Research article

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Exploring the physics of cesium lead halide perovskite quantum dots via Bayesian inference of the photoluminescence spectra in automated experiment

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Abstract: The unique optoelectronic properties of metal halide perovskite quantum dots (QDs) make them promising candidates for applications in light-emitting diodes (LEDs), scintillators, and other photonic devices. The automated micropipetting synthesis platform equipped with an optical reader enables the opportunity for high throughput synthesis and photoluminescent (PL) characterization of metal halide perovskite QDs for the first time. Here, we explore the compositional dependence of the PL behavior and stability of the combinatorial library of cesium lead halide (CsPbX_3) perovskites QDs via the automated platform. To study the stability of synthesized QDs in the binary and ternary configurations, we study the time-dependent PL properties using previously developed machine learning analysis. To systematically explore the PL behavior in the ternary CsPbX_3 QDs system, we introduce the Bayesian inference framework that allows the probabilistic fit of multiple models to the PL data and establishes both optimal model and model parameter robustly. Furthermore, these behaviors can be used as a control parameter for the navigation of the multidimensional compositional spaces in automated synthesis. This analysis shows the nonuniformity of the PL peak behavior in the ternary CsPbX_3 QDs system. Further, the

analysis confirms narrow size distribution and good quality of CsPbBr_3 QDs alloyed with low concentrations of iodide and chloride. We note that Bayesian Inference fit parameters can be further used as a control signal for navigation of the chemical spaces in automated synthesis.

Keywords: automated experiment; Bayesian inference; perovskite; photoluminescent; quantum dots.

In the past five years, there has been a growing interest in nanostructured metal halide perovskites (MHPs), especially quantum dots (QDs) [1], for optoelectronic applications such as light-emitting diodes (LEDs) [2, 3], scintillators [4–6], and solar cells [7], etc. This interest has emerged due to the superior properties of perovskite quantum dots (PQDs) compared to their bulk counterparts. PQDs typically have low trap densities and consequently exhibit high color purity, high photoluminescence quantum yield (PLQY) efficiency, as well as a tunable and narrow emission wavelength [8]. Their size is contingent on the types and amount of long-chained ligands added to the perovskite solution, enabling a precise and facile tunability for encapsulating the crystal. Furthermore, this allows PQDs to have a wide range of bandgap energies in the visible spectrum [8]. PQDs can be categorized into two groups: all inorganic and hybrid organic–inorganic halide perovskites. All inorganic PQDs with a general formula of CsPbX_3 (X: I, Br, Cl) are known to provide more overall stability than hybrid organic–inorganic halide perovskites QDs such as APbX_3 (A: MA, FA; X: I, Br, Cl) [8].

A variety of techniques have been explored to synthesize all inorganic PQDs, including hot injection and ligand-assisted reprecipitation (LARP) [8–10]. The hot injection technique was used to make the first set of PQDs [8, 9] and is usually done at an elevated temperature to create a supersaturated mixture that is then rapidly cooled in an ice bath which produces a multitude of small nuclei and results in nanocrystals. In this technique, the solution temperature controls the size and emissive wavelength of

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QDs, which is advantageous to this technique. The ligand-assisted reprecipitation technique (LARP) was adopted as an alternative method that requires less energy and specialized equipment than the hot injection technique to synthesize QDs [8, 10]. Depending on the perovskite composition, the solution process can be performed at temperatures as low as room temperature and demonstrate the quantum confinement effects [10, 11]. The perovskite precursor solution is made using an organic solvent, typically dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) [10]. Ligands such as oleic acid (OA) and oleylamine (OAM) are commonly added at different ratios in conjunction with an antisolvent under vigorous stirring to create homogenous, luminescent QDs [10].

Although the above techniques can make high-quality QDs, minor differences in approach can alter the size and shape of QDs, thus affecting their optical performance [8, 12]. Additionally, the synthesis in both techniques can be tedious to explore the compositional spaces and optimize the synthesis protocol, leading to irreproducibility due to differences in conditions between the samples and increasing the cost of production. Recently, microfluidic platforms have been developed to accelerate the synthesis of PQDs and improve reproducibility [12, 13]. Microfluidics enhances the synthesis process with more efficient mixing, reduced cost of materials, high heat and mass transfer, high surface to volume ratio, temperature control, and continuous production [13]. Moreover, the microfluidics platform typically enables systematic exploration and control of composition, concentration, flow rate, reaction time, and temperature [12]. However, this method is useful to explore an optimized synthesis reaction but can still not explore large compositional spaces at once [12].

While current PQDs have shown an excellent promise for widely tunable properties due to their high PLQY and extended lifetime, there is still a search for compositions with optimal properties and stability over more extended periods of time. Here, we explore the utility of a micro-pipetting platform to evaluate a broad range of conditions and techniques to automate the synthesis of binary and ternary cesium lead halide (CsPbX_3 , $X=\text{Br, Cl, I}$) QDs at room temperature without any post-synthesis requirements. Via automated pipetting technique, adopted from the synthesis of a combinatorial library of microcrystals of MHPs [14], one is able to synthesize, characterize and compare multiple compositions and properties of interest all at once using a previously developed machine learning (ML) analysis method [14]. We further note that the quality of the QDs can be largely characterized by the photoluminescence (PL) properties and quantum yield calculations [8]. The PL peak, including shape, intensity,

and width, provide information about the optical properties of PQDs, including polydispersity and purity. Here, we develop the Bayesian Inference approach to define the optimal model for the PL emission and map the model and model parameter across the composition space. These parameters provide insight into the chemical and physical behavior of the system and can further be used to navigate the multidimensional chemical spaces of these systems.

