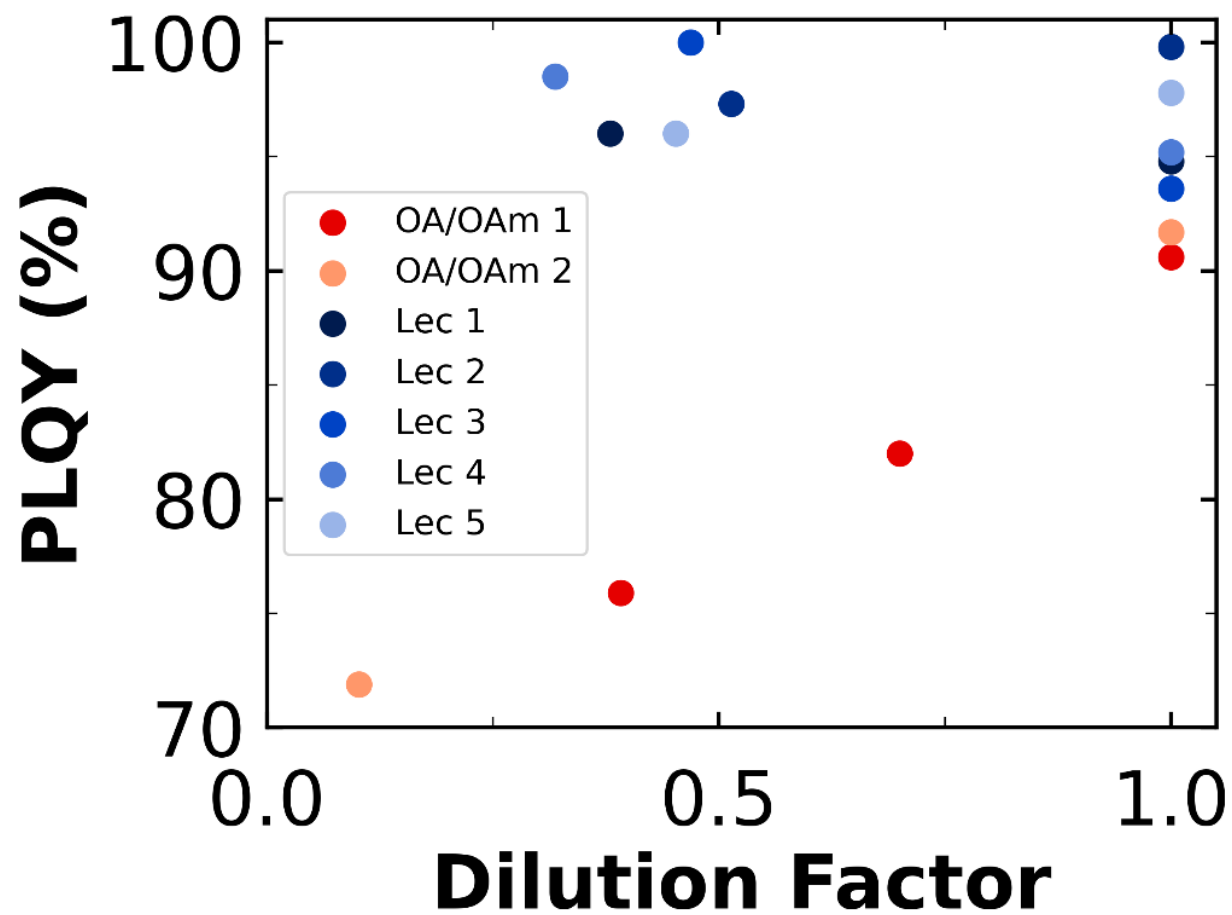


Figure S12. PLQY vs dilution factor for OA/OAm- and lecithin- capped QD solutions at concentrations measurable in an integrating sphere PLQY system.

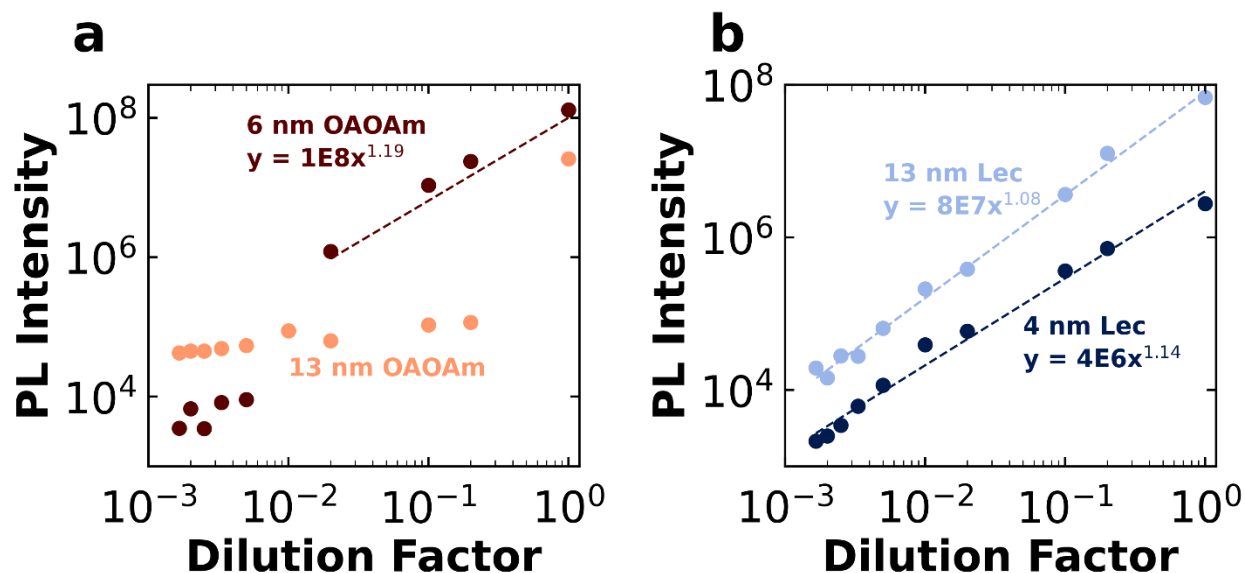


Figure S13. PL linearity for additional QD sizes. a) 6 nm (FWHM = 25 nm, PLQY = 90%) and 13 nm (FWHM = 22 nm, PLQY = 75%) OA/OAm-capped QDs b) 4 nm (FWHM = 30 nm, PLQY = 95%) and 13 nm (FWHM = 20 nm, PLQY = 98%) lecithin-capped QDs

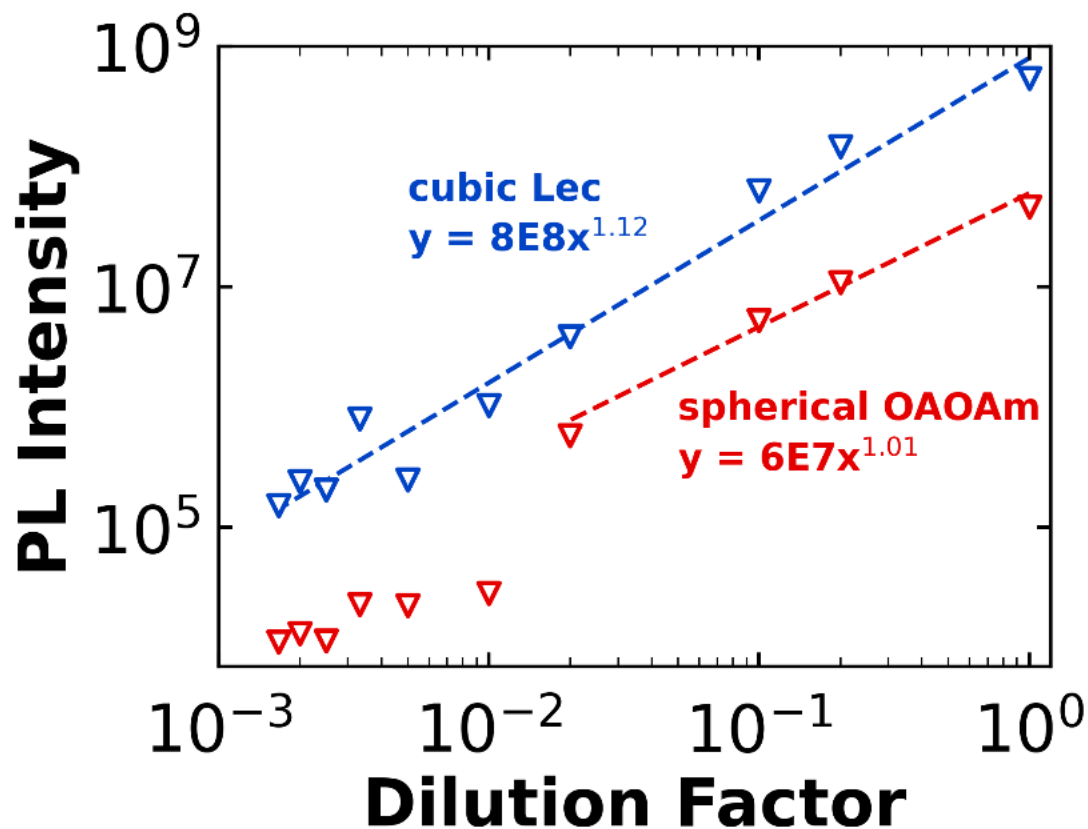


Figure S14. PL linearity for different QD morphologies. Cubic lecithin-capped QDs¹ (FWHM = 20 nm, PLQY = 60%) and spherical OA/OAm-capped QDs (FWHM = 21 nm, PLQY = 80%)

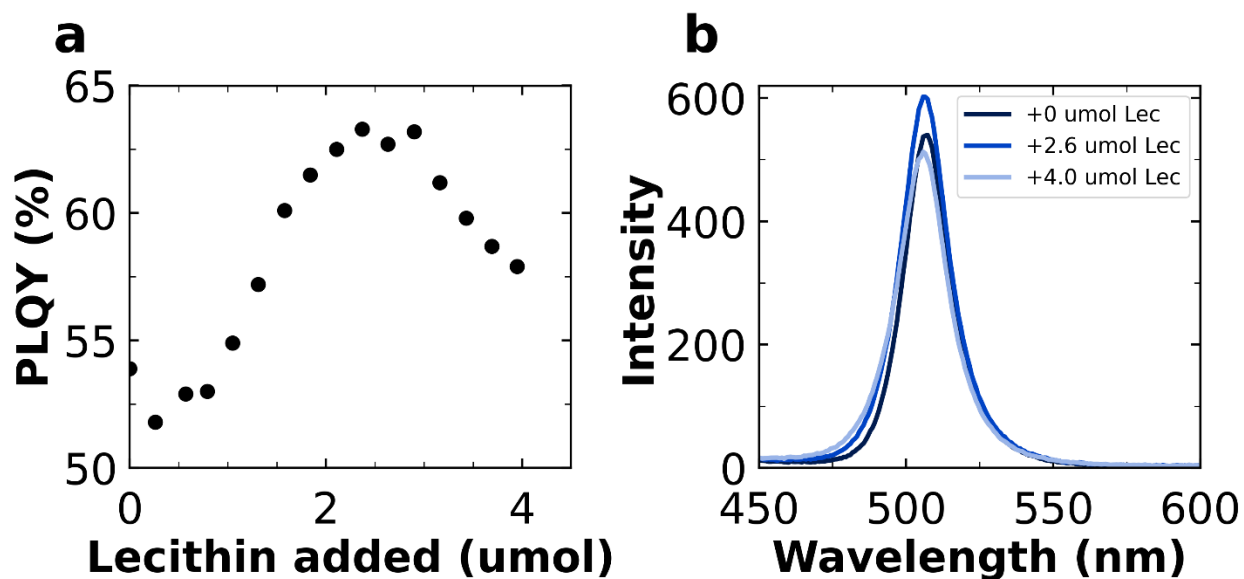


Figure S15. Evidence of etching with excess ligand addition a) PLQY vs. lecithin addition for low surface quality CsPbBr₃ QDs (starting PLQY 52%). b) Blue shift of PL peak position with surface etching in the presence of excess ligand.

