Supporting Information for:

Size-Dependent Biexciton Spectrum in CsPbBr₃

Perovskite Nanocrystals

Matthew N. Ashner, *¹ Katherine E. Shulenberger, *² Franziska Krieg, ^{3,4} Eric R. Powers,¹

Maksym V. Kovalenko,^{3,4} Moungi G. Bawendi,^{2,#} and William A. Tisdale^{1,#}

* Both authors contributed equally

¹ Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States.

² Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States.

³ Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland.

⁴ Laboratory for Thin Films and Photovoltaics, Empa–Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland.

[#]Correspondence: <u>tisdale@mit.edu</u>, <u>mgb@mit.edu</u>

S.1. Experimental Details

S.2. Multiexciton Dynamics Observed in Time-Resolved Photoluminescence Experiments

S.3. Sample Transient Absorption Data in the Single Exciton Regime

S.4. Statistical Uncertainty of Kinetic Parameters and Fits

S.5. Transient Redshift Not Captured by the Two-Component Kinetic Model

S.6. Exciton Lifetime from Transient Absorption and Photoluminescence Experiments

S.7. Unnormalized Component Spectra

S.1. Experimental Details

Sample Preparation

Colloidal CsPbBr₃ nanocrystals were synthesized by a hot injection synthesis as previously described in:

Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; et al. Colloidal CsPbX3 (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. ACS Energy Letters 2018, 3 (3), 641–646.

Cesium oleate (0.4 M): 1.628 g of Cs_2CO_3 (10 mmol, 2 eq. Cs) and 5 mL of oleic acid (16 mmol, 0.8 eq.) were evacuated in a three-neck flask along with 20 mL of 1-octadecene (ODE) at room temperature until the first gas evolution subsided and was then further evacuated at 25-120 °C for 1 hour.

Lead (II)-oleate (0.5 M): 4.6066 g of lead (II) acetate trihydrate (12 mmol, 1 eq.) and 7.6 mL of oleic acid (24 mmol, 2 eq.) were evacuated in a three-neck flask along with 16.4 mL of ODE at room temperature until the first gas evolution subsided and then further evacuated at 25-120 °C for 1 hour.

TOPBr₂ (0.5 M): Trioctylphosphine (TOP) (6 mL, 13 mmol) and Br₂ (0.6 mL, 11.5 mmol) were reacted under inert atmosphere and diluted with toluene (18.7 mL) once the reaction was cooled to room temperature.

CsPbBr₃ Nanocrystals: Pb-oleate (5 mL, 2.5 mmol), Cs-oleate (4 mL, 1.6 mmol), 3-(N,N-dimethyloctadecylammonio)-propanesulfonate (0.215 g, 0.5 mmol) were mixed with 50 mL 1-octadecene and heated to 120° C under vacuum, where the atmosphere was changed to argon. The temperature was further elevated to 100° C- 180° C (depending on the desired NC size) where TOPBr₂ was injected (5 mL, 5 mmol of halides). The reaction was cooled down immediately by an ice bath.

Isolation and Purification: 128 mL of ethyl acetate were added to the 64 mL crude solution (7.5 nm and 6 nm sizes only) and the NCs were precipitated by centrifugation at 29500g for 10 minutes. The NCs were dispersed in 20 mL of toluene and precipitated with 40 mL of ethyl

acetate and centrifugation at 29500g for 1 min. During the second and third purification steps solvents were reduced by factor 2 for each step. The NCs were dispersed in toluene at a concentration of up to 100 mg/mL and centrifuged once more at 29500g for 1 min to make the final suspension.

Spectroscopy Methods

Transient Absorption Spectroscopy

For the femtosecond transient absorption experiments, the 1040 nm output from a high repetition-rate Yb amplifier (Spectra-Physics Spirit) operating at 200 kHz was split into two beams. One arm was used to generate a 400 nm pump pulse by frequency doubling the signal from a commercial non-collinear optical parametric amplifier (Spectra-Physics Spirit-NOPA) in a BBO crystal. The other arm was used to generate a broadband probe pulse (480-650 nm) by focusing the 1040 nm fundamental into a 4 mm YAG window with a 50 mm focal length lens. The pump pulse was compressed to ~50 fs FWHM using a fused silica prism compressor, sent through a mechanical delay stage (Newport) to control the pump-probe delay, and focused into a mechanical chopper (ThorLabs) to modulate the pump at 5 kHz. The pump beam fluence was controlled with a variable neutral density wheel. The pump and probe beams were focused by a 200 mm focal length concave mirror into the sample.