Results and discussion

As mentioned previously, PQDs can be synthesized utilizing a variety of different methods, such as hot injection and LARP [8–10]. In this study, we modified the LARP method to fit our pipetting robot's capabilities for the automated synthesis of binary and ternary combinatorial libraries of CsPbX_3 QDs. The synthesis protocol is written in Opentron's protocol designer controlled by the Python interface for seamless deployment of precursor solutions and mixing in a 96-well plate. The binary and ternary CsPbX_3 QDs are prepared via simple solution mixing of desired quantities of endmember solutions which consist of perovskite solution of cesium lead bromide, cesium lead chloride, and cesium lead iodide (CsPbBr_3 , CsPbCl_3 , and CsPbI_3). This solution is then combined with ligands (OA and OAM) to form the precursor solution, which is added into the antisolvent (toluene) to initiate the formation of QDs. Our approach is similar to other microfluidics methods, which enable the exploration of large compositional spaces yet maintaining control of many aspects of the synthesis. In addition, this technique can be used to synthesize other PQDs, including hybrid organic–inorganic PQDs, and it is highly reproducible. For more details of precursor solutions and mixture ratios, see the information in Supplementary Material Table S1–S3.

Transmission electron microscopy (TEM) images of synthesized CsPbX_3 ($X=\text{Br, Cl, I}$) QDs using the micro-pipetting technique are shown in Figure 1. The CsPbBr_3 QDs (Figure 1a) show a uniform cubic array and have an average size around 10–12 nm. The darker nanodots on the surface of CsPbBr_3 QDs are not specific to our synthesis and are reportedly attributed to excess PbBr_2 attaching to the surface of QDs due to incomplete purification after solvent evaporation [15, 16]. The CsPbBr_3 QDs produced from this procedure show a very similar size and shape throughout literature using both the LARP and hot injection techniques [10, 17]. The CsPbCl_3 QDs (Figure 1b) are more spherical and an average size around 3 nm. CsPbI_3 QDs (Figure 1c) show a more amorphous shape and have a larger-size distribution ranging from around 7 to 15 nm.

Figure 1: Transmission electron microscopy (TEM) images of as synthesized CsPbX₃ QDs in this study.

(a) CsPbBr₃, (b) CsPbCl₃, and (c) CsPbI₃ QDs.

From the above information alone, it can be inferred that the size uniformity and, therefore, the likely bandgap energy uniformity for the CsPbCl₃ and CsPbBr₃ QDs are greater than the CsPbI₃ QDs. When all synthesized QDs in the well plate are excited under a 6 W, 365 nm excitation Ultraviolet (UV) lamp, the pure CsPbCl₃ and CsPbI₃ did not glow, whereas the CsPbBr₃ QDs emitted a bright green color. In theory, all CsPbX₃ QDs should glow under a UV lamp; however, the lack of proper power and wavelength of our UV lamp could be a reason we could not see the glow of the CsPbCl₃ and CsPbI₃ QDs. The emitted colors of all other CsPbX₃ QDs in the ternary and binary mixtures excited under the UV lamp can be seen in the Supplementary Material (Figures S1, S4, and S5, PL and UV-vis absorption measurements of select compositions are shown in Figure S8).

We systematically varied the halide ratios by 10 at% in the automated synthesis protocols to create 66 different ternary mixed-halide QDs. More details of this synthesis can be found in Supplementary Material Table S1. To study the PL properties of as-synthesized CsPb(I_xBr_yCl_{1-x-y})₃ QDs, the microplate containing the 66 samples was excited at 350 and 450 nm wavelengths. PL emissions are measured over 5.5 h. Here, we chose PL to characterize the QDs as it has been widely used to not only measure the optoelectronic properties but also the stability of perovskites [18–20]. While other techniques, such as X-ray diffraction (XRD) have been utilized to explore important dynamical process, such as halide segregation [21], we did not utilize them as we are primarily focused on the evolution of optoelectronic properties and are limited in our capability to perform a high-throughput study utilizing XRD. More information can be found in the Supplementary Material (Figures S2 and S3). This protocol yields a large set of PL spectra as a function of time. To rapidly and efficiently analyze the PL spectral dataset and deduce the optical properties and quality of QDs over time, we use a non-negative matrix factorization (NMF). Details of this analysis were described in our previous work [14]. To interpolate the time-dependent PL behavior in the ternary compositional space and map the emission properties of CsPbX₃ QDs, we implement a Gaussian processing (GP) model. More

explanation of the GP model and the reason for its selection can be found in our previous study [14]. Here, we select three NMF components to represent variability in the ternary QDs system. Shown in Figure 2 is the combined NMF and GP analysis of the time-dependent PL behavior of ternary CsPb(I_xBr_yCl_{1-x-y})₃ QDs at two different excitation wavelengths. CsPbBr₃ rich samples can be seen in Figure 2e and l, CsPbCl₃ rich samples can be seen in Figure 2d, and more mixed CsPb(I_xBr_yCl_{1-x-y})₃ samples can be seen in Figure 2f, j, and k.

