Resolving the Controversy in Biexciton Binding Energy of Cesium Lead Halide Perovskite Nanocrystals through Heralded Single-Particle Spectroscopy

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ABSTRACT: Understanding exciton−exciton interaction in multiply excited nanocrystals is crucial to their utilization as functional materials. Yet, for lead halide perovskite nanocrystals, which are promising candidates for nanocrystal-based technologies, numerous contradicting values have been reported for the strength and sign of their exciton−exciton interaction. In this work, we unambiguously determine the biexciton binding energy in single cesium lead halide perovskite nanocrystals at room temperature. This is enabled by the recently introduced single-photon avalanche diode array spectrometer, capable of temporally isolating biexciton−exciton emission cascades while retaining spectral resolution. We demonstrate that CsPbBr₃ nanocrystals feature an attractive exciton−exciton interaction, with a mean biexciton binding energy of 10 meV. For CsPbI₃ nanocrystals, we observe a mean biexciton binding energy that is close to zero, and individual nanocrystals show either weakly attractive or weakly repulsive exciton−exciton interaction. We further show that, within ensembles of both materials, single-nanocrystal biexciton binding energies are correlated with the degree of charge-carrier confinement.

KEYWORDS: perovskite nanocrystals, quantum dots, biexciton binding energy, single-particle spectroscopy, SPAD arrays

Colloidal semiconductor nanocrystals (NCs) have been extensively studied over the last three decades, owing to the ease of their synthesis and tunability of their photophysical properties. Absorption of a photon by an NC leads to the formation of an exciton, a bound electron-hole pair, whose energy can be precisely tuned by varying the physical dimensions of the NC. In well passivated direct band gap NCs, the dominant relaxation route of excitons is via photoluminescence (PL). Additional complexity is introduced when NCs absorb multiple photons, generating multie excitonic states. In the simplest of these states, the biexciton (BX), two excitons are confined within the NC.

PL from the BX state can serve as a probe to investigate exciton−exciton interaction within the NC. Relaxation from the BX to the singly excited (1X) state can occur through the radiative PL process or via nonradiative Auger processes. Hence, the probability of radiative relaxation from the BX state, the BX quantum yield, is indicative of the relative rates of the two processes. A cascaded radiative relaxation from BX to 1X and further to the ground (G) state results in the emission of two photons in rapid succession. The energy of the first photon \((E_{BX})\) will be shifted from the second \((E_{1X})\), according to exciton−exciton interaction. The value of this shift, the BX binding energy \((\epsilon_b \equiv E_{1X} - E_{BX})\), is defined to be positive for attractive interaction. In intrinsic homogeneous or type-I NCs, where all charge carriers are confined to the same volume, this interaction is typically attractive and stronger than in the bulk, due to the correlation energy of the confined excitons. In type-II heterostructure NCs, where electrons and holes are spatially...
separated, Coulombic repulsion of like-charged carriers can overwhelm this correlation energy and result in an overall repulsive interaction.\textsuperscript{4} Significant effort has been directed at the evaluation and control of this value in II-VI and III-V semiconductor NCs, as it is critical to enhance their performance in various applications, such as sources of quantum light,\textsuperscript{5} lasing media and LEDs,\textsuperscript{6} and photovoltaics.\textsuperscript{6}

In recent years, there has been a surge of interest in lead halide perovskite (LHP) NCs of the form APbX\textsubscript{3}, where A is a monovalent cation and X a halide anion. Their prominent features, near unity PL quantum yield, defect tolerance, and tunable emission across the visible spectrum, have made them a promising candidate for various optoelectronic applications.\textsuperscript{5,6} Additionally, at cryogenic temperatures, they exhibit long PL coherence times, which are desirable for emerging quantum optical technologies such as generation of coherent single photons and entangled photon pairs.\textsuperscript{7} As in their II-VI and III-V counterparts, many of these applications stand to benefit from, or even depend on, reliable estimation of the BX binding energy.

