

Morphological effects on CsPbBr₃ **Perovskite Nanocrystals Photophysics** From Nano to Micro Sol

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Morphological effects on CsPbBr₃ Perovskite Nanocrystals Photophysics: From Nano to Micro

Sol Gutiérrez Álvarez



Morphological effects on CsPbBr₃ Perovskite Nanocrystals Photophysics: From Nano to Micro

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Ph.D. Thesis

Department of Chemistry

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ABSTRACT

CsPbBr₃ perovskite NCs are promising materials for applications such as solar cells, lasers, LEDs, and other optoelectronic devices. Studying the photophysical processes and factors that control them is essential to improve such devices' efficiency. This thesis focuses on how the nano and the microscale morphology affect the excited state dynamics using transient absorption spectroscopy. Nanoscale: We investigated the onephoton linear absorption (OPLA) and two-photon absorption (TPA) properties of NCs with different aspect ratios (AR). We also studied the exciton and biexciton lifetimes and discovered dimensionality independence to their values. The morphology relationship to the optoelectronic properties of CsPbBr₃ NCs is still under discovery. We give a new perspective that can aid in the understanding of such properties by exploring the local field correlation to the TPA coefficient. Microscale: We studied the carrier dynamics in a bisized film of DDAB capped CsPbBr₃ QDs. We reveal how carrier diffusion happens in the large-sized QDs instead of the small-sized QD due to the strong quantum confinement. Combining the carrier diffusion study with a Monte Carlo simulation on the QDs assembly, we can calculate diffusion lengths of charge carriers. The diffusion length of the DDAB capped shows higher values than the ones for the common capping agents oleylamine and oleic acid. Explaining the higher efficiencies of DDAB capped CsPbBr₃ QDs LEDs.

There is no doubt that morphology plays a vital role in designing efficient devices. A deep understanding of nanoscale morphology can help develop new materials with optimized properties. New arrangements in the microscale can beat the electron transfer limitations the current devices face.

ABSTRACT DANISH

CsPbBr₃ perovskit NC'er er lovende materialer til anvendelse i solceller, lasere, LED'er og andre optoelektroniske enheder. Det er afgørende at studere de fotofysiske processer og faktorer, der styrer dem for at forbedre sådanne enheders effektivitet. Denne afhandling fokuserer på hvordan nano- og mikroskalamorfologien påvirker den ved exciterede tilstandsdvnamik brug af transient absorptionsspektroskopi. Nanoskala: Vi undersøgte NC'ers egenskaber for én-foton lineær absorption (OPLA) og to-foton absorption (TPA) med forskellige aspektforhold (AR). Vi studerede også exciton- og biexcitonlevetiderne og opdagede en uafhængighed mellem dimensionalitet og levetidsværdier. Forholdet mellem CsPbBr₃ NC'ers morfologi og optoelektroniske egenskaber bliver stadig undersøgt. Vi bringer et nyt perspektiv, der kan hjælpe med forståelsen af sådanne egenskaber ved at udforske korrelationen mellem det lokale felt og TPA-koefficienten. Mikroskala: Vi undersøgte ladningsbærerdynamikken i en bi-størrelse film bestående af DDAB-omsluttede CsPbBr₃ QD'er. Vi afslører, hvordan ladningsbærerdiffusion sker i store QD'er i stedet for i små QD'er på grund af den stærke kvanteindeslutning. Ved at kombinere undersøgelsen af ladningsbærerdiffusion med en Monte Carlomatchende QD-samling, simulering af en kan vi beregne diffusionslængderne af ladningsbærere. Diffusionslængden for de DDABomsluttede er større end for dem med de almindelige omslutningsmidler oleylamin og oliesyre, hvilket forklarer de højere effektiviteter af DDAB-omsluttede CsPbBr₃ QD LED'er.

Der er ingen tvivl om, at morfologi spiller en afgørende rolle for design af effektive apparater. En dyb forståelse af nanoskalamorfologi kan hjælpe med at udvikle nye materialer med optimerede egenskaber. Nye sammensætninger på mikroskala kan overvinde de begrænsninger med elektronoverførsel som nuværende elektroniske enheder døjer med.

LIST OF PUBLICATIONS

Article I. Morphology dependent one-photon and two-photon absorption properties in Blue Emitting $CsPbBr_3$ nanocrystals.