Due to the wide bandgap energy differences between CsPbX₃ QDs, their PL peaks range from 405, 513, and 700 nm for CsPbCl₃, CsPbBr₃, and CsPbI₃ QDs, respectively [10, 22, 23]. Therefore, to effectively study and capture the wide range of PL behavior of the PQDs, we selected two excitation wavelengths, 350 and 450 nm. Due to the limitations of the optical reader, we need to excite the entire plate at 350 nm, then again at 450 nm. It should be noted that at 450 nm excitation, the CsPbI₃ QDs do not have as intense PL peak compared to the other end members (i.e., CsPbCl₃ and CsPbBr₃) as they can easily degrade in polar solvents such as DMF [24] and therefore may not be as prominently represented in the ternary diagrams and NMF maps in Figure 2. It is also known that at room temperature, the equilibrium phase of CsPbI₃ is the optically inactive δ -orthorhombic phase [25]. However, CsPbI₃ QDs have been successfully synthesized evidenced by TEM image (Figure 1c) and the individual PL spectrum (Supplementary Material Figures S3 and S7). Furthermore, with the same samples, the 350 and 450 both show similar photoluminescence wavelengths (e.g., Figure 2e and l are both CsPbBr₃ rich however Figure 2e was excited at 350 nm and Figure 2l was excited at 450 nm but in Figure 2b and i, the wavelength is similar).

Here, we note that different characteristic PL behaviors will become apparent when performing NMF on the two separate datasets, 350 and 450 nm excitation wavelength. For example, when NMF is performed on the dataset in which 350 nm is the excitation wavelength, we uncover more information about the chloride-rich compositions, while losing information about the iodide-rich compositions. We observe

Figure 2: The multivariate analysis of time-dependent PL properties of ternary $\text{CsPb}(\text{I}, \text{Br}, \text{Cl}_{1-x-y})_3$ QDs system. At an excitation of 350 nm, 2D non-negative matrix factorization (NMF) components of PL behavior of the corresponding phase diagram (represented by a nonzero weight) as a function of wavelength and time where the color describes the intensity of the PL peak (top: (a)–(c)) and Gaussian processing (GP) interpolation of compositional dependencies of the component PL intensities within the ternary diagram where the color is indicative of how the characteristic PL behavior over time describes that compositional region (bottom: (d)–(f)). At an excitation of 450 nm, 2D NMF components (top: (g)–(i)) and compositional dependencies of the component intensities within the ternary diagram (bottom: (j)–(l)).

a similar effect when we perform NMF on the dataset where 450 nm is the excitation wavelength. There, we gain more insight into the iodide-rich compositions and lose information about chloride-rich compositions. Therefore, we utilized the CsPbBr_3 -rich compositions, which are represented well in both datasets, to determine whether there was a difference in PL behavior caused by the excitation wavelength, and we did not observe a distinct difference. However, we do note that the excitation wavelength can affect the stability of the perovskite as demonstrated in literature studies [26]. This effect is not applicable to our study as we alternated between the two excitation wavelengths over time.

At an excitation wavelength of 350 nm, the first NMF component represents chloride-rich samples with PL emission wavelength around 420 nm (Figure 2a and d). The emission decreases in intensity over time signifying that the coupling between the excited and emitted states decreases [27]. This can be due to a slight degradation of the QDs, or increase in the density of defects over time in ambient condition [28]. However, the stability of these QDs prove to hold with only some signs of degradation in ambient conditions over time compared to the QDs synthesized and stored in a nitrogen rich environment [10]. The broad PL emission is most likely due to the combination of three

