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Exploring the Structural Origins of Optically Efficient One-Dimensional Lead Halide Perovskite Nanostructures

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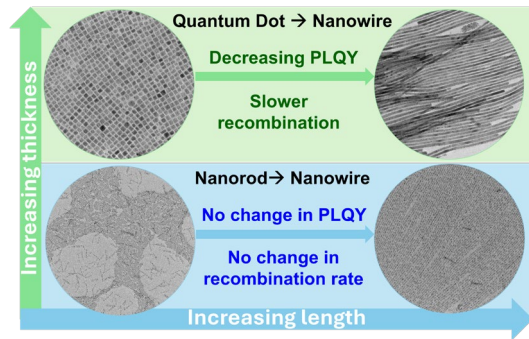
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Abstract

Metal halide perovskites have excellent optoelectronic properties. This study aims to determine how the optoelectronic properties of a model perovskite, cesium lead bromide (CsPbBr_3), change with length and thickness in one dimension (1D). By examining the photophysics of CsPbBr_3 quantum dots (QDs), nanowires (NWs), and nanorods (NRs), we observe the influence of confinement, exciton diffusion, and trapping on their optical properties. Our findings reveal that exciton diffusion to trap states limits the photoluminescence quantum yield (PLQY) of 1D CsPbBr_3 in the weakly confined regime (8-14 nm) and explains their long-lived exciton dynamics, while enhanced radiative rates contribute to achieving near-unity PLQY in the strongly confined regime (<7 nm). Consequently, blue-emitting, 2.4 nm-thick CsPbBr_3 NRs were 3.6X more emissive than the conventional CsPbBr_3 QDs. This study underscores how structural optimization can improve the optoelectronic performance of CsPbBr_3 and provides insight into the complex interplay of radiative and nonradiative processes in 1D ionic semiconductors.

TOC Graphic



Introduction

Metal halide perovskites (ABX_3 , where $A = Cs^+$, MA^+ , FA^+ ; $B = Pb^{2+}$, Sn^{2+} , etc.; $X = Cl^-$, Br^- , I^-) represent a unique class of ionic semiconductors characterized by their exceptional optoelectronic properties.¹ Alongside the initial synthesis of colloidal $CsPbBr_3$ quantum dots (QDs) by Protesescu et al. in 2015,² our group debuted various morphologies of $CsPbBr_3$ nanocrystals (NCs), such as nanosheets and nanowires (NWs), with size-dependent optical properties.³⁻⁶ However, the understanding of structure-property correlations in the latter one-dimensional (1D) perovskite remains incomplete, which is critical for realizing their full potential across various applications.

The photoluminescence (PL) quantum yield (PLQY) serves as an indicator of a semiconductor's efficiency in optoelectronic applications. The typical 8 nm $CsPbBr_3$ QDs exhibit a PLQY that is $<80\%$,^{1,2,7,8} which can be improved by passivating surface trap states.⁹ These trap states are surface-localized due to defect diffusion throughout the ionic perovskite lattice,¹⁰ unlike the internal defects prevalent in class II-VI covalent semiconductors.¹¹ Virtually defect-free, near-unity PLQY QDs can be achieved by performing surface treatment with strong-binding, organic ligands (e.g., zwitterions, benzoic acid, phosphonic acids).¹²⁻¹⁴ Alternatively, our recent work has demonstrated that near-unity PLQY 8 nm QDs can be achieved without surface treatment by avoiding ligand-surface equilibrium-mediated defect formation.¹⁵ This approach, which does not rely on ligand exchange, has also yielded record-high 72% PLQY 8 nm-thick $CsPbBr_3$ NWs, surpassing the previous maximum of 38%, with components of the exciton PL decay exceeding 400 ns.¹⁵

However, the reason for sub-unity PLQY in $CsPbBr_3$ NWs remains unclear, given that QDs of similar confinement and ligand-rich surface conditions exhibit near-unity PLQY.¹⁵ Nonon

et al. expressed that PLQY variations in CsPbBr₃ QDs stem from variations in the density of trap states per particle and the ratio of radiative to nonradiative decay rates.⁸ In 2018, it was hypothesized that exciton diffusion to trap states along the length of 9.5 ± 1.5 nm-thick 1D CsPbBr₃, ranging up to 1.8 μ m-long, could also lead to slower decay rates for a fraction of excitons.¹⁶ The involvement of exciton diffusion was implied by an increase in PL lifetime and decrease in PLQY as the length of 1D CsPbBr₃ increased; however, variations in the trap state density could have also contributed to this behavior.¹⁶ Later, exciton diffusion was directly observed in these NWs using transient absorption microscopy.¹⁷ Currently, the reasons behind subunity PLQY in 1D CsPbBr₃ and the extent to which exciton diffusion is involved remains convoluted, especially as a function of size and morphology.