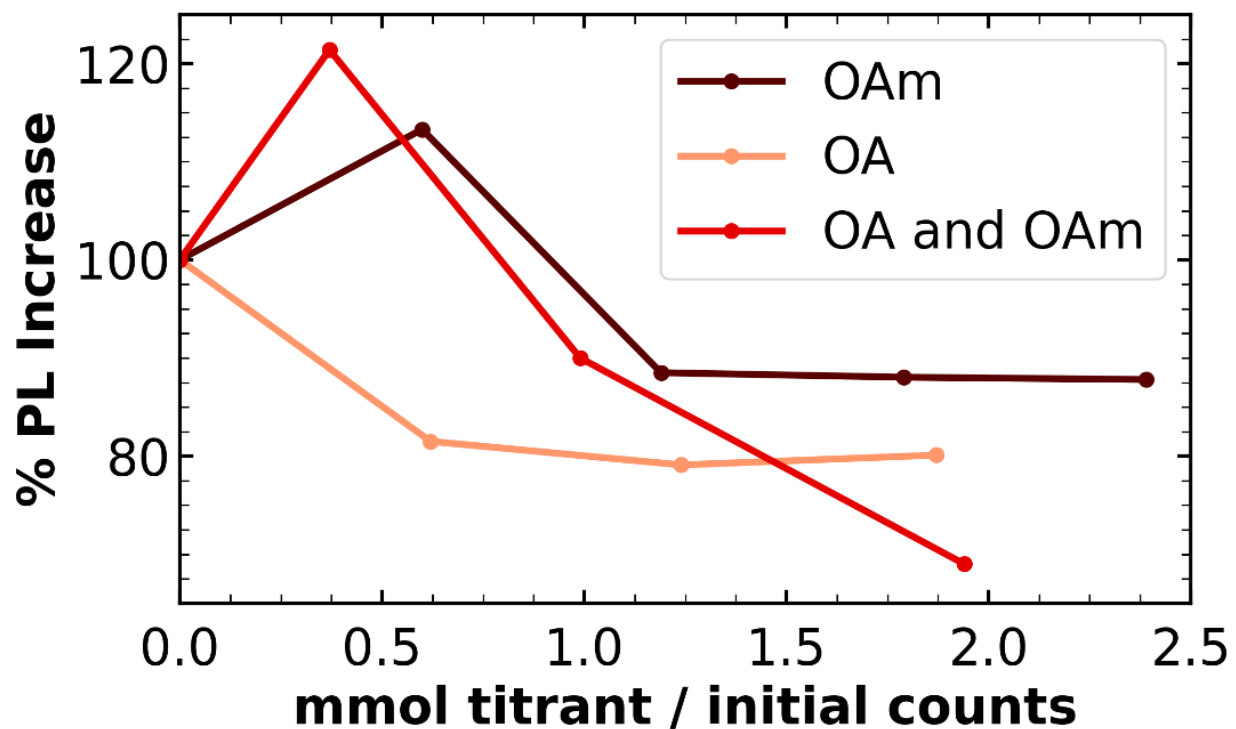


Figure S16. PL increase resulting from the addition of excess ligand to a widefield PL concentration solution of OA/OAm-CsPbBr₃ QDs comparing the addition of neat OAm to neat OA and a 1:1 (v:v) mixture of OA and OAm

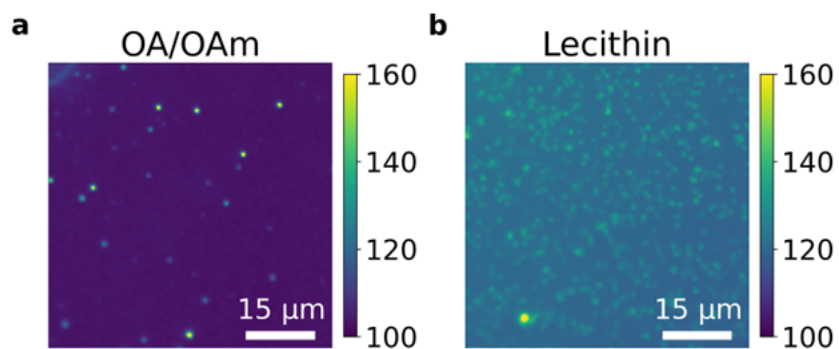


Figure S17. Widefield PL images of a) OA/OAm QDs and b) lecithin QDs. The sample solutions were prepared identically via serial dilution from stock solutions of the same optical density. The images correspond to samples made from solutions B_{OA/OAm} and B_{lec} respectively.

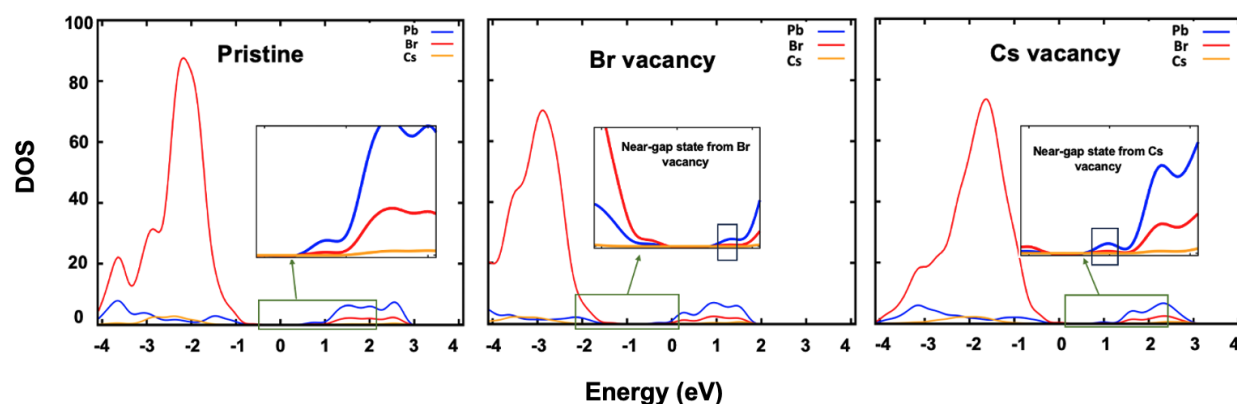


Figure S18. Density of states (DOS) of Cs-terminated slabs of CsPbBr₃. Calculations were performed at the PBE level with spin orbit coupling (SOC) effects on top of PBE-relaxed structures of the pristine slab (a) as well as slabs containing v_{Br} (b) and v_{Cs} (c). Near gap states due to the presence of v_{Br} and v_{Cs} are observed and marked with rectangles in the insets of panels b and c.

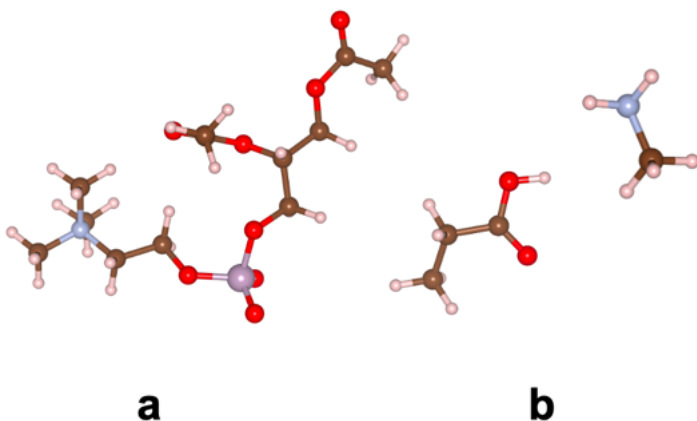


Figure S19. Simplified/truncated forms of the bidentate ligand and monodentate ligand pair used for computational purposes. Truncated lecithin (a), methylamine and propionic acid (b).

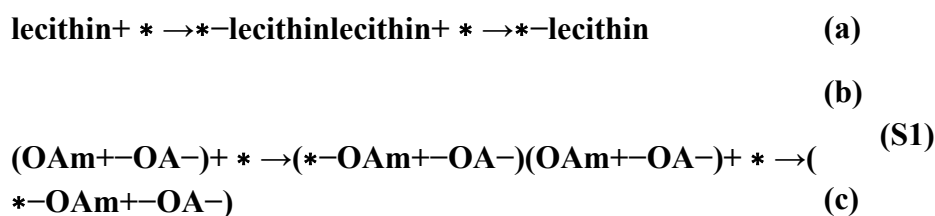
Table S2. Calculated binding energies (eV), including solvent effects, corresponding to the single (OAm or OA) and binary monodentate (OAm/OA) ligands passivating the pristine surface. OAm and OA correspond to oleylamine and oleic acid binding the OA/OAm-passivated pristine slab, while OAm* and OA* represent oleylamine and oleic acid binding the OA⁻/OAm⁺-passivated defective surface.

Passivating ligand(s)	OA/OAm	OAm	OA	OAm*	OA*
Solvated Binding Energy (eV)	-0.42	-0.17	-0.65	-0.25	-0.67

Table S3. Calculated binding energies (eV) corresponding to the binary monodentate (OAm⁺/OA⁻) and the bidentate ligand (lecithin) passivating different types of surface vacancy pairs (shown in Main Text Figure 5d)

Vacancy type	Type <i>i</i>	Type <i>ii</i>	Type <i>iii</i>	Type <i>iv</i>
OAm ⁺ /OA ⁻	-1.95	-1.88	-1.91	-2.07
Lecithin	-3.22	-3.17	-2.96	-2.40

Reaction Mechanism and Binding Energy (BE) Calculation



$$BE = E(* - \text{lig}) - E_{\text{lig}} - E^* \quad BE = E(* - \text{lig}) - E_{\text{lig}} - E^*$$

To compare energetics of lecithin and (OAm⁺-OA⁻) binding the QD surface, we considered comparable binding mechanisms (Equations S1a and S1b) whereby comparatively to the zwitterionic ligand, the monodentate ligand pair (OAm⁺-OA⁻) binds the quantum dot surface (* in Equation S1) as a complex. The corresponding binding energies can therefore be calculated per Equation S1c, where

$$E^*E^*$$

and

$$E(*-lig)E(*-lig)$$

are DFT energies of the bare and ligand-passivated slabs and

$$EligElig$$

represents the energy of either lecithin or the (OAm⁺-OA⁻) complex.