The sample was a solution of nanocrystals in a 2 mm path length quartz cuvette diluted in toluene to an optical density of 0.2 - 0.3 at the first exciton peak. Several precautions were taken to protect the sample from air exposure and avoid the previously reported sample degradation.¹ The dilution was prepared in a glove box under nitrogen atmosphere with anhydrous, air-free solvents, and the cuvette cap was sealed with parafilm and the sample was used immediately. The sample was also stirred vigorously throughout the experiment.

The probe beam was coupled into a spectrometer with a high-speed data acquisition system (Ultrafast Systems) to collect spectra at 10 kHz. The acquisition and chopping were synchronized with the amplifier repetition rate to ensure a consistent number of laser pulses per spectrometer acquisition. Each measurement was the average of 6 scans with 0.5 s acquisition per time point to ensure that dynamics did not change under laser exposure. The raw data were corrected for chirp in the probe pulse and photoluminescence background. The pump-probe cross correlation was measured using the optical Kerr effect in a 1 mm fused silica window. A wavelength-dependent

time zero position was extracted from the cross-correlation and used to correct the data for timing variations due to the probe chirp. After that, the average of 10 spectra from negative time delays was subtracted from the data to remove contributions from spontaneous photoluminescence to yield the processed data.

Time-Resolved Photoluminescence

The photoluminescence experiments used the same 400 nm light source described above. The 400 nm light was focused using a 25.4 mm lens into a solution of NCs diluted to an optical density of 0.01 at the first exciton peak and held in a 2 mm path length quartz cuvette. The sample was stirred vigorously throughout the experiment to prevent photocharging. The emitted photoluminescence was collected with a 75 mm focal length lens and focused into a 150 mm focal length monochromator equipped with a 150 gr/mm grating (Princeton Instruments SP2150). The monochromator output was collected and focused into a single photon counting avalanche diode (MPD). Photoluminescence lifetimes were collected by sending the electrical pulses from the APD to a time-correlated single photon counting unit (Picoquant Picoharp 300). The synchronization signal was generated by frequency doubling the other arm from the laser, focusing it into a high-speed photodiode (Thorlabs), and using the photodiode output to trigger a digital delay generator (Stanford Research Systems DG645) to send pulses of the correct voltage and polarity to the TCSPC unit. The complete system had an IRF of 160 ps, and the count rate at the detector was maintained at 1500 counts per second to avoid artifacts. A PL decay trace was collected at each spectral position by scanning the monochromator in 2 nm increments.

S.2. Multiexciton Dynamics Observed in Time-Resolved Photoluminescence Experiments

Figure 1c-d in the main text shows there is no spectral shift in the emission associated with the decay of biexcitons in the 10 nm NCs, and Figure S1 shows that the same is true for the 6 and 7.5 nm NCs. Despite the lack of a transient spectral shift associated with emission from the biexciton state even at particularly high excitation fluences, photoluminescence dynamics indicate that such states are being generated and contribute to the observed emission as shown in Figure 1e, Figure S1c, and Figure S1f for all three sizes. At high fluences, a fast decay component emerges at early time delays in the dynamics of the photoluminescence peak intensity. Furthermore, we know from the solution g(2) measurements that the biexcitonic state has a high enough quantum yield that it contributes to the measured spectrum at early time delays.¹ This leads us to the conclusion that the biexciton emission spectrum is heavily overlapped with the exciton emission spectrum and cannot be separately resolved in an ensemble photoluminescence experiment. The exciton-exciton interaction must be weak enough that no shift is observed within the resolution of the measurement.