Confinement can enhance the radiative rate and PLQY of semiconductors when their size becomes smaller than the exciton Bohr diameter. Therefore, tuning confinement through structural modifications may motivate further improvements in the optical properties of 1D CsPbBr₃. Moreover, the impact of exciton diffusion on the optical properties of “ultrathin” 1D CsPbBr₃ (<5 nm-thick), and their photophysics in general, remains unexplored. In this study, we examine the photophysics of 1D CsPbBr₃ as a function of both thickness and length. Herein, the PLQY and PL decay are compared across five systems: 8 nm QDs, 8 nm NWs, 3.2 nm NWs, 3.2 nm nanorods (NRs), and 2.4 nm NRs, where the number denotes material thickness. We elucidate the impact of the exciton diffusion and trapping/detrapping processes by deconvoluting the radiative and nonradiative processes using variable-temperature time-resolved PL spectroscopy, as well as electronic structure calculations and kinetic Monte Carlo simulations. Our findings confirm that exciton diffusion is responsible for limiting the PLQY of 8 nm CsPbBr₃ NWs by allowing excitons to access trap states further along the nanostructure. Conversely, enhanced radiative rates due to

confinement in strongly confined systems collectively minimize the effect of exciton diffusion and work to achieve near-unity PLQY 1D CsPbBr₃, without ligand exchange, in the strongly confined regime (<7 nm) despite the observation of strong trapping behavior. The near-unity PLQY 2.4 nm NRs are more emissive as blue emitters than the near-unity PLQY 8 nm QDs by a factor of 3.6 because of their shorter PL lifetime. This analysis underscores the potential for structural optimization to boost the optical performance of a model perovskite and outlines the obscure consequences granted by a 1D morphology.

Results & Discussion

All CsPbBr₃ NCs herein were colloiddally synthesized via the hot injection of cesium-oleate into a solution of PbBr₂ dissolved in a mixture of organic ligands at elevated temperatures. The synthesis of QDs followed the procedure established by Protesescu et al.,² while the synthesis of 1D NCs was based on our previously reported methods, which employ octylamine, low reaction temperature, and long reaction time to promote 1D growth.^{5,16,18} Thickness control was achieved using hexanoic acid, following Imran et al.¹⁹ Unless stated otherwise, all optical measurements were conducted in a concentrated solution-state to prevent dilution-induced defect formation and structural degradation, while optically dilute conditions were achieved by using a 0.1 mm pathlength cuvette.^{15,20} Transmission electron microscopy (TEM) imaging of the samples was conducted under these concentrated conditions.

TEM imaging confirmed morphologically pure 8 ± 1 nm QDs, 8 ± 1 nm NWs, 3.2 ± 0.1 nm NWs, 3.2 ± 0.1 nm NRs, and 2.4 ± 0.1 nm NRs (Figure 1a-f). Figures S1-S5 contain additional TEM images of the NCs taken at different magnifications. The NWs were >1 μ m and the NRs were around 30 nm in length with a standard deviation around 20%. The aspect ratios of the NWs exceeded 160, while those of the NRs were less than 20. To our knowledge, this is the first direct

synthesis of highly monodisperse 2.4 nm-thick CsPbBr₃ NRs. Molecular dynamics simulations supported that the NCs adopted a distorted cubic unit cell of 1D CsPbBr₃ (Figure 1g). Powder x-ray diffraction (PXRD) patterns of the NCs can be found in Figure S6. Distortions from cubic to orthorhombic in 3.2 nm 1D CsPbBr₃ are consistent with findings reported by Zhu et al.²¹ Additionally, the square unit cell of CsPbBr₃ was directly observed using high-resolution TEM (HR-TEM, Figure 1h-j and Figures S7-S9), with a Pb-Br bond length of 3.0 ± 0.1 Å.