Solvation Effects on Ligand Binding the QD Surfaces

In principle, the rate of reactions can be controlled by the solvent's polarity, and therefore its dielectric constant, as well as its acceptor (AN) or donor number (DN). To account for the effect of ACN and acetone which are both polar aprotic solvents and used in the washing process of our synthesized QDs, we employed an explicit solvent model.

$$Esolvnx*solv=E(*-ligand)x*solv-E(*-ligand)-x.EsolvEsolvnx*solv=E(*-ligand)x*solv-E(*-ligand)-x.Esolv \quad (S2)$$

$$BE ||solv=BE+ (Esolvn)(*-lig)-(Esolvn)lig-(Esolvn)*BE |solv=BE+ (Esolvn)(*-lig)-(Esolvn)lig-(Esolvn)* \quad (S3)$$

We used periodic solvated slab models including a layer of liquid solvents on top of the slabs that were used for binding energy calculations. We first attained the number of solvent molecules required to sufficiently solvate the ligands as well as bare and passivated slabs, by gradually adding solvent molecules (x) to the system and calculating the solvation energy (

$$Esolvnx*solvEsolvnx*solv$$

) per Equation S2. In this equation,

$$x.Esolvx.Esolv$$

, represents the energy of x solvent molecules in liquid phase, and

$$E(*-ligand)E(*-ligand)$$

and

$$E(*-ligand)x*solvE(*-ligand)x*solv$$

are total energies of the passivated slab without solvent and containing x solvent molecules, respectively. As a representative, the onset of the plateau in Figures S13b and S13c shows the

minimum number of solvent molecules required to sufficiently solvate the (OAm⁺-OA⁻)-passivated and lecithin-passivated slabs of CsPbBr₃. Accordingly, we used 10 and 20 solvents for the adjacent and non-adjacent (twice as large unit cell) vacancy cases, respectively. Finally, to obtain the net effect of solvation on the binding energy, we calculated the solvation energy for the ligand.

(*E*_{solv})_{lig}(*E*_{solv})_{lig}

, clean slab

(*E*_{solv})*(*E*_{solv})*

and the ligand-passivated slab

(*E*_{solv})(*-lig)(*E*_{solv})(*-lig)

, and computed the binding energy in the presence of solvents (

BE |_{solv} BE |_{solv}

) by applying the obtained net solvation energy to the BE, per Equation S3.

Binding Energy Calculation of Mono-ligand Passivated Single-vacancy Surfaces

In addition to vacancy pairs, we studied Br⁻-rich and OAm⁺-rich conditions where the single vacancy surface is passivated by a monodentate ligand. We calculated the BE of OAm⁺ passivating CsPbBr₃ by gradually pulling the ligand off the surface and obtained the corresponding energy vs. distance plot (Figure S13a). *E_d* is the energy required to pull the ligand off the surface by a distance of *d* (Å), marked on the x-axis, *d* = 0 (Å) refers to the ligand binding the surface, and *d* = -1 (Å) corresponds to the ligand filling the vacant site. It can be seen that OAm⁺ strongly binds the surface (BE = -4.1 eV) which can primarily be attributed to the size of the ligand and therefore, the capability of the ammonium moiety to access and occupy the vacant site (*v'*_{Cs}).

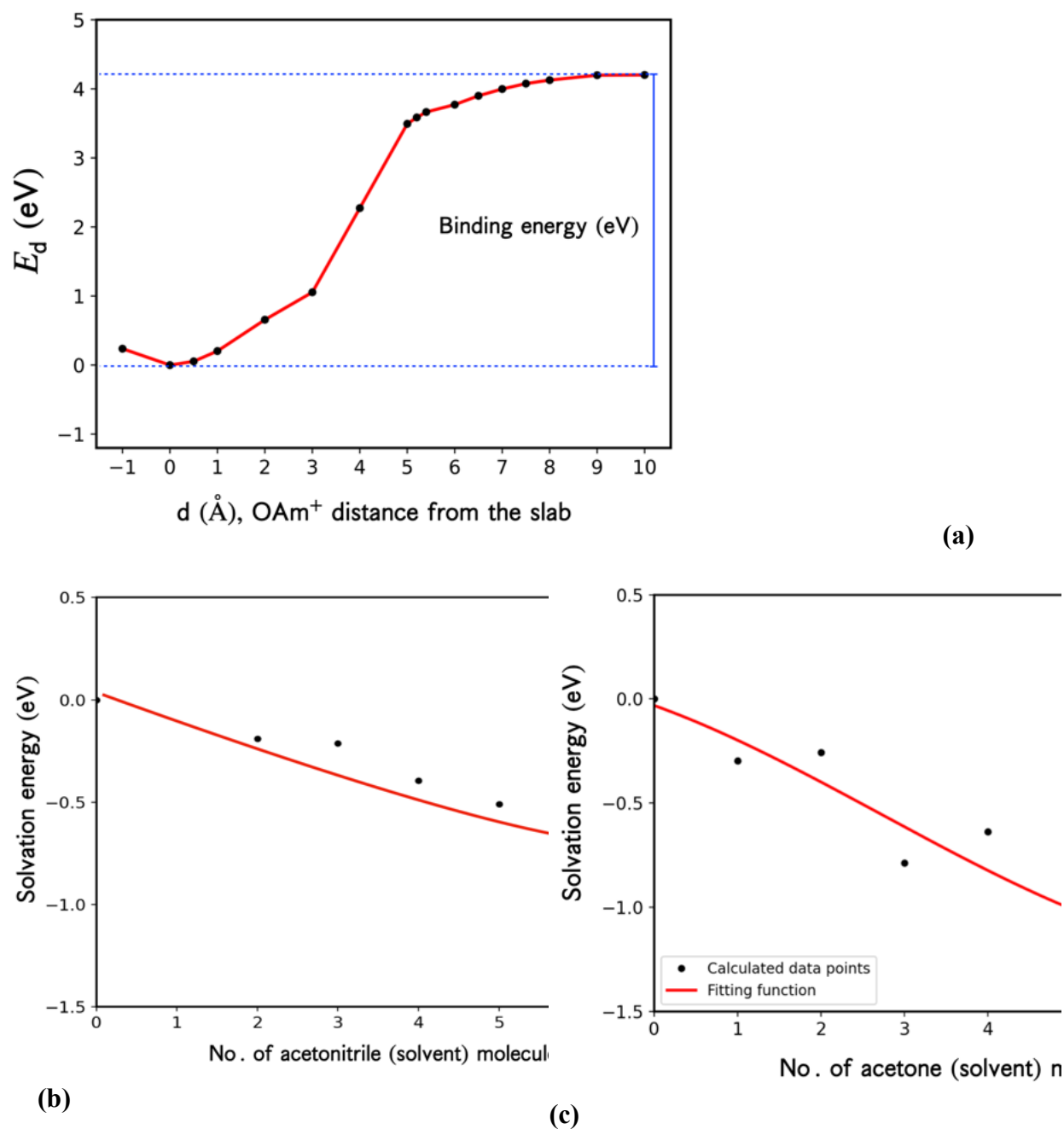


Figure S20. (a) Binding energy calculation of the OAm⁺-passivated slab containing a single Cs vacancy (v'_{Cs}). E_d is the energy required to pull the ligand off the surface by d (Å) (shown on the x-axis), $d = 0$ (Å) refers to the ligand binding the surface, and $d = -1$ (Å) corresponds to the ligand filling the vacant site. (b) Solvation energies versus the number of solvent molecules, calculated per Equation S3, for (OAm⁺-OA⁻)-passivated and (c) lecithin-

passivated slabs of CsPbBr₃ are shown. Solid blue lines indicate the solvation energies at the onset of the plateau corresponding to the number of solvent molecules sufficient to solvate the passivated slabs.

Experimental Equilibrium Constants and Binding Energies

To better understand the calculated binding energies in the context of the system – we compute the ligand binding equilibrium constant from both the DFT binding energies (Main Text Figure 5d) and the experimental PL dilution results (Main Text Figure 4c).

The ligand binding equilibrium constant from DFT was calculated with equation S4:

$$\Delta G^\circ = -RT \ln(K_{ligand}) \quad \Delta G^\circ = -RT \ln(K_{ligand})$$

(S4)

where

$$\Delta G^\circ$$

is the binding energy in J/mol, R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature and K_{ligand} is the ligand binding equilibrium constant.

The experimental ligand binding equilibrium constant was calculated through a series of steps. First to determine the ligand and nanocrystal solutions we dried 2 mL of a 290 nM solution of the OA/OAm-capped QDs in a centrifuge tube of known weight and measured the total QD and ligand mass to be 3 ± 1 mg. The total mass contribution from the OA/OAm-capped QDs was calculated to be 1 mg so the maximum ligand contribution was 2 mg. The dry mass of 2 mL of a 140 nM solution of lecithin-capped QDs was measured to be 2 ± 1 mg. The total mass contribution from the lecithin-capped QDs was calculated to be 0.3 mg so the maximum ligand contribution was 1.7 mg.

Assuming 100 binding sites per QD and that the QDs start as completely bound, the initial concentrations at the drop-off point (solution 6, 0.04 nM) were calculated to be [OA/OAm-QD] = 3.6E-11 M, [free OA/OAm] = 1.9E-7 M, [lecithin-QD] = 3.6E-11 M and [free lecithin] = 1.3E-7 M.

Based on Figure 4c the OA/OAm the integrated PL intensity at 0.04 nM is ~7 times lower than expected, meaning that at equilibrium only 15% of the QDs are still bound by ligand and emissive. For lecithin the PL intensity is nearly linear and an estimated 99% of the QDs are still bound by ligand and emissive. From these numbers K_{ligand} can be calculated using equation S5

$$K_{ligand} = \frac{f_{emissive}[QD-ligand]}{(1-f_{emissive})[QD-ligand][free\ ligand]} \quad K_{ligand} = \frac{f_{emissive}[QD-ligand]}{(1-f_{emissive})[QD-ligand][free\ ligand]}$$

(S5)

Where $f_{emissive}$ is the fraction of quantum dots which are still bound and emissive, [QD-ligand] is the starting concentration of fully bound QDs in solution 6 and [free-ligand] is the starting concentration of free ligand in solution 6.