different halides self-assembling over time and therefore forming heterogenous size distribution or the ligands are not as strongly bonded to QDs and therefore increasing their sizes over time (Figure 2a). The chloride-rich QD compositions exhibit this behavior most prominently and are highlighted in red color in the ternary map (Figure 2d). The white lines in Figure 2d guide to the solid solution between 87% CsPbCl_3 , 8% CsPbI_3 , and 5% CsPbBr_3 possibly forming $\text{CsPb}(\text{I}_{0.08}\text{Br}_{0.05}\text{Cl}_{0.87})_3$ QDs as a representative composition at the center of the dark red region. The second NMF component and the corresponding ternary diagram describe emissions from bromide-rich QDs excited with 350 nm wavelength (Figure 2b and e). When CsPbBr_3 is the dominant composition, the emission wavelength is close to that of pure CsPbBr_3 QDs. As can be seen in Figure 2b, the PL emission initially appears at around 520 nm and the intensity increases with time and then slightly degrades after 1.5 h, however it remains relatively stable throughout the 5.5 h in ambient conditions. The PL peak width follows the same trend as the peak intensity where the peak starts to narrow and after an hour in ambient condition, becomes broader up until about 3.5 h. As with the chloride rich QDs, these changes could be due to QD oxidation in air, increases in defect density, expansion of the size distribution, or alterations in the ligand binding ratios. The QDs that follow this trend at the center of red regions have a representative composition of $\text{CsPb}(\text{I}_{0.15}\text{Br}_{0.40}\text{Cl}_{0.45})_3$ and also $\text{CsPb}(\text{I}_{0.15}\text{Br}_{0.70}\text{Cl}_{0.15})_3$ as shown by white lines in Figure 2e. The third NMF component illustrates a narrow emission centered around 450 nm wavelength when QDs are excited at 350 nm (Figure 2c). The corresponding compositional dependency map guides to the compositions closer to the center of the ternary diagram such as $\text{CsPb}(\text{I}_{0.35}\text{Br}_{0.35}\text{Cl}_{0.30})_3$ as well as chloride rich compositions (Figure 2f). In general, since the iodide rich QDs cannot be emitted at this excitation wavelength the emission is in between the PL properties of CsPbBr_3 and CsPbCl_3 QDs. It is noted that the PL emission is narrow with high intensity up to 2.5 h in ambient condition indicating the high quality of these QDs. While these QDs hold the stability during the entire measurements the emission intensity gradually decays indicating degradation.

To capture the PL properties of QDs with higher concentration of iodide, the well plates are excited at 450 nm wavelength and similar PL analysis is performed. The first NMF component in Figure 2g illustrates a tail of PL emission centered at around 475 nm wavelength. The PL emission is most intense at the beginning and then loses the intensity with time. By analyzing the ternary diagram of compositional dependency in Figure 2j, this can be attributed to the presence of chloride in the compositions affecting on the overall composition of the QDs and blue

shifting the peak emission wavelength and the 450 nm excitation cutting off part of the emission peak. Other representative compositions with similar properties are around $\text{CsPb}(\text{I}_{0.30}\text{Br}_{0.30}\text{Cl}_{0.40})_3$ and $\text{CsPb}(\text{I}_{0.30}\text{Br}_{0.60}\text{Cl}_{0.10})_3$. These PL data are also similar to that of Figure 2g and j. The PL emission wavelength is around 540 nm in the second NMF component (Figure 2h). In the beginning, the emission is not intense, however, with time the intensity increases. The corresponding ternary map in Figure 2k shows central regions with higher iodide concentration such as compositions around $\text{CsPb}(\text{I}_{0.45}\text{Br}_{0.20}\text{Cl}_{0.35})_3$. In this case, the higher concentration of iodide can shift the PL emission to higher wavelengths. Noticeably the emission width increases throughout time indicating either phase segregation or peak splitting due to a nonuniform mixture of this ternary system. Finally, the third NMF component in the 450 nm excitation (Figure 2i) shows the emission wavelength around 515 nm close to the emission from pure CsPbBr_3 QDs. This trend is also similar to that of CsPbBr_3 rich samples excited at 350 nm shown in Figure 2b and e. The QDs that mostly represent this trend are in multiple regions of phase diagram including $\text{CsPb}(\text{I}_{0.10}\text{Br}_{0.42}\text{Cl}_{0.48})_3$; $\text{CsPb}(\text{I}_{0.10}\text{Br}_{0.70}\text{Cl}_{0.20})_3$; and $\text{CsPb}(\text{I}_{0.10}\text{Br}_{0.85}\text{Cl}_{0.05})_3$ QDs (Figure 2l). These bromide rich QDs show up well in both the 350 and 450 nm excitation wavelengths (Figure 2b and i). There is a slight blue shift in the peak position over time possibly due to changes in the size and crystallization of the QDs with time. The intensity of PL emission is fairly constant with nearly narrow peak width throughout 5.5 h indicating the high quality and stability of these QDs in ambient conditions.

Here, the intervals of the samples in the ternary diagram are farther apart compositionally (X-site doping changes by 10 at% increments). Since there are fewer samples for the compositional space, the uncertainty between each data point is higher and therefore the test will have a greater margin of error. To develop a better understanding of the time-dependent PL behavior of QDs, we synthesized and studied the binary $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ and $\text{CsPb}(\text{Br}_x\text{I}_{1-x})_3$ QDs based on the two endmembers on the edges of ternary phase diagram (for details see Supplementary Material Figures S4–S7). Within these binary systems, we sampled compositions approximately 1 at % apart yielding a total of 101 samples in each system (see Tables S2 and S3), thus decreasing the margin of error.