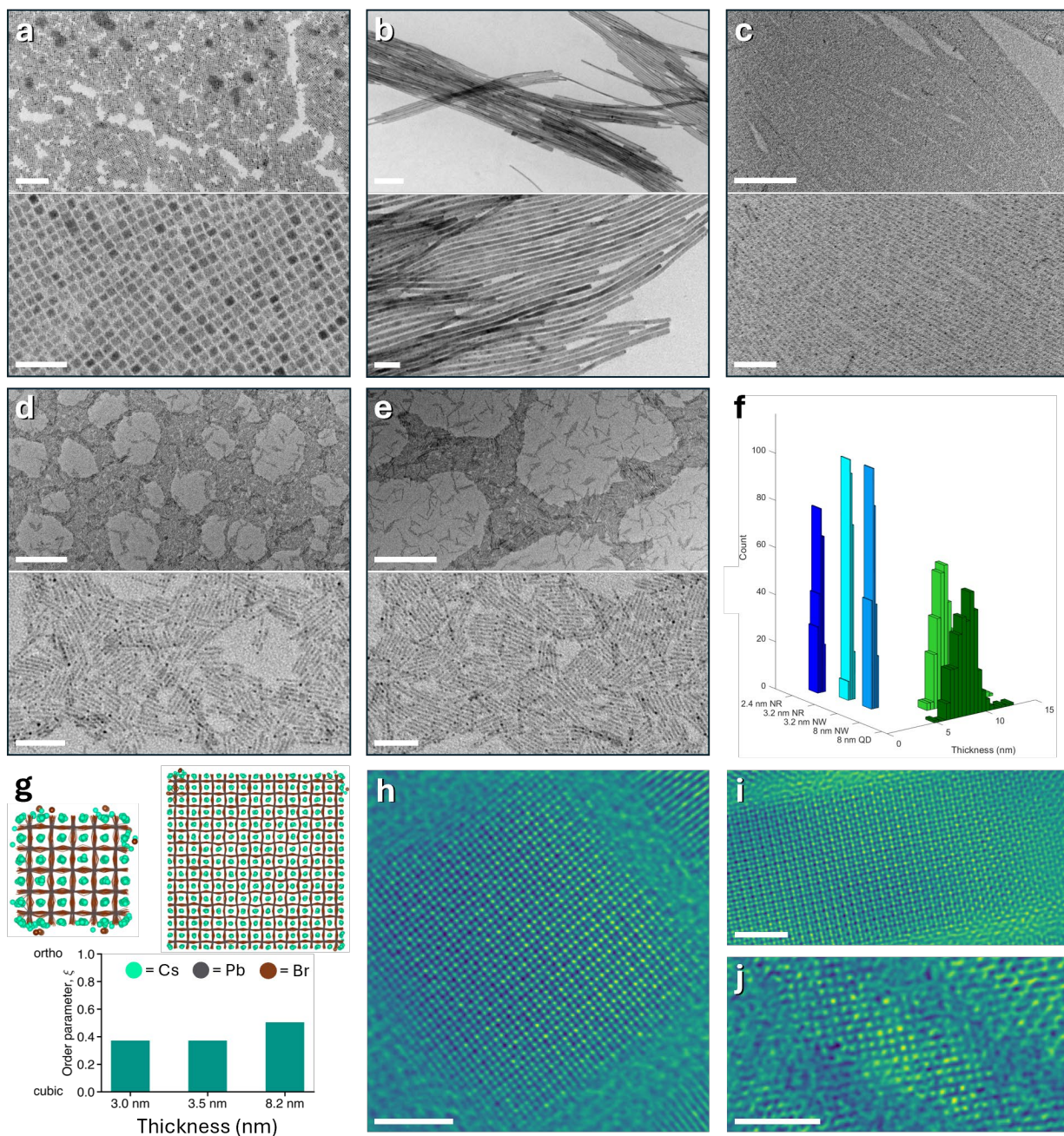


Figure 1. Structural characterization of CsPbBr₃ NCs. Low magnification TEM images of (a), 8 nm QDs, (b), 8 nm NWs, (c), 3.2 nm NWs, (d), 3.2 nm NRs, and (e), 2.4 nm NRs. Upper panel scale bar: 200 nm. Lower panel scale bar: 50 nm. (f), Histogram of NC thicknesses sampled from 250 particles. (g), Molecular dynamics simulation of 3 nm-thick and 8.2 nm-thick CsPbBr₃ NWs with infinite length defined by periodic boundary conditions and the order parameter, ζ , representing distortion to the orthorhombic crystal structure, as a function of thickness. HR-TEM images of (h), 8 nm QDs, (i), 8 nm NWs, and (j), 3.2 nm NWs. Scale bar: 5 nm. The corresponding Fast Fourier transforms displaying a square pattern can be found in Figures S7-S9.

Under ultraviolet excitation, the 8 nm QDs and NWs emitted green light, while the <4 nm-thick systems emitted blue light (Figure 2a). The excitonic absorption maxima were observed at 508 nm for 8 nm QDs, 508 nm for 8 nm NWs, 445 nm for 3.2 nm NWs, 445 nm for 3.2 nm NRs, and 434 nm for 2.4 nm NRs (Figure 2a). The corresponding excitonic PL maxima were observed at 521 nm for 8 nm QDs, 521 nm for 8 nm NWs, 469 nm for 3.2 nm NWs, 469 nm for 3.2 nm NRs, and 459 nm for 2.4 nm NRs (Figure 2a). These maxima matched those reported for CsPbBr₃ NCs of the aforementioned thicknesses and did not coincide with potential impurities, such as the ultraviolet-emitting, hexagonal Cs₄PbBr₆ or blue-emitting, tetragonal CsPb₂Br₅ compositions.^{2,6,15,21-23} The PL full width at half maximum was 77.8 meV for 8 nm QDs, 89.5 meV for 8 nm NWs, 135.4 meV for 3.2 nm NWs, 131.0 meV for 3.2 nm NRs, and 86.5 meV for 2.4 nm NRs.