Table S4. Ligand binding equilibrium constant K_{ligand} for solvated OA/OAm and lecithin QDs computed from DFT and experimental results

		K_{ligand}
DFT	<i>OA/OAm</i>	3.7 E4
	<i>lecithin</i>	1.3 E34
Experimental	<i>OA/OAm</i>	9.1 ± 0.3 E5
	<i>lecithin</i>	7.4 ± 0.6 E8

Using equation S4 the experimental binding energy of OA/OAm to CsPbBr₃ is -0.34 eV. For lecithin the experimental binding energy is -0.50 eV. The observed discrepancy between our theoretical and experimental binding energies for lecithin can likely be attributed to our decision to use a truncated version of the molecule for computational feasibility. We anticipate that the solvent effects would have been more pronounced, aligning the calculated binding energies more closely with experimental values, had the full molecular structure been incorporated in our analysis.

Table S5. Serial dilutions resulting in QD solutions used for concentration dependent PL. Solutions used for TRPL are indicated with a star.

	Volume of OA/OAm QD Solution	Concentration of OA/OAm QDs (mg/mL)	Volume of lecithin QDs	Concentration of lecithin QDs (mg/mL)	Volume of Hexanes (mL)	Dilution Factor
Solution 1 (Ensemble PLQY Concentration)*	100 μ L of stock solution	3.3E1	200 μ L of stock solution	6.3E-1	4	1
Solution 2*	20 μ L of stock solution	6.6E0	40 μ L of stock solution	1.3E-1	4	2E-1
Solution 3*	10 μ L of stock solution	3.3E0	20 μ L of stock solution	6.3E-2	4	1E-1
Solution 4*	2 μ L of stock solution	6.6E-1	4 μ L of stock solution	1.3E-2	4	2E-2
Solution 5	1 μ L of stock solution	3.3E-1	2 μ L of stock solution	6.3E-3	4	1E-2
Solution 6	200 μ L of solution 3	1.7E-1	200 μ L of solution 3	3.2E-3	4	5E-3
Solution 7	133 μ L of solution 3	1.1E-1	133 μ L of solution 3	2.1E-3	4	3.3E-3
Solution 8	100 μ L of solution 3	8.3E-2	100 μ L of solution 3	1.6E-3	4	2.5E-3
Solution 9 (Microscopy Concentration)*	400 μ L of solution 4	6.6E-2	400 μ L of solution 4	1.3E-3	4	2E-3
Solution 10	333 μ L of solution 4	5.5E-2	333 μ L of solution 4	1.1E-3	4	1.7E-3

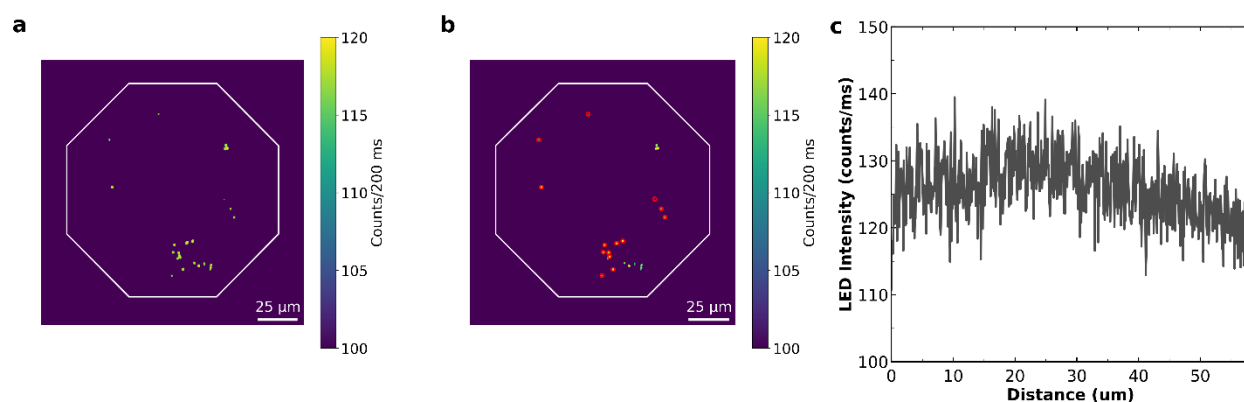


Figure S21. a) quantum dot sample illuminated with the field-stop (white octagon) partially closed to demonstrate the quality of particle selection. b) quantum dot sample illuminated with the field-stop (white octagon) partially closed and selected particles circled in red to demonstrate the quality of particle selection. The particle selection algorithm accounts for particle brightness, size and nearest neighbor distance. c) Illumination homogeneity of the LED across the objective flat field of view. Y-axis limits represent $\pm 20\%$ of the mean illumination intensity.

		CPA Identified Intensity States						
		1	2	3	4	5	6	7
True Number of Intensity States	1	1.00	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.00	0.84	0.16	0.00	0.00	0.00	0.00
	3	0.00	0.00	1.00	0.00	0.00	0.00	0.00
	4	0.00	0.00	0.00	1.00	0.00	0.00	0.00
	5	0.00	0.00	0.00	0.08	0.92	0.00	0.00
	6	0.00	0.00	0.04	0.18	0.44	0.35	0.00
	7	0.00	0.00	0.96	0.04	0.00	0.00	0.00

Figure S22. Confusion matrix quantifying the performance of our custom CPA package. Confusion matrix was generated by creating synthetic blinking traces with a power law exponent of $\alpha = 1.5$, a time step size of 50 ms and n states evenly spaced between 100 and 140 counts/50 ms. 100 synthetic traces² were generated for each n in the range of 1 to 7 (the true number of states). The synthetic traces were analyzed using our CPA package and the number of fit states was extracted (the number of CPA determined states). This test shows that we can reliably resolve up to 5 intensity states in blinking traces at the experimental conditions (time step size = 50 ms and intensity range of 100 to 140 counts/50 ms).

Change Point Analysis to Blinking Statistics

Our analysis package uses CPA to determine the number of intensity levels in each trace and which intensity level each time point belongs to.^{3,4} From this information we calculate the dwell time probability distribution for each level and fit to a power law⁵ (Equation S6) and a truncated power law⁶ (Equation S7). The fit that yields a larger R^2 value is used for further analysis of the intensity level.

$$P(t)=Ct^{-\alpha}Pt=Ct^{-\alpha}$$

(S6)

[Equation]

(S7)

Where $P(t)$ is the dwell time probability distribution, C is an exponential pre-factor, t is the dwell time, α is the power law exponent and T_c is the cutoff time. From these fits the dwell time expectation value [Equation] can be calculated according to Equations S8 (power law) or S9 (truncated power law).

[Equation]

(S8)

[Equation]

(S9)

Where t_{max} is the maximum observed dwell time, t_{min} is the minimum observed dwell time and Γ is the upper incomplete gamma function.

For the purposes of the post-CPA analysis an ON-state is defined as the most intense CPA identified level and all other CPA identified intensity levels are defined as OFF-states. From the above information we can calculate our blinking statistics.

[Equation]

(S10)

[Equation]

(S11)

[Equation]

(S12)

[Equation]

(S13)

Where T_{ON} is the total dwell time of the ON-state, T_{total} is the total measurement time, n is the number of OFF states, T_n are the total dwell times of each OFF-state, τ_{ON} is the expected ON event dwell time (Figures S5c and S7c), τ_{OFF} is the weighted expected OFF event dwell time (Figure Figures S5d and S7d) and $\tau_{ON/OFF}$ is the weighted ON/OFF ratio (Figure 3d).

References:

- (1) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *J Am Chem Soc* 2019, *141* (50), 19839–19849. https://doi.org/10.1021/JACS.9B09969/SUPPL_FILE/JA9B09969_LIVESLIDES.MP4.
- (2) Palstra, I. M.; Koenderink, A. F. A Python Toolbox for Unbiased Statistical Analysis of Fluorescence Intermittency of Multilevel Emitters (). *Journal of Physical Chemistry C* 2021, *125* (22), 12050–12060. <https://doi.org/10.1021/acs.jpcc.1c01670>.
- (3) Watkins, L. P.; Yang, H. Detection of Intensity Change Points in Time-Resolved Single-Molecule Measurements. *Journal of Physical Chemistry B* 2005, *109* (1), 617–628. <https://doi.org/10.1021/jp0467548>.
- (4) Li, H.; Yang, H. Statistical Learning of Discrete States in Time Series. *Journal of Physical Chemistry B* 2019, *123* (3), 689–701. <https://doi.org/10.1021/acs.jpcb.8b10561>.
- (5) Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. Nonexponential “Blinking” Kinetics of Single CdSe Quantum Dots: A Universal Power Law Behavior. *J Chem Phys* 2000, *112* (7), 3117–3120. <https://doi.org/10.1063/1.480896>.
- (6) Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G. Blinking Statistics in Single Semiconductor Nanocrystal Quantum Dots. *Phys Rev B Condens Matter Mater Phys* 2001, *63* (20). <https://doi.org/10.1103/PhysRevB.63.205316>.

Appendix C: Supporting Information for Chapter 4

This work is taken from a draft of an in preparation publication.

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Methods:

Chemicals

Cesium carbonate (Cs_2CO_3 , 99.9% metals basis), diisooctylphosphinic acid (DOPA, 90%), trioctylphosphine oxide (TOPO, 99%), hexanes (anhydrous 95%), hexanes ($\geq 95\%$), polystyrene (PS, MW 280,000), toluene (anhydrous 99.8%), octane (anhydrous $\geq 99\%$), acetone (90%), isopropyl alcohol (IPA, 90%) and acetonitrile (ACN, anhydrous 99.8%) were purchased from Millipore Sigma. Lecithin (90%) and lead (II) bromide (PbBr_2 , 99.998% metals basis) were purchased from Alfa Aesar. Cs_2CO_3 was dried in a vacuum oven at 120°C for 8 hours and stored in a glovebox. All other chemicals were used as received.

Synthesis of Lecithin-Capped CsPbBr_3 QDs

The precursor solutions for lecithin-capped CsPbBr_3 were prepared according to Akkerman et al.⁵² The QDs were synthesized under ambient conditions in 6 mL hexanes with 160 μL of 0.04 M PbBr_2 -TOPO, 320 μL of 0.2 M TOPO, 80 μL of 0.02 M Cs-DOPA. After 30 minutes of stirring at room temperature 80 μL of 0.13 M lecithin was added to the reaction. The QDs were subsequently washed by adding acetone in a 3:1 v:v ratio and centrifuged at 10,000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was dissolved in 2 mL anhydrous toluene, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Synthesis of C8C12 PEA-Capped CsPbBr_3 QDs

The precursor solutions for lecithin-capped CsPbBr_3 were prepared according to Akkerman et al.⁵² The QDs were synthesized under ambient conditions in 6 mL hexanes with 160 μL of 0.04 M PbBr_2 -TOPO,

320 μL of 0.2 M TOPO, 80 μL of 0.02 M Cs-DOPA. After 30 minutes of stirring at room temperature 80 μL of 0.13 M lecithin was added to the reaction. The QDs were subsequently washed by adding ethyl acetate in a 3:1 v:v ratio and centrifuged at 10,000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was dissolved in 2 mL anhydrous hexanes, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Synthesis of DC-Capped CsPbBr₃ QDs

The precursor solutions for lecithin-capped CsPbBr₃ were prepared according to Akkerman et al.⁵² The QDs were synthesized under ambient conditions in 6 mL hexanes with 160 μL of 0.04 M PbBr₂-TOPO, 320 μL of 0.2 M TOPO, 80 μL of 0.02 M Cs-DOPA. After 30 minutes of stirring at room temperature 80 μL of 0.13 M lecithin was added to the reaction. The QDs were subsequently washed by adding acetone in a 3:1 v:v ratio and centrifuged at 10,000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was dissolved in 2 mL anhydrous toluene, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Synthesis of DDAB-Capped CsPbBr₃ QDs

The precursor solutions for lecithin-capped CsPbBr₃ were prepared according to Akkerman et al.⁵² The QDs were synthesized under ambient conditions in 6 mL hexanes with 160 μL of 0.04 M PbBr₂-TOPO, 320 μL of 0.2 M TOPO, 80 μL of 0.02 M Cs-DOPA. After 30 minutes of stirring at room temperature 80 μL of 0.13 M lecithin was added to the reaction. The QDs were subsequently washed by adding ethyl acetate in a 3:1 v:v ratio and centrifuged at 10,000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was dissolved in 2 mL anhydrous toluene, filtered through a 0.45 μm PTFE filter and stored at 0°C in a glovebox.