The top row in Figure 3 shows the NMF decompositions of time dependent PL for the solid solutions between CsPbBr_3 and CsPbCl_3 . The synthesized QDs were excited at 350 nm and show narrow and intense PL peaks throughout the 6 h in the ambient air. The PL emission peak in the first component (Figure 3a) starts at around 412 nm when the

QDs are rich in CsPbCl_3 concentration. The PL emission gets more intense throughout time and reaches its peak intensity around 1.5 h in ambient conditions. This can be due to the QDs having more time to crystallize and self-assemble, thus allowing for less defect and higher emission yield evidenced by their overall narrow emission range. In the same binary system, where more bromide concentration is present (Figure 3b), the PL emission is around 500–512 nm. The PL spectra are broader than the spectra for QDs with higher chloride concentration partially due to bigger size of bromide based QDs and a more heterogenous size distribution. Another notable difference in the bromide-rich QDs are that the PL spectra are initially more intense. This is most likely due to a better crystal quality of the bromide-rich samples as previously seen in the TEM images in Figure 1a. At the end, the QDs are still stable, and the intensity of the PL emission has only slightly decreased. The width of these PL emissions also increases slightly throughout time. The bromide rich QDs indicate to be the most stable after 6.5 h. In the third NMF component, the PL emission between 425 and 475 nm becomes more intense around 1.5 h in ambient conditions (Figure 3c). Again, this can be due to the QDs having more time to crystallize. The peaks after about 5 h tend to get narrower and less intense. This intensity change could be because the QDs start to degrade with time at these compositions or the defect densities increase. The narrow PL width can indicate the more homogenous size distribution of these QDs as time continues.

The bottom row in Figure 3 shows the NMF decompositions of time dependent PL for the solid solutions between CsPbBr_3 and CsPbI_3 binary system excited at

450 nm. Overall the as synthesized $\text{CsPb}(\text{Br}_x\text{I}_{1-x})_3$ binary QDs show broader PL peaks as compare to PL behavior in the $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ system possibly due to the wider emission wavelength differences between the endmembers or the inherent different sizes of the halides. The PL emission is at higher wavelengths and the emission become more intense over time as shown in Figure 3d–f. In the compositions that are more iodide rich (Figure 3f), the peak emission wavelength is around 700 nm at the very beginning in ambient conditions confirming the formation of iodide rich QDs. However, with time, the peaks get more intense, slightly blue shift and broaden. This can indicate that the iodide-rich samples are not as stable in ambient conditions and even though the bromide is the minority concentration in this case, it shifts the PL emission slightly. The peak widening can also be due to phase segregation or peak splitting due to degradation and therefore a nonuniform mixture results. The second NMF component in Figure 3e can be attributed to the QDs with compositions that are rich in bromide. The starting emission wavelength is around 515 nm which is consistent with the mission of pure CsPbBr_3 QDs [10]. This PL behavior may be different than the bromide-rich samples in the $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ binary system (Figure 3a–c) because of the different excitation wavelength (350 vs. 450 nm), along with the iodide-based QDs not forming as well as the chloride-based QDs. On the other hand, the CsPbCl_3 QDs even at low concentrations form faster and are more intense than the iodide-based QDs which can also impact the results of the NMF data. In this binary system, the bromide-rich QDs also have slightly broader PL peaks than the bromide-rich QDs in the $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ binary system (Figure 3b) partially due to

Figure 3: The NMF analysis of time dependent PL behavior in $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$, $\text{CsPb}(\text{Br}_x\text{I}_{1-x})_3$ binary QDs systems. Compositional dependencies of the component intensities within the CsPbBr_3 and CsPbCl_3 binary system excited at 350 nm (Top: (a)–(c)). Compositional dependencies of the component intensities within the CsPbBr_3 and CsPbI_3 binary system excited at 450 nm (bottom: (d)–(f)).

the inherent size of the bromide- and iodide-based QDs being larger than the mixed bromide and chloride QDs. This can be also seen in the TEM images in Figure 1. The second possibility can be phase segregation and peak splitting.

Finally, the third NMF component in Figure 3d shows a wide PL emission. It appears that these QDs cannot be formed until about an hour in ambient conditions. This could be due to the solid solution between iodide- and bromide-based perovskites cannot initially form stable QDs but throughout time the bromide helps stabilizes the QDs based on their environment [29]. Since CsPbI₃ tends to be the most unstable in ambient conditions, it is surprising that the PL peaks get more intense as time goes on [24]. The peaks are also much wider than those of more CsPbBr₃- and CsPbCl₃-rich samples. This can be due to the iodide-based QDs having the largest size distributions.

We proceed further by exploring the compositional dependence on the shape of the PL spectra. As mentioned previously, for monodispersed PQDs, the expected emission spectrum is a Lorentzian shape with its full width at half maximum (FWHM) corresponding to the photoluminescence quantum yield (PLQY) [30]. However, in the presence of any disorder, the emission shape begins to adopt a Gaussian profile, which can become more complex in the presence of polydispersity. Additionally, multiple well-defined peaks can be observed if the system separates into different phases.

Here, we explore the evolution of PL properties across the ternary system's compositional space. Initially, we found using a simple least square fits approach implemented via the lmfit library in Python to be unstable and very sensitive to the initial choice of parameters. Whereas well-defined peaks can be fitted well, systems with multiple peaks yield spurious parameter values, especially when clear peaks are absent. Correspondingly, the least square fit is also impractical because of analysis across the compositional space containing examples of different behaviors.