However, the value of the BX binding energy in LHP NCs is a subject of current debate. Reported values for the prototypical all-inorganic CsPbBr\textsubscript{3} NCs span the range between strongly attractive to strongly repulsive interaction ($ε_b \approx 100$ meV\textsuperscript{11} to $−100$ meV;\textsuperscript{12} see Supporting Information Table S1). Common to all previous experimental works is their reliance on ensemble measurements. While these techniques proved invaluable in studying multie excitonic states in NCs, their ensemble nature introduces several possible sources for the estimation errors which may underlie the existing discrepancies. First, ensemble methods require fitting data to a model, and quantitative results often depend on the model chosen to analyze and interpret the data.\textsuperscript{13,14} In particular, the BX contribution might be hard to disentangle from other photophysical or chemical processes such as charging or sintering\textsuperscript{15,16} leading to ambiguities. Additionally, most methods require resolving the BX and 1X peaks spectrally, which might prove challenging when $ε_b$ is much smaller than the 1X homogeneous and inhomogeneous spectral broadenings.\textsuperscript{15,16} Finally, the size heterogeneity, inherent to colloidal synthesized NC ensembles, can introduce systematic biases due to the size dependent absorption cross section of the 1X and BX states.

Room temperature single-particle heralded spectroscopy has been recently introduced as a way to overcome these shortcomings of ensemble approaches.\textsuperscript{16,17} This is achieved by temporally isolating photon pairs originating from the BX→1X→G cascade of single particles and is hence free of all the aforementioned biases and ambiguities. In this work, we utilize this technique to unambiguously determine the BX binding energies of the prototypical LHP NCs CsPbBr\textsubscript{3} and CsPbI\textsubscript{3}. All CsPbBr\textsubscript{3} single particles measured featured an attractive exciton–exciton interaction ($ε_b = 10 \pm 6$ meV), and a clear correlation of the BX binding energy with charge-carrier confinement was observed. Interestingly, CsPbI\textsubscript{3} NCs showed either weakly attractive or weakly repulsive exciton–exciton interaction with an average around zero binding energy ($ε_b = 1 \pm 9$ meV).

**RESULTS**

**Nanocrystals in This Work.** Perovskite NCs investigated in this work were synthesized according to refs 18 and 19 (CsPbBr\textsubscript{3}), and ref 20 (CsPbI\textsubscript{3}), with minor modifications (see Methods section and Supporting Information section S2). CsPbBr\textsubscript{3} NCs, seen in Figure 1a, feature an edge size distribution of $5.9 \pm 1.3$ nm, 2.44 eV ensemble emission peak, and $\sim 100\%$ quantum yield. For CsPbI\textsubscript{3}, seen in Figure 1b, two size populations are visible. Smaller NCs ($\sim 80\%$ of the particles) with an edge size distribution of $7.2 \pm 1.9$ nm, and larger NCs with an edge size distribution of $15.4 \pm 3.3$ nm. The ensemble emission peak is at 1.84 eV, and the quantum yield is $\sim 42\%$. Samples of isolated nanocrystals were prepared by spin coating a dilute solution of the NCs dispersed in a 3 wt % solution of poly(methyl methacrylate) (PMMA) in toluene on a glass coverslip.

**Single-Particle Heralded Spectroscopy.** In order to measure the BX binding energy in single NCs, we use heralded spectroscopy, a technique that utilizes the temporal correlation of photon detections to unambiguously resolve the BX and 1X emission spectra. This technique was recently introduced and utilized to measure the BX binding energy of single CdSe/CdS/ZnS quantum dots at room temperature.\textsuperscript{16} Briefly, an inverted microscope with a high numerical aperture objective is used to focus pulsed laser illumination on a single NC, and collect the emitted fluorescence. The collected fluorescence is then passed through a Czerny–Turner spectrometer with a single-photon avalanche diode (SPAD) array detector, so that each detected photon is time-stamped according to its arrival time, and energy-stamped according to the array pixel it was detected in (Figure 2a). Post-selecting only photon pairs that follow the same excitation pulse robustly isolates BX-1X emission cascades from emission of other overlapping emitting states, such as 1X or trions. The pump power is adjusted so that the average number of photons absorbed by an NC per pump pulse ($⟨N⟩$) is low ($<0.4$; see Supporting Information section S3). This helps prevent rapid deterioration of the NCs.