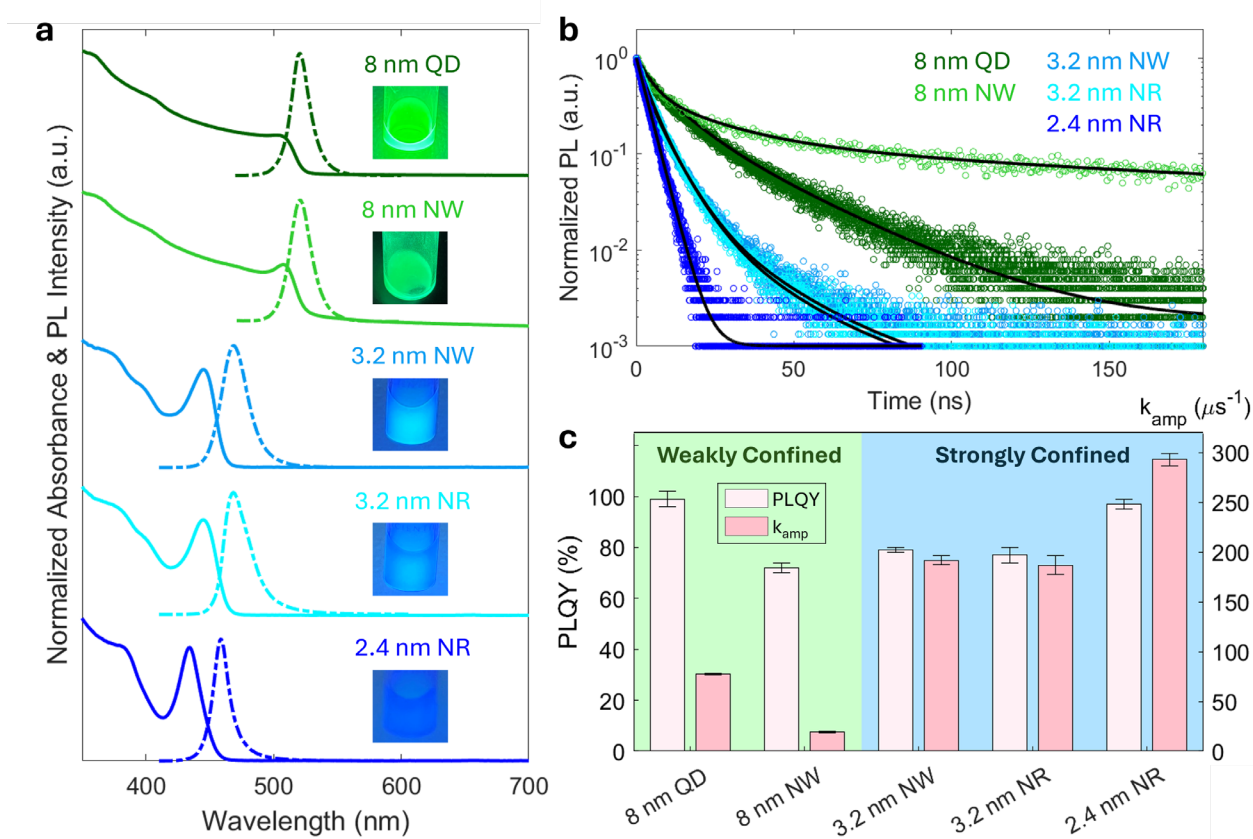


Figure 2. Optical characterization of CsPbBr₃ NCs. (a), Absorption and PL spectra of the 8 nm NWs, 8 nm QDs, 3.2 nm NWs, 3.2 nm NRs, and 2.4 nm NRs accompanied by images of their PL under ultraviolet photoexcitation. (b), Fitted PL decay of the aforementioned NCs. (c), The PLQY and k_{amp} values of the NCs. The PLQY error bars are the standard deviation of five reproductions of each sample while the k_{amp} error bars represent the error of the PL decay fit.

The PL maxima were identical between the 8 nm QDs and NWs, as well as between the 3.2 nm NWs and NRs. However, a blue shift in the PL maximum of 1D CsPbBr₃ was observed as its thickness decreased from 8 nm to 2.4 nm. This blue shift is consistent with confinement effects, which cause the exciton transition energy to increase when at least one dimension of CsPbBr₃ becomes smaller than its exciton Bohr diameter (~ 14 nm) and to remain unchanged above it.^{1,2} Hence, we denote the green-emitting 8 nm QDs and NWs, “weakly confined,” and the blue-emitting <4 nm systems, “strongly confined.” Furthermore, the PL spectra for each NC contained a singular excitonic peak. Particularly for the strongly confined systems, this high spectral purity

indicated that they were relatively monodisperse in thickness as confinement effects are discrete to thickness. Achieving such thickness purity was previously an obstacle preventing the unambiguous study of structure-property correlations in 1D CsPbBr₃.^{19,24,25}

The PLQY was $99 \pm 3\%$ for 8 nm QDs, $72 \pm 2\%$ for 8 nm NWs, $79 \pm 1\%$ for 3.2 nm NWs, $78 \pm 3\%$ for 3.2 nm NRs, and $97 \pm 2\%$ for 2.4 nm NRs. To our knowledge, this near-unity PLQY for 2.4 nm NRs is the highest reported value for 1D CsPbBr₃ and without any surface-ligand treatment. The PL decay for each NC (Figure 2b) was exponentially fitted and the amplitude-averaged PL lifetimes were calculated using equation (1), where A_i is the pre-exponential amplitude and τ_i is the PL lifetime of the i^{th} component. The lifetime components correspond to radiative recombination under the influence of nonradiative processes based on the observation that defect-free CsPbBr₃ NCs exhibit monoexponential PL decay. The amplitude-averaged PL lifetime (τ_{amp}) was 12.8 ± 0.6 ns for 8 nm QDs, 52 ± 2 ns for 8 nm NWs, 5.2 ± 0.1 ns for 3.2 nm NWs, 5.4 ± 0.3 ns for 3.2 nm NRs, and 3.42 ± 0.01 ns for 2.4 nm NRs. The τ_{amp} value of 52 ns for 8 nm NWs is the longest reported for colloidal CsPbBr₃, with a τ_4 of 730 ns indicating good potential for carrier transport. Figure S10 and Table S1 contain the PL fitting details.

$$\tau_{amp} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \quad (1)$$

Although the PLQY of 1D CsPbBr₃ generally increased as its thickness decreased, the magnitude of the PLQY increase did not strictly correlate with the amplitude-averaged PL decay rate (k_{amp} , Figure 2c), adopting the rate formalism where $k = 1/\tau$. This discrepancy arises when nonradiative processes also contribute toward electron-hole recombination, evident to varying extents across our NCs based on their diverse PL decay profiles. Hence, $k_{amp} = k_r + k_{nr}^*$, where k_r is the rate of purely radiative bimolecular recombination and k_{nr}^* is the apparent nonradiative

rate that influences the PL decay. As dictated by equation (2), the PLQY increases with the ratio of k_r to the total decay rate, which is a sum of k_r and the nonradiative decay rate (k_{nr}).

$$PLQY = \frac{k_r}{k_r + k_{nr}} = \frac{k_r}{k_r + N_{trap}k_{nr,trap}} \quad (2)$$