To systematically explore compositional dependence of the PL, we implement the Bayesian framework for the analysis of the emission spectra. In general, Bayesian inference (BI) is based on the concepts of prior and posterior probabilities. The prior, $p(\theta_i)$, represents the level of knowledge about the system before the experiment. The experiment yields the data, D , based on which the posterior distribution is calculated via Bayes formula [31, 32]:

$$p(\theta_i|D) = \frac{p(D|\theta_i)p(\theta_i)}{p(D)} \quad (1)$$

Here, $p(D|\theta_i)$ represents the likelihood that this data can be generated by the theory, e.g., given choice of model i , and

model parameters θ . The $p(D)$ is the denominator, that defined the total space of possible outcomes.

It is instructive to compare the Bayesian inference (BI) and classical least square (LS) fitting approach. Here, we assume that the experimental observations are given in the form of measured scalar values y_i for the points x_i . In LS fitting, we assume that the observed behavior is described by the function $f(\theta)$, and seek to find the function parameter vector θ . The optimization is performed by minimizing the least square error between the data and prediction, defined as a calculated version of function over the data points, $f(x_i)$. The minimum of mean square error in the space of parameters θ defines the point estimate of the function. Note that in a classical least square fits the parameter can be fixed, free, or rigidly constrained (e.g., non-negative).

The BI approach treats the prior information on parameters θ as a joint probability distribution. For convenience, the prior distributions are often marginalized, meaning that the distributions are considered to be independent. If the specific parameter is well known, the corresponding distribution is narrow and can be chosen based on prior experiments, available published data, or physical model. If the parameter is known poorly, the distribution is broad and for bound parameters is typically chosen as a uniform distribution and for the unbound parameter as a Gaussian (weakly-informed priors). The result of the BI is then the posterior parameter distribution, reflecting the updated knowledge on the parameters. Note that this approach allows considerably more flexibility compared to LS. For example, if several parameter values can describe experimental data, the posterior distribution will be multimodal. Second, the unique strength of Bayesian approach is that the model selection can be incorporated as a part of inference process. In this case, the models can be drawn from a list of possible models with certain probability, and posterior distribution will update this probability to define model selection.

Here, we consider five primary models, namely single Lorentzian,

$$y(x) = y_0 + \frac{A}{((x - x_0)^2 + w^2)^{1/2}} \quad (2)$$

Single Gaussian,

$$y(x) = y_0 + Ae^{-\left(\frac{(x-x_0)}{w}\right)^2} \quad (3)$$

and double Lorentzian, double Gaussian, and Lorentzian-Gaussian defined similarly as sum of Eqs. (2) and (4).

The Bayesian regression is implemented via the PyMC3 library in Python. We have used the Metropolis-Hastings (MH) algorithm to sample the distributions of model

Table 1: Priors used in sampling.

	Lorentzian priors	Gaussian priors
Offset	$y_0 \sim \text{Uniform}(-1, 1)$	$y_0 \sim \text{Uniform}(-1, 1)$
Amplitude	$A \sim \text{HalfNormal}(0, 10)$	$A \sim \text{HalfNormal}(0, 10)$
Peak position	$x_0 \sim \text{Normal}(x_{avg}, x_{sd})$	$x_0 \sim \text{Normal}(x_{avg}, x_{sd})$
Width	$w \sim \text{Normal}(10, 30)$	$w \sim \text{Normal}(10, 30)$
Data variance	$\eta \sim \text{Gamma}(0.1, 0.1)$	$\eta \sim \text{Gamma}(0.1, 0.1)$

parameters with the assumption that the measurement error η comes from a normal distribution with a variance of σ^2 , i.e., $\eta \sim N(\mu, \sigma^2)$. Therefore, in addition to the model parameters, the data variance is also estimated. The priors for the two models are given in Table 1. We also placed bounds on two parameters, peak position and width. For the peak position, the bounds were the measurable wavelength range. For the width parameter, the minimum width allowed was at least 2 nm as this measurable wavelength step size. We compared convergence for 4 to 16 chains for variable chain length and burn length. Based on these analyses, we have chosen four chains of the 3000 steps with the burn of 500.

To illustrate the principle and performance of Bayesian regression, shown in Figure 4 is the example of the BI analysis on the synthetic data set with known ground truth.

Here, the synthetic data are generated to follow the double Lorentzian form with the parameters: $y_0 = 0$, $x_{01} = 1$, $A_1 = 0.5$, $w_1 = 1$, $x_{02} = 6$, $A_2 = 1$, and $w_2 = 1$. The results of the BI

fit for different levels of the Gaussian noise are shown in Figure 4. Note that for low noise level, the fit reproduces the data as expected, while for higher noise level, the confidence interval becomes broader. This behavior is illustrated more systematically in Figure 4e, showing the evolution of the mean of reconstructed function and the reconstruction uncertainty. Clearly, BI allows to reconstruct the function behavior for noise level up to approximately 0.1. Above this level, the reconstructed function deviates from the ground truth and the corresponding uncertainty increases rapidly. It should be noted that using more restrictive priors (e.g., known peak positions, etc.) allows to reconstruct the function for much higher noise levels.

In comparison, shown in Figure 4g and h is the noise dependence of the reconstruction for the same data set using the Lorentzian–Gaussian model, i.e., using functional form different from the ground truth. Here, the uncertainty is significantly higher for all noise levels and the fit starts to fail for lower noise levels. This analysis illustrates that “correct” model allows for better fit of the data and the tunability of BI via priors.