Sol Gutiérrez Álvarez, Christina Basse Riell, Mahtab Madani, Mohamed Qenawy, Qian Zhao, Xianshao Zou, Tõnu Pullerits, Kaibo Zheng*

Submitted

Article II. Charge Carrier Diffusion Dynamics in Multi-sized Quaternary Alkylammonium-Capped CsPbBr₃ Perovskite Nanocrystal Solids.

Sol Gutiérrez Álvarez, Weihua Lin, Mohamed Qenawy, Jie Meng, Karel Zidek, Tonu Pullerits, Kaibo Zheng*

ACS Appl. Mater. Interfaces 2021, 13, 44742-44750

My contribution to Papers

Article I. I designed the experiments, Co-supervised the nanocrystal synthesis, co-performed the spectroscopy experiments, analyzed the experiment data, and drafted the manuscript. I supervised the analysis of TEM, UV-Vis, and XPS data.

Article II. I designed the experiments, synthesized the nanocrystals, co-performed the spectroscopy experiments, analyzed the data, and drafted the manuscript.

OTHER PAPERS NOT INCLUDED IN THIS THESIS

1- Role of the Metal Oxide Electron Acceptor on Gold-Plasmon Hot-Carrier Dynamics and Its Implication to Photocatalysis and Photovoltaics.

Yocefu Hattori, **Sol Gutiérrez Álvarez**, Jie Meng, Kaibo Zheng, Jacinto Sá*****

ACS Appl. Nano Mater. 2021, 4, 2, 2052–2060

2- Exploring the light-induced dynamics in solvated metallogrid complexes with femtosecond pulses across the electromagnetic spectrum.

Maria A. Naumova, Aleksandr Kalinko, Joanne W. L. Wong, **Sol Gutierrez Alvarez**, Jie Meng4, Mingli Liang, Mohamed Abdellah, Huifang Geng, Weihua Lin, Katharina Kubicek, Mykola Biednov, Frederico Lima, Andreas Galler, Peter Zalden, Stefano Checchia, Pierre-Adrien Mante, Jennifer Zimara11,a), Dirk Schwarzer, Serhiy Demeshko, Vadim Murzin, David Gosztola, Martin Jarenmark, Jianxin Zhang, Matthias Bauer, Max Latevi Lawson Daku, Dmitry Khakhulin, Wojciech Gawelda, Christian Bressler, Franc Meyer, Kaibo Zheng, and Sophie E. Canton.

J. Chem. Phys. 152, 214301 (2020)

3- Modulating Charge-Carrier Dynamics in Mn-Doped All-Inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States.

Jie Meng, Zhenyun Lan, Mohamed Abdellah, Bin Yang, Susanne Mossin, Mingli Liang, Maria Naumova, Qi Shi, **Sol Laura Gutierrez Alvarez,** Yang Liu, Weihua Lin, Ivano E. Castelli, Sophie E. Canton, Tönu Pullerits, and Kaibo Zheng*

J. Phys. Chem. Lett. 2020, 11, 9, 3705-3711

4- Revealing Hot and Long-Lived Metastable Spin States in the Photoinduced Switching of Solvated Metallogrid Complexes with Femtosecond Optical and X-ray Spectroscopies. Maria A. Naumova, Aleksandr Kalinko, Joanne W. L. Wong, Mohamed Abdellah, Huifang Geng, Edoardo Domenichini, Jie Meng, Sol Gutierrez Alvarez, Pierre-Adrien Mante, Weihua Lin, Peter Zalden, Andreas Galler, Frederico Lima, Katharina Kubicek, Mykola Biednov, Alexander Britz, Stefano Checchia, Victoria Kabanova, Michael Wulff, Jennifer Zimara, Dirk Schwarzer, Serhiy Demeshko, Vadim Murzin, David Gosztola, Martin Jarenmark, Jianxin Zhang, Matthias Bauer, Max Latevi Lawson Daku, Wojciech Gawelda, Dmitry Khakhulin, Christian Bressler, Franc Meyer, Kaibo Zheng, and Sophie E. Canton*