The relevant processes that contribute to k_{nr} in CsPbBr₃ NCs are trapping, detrapping, exciton diffusion.^{16,26} The value of k_{nr} scales with the number of trap states (N_{trap}) and the nonradiative decay given one trap state ($k_{nr,trap}$), which encodes nonradiative behavior unique to the NC.⁸ Auger recombination and other multiexciton processes are neglected given the low photoexcitation power densities applied throughout this study ($\sim 6 \mu\text{W cm}^{-2}$ from lamp following monochromation). The nonradiative recombination of free carriers is also neglected because the photoexcited population consists mostly of excitons ($\sim 99\%$) across these CsPbBr₃ NCs with high exciton binding energies, especially at low excitation fluences.²⁶

The rates of trapping, detrapping, and exciton diffusion can be traced back to the dimensionality and morphology of CsPbBr₃, necessitating an understanding of their structure-property correlations. In short: 1) Quantum confinement can enhance k_r due to increased wavefunction overlap between electrons and holes.²⁶ 2) Quantum confinement can deepen trap states in CsPbBr₃, increasing the ratio of trapping to detrapping rates.^{27,28} 3) Quantum confinement can strengthen the exciton-phonon coupling due to increased wavefunction overlap between excitons and phonons.²⁹ The amplified thermal energy of the system may enhance nonradiative processes, such as trapping, detrapping, exciton diffusion, and exciton disassociation into free carriers. 4) The NC size may limit exciton diffusion below the exciton diffusion length and enhance many-body, exciton-phonon interactions.^{16,17} 5) Finally, NCs exhibit different susceptibilities to the formation of surface vacancies depending on their molecular weight, or colloidal stability.^{14,15}

The PL decay of all NCs was measured as a function of temperature (Figure S10). The temperature dependence of τ_{amp} was characterized by a thermal component and a nonthermal component (Figure 3a). The contribution of the nonradiative processes towards the PL decay, given that these processes are thermally activated, was deconvoluted using the Arrhenius model, equation (3). The data for each NC was in good agreement with the monoexponential Arrhenius fit of the temperature-dependent τ_{amp} data (Figures 3a, S12, and S13), where τ_r is approximated as the temperature-independent radiative decay lifetime, τ_{nr0}^* is the apparent nonradiative decay lifetime at 0 K, E_a is the activation energy of the nonradiative processes, k_B is Boltzmann's constant, and T is temperature.

$$\tau_{amp} = \tau_r + \tau_{nr0} e^{\frac{E_a}{k_B T}} \quad (3)$$

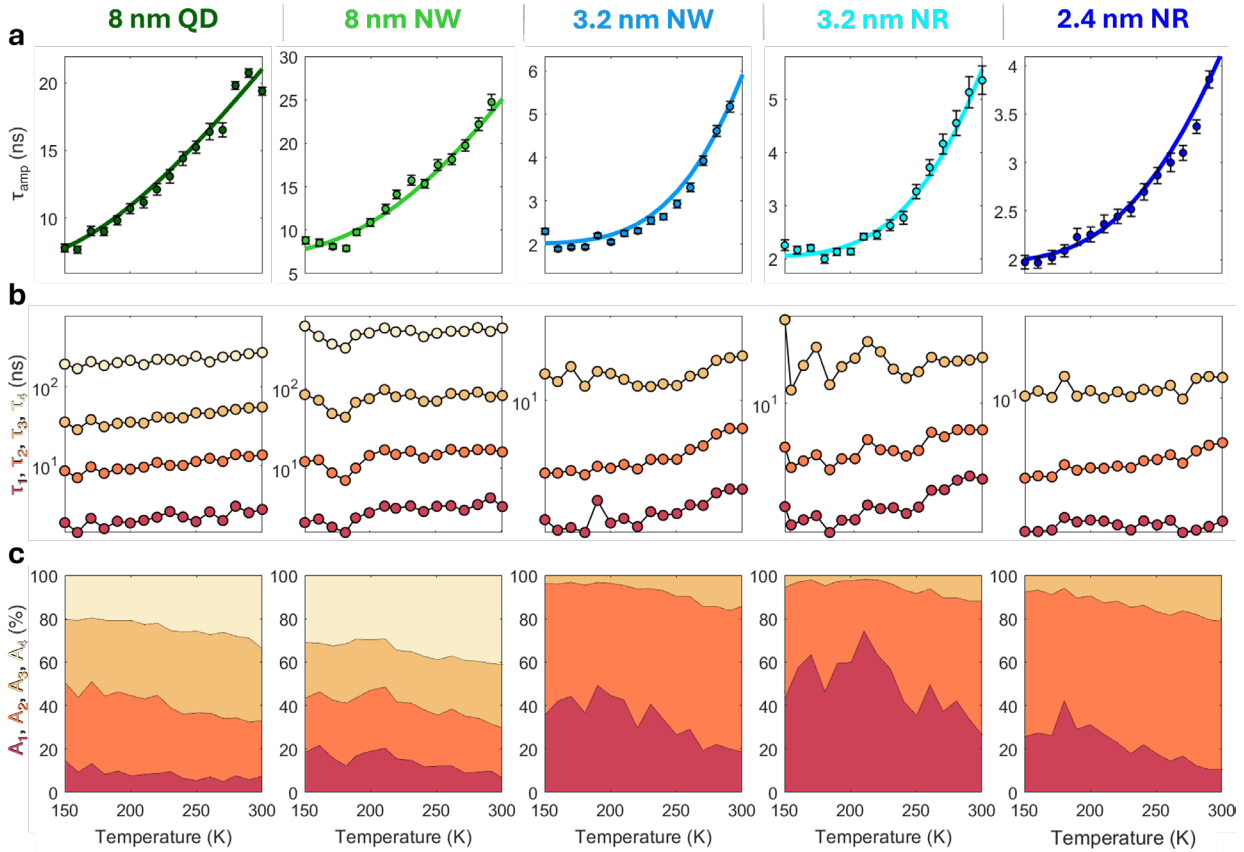


Figure 3. The temperature dependent photodynamics of CsPbBr₃ NCs. of **a**, τ_{amp} , **b**, the individual lifetime components (τ_1 , τ_2 , τ_3 , τ_4), and **c**, their relative contributions (A_1 , A_2 , A_3 , A_4) for 8 nm QDs, 8 nm NWs, 3.2 nm NWs, 3.2 nm NRs, and 2.4 nm NRs.