The unique strength of the BI approach is that it allows to distinguish different models. In general, this can be accomplished via the hierarchical Bayesian model, where the model is drawn from the multinomial distribution $M(i)$ and the model parameters are optimized in a usual fashion. Alternatively, the probabilities of the models can be

Figure 4: (a–d) Demonstrate how a synthetic dataset is created utilizing a known function and a certain amount of noise is produced. Shown in (e) and (f) is the fitting of the Double Lorentzian model as a function of noise. As indicated by the arrow in (e), at a particular amount of noise, this model begins to fail at describing the dataset. Utilizing the Lorentzian-Gaussian model as shown (g) and (h), this fail point begins at a lower amount of noise.

estimated from the posterior densities using the widely applicable information criterion (WAIC) [33] as proposed by Gelman et al. [34]. The WAIC is defined as:

$$WAIC = \sum_{i=1}^n \log \left(\frac{1}{S} \sum_{s=1}^S p(y_i | \theta^s) \right) - \sum_{i=1}^n \text{var}_{post}(\log p(y_i | \theta)) \quad (4)$$

Here, S is the number of simulations draws and n is the number of available datapoints. The first term in Eq. (4) is the logarithm of predictive density defining the quality of the fit. The second term is the effective number of parameters, $pWAIC$, determined by the total variance of the log likelihood, $\log p(y_i | \theta)$. This term defines the complexity of the fitting function. Note that similar to calculation of the Bayesian estimate and uncertainty as shown in Figure 4, calculation of WAIC requires traces acquired during the sampling rather than just the point estimates. Subsequently, the probability of the model $p(M)$ is recovered via a Bayesian model averaging approach [35].

The fit of the synthetic data set using dissimilar models for low noise levels is shown in Figure 5. Here, the use of the

correct model gives an excellent fit as shown in Figure 5d. The use of the single peak Lorentzian (Figure 5b) and Gaussian (Figure 5c) functions allows to identify the dominant peak in the robust manner. Remarkable is that the remainder of the data is interpreted as the offset. Correspondingly, dependent of the level of the prior knowledge (e.g., using constrained distribution of the offset) allows to control the inference process. Finally, the use of the Lorentzian–Gaussian and double Gaussian leads to slightly worse prediction. It is also important to note that the nature of the fit procedure suggest that the width, amplitudes, and positions of the peaks are relatively insensitive to the choice of the fit function. Therefore, we consider the best model and the effective model parameters complementary descriptors.

The dependence of the WAIC score and the model probability on noise level is shown in Figure 5g and h. Here, it can be seen that for low noise levels, the correct model gives noise-independent $pWAIC$, whereas as for incorrect model the value strongly depends on the specific realization of the data set. The use of simple Gaussian and

Figure 5: Shown in (a) is the Double Lorentzian function (known truth) utilized for the synthetic dataset. The fit and uncertainty for the (b) Lorentzian, (c) Gaussian, (d) Double Lorentzian, (e) Double Gaussian, and (f) Lorentzian-Gaussian models are shown. Shown in (g) is how the WAIC parameters changes for each model as a function of noise. Similarly, (h) shows how the weight parameters changes for each model as a function of noise.

Figure 6: Fitting of each model for characteristic PL behaviors represented by three different compositions.

(a) $\text{CsPb}(\text{I}_{0.30}\text{Br}_{0.60}\text{Cl}_{0.10})_3$, (b) $\text{CsPb}(\text{I}_{0.60}\text{Br}_{0.10}\text{Cl}_{0.30})_3$, and (c) $\text{CsPb}(\text{I}_{0.90}\text{Cl}_{0.10})_3$. Exploration of the WAIC parameter for each model across the ternary phase diagram is shown in (d–h). Similarly, the compositional dependence of the weight parameter for each model is shown in (i–m). The fits and uncertainties of the five models for the PL spectra in (a) are shown in Figure S8.

Lorentzian function leads to low p WAIC values. The model probability is shown in Figure 5h and here the critical behavior as a function of noise level is clearly seen. Note that similar analysis can be performed as a function of discretization (corresponding to the wavelength at which measurements are performed), thus allowing to pinpoint optimal experimental parameters. Similarly, such analysis can also be performed as a function of the priors' strength, illustrating to which extent prior knowledge of the system affects interpretability.

As illustrated for the examples of the synthetic data, the BI allows a natural and flexible framework for the analysis of the PL behavior in the combinatorial library of ternary CsPbX_3 QDs. We further explore this analysis for the experimental data set.