![Figure 1](https://doi.org/10.1021/acsnano.1c06624)  
**Figure 1.** Particles investigated in this work. (a) Transmission electron micrograph of the CsPbBr\textsubscript{3} NCs investigated in this work. (b) Transmission electron micrograph of the CsPbI\textsubscript{3} NCs investigated in this work. Both scale bars are 20 nm. (c) Ensemble emission (solid lines) and absorption (dashed dotted lines) of the CsPbBr\textsubscript{3} (green) and CsPbI\textsubscript{3} (red) NCs. Blue line marks the excitation wavelength (470 nm).
and minimize excitation of higher multie excitonic states. A thorough description of the system and technique is given in ref 16, and some modifications made to accommodate the different fluorescence parameters of the LHP NCs are described in the Methods section and in Supporting Information section S4.

Figure 2b is a 2D histogram of such post-selected photon pairs from a 5 min measurement of a single CsPbBr3 NC. It shows the energy of the first arriving photon ($E_{\text{BX}}$) as a function of the second arriving photon ($E_{1X}$) of the pair. The green dashed line is a guide to the eye, marking the same energy for both photons (undetectable by the system due to pixel dead time). The asymmetry of the histogram around this diagonal is indicative of an attractive exciton–exciton interaction ($E_{\text{BX}}$ is typically smaller than $E_{1X}$). This energy difference is quantified in Figure 2c where the BX (red dots) and 1X (blue circles) spectra are extracted by full horizontal and full vertical binning, respectively, of Figure 2b. This identification is corroborated by the good agreement between the 1X spectrum, and the spectrum of all detected photons (gray area, normalized). The emission peaks of the BX and 1X spectra are estimated from fits to Cauchy–Lorentz distributions (matching color lines), and the BX binding energy is estimated as the difference in peak positions. For this specific NC, $\varepsilon_b = 13.5 \pm 1.8$ meV (all errors in this paper are estimated as the 68% confidence interval of the fit).

Two further insights were extracted from the same data set. First, the normalized second order correlation of photon arrival times ($g^{(2)}(0)$) was calculated by the method described in ref 21. This value is defined as the ratio between the number of detection pairs following the same excitation pulse and the expected number for a classical Poissonian emitter. The presence of the additional exciton in a doubly excited NC increases the probability of nonradiative BX to 1X decay via Auger recombination. As a consequence, fewer photon pairs are emitted, leading to $g^{(2)}(0) < 1$, a phenomenon termed photon antibunching. Hence, the value of $g^{(2)}(0)$ helps quantify the PL quantum yield of the BX state.

Second, the time-gated second order correlation of photon arrival times ($g^{(2)}(0)$) was calculated. This is performed by post-selecting only detections arriving within a time window of 1–30 ns after any excitation pulse, and applying the same $g^{(2)}(0)$ calculation procedure to the resulting filtered data. Most multie exciton emission processes occur at time scales shorter than 1 ns (see Supporting Information section S5), and are therefore, filtered out by this time window. In single NCs, multie exciton states are the only source for multiple photon detections following the same excitation pulse. Therefore, a low $g^{(2)}(0)$ is a good indication of whether the observed emission originates from a single particle or not1,6,24 ($g^{(2)}(0)$ and $g^{(2)}(0)$ are further discussed in Supporting Information section S3). For this specific NC, $g^{(2)}(0) = 0.175 \pm 0.008$ and $g^{(2)}(0) = 0.012 \pm 0.003$.