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ABBREVIATIONS

HP: Halide Perovskite	SOC-DFT: Spin-Orbit Coupling		
LED: Light Emitting Diode	Density Functional Theory		
OPLA: One Photon Linear Absorption	OLA: Oleylamine		
TPA: Two-photon Absorption	OA: Oleic Acid		
MPA: Multiple photon Absorption	DOS: Density of States		
QD : Quantum Dot	PL: Photoluminsescense		
NPL: Nanoplatelets	DDAB: Didodecyldimethylammonium		
NW: Nanowires	bromide		
p-NC: Perovskite Nanocrystals	TEM: Transmission Electron		
PLQY: Photoluminescence Quantum	Microscopy		
Yield	XPS: X-Ray Photoelectron		
VB: Valance Band	Spectroscopy		
CB : Conduction Band	TAS: Transient Absorption		
VBM: Valance Band Maximum	Spectroscopy		
CBM: Conduction Band Maximum	SVD: Singular Value Decomposition		
GS : Ground State	DAS: Decay Associated Spectra		
EQE: External Quantum Efficiency	AR: Aspect Ratio		
FRET: Förster Energy Transfer			
DFT: Density Functional Theory			

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1 INTRODUCTION

MOTIVATION

The rise of pollution and increased damages of climate change due to energy production and consumption requires extraordinary efforts in all fields to mitigate its effects. ^{1,2} Renewable energies have great potential to offset greenhouse gas emissions from fossil fuel combustion and reduce climate change.³ The use of renewable energy has great benefits aside from environmental reasons. Countries that generate renewable energy become independent from the petroleum market. Developing energy stability, promoting economic growth and social development. Access to a safe and sustainable energy supply reduces negative impacts on the environment and human health.^{4, 5, 6}

Materials scientists have joined forces to tackle the current pollution and energy challenges through different strategies. One strategy is developing, improving, and discovering materials as central components of new energy solutions. The second strategy is to replace high-demand everyday materials with efficient materials made with earth-abundant compounds and cheap synthesis methodologies that cause less pollution and require less energy to operate.³ Having these two strategies in mind, perovskite nanocrystals (p-NC) have emerged.

Initially, perovskites caught the attention of scientists for their use as light harvesters in solar cells. In a short lifespan, perovskite solar cells have reached efficiencies of 25.5%⁷, competing with the leading technology in the market, the Si solar cells. That is not the only applicability of this material. Light-emitting diodes (LED) have taken over older lighting devices and screens applications. Quantum dot (QD)-LED devices for light-harvesting have significant potential to save energy with a projected reduction of 50% in the electricity consumption occurring due to lighting only.^{8,9} p-NC have also attracted significant attention as emitting materials in this field.¹⁰ The success and potential of p-NCs for these two applications rely on their outstanding optical properties. They have size-tunable optical bandgap, and near-unity photoluminescence quantum yields (PLQYs), together with narrow emission bandwidth. The raw bulk materials of perovskites and equipment for preparing them are cheap and present high carrier transport capabilities. Enabling efficient and high-power devices with prolonged carrier lifetimes.^{11,12}

p-NCs show enhanced PL emission compared to the bulk due to increased exciton binding energy and surface passivation. The increase in exciton binding energy can prevent dissociation of the exciton prior to its radiative decay in NCs. As a result the PLQY can reach values > 95% in CsPbBr₃¹³ and CsPbI₃¹⁴. By confining perovskites in small spaces, optical properties such as light absorption and emission become tunable to size and shape. The material's tunability and exceptional properties have unlocked many different research lines.¹⁵ These properties render the material's potential in many optoelectronic applications.

Photophysical processes such as light absorption, carrier or energy transfer, carrier diffusion, and relaxation are essential for the performance of the above-mentioned devices, but are sensitive to material structures. Understanding how the structural factors affect these processes is crucial for device engineering. This thesis aims to rationalize the relationships of different factors have on the aforementioned photophysical processes. In particular, we are emphasizing our experimental results from the effects of the morphologic factors, including the nanoscaled morphology of individual NCs and macroscopic morphology of NC assembly in film solids, which has been proved critical during device fabrication but seldomly been fully understood. We tried to rationalize the correlation of those structural factors on a series of intrinsic optical properties of NCs such as one photon linear absorption (OPLA) cross-section and two-photon absorption (TPA), photogenerated carrier diffusion, and other excited-state dynamics. These analyses are expected to highlight the steps needed to improve further and optimize those materials for the optoelectronic application.