First, we apply this method to a few characteristic PL behaviors at time zero in the ternary system. Shown in Figure 6a is the fitting of the PL behavior of $\text{CsPb}(\text{I}_{0.30}\text{Br}_{0.60}\text{Cl}_{0.10})_3$ QDs. For this composition, we observe a high-intensity, single peak at approximately 540 nm. We

explore the PL behavior of this composition in detail in Figure S8; however, here, we observe that the Gaussian model better describes this PL behavior. Another typical PL behavior observed in this ternary system is a broad peak spanning over 100 nm for $\text{CsPb}(\text{I}_{0.60}\text{Br}_{0.10}\text{Cl}_{0.30})_3$ QDs, as shown in Figure 6b. Overall, this PL behavior is described well by a broad Gaussian profile. Finally, we observe a characteristic PL behavior in Figure 6c in which we see the same broad peak; however, this is combined with another broader peak at higher wavelengths, indicating phase separation between the iodide and chloride in this binary $\text{CsPb}(\text{I}_{0.90}\text{Cl}_{0.10})_3$ composition.

Next, we explore the compositional dependence of PL behavior across the entire ternary phase space utilizing two metrics: WAIC (Figure 6d–h) and weight (Figure 6i–m). Here, we measure the PL behavior using a 450 nm excitation wavelength. This analysis was also performed on the ternary system characterized by a 350 nm excitation wavelength and is shown in Figure S9. Notably, we observe that the weight for the Lorentzian model is considerably

smaller in magnitude than the other models, as shown in Figure 6i, indicating this model does not describe the PL behavior of this ternary system well, possibly due to disorder, polydispersity, and phase separation throughout this system. As shown in Figure 6j and m, the weight of Double Lorentzian and Lorentzian–Gaussian models are high only for some compositions including red regions close to the CsPbCl_3 rich compositions and center of the ternary diagram, signifying the presence of double peaks and phase separation in these regions. Interestingly, the CsPbBr_3 -rich compositions are best described by a Gaussian fit as indicated by the high magnitude in weight for this model (shown in Figure 6k), implying single peak with no phase separation, and slight disorder in these compositions. Finally, the remainder of the ternary phase system (Figure 6l), specifically CsPbI_3 -rich compositions, are best described by the Double Gaussian model, indicating possibility of phase separation and disorder.

With information about each model's fit, we can then calculate the posteriors, such as offset, peak amplitude, and peak width, across the ternary compositional space. We take a particular interest in the peak width parameter as it is related to the FWHM and, therefore, the PLQY. The mapping

of these parameters is shown in Figure 7 and S11–S15. We primarily focus on the 450 nm excitation wavelength dataset, which is shown in Figure 7. As mentioned earlier, we observed that the Lorentzian, Double Lorentzian, and Lorentzian Gaussian models did not fit the PL behavior of QDs well; however, we include how the posteriors change for this model in Figure S10. For the CsPbBr_3 -rich compositions, which were primarily described by the Gaussian model (Figure 7a–d). For these compositions, we observe a high-amplitude and narrow peak width, indicating high PLQY. Next, for the compositions described in the Double Gaussian model, which is primarily composed of CsPbCl_3 -rich compositions doped mostly with CsPbI_3 , the amplitude is small, and the width is broad, as shown in Figure 7d. The CsPbI_3 -rich compositions, which are also fitted with the Double Gaussian model, exhibit the same behavior as the CsPbCl_3 -rich compositions doped mostly with CsPbI_3 . However, these regions represent phase segregations due to presence of double peaks. For the CsPbCl_3 -rich compositions described well by the Double Gaussian model, we observe a general trend in which one of the peak width (Figure 7h and k) is large, indicating a broad peak such as the one seen in Figure 6c. The other width parameter is considerably

Figure 7: Shown is the Bayesian fit parameters, specifically the offset, peak positions, amplitudes, and widths, for the (a–d) Gaussian and (e–k) Double Gaussian, models.

The parameters for the Lorentzian, Double Lorentzian, and Lorentzian Gaussian model are shown in Figure S10.

smaller. This result further confirms the capability of BI analysis providing new insight on the formation and quality of ternary solid solution of CsPbX_3 QDs which cannot be revealed solely by the GP approach.

To summarize, here we synthesized cesium lead halide QDs in the binary and ternary solid solution configuration via an automated micropipetting platform. The synthesis of vast compositional spaces of CsPbX_3 QDs is highly reproducible using this platform and can be extended to other PQDs including hybrid organic–inorganic perovskites. We explored the ambient stability of QDs by studying the time-dependent PL spectra. The stability and the PL shape behavior was analyzed using non-negative matrix factorization and Bayesian inference analysis. The Bayesian inference approach allows us to obtain the model that best describes the PL behavior and yields the model parameters and associated uncertainties. This analysis allows characterization of size distribution and phase segregation of ternary QDs by analysis of PL peak shape and width. Overall, we observe better performance of the chlorine doped CsPbBr_3 QDs than the iodide-doped CsPbBr_3 QDs with CsPbBr_3 performing the best as it maintains a high intensity and narrow PL peak over time.

More generally, we believe that the capability of the Bayesian inference methods to use the prior knowledge on the system and update it based on the experimental observations can provide a complementary approach for navigating multidimensional compositional spaces in automated synthesis. Traditionally, this approach is based solely on the Bayesian optimization methods using the combination of the uncertainty and functional properties to define corresponding acquisition function. Here, the Bayesian inference yields additional parameters that characterize the physical responses in the systems, as well as associated uncertainties. These provide an additional spectrum of descriptors to navigate the chemical space of these systems.

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