CsPbBr3 NCs. Figure 3a shows the BX binding energy of 60 single CsPbBr3 NCs, determined using the procedure illustrated in Figure 2. In our measurements, we maintain $(N) \sim 0.1$ and obtain a mean single-particle $\varepsilon_b$ error of $\pm 3.1$ meV. To filter out accidental measurements of non-isolated NCs, only measurements where $g^{(2)}(0) < 0.2$ are considered. All particles feature an attractive exciton–exciton interaction ($\varepsilon_b > 0$), and the distribution is centered around $\varepsilon_b = 10 \pm 6$ meV. Figure 3b displays the binding energy of each NC as a function of the 1X emission peak position. A clear correlation between the two values is evident. This can be interpreted as the effect stronger charge-carrier confinement has on both the 1X emission peak (stronger confinement is correlated with higher energy emission peak) and the binding energy (stronger confinement is correlated with stronger interaction of the two excitons). The trend and magnitude are in reasonable agreement with theoretical predictions recently made by Nguyen et al.25 and bounds suggested by Shulenberger et al.15

The suggested interpretation is further corroborated in Figure 3c. Here, the BX binding energy is plotted as a function of $g^{(2)}(0)$, another value indicative of charge-carrier confinement. Namely, tighter confinement increases the rate of Auger processes3 and, consequently, reduces the yield of the competing radiative BX decay process, evident in lower $g^{(2)}(0)$. Therefore, the inverse correlation of $\varepsilon_b$ with $g^{(2)}(0)$ evident in Figure 3c can be seen as pointing to the same underlying correlation of the BX binding energy with charge-carrier confinement.

CsPbI3 NCs. CsPbI3 NCs BX binding energies were measured by the same technique (Figure 4). Results feature $\varepsilon_b$ values distributed around zero ($\varepsilon_b = 1 \pm 9$ meV, $(N) \sim 0.3$, ...
mean single-particle $\epsilon_b$ error: $\pm 4.8$ meV). The trends observed for CsPbBr$_3$ are visible here as well, where higher 1X emission peak energy and lower $g^{(2)}(0)$, or stronger confinement, are correlated with stronger attractive interaction (Figure 4b,c). As a result, while $\epsilon_b$ values are mostly within reasonable error from zero, NCs featuring a 1X emission peak lower (higher) than 1.845 eV or $g^{(2)}(0)$ higher (lower) than 0.25 typically display a small negative (positive) $\epsilon_b$ value. While the results are not as conclusive as for CsPbBr$_3$, they suggest that the weak exciton–exciton interaction in CsPbI$_3$ NCs can be either repulsive or attractive, depending on the exact parameters of the single particle.

It is noteworthy that CsPbI$_3$ measurements were significantly more challenging than their CsPbBr$_3$ counterparts. This is due to two factors. First, CsPbI$_3$ NCs synthesized were typically less emissive and less stable under the conditions of our measurements. That resulted in many NCs deteriorating during the measurement (PL declines to near zero), before enough photon pairs were detected to extract reliable spectra fits. Second, current SPAD array technology is less sensitive at these longer wavelengths. The SPAD array detector used in this work has roughly twice the photon detection efficiency at the CsPbBr$_3$ emission peak compared to the CsPbI$_3$ emission peak. These two factors resulted in the smaller statistics and larger errors for CsPbI$_3$ NCs in this work.

**DISCUSSION**

The BX binding energies presented in this paper are at the lower range of values previously reported in the literature for these NCs (see a table of previously reported values in Supporting Information section S1). While in some cases this might be attributed to the potential pitfalls associated with ensemble measurements discussed in the introduction, it is also important to consider the possibility that heralded spectro-
copy and ensemble measurements probe the NC in a qualitatively different excitation state. For example, one widely adopted ensemble technique for estimating BX binding energy involves recording the transient absorption (TA) spectrum of a probe pulse at very short (<1 ps) delays from a pump pulse, that is, before the relaxation of hot carriers to the band edge.27,28 The hot carrier pair generated by the pump shifts the spectral position of the absorption resonance for the probe photon, and this shift is recorded as the exciton–exciton interaction energy. In contrast, results presented in this paper rely on measurements of photon pairs emitted from individual BX→BX→G cascades following the excitation pulse. Since the PL decay lifetimes of the BX and 1X states are significantly longer than the time scales of hot carrier relaxation in the NCs (see Supporting Information section S5), our measurements probe the NC only after the hot carrier pairs have relaxed to the band edge.