The thesis is organized in the following way. Chapter 1 introduces the perovskite structure's fundamental photophysical behavior of CsPbX₃ NCs and examines the factors affecting photophysics. Chapter 2 is about the depiction of the synthesis method followed by the description of experimental methods and motivation for using them. Chapter 3 describes our research on the nano morphology's effect on OPLA and TPA properties of CsPbBr₃ NCs. Chapter 4 investigates the micromorphology of a bi-sized film and its effects on carrier transfer and diffusion. Chapter 6 gives the Future Outlook.

PEROVSKITE NANOCRYSTALS: BASICS

In 1839 the geologist Gustav Rose discovered the mineral CaTiO₃ in the Ural Mountains. The name perovskite is accredited to the Russian mineralogist Count Lev Alexevich von Perovski in honor of his work¹⁶. Perovskite refers to a large family of crystalline ceramics with 3D structures based on that of the natural mineral

calcium titanium oxide with the ABX₃ structure, where "X= oxygen or halogen" is an anion bonding with "A" and "B" cations with different sizes. A and B cations are coordinated with 12 and 6 X anions, respectively. The structure of CsPbBr₃ is shown in Figure 1.



Figure 1. Crystal structure Perovskite CsPbBr₃.¹⁷

The ideal cubic structure of perovskite is not very common, and even the mineral perovskite is a bit distorted.^{18,19} This distortion is one of the main reasons for this family's many piezoelectric and ferromagnetic materials. Other properties such as insulating, semiconductor, magnetic, and superconducting compounds can also be found.

In recent decades, the optoelectronic properties of these materials have catapulted them to the forefront of interest in the scientific community, reaching 25,7% efficiency on perovskite solar cells this year.²⁰ Specifically, the family of halide perovskites (HP) entered the solar energy field as light absorbers, as we mentioned

before. Characteristics include their high absorption coefficient and broad absorption spectrum, the high mobility of holes and electrons, and long diffusion lengths. These characteristics are due to the structure and chemical composition, which will be explained later. In addition to their excellent capabilities as light absorbers in solar devices, they are also significant light emitters. For this reason, HPs have also created a niche in this type of application, such as light-emitting diodes.^{21–25} HPs are a promising platform for these applications, mainly because of their excellent charge transport and bandgap tunability. The highest efficiency reported for perovskite NCs is 23.4% of external quantum efficiency (EQE).²⁶ This EQE value surpasses the highest EQE in InP-based greenemitting QD-LEDs (EQE = 16.3%)²⁶ and gets closer to the theoretical value of LED EQE of 30%.²⁷

Low dimensional perovskites, which possess perovskite domains spatially confined at the nanoscale, have further extended the tunability and functionality of this material.¹⁵ The most notable success of p-NC in this area lies in its narrow emission spectrum and extremely high PLQY, reaching 100%.

Besides the conventional features of NC materials, such as the increased surface area and reactivity, quantum confinement is the most critical factor explaining their anomalous behaviors compared with bulk counterparts, which is worthwhile to stress here.

In general, a NC size ranges from 1 nm to 100 nm.²⁸ The quantum confinement occurs when semiconductor NCs are comparable in size to the bulk exciton Bohr radius. The exciton Bohr radius (2a₀) of CsPbBr₃ is 7 nm. ^{29,30} The confinement can be created due to electrostatic potentials, the presence of an interface between different semiconductor materials, and the presence of a

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semiconductor surface.³¹ This boundary makes the motions of electrons and holes in a semiconductor restricted. Their electronic behavior can be explained from the perspective of quantum mechanics in its simplest form as a particle in a box. In this model and considering only one dimension, a particle of mass m is confined along a stretch length L, the box. Inside the box, the potential is 0. Outside, it is infinite. The energy of an electron excited by light in a NC experiencing quantum confinement is expressed by eq 1.³². The boundaries of the NC determine the box length.

$$\Delta E = \frac{(2n-1)\hbar^2 \pi^2}{2mL^2} \qquad 1$$

We observe that as "L" increases, ΔE decreases, meaning an electron will need less energy to be excited as the radius increases. If the energy gap refers to the optical bandgap for the optical transition, the material's absorption band will then shift towards the red with such increased dimension. As seen in Figure 2, the gray bands represent the conduction and valance band of the bulk semiconductor. As the diameter of the NC decreases, the bandgap energy is higher. Consequently, NC absorption and emission spectra are strongly size-dependent, with the band edge features of both shifting to shorter wavelengths with decreasing particle size.