The value of k_{nr} was calculated by inputting the PLQY and $k_r = 1/\tau_r$ into equation (2). Equation (2) and the radiative variables are used to determine k_{nr} rather than equation (3) because PL spectroscopy cannot be used to directly obtain k_{nr} . Table 1 compares the values of PLQY, k_{amp} , k_r , k_{nr} , and E_a . For each NC, k_r was greater than k_{amp} , reinforcing that nonradiative processes influence the photodynamics to produce the observed PL decay. Indeed, the k_r values were slightly faster than the fastest PL decay component, $k_1 = 1/\tau_1$, measured at room temperature for each NC, which is conventionally thought to represent recombination that is least affected by nonradiative processes.

Table 1. The PLQY, k_{amp} , k_r , k_{nr} , and E_a values for each NC studied herein.

	PLQY (%)	k_{amp} (μs^{-1})	k_r (μs^{-1})	k_{nr} (μs^{-1})	E_a (meV)
8 nm QD	99	77.8	157	1.58	61.0
8 nm NW	72	19.3	137	53.3	83.3
3.2 nm NW	79	192	615	163	120
3.2 nm NR	77	187	550	164	123
2.4 nm NR	97	293	507	15.7	111

The k_r values for the 8 nm QDs and NWs were similar, corroborating similar confinement effects between the two, consistent with their matching absorption and PL maxima. The τ_3 and τ_4 PL lifetimes of the 8 nm QDs and NWs that are long-lived enough to accommodate the trapping/detrapping process also make up a larger contribution of their PL decay (Figure 3b,c).

Yet, the k_{nr} for 8 nm NWs was 34X faster than for QDs. Given similar confinement, exciton diffusion to trap states present along the length of the NW may be responsible for significantly enhancing the k_{nr} of the 8 nm NWs relative to QDs, thereby limiting the PLQY of CsPbBr₃ in the weakly confined regime. This suggests that exciton diffusion helps to facilitate the long trapping/detrapping process, observed within the abnormally long-lived τ_3 (114 ns) and τ_4 (730 ns) of 8 nm NWs, their dominant contributions to the PL decay, and the slow k_{amp} (19.3 μs^{-1}). Conversely, QDs can surpass the 72% PLQY of the NWs because, as the length of CsPbBr₃ decreases, the exciton is physically limited from accessing additional, nonlocal trap states through diffusion, achieving near-unity PLQY with lower k_{nr} .

The k_r values for the strongly confined systems were >3.2X faster than those for the 8 nm QDs and NWs, likely because of confinement. The E_a values of nonradiative processes were also greater than those for the 8 nm QDs and NWs. Notably, the k_r , E_a , and PLQY values for the strongly confined systems were such that k_{nr} was high relative to the QDs. Between the 3.2 nm NWs and NRs, the k_r , E_a , k_{nr} , and PLQY values were similar, and even their PL decay profiles were almost indistinguishable, unlike 8 nm QDs and NWs. This contrasting behavior between the weakly confined 8 nm NWs and strongly confined 3.2 nm NWs exemplifies that the length of 1D CsPbBr₃ has different consequences at different thicknesses. Whereas exciton diffusion to trap states dominated the PL decay of 8 nm NWs, this process did not cause the PLQY, PL decay, k_{amp} , k_r , and k_{nr} values of the 3.2 nm NRs to deviate significantly from the 3.2 nm NWs. Accordingly, the most short-lived, least nonradiative PL lifetime, τ_1 , contributed more to the PL decay of the strongly confined systems than that of the weakly confined systems across all temperatures despite comparable PLQY values. This observation supports that radiative recombination outcompetes

diffusion and limits excitons from accessing to additional trap states along 1D CsPbBr₃ when it is sufficiently confined.

The k_r for the 2.4 nm NRs was slightly slower than those for the 3.2 nm NWs and NRs, despite the expectation for k_r to increase with confinement. Nonetheless, the 2.4 nm NRs achieved near-unity PLQY with its observed k_r , k_{nr} , and E_a . Notably, the cause of sub-unity PLQY for the 3.2 nm NWs and NRs may be their outstanding trapping behavior represented within relatively fast k_{nr} values, as their k_r values were at least faster than k_r of near-unity PLQY 2.4 nm NRs and with similar E_a values. This particularly strong trapping behavior of the 3.2 nm NWs and NRs was also indirectly apparent in their PL spectra, which were significantly broader than the other NCs. Even for the 2.4 nm NRs, k_{nr} was 9.9X faster than that of the QDs despite both systems having near-unity PLQY. This significant trapping behavior affirms that strongly confined 1D CsPbBr₃ either has a large density of surface trap states or it has a lower, so-called “defect tolerance,” the extent to which a trap state impinges the optoelectronic properties. A lower defect tolerance in strongly confined CsPbBr₃ may be explained by increased wave function overlap between the excitons and trap states, as well as exciton localization, resulting in deeper trap states.^{27,28} However, k_r was still fast enough in these strongly confined systems to maintain high to near-unity PLQY despite faster k_{nr} values than the near-unity PLQY QD. Interestingly, the 2.4 nm NRs achieve near-unity PLQY at a k_{amp} 3.8X faster than that of QDs, making the PL effectively 3.6X brighter with a negligible 2% loss of efficiency. This relative emissivity was calculated according to equation (4). This result highlights the potential of optimizing the structure and morphology of ionic semiconductors to achieve better optical performance.