Since the wave function of the hot exciton differs from that of a band-edge 1X state, the interaction energies may be different in the two cases. Studies on PbS nanocrystals indicate that the magnitude of interaction between a hot exciton and a band-edge exciton is larger than between two band-edge excitons.29 For CsPbI3 NCs, a recent study indicates that the estimated εb increases as the pump wavelength decreases in short-delay TA experiments.30 Similar trends have been demonstrated for CsPbBr3 at cryogenic temperatures using two-dimensional electron spectroscopy.31 In addition, analyses of TA measurements by Ashner et al., that do not employ short-delay spectra, did not result in large positive values (but rather in small negative values of a few meV).14 Together, these observations suggest that εb measured when both excitons are at the band edge would be lower than that measured when the first exciton is still hot. In this sense, heralded spectroscopy and short-delay TA are complementary measurements of band-edge and hot exciton–exciton interaction, respectively, and a careful comparison of the two can help uncover insights into dynamics of exciton interactions in NCs.

Negative εb values, observed only for CsPbI3 NCs in this work, are less often reported in the literature for similar NCs (see Supporting Information section S1). The origin of this repulsive interaction is not immediately apparent from existing theoretical models of intrinsic homogeneous semiconductor NCs.25,32 One possible explanation is a modification of the charge-carrier wave functions induced by surface ligands.33 This can result in a type-II potential landscape, where the electrons or the holes are localized at the NC surface, and Coulomb repulsion might dominate the exciton–exciton interaction. Alternatively, the electrostatic field generated by charge carriers trapped in the ligand-induced trap states can result in charge separation, and a similar repulsive interaction. Another possibility, suggested by Ashner et al.,14 is the formation of polarons, supported by the deformable nature of the perovskite lattice. The results presented in this work cannot pinpoint a certain mechanism, and present limited statistics of negative εb values. However, the apparent observation of a repulsive exciton–exciton interaction in a homogeneous nanocrystal highlights the importance of further investigating the effect of surface chemistry, environment, and perovskite lattice on charge-carrier interaction in LHP NCs.

In addition to the BX binding energy, the single-particle nature of our technique also allows the investigation of the BX spectral line width. As is evident from Figure 2c and Figure S5, the CsPbBr3 NCs BX spectrum is broader by a factor of 1.4 ± 0.4 compared to the 1X spectrum (measurements of CsPbI3 NCs suggest a similar factor, but at a lower confidence). A possible explanation for this broadening is the presence of multiple decay routes from the BX to the 1X state, possibly through thermally excited hot BX states which are close energetically to the lowest BX state.31,34 We note that this is qualitatively different from observations in core/shell/shell CdSe/CdS/ZnS NCs.16,17 However, II-VI semiconductor NCs feature more pronounced spectral diffusion compared to LHP NCs.35,36 As demonstrated in ref 16, attenuation of the BX spectral diffusion as compared to the 1X spectral diffusion can overwhelm BX broadening effects, if they exist, and lead to a BX spectrum that is narrower than the 1X.

CONCLUSIONS

Heralded spectroscopy enables us to unambiguously determine the bie exciton binding energy (εb) of single lead halide perovskite nanocrystals. Using this technique, we demonstrate that ~6 nm edge CsPbBr3 nanocrystals feature an attractive exciton–exciton interaction of εb = 10 ± 6 meV, which lies at the lower range of previously reported values. Interestingly, within the ensemble of ~7 nm edge CsPbI3 nanocrystals, some exhibit weak attractive interactions, whereas others appear to exhibit weak exciton–exciton repulsion. This rarely observed phenomenon in homogeneous nanocrystals warrants further investigation of charge-carrier interactions in these particles. In nanocrystals of both materials, the strength of attractive interaction exhibits a clear correlation with single-exciton emission peak position and photoluminescence antibunching (g(2)(0)), highlighting the dependence of εb on charge-carrier confinement. These insights into the physics of exciton interactions in lead halide perovskite nanocrystals can enable the development of better engineered nanocrystals for future optoelectronic technologies. Moreover, the ability to determine the bie exciton binding energy of single nanocrystals at room temperature is instrumental to their utilization in quantum technologies.