4 nm	9 nm	15 nm	30 nm	50 nm	Bulk
	■				
			↓ ↓	1	\$

Energy



Another aspect of quantum confinement is that the behavior is no longer a continuum but as discrete energy levels (represented in Figure 2 with fewer lines). As the diameter decreases, there are more discrete energy levels.³³ The degree of confinement can be expressed as $L/2a_0$, L is the diameter of the NC, and $2a_0$ is two times the Bohr radius. When $0.5 > L/2a_0$ the NCs is in strong confinement regime for values between $0.5 < L/2a_0 < 2$ it's the intermediate quantum confinement and for $L/2a_0 > 2$ the NC is under weak confinement to bulk behavior.³⁴

The HP family comprises hybrid compounds such as MAPbX₃ (MA = CH₃NH₃, X = Cl, Br, and I) and all inorganic compounds such as CsPbX₃. The p-NC that has caught most attention has been the allinorganic CsPbBr₃. The synthesis and crystallography of CsPbX₃ have been reported since 1958.³⁵ However, as colloidal nanomaterials, they were first synthesized in 2015 by Loredana et al. ²⁹ The nature of the perovskite combined with the nanostructure allows them an easy synthesis process, wide color tenability, high quantum yields reaching 100% efficiency.

PHOTOPHYSICS OF PEROVSKITE NCS

The meticulous study of the processes after light excitation in CsPbBr₃ is crucial to developing and optimizing excellent optoelectronic devices. The photophysical cycle will be detailed in this chapter. In the initial step of the photophysical cycle (Figure 3), electrons and holes are excited to the conduction (CB) and valence bands (VB). After excitation, two pathways to excited state depopulation can occur: 1-If the charge separation happens, free carriers travel until the recombination process happen. 2-energy transfer happens until the recombination phase starts. The relaxation processes result from the competition among different possible radiative and non-radiative pathways. The photophysical process is strongly influenced by the perovskite structure, which will be explained further in Chapter 3.¹⁵

In order to understand the parameters governing this interaction in perovskites, special the CsPbX₃ we are targeting, the photophysical cycle will be divided into three main stages light absorption, charge carrier diffusion, and recombination. These three processes will be explained further in this chapter.



Figure 3. Photophysical cycle main events in p-NC

LIGHT ABSORPTION

The following three scenarios can induce light absorption in p-NCs. **OPLA 1**-When light has the close energy to the optical bandgap of the material excited: An electron from the valance band is excited to the conduction band at the band edge states, creating an exciton or electron-hole pair. **OPLA 2**- When the photon absorbed is of greater energy than the material's bandgap, excited hot electrons and holes undergo a cooling process. In the cooling process, the excess energy is typically converted into heat on a picosecond timescale or even faster when hot carriers relax to conduction band maximum (CBM) and valance band maximum (VBM) correspondingly.¹⁵ Both these processes are one photon linear absorption (OPLA). They use one photon to generate one electron-hole pair. **TPA**-When two or more photons (of less energy than the bandgap) are absorbed simultaneously to excite one electron from VB to CB. This process is called two-photon absorption (TPA) or multiphoton absorption (MPA) if more than two photons are absorbed. Since the TPA process plays a crucial role in this thesis, a brief introduction of the applicability of this property and the most important features will be introduced.

Göppert-Mayer proposed the TPA process in 1931. The Göppert-Mayer (GM) is also the unit in which the TPA cross-section is reported (1 GM = 1×10^{-50} cm⁴ s photon⁻¹). The mechanism proposed for TPA is generally described in terms of an intermediate state in resonance with single-photon energy, this intermediate state can either be virtual or real with negligible single-photon absorption.³⁶ TPA shows a more extended penetration depth than OPLA for the same materials because the TPA excitation photon energy is usually in the NIR range, which undergoes decreased absorption (NIR energy < bang gap) and reduced scattering by matters.³⁷ For this reason, TPA materials are currently attracting considerable attention in applications such as photodynamic therapy, 3D optical data storage, information technology, multiphoton imaging, bio-imaging, frequency up-conversion, lasing amplification, and 3D material microfabrication.^{36,38}

State-of-the-art materials with visible MPA are primarily organic and polymeric materials. However, their MPA absorption cross-sections are still far from satisfactory device application. Their values are between (100 GM to 10⁴GM). CsPbX₃, on the other hand, has shown MPA cross-sections of 10⁶ GM.³⁸ We report in

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Article I TPA cross-sections between (1.3 to 2.3)*10 6 GM for CsPbBr₃ NPLs and NW.