Figure S1. Time-resolved photoluminescence spectra for different NC sizes and fluences normalized to the same peak intensity. (a) 6 nm at low fluence $(0.26 \,\mu\text{J/cm}^2, \langle N \rangle = 0.01)$. (b) 6 nm at high fluence (26 $\mu\text{J/cm}^2, \langle N \rangle = 1$). (c) Spectrally integrated TRPL dynamics under low fluence (blue trace) and high fluence (red trace) excitation for the 6 nm NCs. (d) 7.5 nm at low fluence (5 $\mu\text{J/cm}^2, \langle N \rangle = 0.3$). (e) 7.5 nm at high fluence (1600 $\mu\text{J/cm}^2, \langle N \rangle = 116$). (f) Spectrally integrated TRPL dynamics under low fluence TRPL dynamics under low fluence (blue trace) and high fluence (blue trace) and high fluence (red trace) excitation for the 7.5 nm NCs.

S.3. Sample Transient Absorption Data in the Single Exciton Regime

Figure S2 shows example TA spectra for the same NCs as Figure 2 in the main text excited with a lower pump fluence such that contributions from the biexciton state is negligible. This data lacks the spectral changes over the 2-200 ps pump-probe delay range in Figure S2b that is evident at higher excitation fluences in Figure 2b.



Figure S2. Transient absorption spectral dynamics of 7.5 nm NCs with a pump fluence that generates an average of 0.2 excitons per NC per pulse over the same pump-probe time delay regimes as Figure 2 in the main text: (a) 0-2 ps, (b) 2-200 ps, and (c) >200 ps.

S.4. Statistical Uncertainty of Kinetic Parameters and Fits

The Markov Chain Monte Carlo (MCMC) sampling method can be used to produce visualizations of the uncertainty in the kinetic parameters as described in our previous publication.² These visualizations take the form of corner plots, shown in Figures S3, S4, and S5 for the 10 nm, 7.5 nm, and 6 nm NCs respectively. The corner plots represent the contents of every state in the Markov chain, in contrast to the random samples used to generate Figure 3 in the main text. The diagonal panels are histograms of the distribution of each individual parameter. If any individual parameter has asymmetric uncertainty or a bimodal distribution, it will be visible in its histogram. The off-diagonal panels display cross-correlations between each pair of parameters. If a pair of parameters appear correlated in the Markov chain, but should not be correlated in the physical system, that would be an indicator that the model contains a redundancy and should be modified. The corner plots shown here reveal largely uncorrelated fitting parameters, indicating that the 2-component kinetic model does not over-specify the true physical system.



Figure S3. Corner plot displaying the probability distributions for each parameter and parameter pair extracted from the MCMC analysis for the 10 nm NCs. The diagonal panels show histograms for each of the individual parameters. The off-diagonal panels show the cross-correlations between each pair of parameters produced by applying a kernel smoothing estimation algorithm to the MCMC samples. The contour lines are 10% intervals.



Figure S4. Corner plot for the 7.5 nm NCs.



Figure S5. Corner plot for the 6 nm NCs.

Figure S6 presents a comparison of the fit results with the raw data for each NC size and pumpprobe delay times of 2 ps, 200 ps, and 2.25 ns. The colored circles in each panel represent the raw TA data at each fluence for the respective NC size and delay, and the black lines are the fits produced from a random sample of 100 parameter sets from the MCMC population overlaid with some transparency as in Figure 3 in the main text. Like Figure 3, the individual traces are close enough together that they are rendered as a single trace and the line weight has been adjusted for visibility. The spread in the individual samples is less than the thickness of the line as rendered indicating a very high certainty that the black lines represent the best fit of the proposed model to the data.



Figure S6. Comparisons of the raw data and a sample of the fits extracted from the MCMC ensemble at a pump-probe time delays of (a-c) 2 ps, (d-f) 200 ps, and (g-i) 2.25 ns for the (a, d, g) 10 nm, (b, e, h) 7.5 nm, and (c, f, i) 6 nm NCs. The colored circles are the data collected at a series of pump fluences, and the black lines are 100 superimposed sample fits. The individual fits are indistinguishable on this scale as they all lie within the thickness of the individual lines. Pump fluence values shown in panels a-c apply to all panels in their respective columns.