$$Relative\ Emissivity = \frac{PLQY_{NR} k_{amp,NR}}{PLQY_{QD} k_{amp,QD}} \quad (4)$$

Electronic structure calculations on various sizes of 1D halide perovskite were performed to explain the observed size-dependent photophysics. The excited state calculations were performed within the atomistic semi-empirical pseudopotential framework,³⁰ which was designed for the calculation of band gap, density of states, oscillator strengths, and radiative recombination rates of nanoscale semiconductors. The ambient temperature k_r values were predicted as the Boltzmann weighted sum of rates from each excitonic state, an approach validated in lead-halide perovskites by recovering non-monotonic radiative lifetime trends induced by thermal population of high-lying dim states, equation (5),³¹ where ϵ_0 is the vacuum permittivity, $\hbar$ is the reduced Planck constant, c is the speed of light, and Z is the partition function of the electronic energy levels. The parameters, ω_n and μ_n , are the transition frequency and the transition dipole strength of the n^{th} exciton, respectively.

$$k_r = \frac{1}{Z} \sum_n e^{-\beta E_n} \frac{\omega_n^3 |\mu_n|^2}{3\pi\epsilon_0 \hbar c^3} \quad (5)$$

We investigate the qualitative trends for CsPbBr₃ through analogy with CsPbI₃, for which there is a previously parametrized pseudopotential that includes spin-orbit coupling and angular momentum dependent terms.³² The k_r values of 1.3 nm and 1.9 nm-thick 1D CsPbI₃ were calculated as a function of length (Figure 4a). In the strongly confined thickness regime, k_r increased as a function of the length of 1D CsPbI₃, however they eventually plateaued as the length approached the exciton Bohr diameter, supporting the experimental observation of similar k_r values between the 3.2 nm CsPbBr₃ NRs and NWs. On the other hand, it is noteworthy that, below the exciton Bohr diameter, k_r increases as the length of 1D CsPbI₃ increases because of an increase in the oscillator strengths of the bright excitons that outcompetes modifications to the exciton transition energy caused by confinement (Figure 4b). Our pseudopotential model captures the band

edge wavefunction characteristics of CsPbI₃ perovskites, demonstrated by the single particle densities visualized in Figure 4c and S14. The HOMO (valence band edge) state has a Bloch function composed of Pb 6s and I 5p orbitals, while the LUMO (conduction band edge) state is mostly Pb 6p character. The confinement potential of the crystal structure leads to anisotropic spatial distribution of the single particle carrier densities along the unconfined length. Thus, the lowest energy bright exciton is polarized along the length of 1D CsPbI₃. The oscillator strength of this bright state increases linearly with the length of 1D CsPbI₃ as the exciton wavefunctions extend along the unconfined direction. Thus, theory also predicts that an extended 1D morphology can enable faster emission as compared to 0D structural analogs in the strongly confined regime.