Ensemble Characterization

Absorbance spectra of the QD solutions were performed using a Perkin-Elmer Lambda 950 UV/Vis/NIR Spectrometer with a range of 400-600 nm, with a step size of 0.5nm and an integration time of 0.5 s. Absorbance spectra were transformed from wavelength to energy according to equation S1.¹

$$A(E) \propto \frac{A(\lambda)}{\nu} \quad (\text{S1})$$

Steady-state photoluminescence spectra of solution samples were acquired using a fiber coupled Ocean Optics HDX spectrometer. Spectra were collected using an excitation wavelength of 405 nm. Spectral correction was performed using a calibrated white light source (Ocean Insight HL-3P-INT-CAL) to correct for the responsivity of the detector. Steady state PL spectra were acquired with integration times of 200ms, with 20 scan averaging.

Steady-state photoluminescence spectra of film samples on glass were acquired using an Edinburgh Instruments FLS1000 Photoluminescence Spectrometer. The film samples were excited with a Xenon arc lamp, with wavelength selection provided by an excitation monochromator. Spectra were collected using an excitation wavelength of 405 nm with an excitation bandwidth of 0.5nm. Steady state PL spectra were acquired with a hold time of 1s, 0.5nm step size and with 3 scan averaging. Photoluminescence spectra were transformed from wavelength to energy using equation S2.¹

$$I(E) \propto IE \propto I(\lambda)\nu^3E^2 \quad (\text{S2})$$

Time resolved photoluminescence measurements were acquired using a commercial PicoQuant FluorTime 100 system with LDH-405 laser diode, a 405 nm picosecond pulsed diode laser. The repetition rate is controlled by an external trigger input from a PicoHarp PDL 800-B laser driver and was set to 5 MHz. A photomultiplier tube (PMT) detector was used in TCSPC mode with an instrumental response function (IRF) of approximately 400 ps. The instrument response function (IRF) was measured via laser scatter from a commercial solution of colloidal silica (LUDOX). Concentration dependent

photoluminescence was collected on the same instrument with a laser repetition rate of 50 MHz. TRPL lifetime analysis was performed using a custom Python IRF-reconvolution package. Lifetimes were fit using a stretch exponential decay (Equation 1).

(S3)

Where A is the pre-exponential factor, τ_k is the lifetime of the decay, C is the background of the measurement and β is the distribution of decay rates. τ_{str} , the average lifetime of a stretch exponential, is calculated according to Equation 2 where Γ is the gamma function.

(S4)

Photoluminescence quantum yield measurements (PLQY) were performed on a commercial integrating sphere system (Hamamatsu Photonics K.K). PLQY values are determined using a white light source (Hamamatsu Mercury Xenon Lamp) and a monochromator for wavelength selection (405 nm) as the excitation source to illuminate the samples in an integrating sphere (Hamamatsu Photonics K.K). The optical density of samples was kept below 0.1 at the excitation wavelength to minimize reabsorption effects. Spectral correction was performed using a calibrated white light source (Ocean Insight HL-3P-INT-CAL) to correct for the responsivity of the detector.

Small-angle x-ray scattering (SAXS)

CsPbBr₃ quantum dots in toluene were sealed in quartz capillaries under inert atmosphere. SAXS data were taken on a Xenocs XEUS 3.0 instrument with a Cu K α source. Scans at four sample-to-detector distances were merged to obtain $I(q)$ over a large q -range. A capillary of solvent was likewise measured; scattered intensity scaled to the sample data and subtracted as background.

Transmission electron microscopy (TEM)

TEM was performed with a FEI Tecnai G2 20 S-Twin operated at 200kV. Samples were prepared by drop-casting solutions of CsPbBr₃ QDs onto ultrathin carbon film TEM grids (Ted Pella, Prod # 01824, ultrathin carbon film on lacey carbon support film, 400 mesh, Cu). To minimize air exposure, grid prep was performed in a glovebox with an argon atmosphere. After drop-casting, the grids were dried under vacuum in the glovebox antechamber for roughly 30 min, before being transferred back into the glovebox, sealed in an air-tight container, and transported to the microscopy facility.

Quantum Dot Microscopy Sample Preparation

Low fluorescence glass coverslips (VistaVision #1.5 22x22 mm, VWR) were cleaned through a sequential sonication of 10 minutes in soap solution, de-ionized water (x2), acetone and IPA. Each side of the coverslips were ozone cleaned for 23 minutes before spin coating.

Low concentration QD solutions were prepared in 5 wt% PS in toluene via serial dilutions. For lecithin-capped QDs 1 μ L of stock QD solution were added to 2 mL of PS-toluene (solution A_{lec}). 100 μ L of solution A_{lec} were added to 2 mL of PS-toluene (solution B_{lec}). 100 μ L of solution B_{lec} were added to 2 mL of PS-toluene (solution C_{lec}). Single QDs films were prepared via spin coating solution B_{oleic acid/oleylamine} (60 μ L) or solution C_{lec} (60 μ L) onto the cleaned coverslips at 2,000 rpm for 40 seconds. The films were stored in a glovebox until measurement.

Widefield Microscopy

Widefield microscopy measurements were performed on a Nikon TE2000 inverted optical microscope using a CFI Super Fluor 40x Oil immersion objective (NA = 1.3), with Olympus F immersion oil. The illumination source was a 415 nm LED (SOLIS-415C, Thor Labs) at a power density of 9 mW/cm². The

following filters were used for the measurement: ET510/80m (Chroma), FF01-424/SP-25 (Semrock) and ZT442rdc (Chroma) mounted in Chroma Laser TIRF for Nikon TE2000/T filter cube. Videos of the sample photoluminescence in time were collected on a Prime 95B (Photometrics) camera for 6 minutes and 40 seconds (8000 images in total) with an integration time of 50 ms per image. Individual QD blinking traces were extracted from the videos using a custom-built Python package for selecting bright objects from a dark background.⁶³ Briefly, individual quantum dots were selected using the Laplacian of Gaussian method to automatically identify bright single particles from the mean image. The image coordinates of these identified particles were used to extract the relevant single particle time traces from the image sequence for further analysis. The efficacy of particle identification was assessed by constricting the microscope field of view to rule out false positive selections.²

Analysis of Blinking Traces Using Change Point Analysis

We used Change Point Analysis (CPA) adapted for a Gaussian-distributed time series. Our home-built Python CPA package is based on the equations published by Yang et al.⁶¹ A more detailed explanation of our CPA package can be found in the supporting information – including a confusion matrix quantifying the performance of our CPA package on synthetically generated blinking data (Figure S22) and a detailed breakdown of how we extract our statistics from CPA fit traces. Our particle selection and CPA code is publicly available at: <https://github.com/GingerLabUW/Widefield-CPA>.

Microscope Cryostat

Variable temperature and single QD linewidth experiments were performed on a homebuilt confocal microscope coupled to an AttoCube AttoDry800 optical cryostat with internal microscope objective (LT APO). QDs were located via piezo stage scanning (ANSxyz100std stages) controlled via a homebuilt python interface connected to the scanning controllers (ASC 500 and ANC300). Samples were excited by a NKT Super K Fianium tunable laser source with an excitation source set to 470nm. Sample emission was directed to either a HBT Interferometer with APD Detectors (MPD-PDM) connected to TCSPC Hardware (Swabian Photonics TimeTagger Ultra) or to a spectroscopy path (Princeton Instruments IsoPlane320 and PIXIS 400) via a motorized flip mirror.

Variable temperature PL

Samples for variable temperature PL experiments were prepared by drop casting in a nitrogen filled glovebox. Samples were loaded into the cryostat and cooled to base temperature (3.6K). Variable temperature measurements were performed in ascending order after allowing for equilibration at the set temperature (several hours).

Nuclear Magnetic Resonance Characterization (NMR)

Prior to measurement quantum dot samples were dried on a rotary evaporator (IKA RV8) into a 20mL vial. After solvent removal the sample was further dried overnight on a Schlenk line. The dried QD samples were dissolved in 2.5mL of deuterated DMSO. 2.5uL of mesitylene was added to each sample to act as an internal standard for NMR quantitation. NMR integration values relative to this internal standard were used to quantify mmols of ligand for each sample.

Figure S1. Stokes shift

Figure S2. Lifetimes

Figure S3 Additional Structural characterization of Ligand Exchanged QDs.