S.5. Transient Redshift Not Captured by the Two-Component Kinetic Model

Figure S6 shows that the model accurately reproduces the spectral line shapes within the first 200 ps, the time frame relevant for biexciton dynamics. However, Figure S6g-i shows a feature that the model fails to capture. There is a subtle fluence dependent red-shifting of the band edge bleach feature over ns time scales that is more prominent in the smaller NC sizes. Given the high statistical certainty of the fit, this dynamic spectral shift must be due to an effect not included in the 2-component kinetic model. We hypothesize that this ns-timescale red-shifting of the bleach feature is due to size dependent exciton lifetimes within the polydisperse NC ensemble, because any effect due to polydispersity will become more prominent as quantum confinement increases. Although this should not affect any conclusions about the biexciton state or the biexciton spectrum - since the redshift occurs on time scales much slower than the biexciton lifetime - it is worth noting the possibility of a bias where the extracted exciton component spectrum may be blueshifted from the true spectrum. Such a bias would lead to an overestimation of the attractive character of the exciton-exciton interaction, as the energy of the exciton state would be overestimated. Although this bias impacts our ability to quantitatively measure the exciton-exciton interaction energy, its direction increases our confidence that the interaction is indeed repulsive, as correcting for it would lead to concluding that the interaction is more repulsive than the data in Figure 4 indicate.

S.6. Exciton Lifetime from Transient Absorption and Photoluminescence Experiments

Extracting an accurate lifetime for the single exciton state from our 200 ps fitting window presents a challenge because the decay kinetics are not exponential and occur over a significantly longer time regime than our TA measurements can access, as shown in Figure S2. As a result, the first-order kinetic model that we employ is not truly accurate for the exciton decay, and the fitted exciton lifetimes may not be indicative of the true single-exciton dynamics because of the limited time-window of the fit. Due to this behavior, the exciton lifetimes extracted from our model do not exhibit a consistent trend like the biexciton lifetimes and absorption cross-section parameters do. Table S1 compares the exciton lifetimes extracted from the TA data using the target analysis model with lifetimes extracted from time-resolved PL data by fitting just the window of the TA measurement (0-2.5 ns) and the 1/e lifetime extracted from the PL traces.

Table S1. Single exciton lifetimes extracted from various methods. The lifetimes from the TA fits are reported with the central 90% credible intervals as in Table 1 of the main text.

NC Size (nm)	6	7.5	10
τ_{χ} from TA fits (ns)	$3.026_{3.023}^{3.028}$	$4.902_{\scriptstyle{4.898}}^{\scriptscriptstyle{4.906}}$	$3.431_{3.426}^{3.435}$
PL 0-2.5 ns Fit Lifetime (ns)	4.1±0.1	4.35±0.09	11.6±0.8
PL 1/e Lifetime (ns)	4.5	4.5	12.3

S.7. Unnormalized Component Spectra

Figure S7 shows the unnormalized biexciton and exciton component spectra for all three sizes of NCs. The traces were generated and rendered in the same fashion as Figure 3 in the main text, and the spread of the sample traces is less than the rendered line thickness. This indicates a high statistical certainty in these unnormalized spectra as in the normalized spectra and that the model accurately captures the overall intensity of the spectra and not just the shape. The dOD intensities of these spectra are quantitative in that they show the expected TA signal that would be measured if every NC in the measurement focal volume had an exciton or biexciton present for the specific sample concentration.



Figure S7. Unnormalized component spectra for the exciton (black trace) and biexciton (red trace) states for the (a) 10 nm, (b) 7.5 nm, and (c) 6 nm NCs. The plots were generated by superimposing the component spectra recovered from 100 random samples of the Markov chain. The variation among the samples is within the width of the traces.

References

- Shulenberger, K. E.; Ashner, M. N.; Ha, S.K.; Krieg, F.; Kovalenko, M.V.; Tisdale, W. A.; Bawendi, M. G. Setting an Upper Bound to the Biexciton Binding Energy in CsPbBr₃ Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2019**, *10*, (18), 5680-5686.
- (2) Ashner, M. N.; Winslow, S. W.; Swan, J. W.; Tisdale, W. A. Markov Chain Monte Carlo Sampling for Target Analysis of Transient Absorption Spectra. *J. Phys. Chem. A* 2019, *123* (17), 3893–3902.