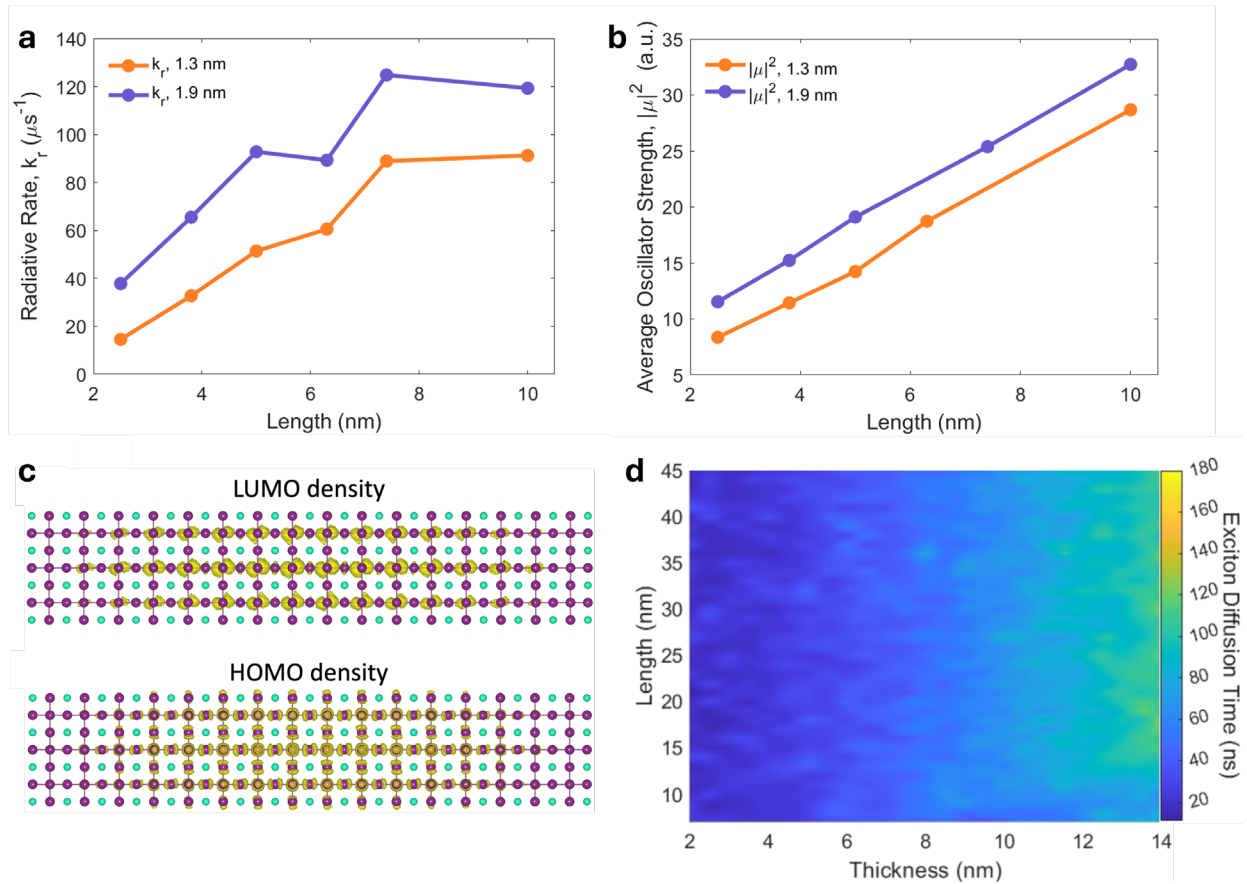


Figure 4. Theoretical calculations on 1D halide perovskite. (a), The radiative rate of CsPbI₃ as a function of length. (b), The average oscillator strength of CsPbI₃ as a function of length. (c), The LUMO (bottom of conduction band) and HOMO (top of valence band) states in a 1.9 nm x 1.9 nm x 10.0 nm CsPbI₃ NR. (d), Mapping of the average exciton diffusion time recorded from the kinetic Monte Carlo simulation for NCs of different thicknesses and lengths.

Additionally, our calculations show that the k_r values increase with thickness in the strongly confined regime (1.3-1.9 nm). While the measured k_r values of the 2.4 nm (507 μs^{-1}) and 3.2 nm (550 μs^{-1}) CsPbBr₃ NRs weakly followed this trend, the total decay rates, k_{amp} , decrease from the 2.4 nm NRs (293 μs^{-1}) to 3.2 nm NRs (187 μs^{-1}). This difference further suggests that nonradiative channels suppress radiative recombination in the larger systems. This is supported by the near-unity PLQY of 2.4 nm NRs contrasted with the 77% PLQY of 3.2 nm NRs, suggesting that additional trap states prevent efficient emission. Further theoretical developments will enable direct investigation of non-radiative channels including trapping, hot carrier cooling, and Auger processes in lead-halide perovskites.

Exciton diffusion in NCs of varying sizes can also be modeled classically with a kinetic Monte Carlo simulation. In a typical simulation, an NC of given size was modeled as a three-dimensional grid of lattice sites spaced by the Pb-Br bond length, 3 Å. The photoexcitation was initiated at a random site, then the exciton was allowed to diffuse via random walk. With each iteration of the random walk, a new velocity was assigned to the exciton until radiative or nonradiative decay occurred. Nonradiative decay occurred when the exciton became trapped by a surface defect, with a 5% probability of detrapping. The exciton diffusion time was tracked for 5000 photoexcitation events across 10 NCs, which effectively averaged out surface defect inhomogeneity. The exciton diffusion time tended to increase with increasing NC length if they were thick enough (Figure 4d), which qualitatively supported the experimental observation that k_{amp} increases as 8 nm-thick CsPbBr₃ decreases in length. Furthermore, this simulation

demonstrated that presence of the trapping/detrapping mechanism was critical for observing long-lived exciton decay, as shown previously,¹⁶ revealing the interplay between exciton diffusion and trap states in 1D CsPbBr₃. The Monte Carlo simulations also show no change in the exciton diffusion time as the thickness of 1D CsPbBr₃ becomes smaller than average exciton diffusion distance, further supporting that exciton diffusion may be insignificant in the strongly confined regime.

Conclusion

This structure-property study clarifies the influence of confinement, exciton diffusion, and trapping on the optical properties of CsPbBr₃ NCs. By systematically comparing the PLQY and decay rates of CsPbBr₃, with varying thicknesses and lengths, we ascertain that exciton diffusion to trap states is the primary factor limiting the PLQY of 8 nm NWs in the weakly confined regime. The enhancement of radiative rates caused by confinement and high oscillator strengths in strongly confined systems collectively minimize the role of exciton diffusion and trapping/detrapping, enabling near-unity PLQY in 2.4 nm NRs despite pronounced trapping behavior. These findings show, through a model system, how structural and morphological optimization can further improve the optical performance of perovskites by making CsPbBr₃ 3.6X more emissive. This work can also provide valuable insights into the design principles of high-efficiency perovskite-based optoelectronics. As a technology, 1D perovskite is a hotbed for the exploration of previously studied phenomena in QDs (Supporting Discussion 1).

Data Availability

The data that support this study are available from the corresponding author upon reasonable request.

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Competing interests

The authors declare no competing interests.

Additional information

Supporting information The online version contains supporting material available at _____

- Supplementary tables and figures, detailed procedures for synthesis and characterization, and additional discussion on stability and anion exchange.

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