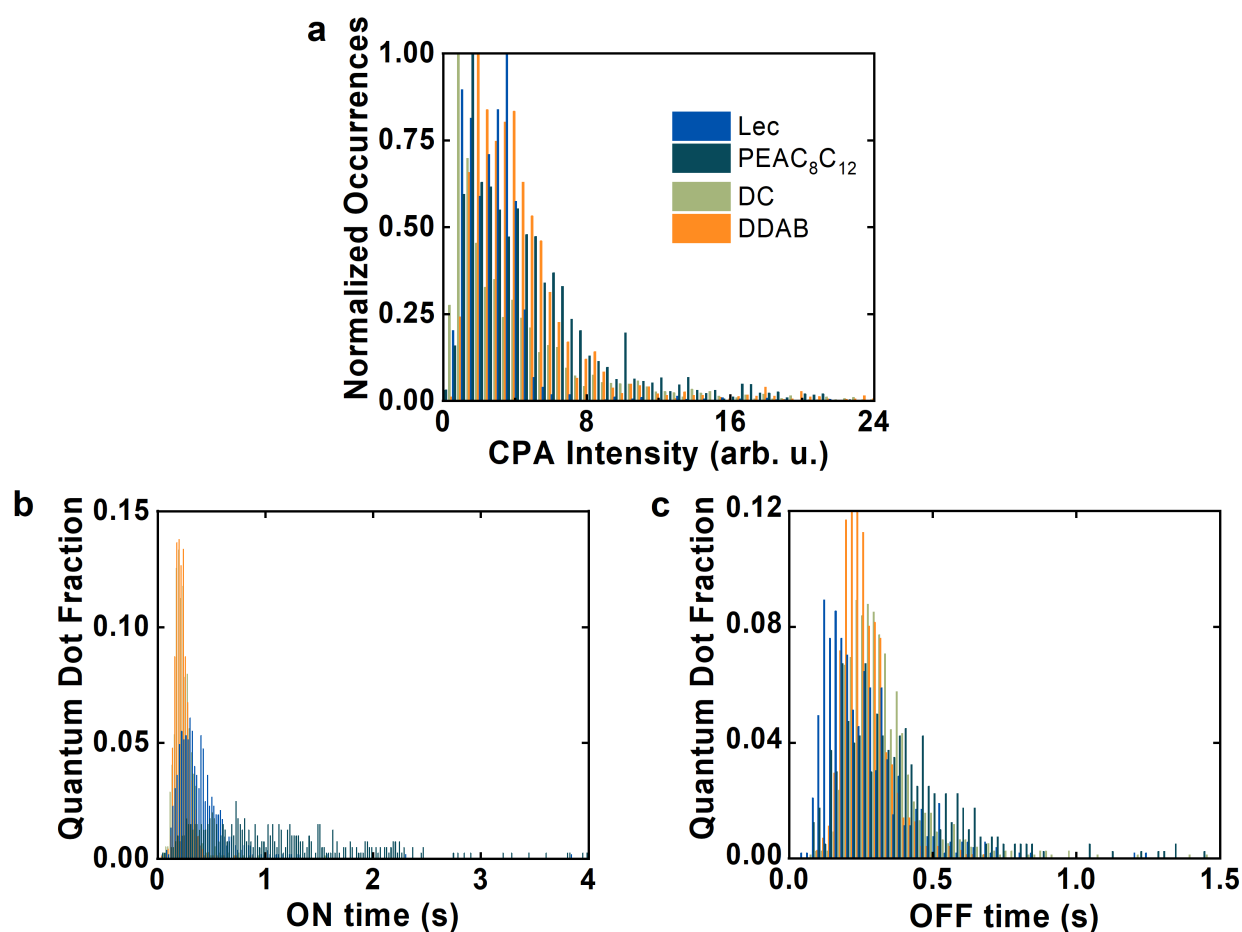


Figure S6 Additional blinking metrics. Comparison of blinking behavior between the lecithin, PEAC₈C₁₂, DC and DDAB capped QDs across three additional metrics **a**) distribution of intensities in the blinking traces according to the CPA fits **b**) distribution of the expected ON times from power-law dynamics and **c**) distribution of the expected OFF times from power-law dynamics.

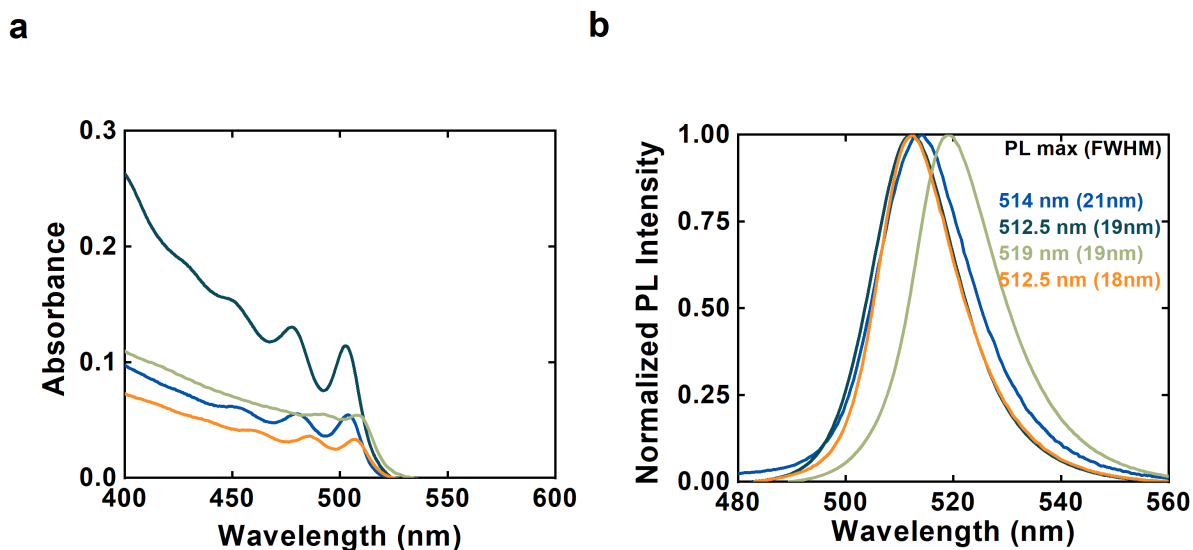


Figure S7 QD Film characterization. Ensemble Characterization of drop-cast QD film samples used in variable temperature PL experiments for lecithin, PEAC₈C₁₂, DC and DDAB capped QDs including **a)** QD film absorbance and **b)** photoluminescence showing a red shift and increased broadening consistent with energy transfer in the solid state.

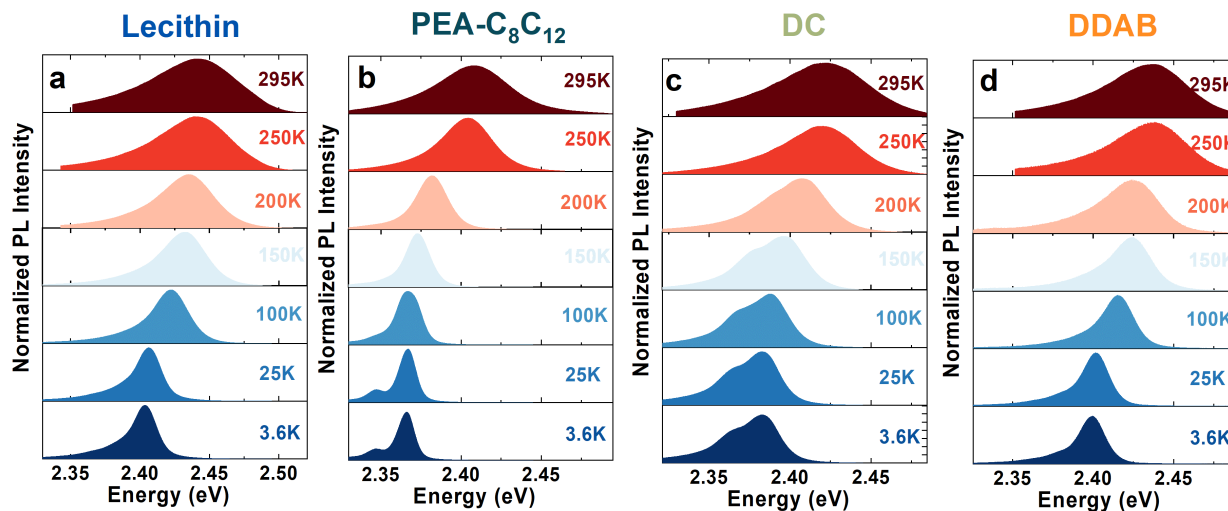


Figure S8 QD Film characterization. Selected temperature dependent QD Film experiments for lecithin, PEAC₈C₁₂, DC and DDAB capped QDs (**a-d** respectively). Spectra are shown for sample temperatures of 3.6, 25, 100, 150, 200, 250 and 295K.

From these data fwhm and pl peak position were extracted for each temperature and plotted in Figure S9.

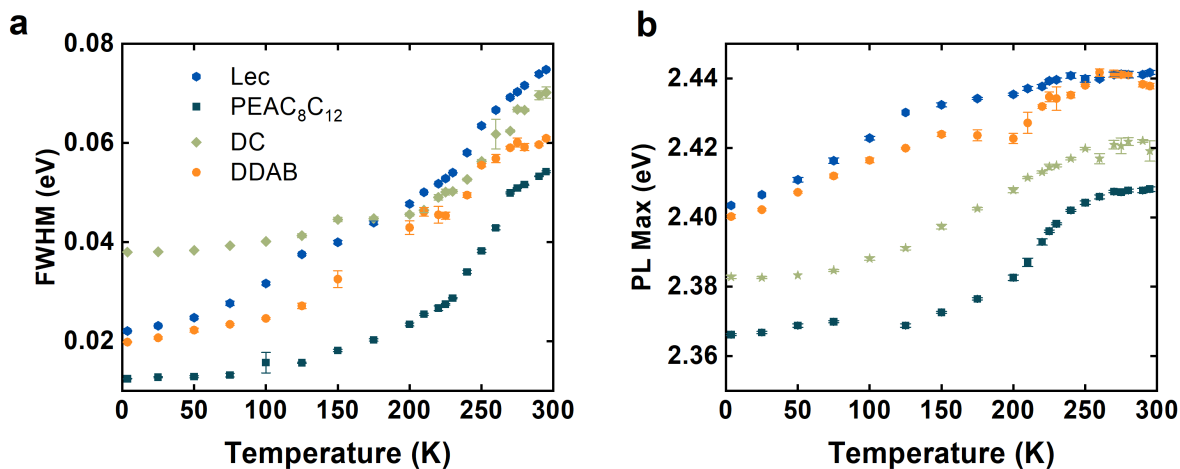


Figure S9 Variable Temperature Ensemble Peak Position and PL FWHM **a)** Full width at half max (fwhm) of Ensemble Photoluminescence and peak position vs temperature