METHODS

Synthesis of CsPbBr3 Nanocrystals. CsPbBr3 NCs were synthesized according to a reported recipe18 with slight modifications. ODE (5 mL) and PbBr2 (69 mg) were mixed and dried under vacuum for 1 h at 120 °C. Then, under an Ar atmosphere, dried OA (0.5 mL) and PbI2 (0.5 mL) were injected to the mixture and the temperature was raised to 180 °C and kept for 10 min. Then, Cs-oleate solution (0.4 mL) was swiftly injected, and after 25 s, the reaction mixture was cooled by an ice water bath. The NCs were purified from the crude solution by centrifugation and dispersed in anhydrous toluene. Following, surface treatment was performed by a saturated NH4BF4 toluene solution (1 mL) stirred together with 25 mL of CsPbBr3 NCs in toluene (following ref 19 with slight modifications).

Synthesis of CsPbI3 Nanocrystals. CsPbI3 NCs were synthesized according to the recipe reported in ref 20 with minor modifications. ODE (5 mL), PbI2 (87 mg), OLA (1 mL, dry), TDPA (120 mg), and TOPO (1.5 mg) were mixed and dried under vacuum for 1 h at 120 °C. The temperature was raised to 280 °C and kept for 10 min under an Ar atmosphere. Then Cs-oleate solution (0.4 mL) was quickly injected, and after 15 s, the reaction mixture was cooled by an ice-water bath. The crude solution was purified by two-step centrifugation in hexane.

See further details of the synthesis protocols in Supporting Information section S2.
Optical Setup. The SPAD array spectrometer is built around a commercial inverted microscope (Eclipse Ti-U, Nikon). An oil immersion objective (x100, 1.3 NA, Nikon) is used to focus light from a pulsed laser source (470 nm, 5 MHz, LDH-P-C-470B, PicoQuant) on a single NC and collect the emitted PL. The emitted light is then filtered through a dichroic mirror (FF484-FDi02-t3, Semrock) and a long-pass filter (BLP01-473R, Semrock). The magnified image plane (x150) serves as the input for a Czemy–Turner spectrometer that consists of a 4-f system (AC254-300-A-ML and AC254-100-A-ML, Thorlabs) with a blazed grating (53.5°–321R, Richardson) at the Fourier plane. At the output image plane of the spectrometer, a 512 pixel on-chip linear SPAD array is placed. In our experiments, 30–43 pixels of the array were used (see Supporting Information section S4). The physical pixel pitch is 52.4 μm, corresponding to ∼1.5 nm wavelength difference of impinging photons between neighboring pixels. Time tagging is done by an array of 64 time-to-digital converters (TDCs) implemented on a field-programmable gate array (FPGA). The temporal instrument response function of the system features a ∼180 ps full width at half maximum (FWHM).

See further details of the experimental setup in ref 16 and Supporting Information section S4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge from https://pubs.acs.org/doi/10.1021/acsnano.1c06624.

List of previously reported biexciton binding energies; nanocrystal synthesis protocol; details of supporting analyses of (N), g(2)(0), and g(2)(0); system parameters; photoluminescence decay lifetime estimation; biexciton spectrum broadening (PDF)

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Notes

The authors declare the following competing financial interest(s): The authors have filed a patent application on the presented method. For the sake of transparency, the authors would like to disclose that (i) Edoardo Charbon holds the position of Chief Scientific Officer of Fastree3D, a company making LiDARs for the automotive market, and that (ii) Ivan Michel Antolovic, Claudio Bruschini and Edoardo Charbon are co-founders of Pi Imaging Technology. Both companies have not been involved with the paper drafting.

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