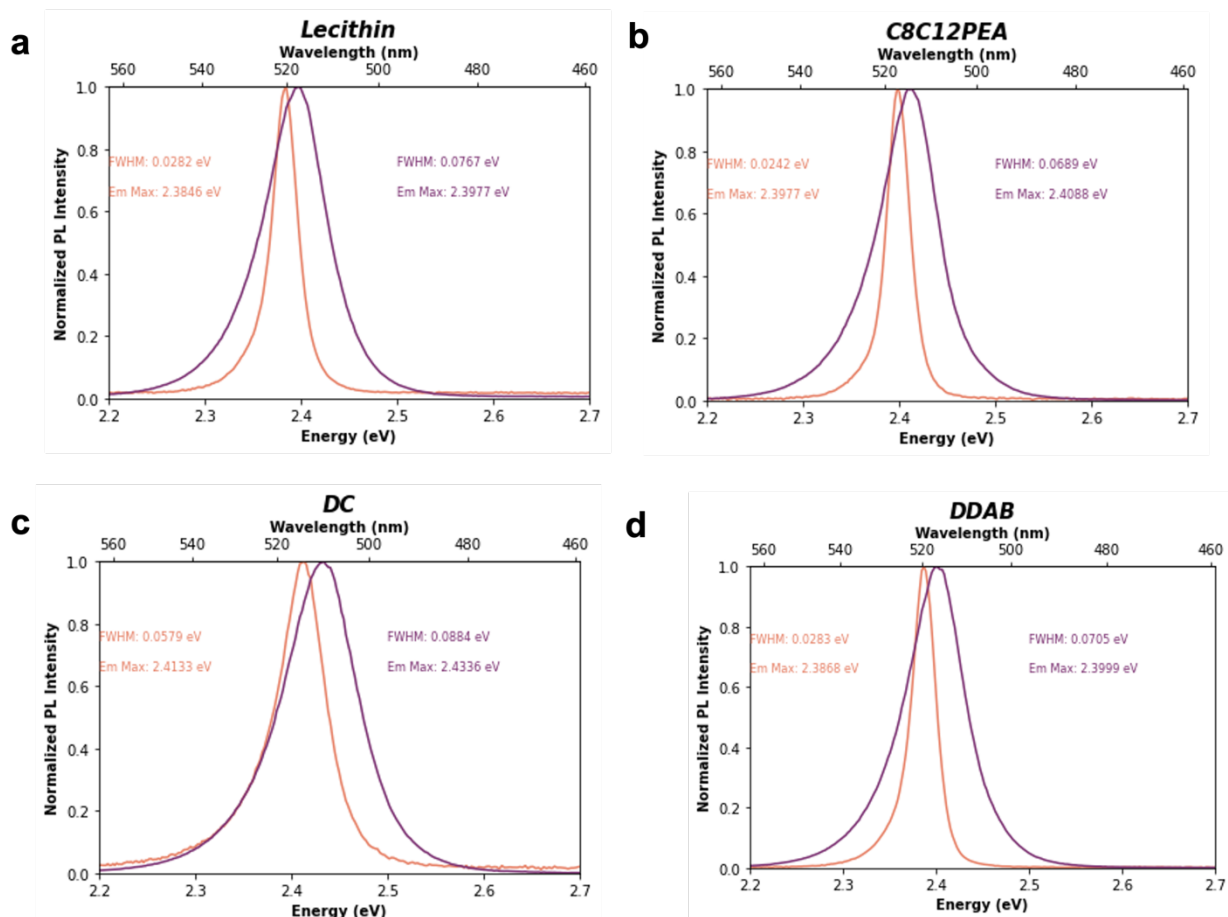


Figure S10 Heptamethyl nonane matrix. Comparison of QD PL at RT and “flash-frozen” in liquid nitrogen to form a glassy-matrix in heptamethyl nonane solvent for lecithin, PEAC₈C₁₂, DC and DDAB capped QDs (a-d). FWHMs extracted from the PL data are consistent with the linewidth trends reported in Figure 4(b).

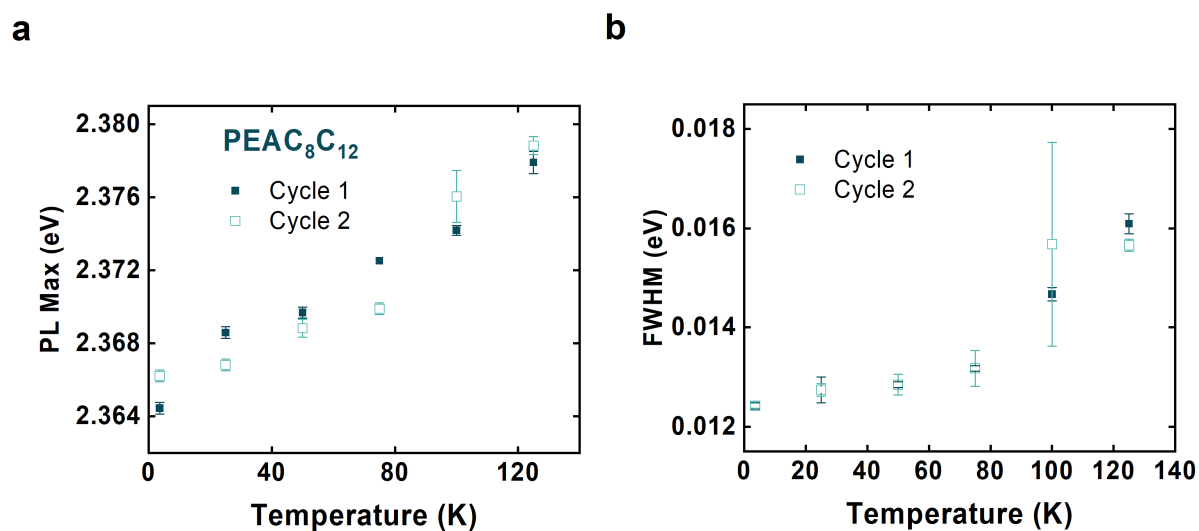


Figure S11 Cryostat cycling stability PEAC₈C₁₂. Comparison of temperature dependent FWHM values for the same PEAC₈C₁₂-capped QD sample upon first and second cooling cycles. Data for FWHM and PL peak position are plotted in **a)** and **b)**. These data show repeatability after more than 1 cycle, results are within in error (or comparable) for both FWHM and PL max.

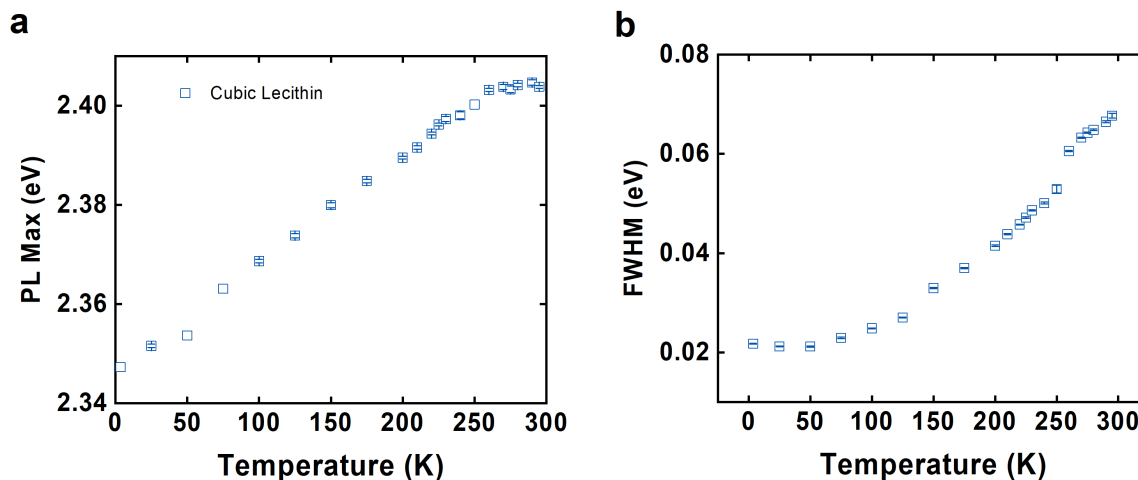


Figure S12 Cubic Lecithin Samples. Variable temperature PL Data for cubic lecithin-capped QDs. Extracted PL peak position and FWHM values are plotted in **a)** and **b)**.

Ligands per Quantum Dot Calculations:

We obtained the quantum dot concentration in each sample by performing absorbance spectroscopy (as shown in Figure S13) to determine both the average size and concentration of Quantum Dots via the method published by Maes et al.³ Quantum dot size was determined from the bandgap by equation 2.

Calculation of the number of ligands per nanocrystal was calculated via quantum dot digestion in deuterated DMSO.⁴

The Molar Absorptivity of the Quantum Dots was calculated via Equation 3:

$$\varepsilon_{335} \approx (0.052 \pm 0.002) \frac{4}{3} \pi r^3 \text{cm}^{-1} \mu\text{M}^{-1}$$

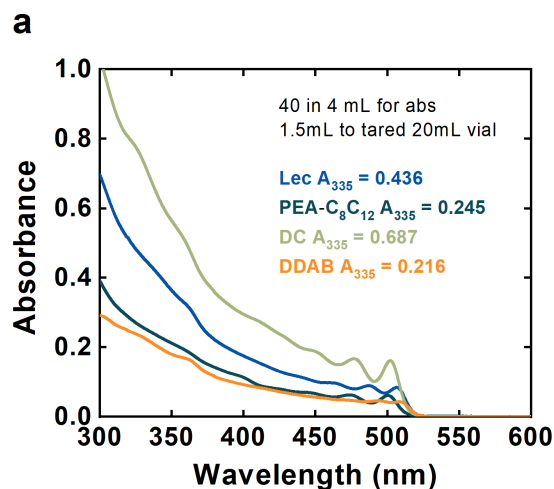


Figure S13: Absorbance Spectra for concertation and sizing determination. a) Absorbance spectra acquired with 100-fold dilution of initial concentration.

Calculation of the number of ligands per nanocrystal was calculated via quantum dot digestion in deuterated DMSO.⁴ For these measurements mesitylene was used as an internal standard to quantify mmols of recovered ligand post digestion.

Figure S14-17 show ¹HNMR spectra for the DMSO digested samples.

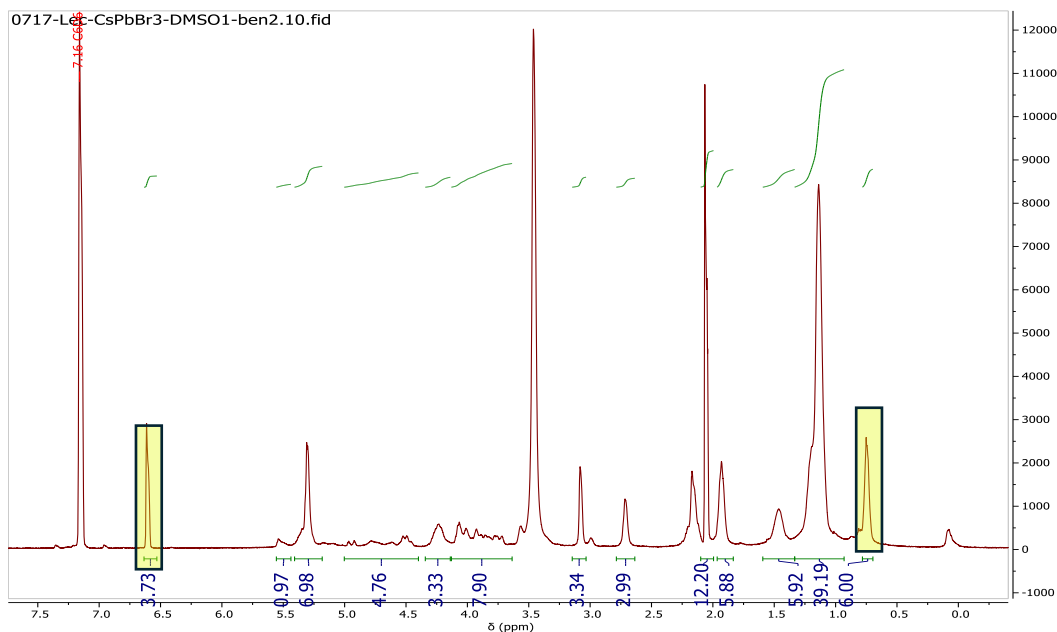


Figure S14: ¹H NMR of Lecithin capped QDs showing peaks used for ligand calculation in yellow boxes.

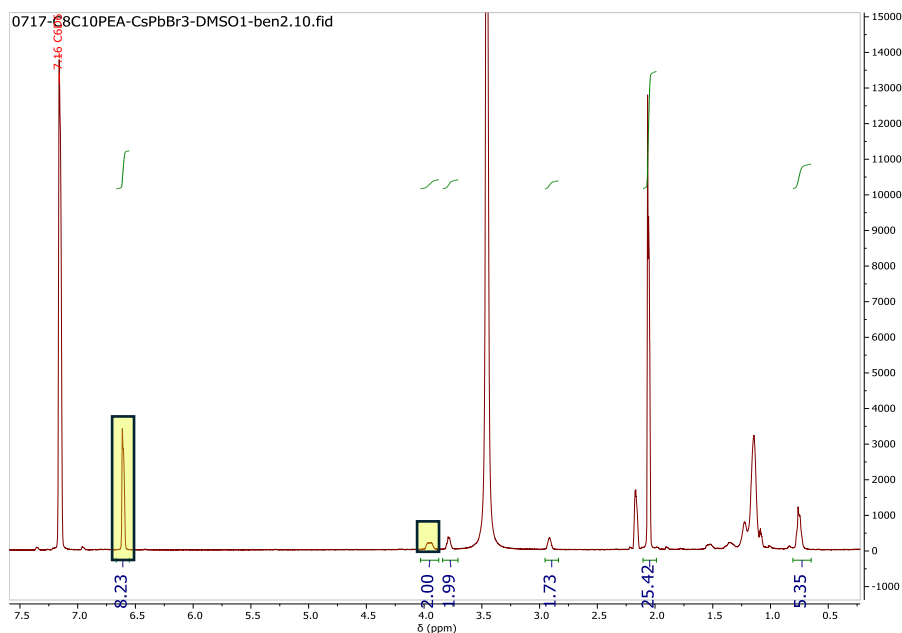


Figure S15: ^1H NMR of PEA- C_8C_{12} capped QDs showing peaks used for ligand calculation in yellow boxes.

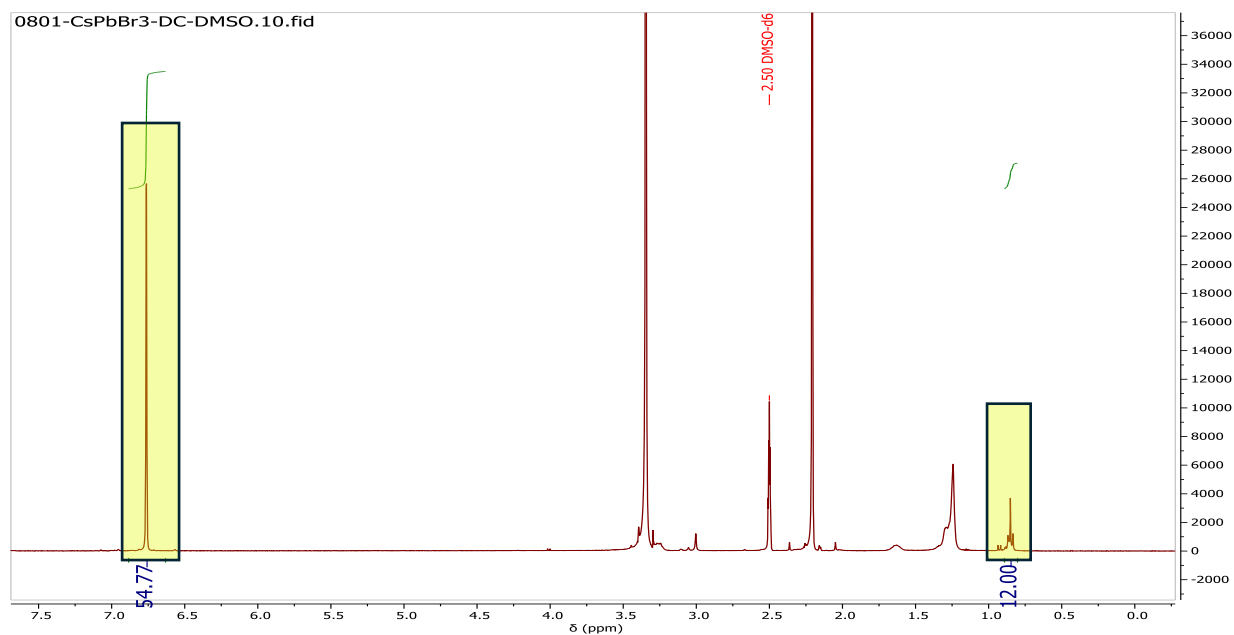


Figure S16: ^1H NMR of DC capped QDs showing peaks used for ligand calculation in yellow boxes.

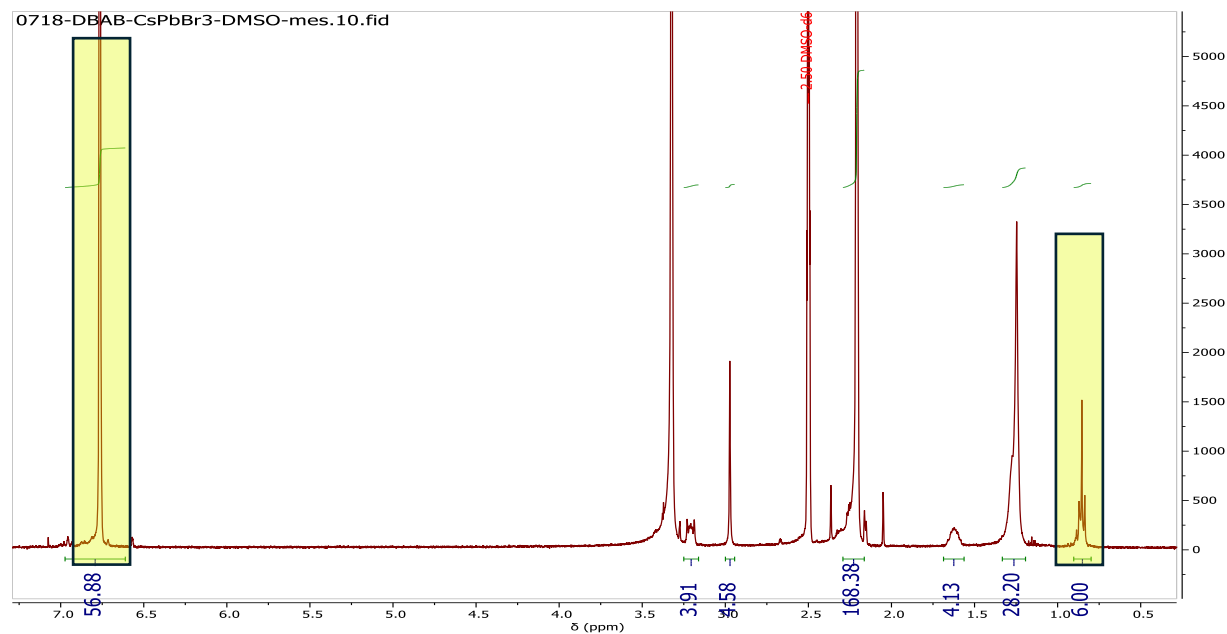


Figure S17: ^1H NMR of PEA- C_8C_{12} capped QDs showing peaks used for ligand calculation in yellow boxes.

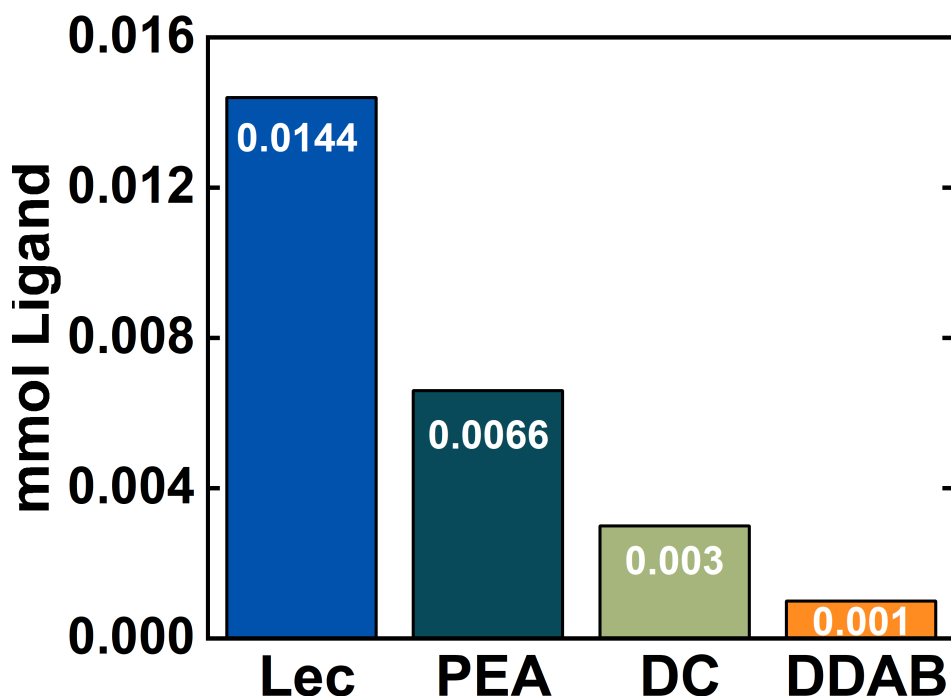


Figure S18: Milimol of Ligand per QD from NMR spectroscopy.

References:

- (1) Mooney, J.; Kambhampati, P. Get the Basics Right: Jacobian Conversion of Wavelength and Energy Scales for Quantitative Analysis of Emission Spectra. *Journal of Physical Chemistry Letters*. American Chemical Society October 3, 2013, pp 3316–3318. <https://doi.org/10.1021/jz401508t>.
- (2) Gallagher, S.; Kline, J.; Jahanbakhshi, F.; Sadighian, J. C.; Lyons, I.; Shen, G.; Hammel, B. F.; Yazdi, S.; Dukovic, G.; Rappe, A. M.; Ginger, D. S. Ligand Equilibrium Influences Photoluminescence Blinking in CsPbBr₃: A Change Point Analysis of Widefield Imaging Data. *ACS Nano* **2024**, *18* (29), 19208–19219. <https://doi.org/10.1021/acsnano.4c04968>.
- (3) Maes, J.; Balcaen, L.; Drijvers, E.; Zhao, Q.; De Roo, J.; Vantomme, A.; Vanhaecke, F.; Geiregat, P.; Hens, Z. Light Absorption Coefficient of CsPbBr₃ Perovskite Nanocrystals. *Journal of Physical Chemistry Letters* **2018**, *9* (11), 3093–3097. <https://doi.org/10.1021/acs.jpclett.8b01065>.
- (4) Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; Ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C. J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for

Improved Durability and Stability. *ACS Energy Lett* **2018**, 3 (3), 641–646.
<https://doi.org/10.1021/acsenergylett.8b00035>.