ENERGY AND CHARGE CARRIER TRANSFER

After light absorption, there are two main processes in which the energy generated can travel in semiconductor NCs. Energy transfer process: There are different ways energy transfer happens: Dexter energy transfer, or förster energy transfer (FRET). In semiconductor NCs the most common process reported is FRET. Excitation energy migrates from one system **Donor (D)** to another **Acceptor (A)**. This energy transfer is a consequence of mutual electrostatic repulsion between the electrons of the donor and acceptor species. As D* relaxes to D, the transition dipole thus created interacts by Coulombic (electrostatic) repulsion with the transition dipole created by the simultaneous electronic excitation of A to A* as seen in Figure 4.^{39,40}



Figure 4. Forster Energy transfer (FRET) electron movement diagram.

For FRET to happen, several requirements need to be met. There should be a spectral overlap of the donor emission and acceptor absorption. There should be a favorable orientation of transition dipole. The rate of energy transfer is also highly dependent on the distance between Donor and Acceptor.

Charge transfer process: The photogenerated excitons dissociate into electrons and holes, and those charge carriers can diffuse or transport within the materials in this process. Our results in **Article II** indicate an electron transfer process happening instead of energy transfer in QD solid film. The low exciton binding energy of CsPbBr₃QD (40 meV- for 8 nm QD)³⁰ indicates predominantly free carriers at room temperature, making carrier transfer more probable. The energy band alignment between the donors and acceptors obtained is also more probable for carrier transfer processes than energy transfer.^{24,41-43}

The diffusion of electrons and holes is mainly determined by the carrier mobility of the materials, which depends on intrinsic and extrinsic factors of the materials. The intrinsic factors depend on the carrier interactions with the underlying lattice. Material parameters such as the carrier effective mass and mean scattering time determine the intrinsic mobility⁴⁴. The carrier effective mass depends on the band structure of the CsPbBr₃ perovskite. They are determined by the valence and conduction band's dispersion and interaction of charge-carriers with crystal vibrations. The higher the effective mass has, the lower mobility. The scattering time reflects the average frequency carriers experience a scattering event that alters their momentum state. On the other hand, material imperfections account for the extrinsic effects, such as grain boundaries, energetic disorder, or impurities, this can be avoided by material processing. The observed result in this method is a combination of both.45

Computational studies on the effective mass of CsPbBr₃ NCs charge carriers are not yet consistent. However, they show how the effective mass of electrons and holes are fairly similar. Density functional studies (DFT) by Protescue²⁹ show m_e =0.14 and m_h = 0.15 and by Rossi⁴⁶ m_e = 0.121 and m_h = 0.117, although none of these models consider the Coulomb interaction between the electron and the hole. ⁴⁷ A study by Akkerman⁴⁸ uses DFT to incorporate spinorbit coupling (SOC-DFT) and studies the reduction of the size on the effective mass. The results show the effective mass of holes and electrons very close to each other m_e = 0.172, m_h =0.171 of CsPbBr₃ bulk, and as the size is reduced, both effective masses increase, with the carrier's effective masses remaining very close to each other along with the series. These results imply that electron and hole mobilities are expected to be very similar in CsPbBr₃ NCs.

Nevertheless, a factor to consider is the scattering affected by the presence of polarons in CsPbBr₃ perovskites. Polarons involve excited charges and corresponding lattice deformation via electron-phonon coupling, inducing a polarization of the surrounding lattice. Research revealed that the excited electrons form large polarons while holes form small polarons. When the radius of a polaron is much larger than the lattice constant of the material, they are called large polarons. The carriers that become trapped in potential wells of their own creation are small polarons.⁴⁹ A small polaron is usually more confined, while a large polaron allows a relatively free movement, explaining why even with similar effective masses between electrons and holes, higher mobility in the electron than the hole is expected CsPbBr₃. ⁵⁰ As we report in **Article II**, the mobility of electrons is 2.1 cm²/ Vs, and the mobility of holes is 0.69 cm²/ Vs for CsPbBr₃ (10 nm QD).

RECOMBINATION

There are numerous recombination channels, and they depend on a variety of conditions. In general, the recombination process happens through radiative and non-radiative processes. photoluminescence is the radiative decay pathway, and the main non-radiative processes involve Auger, free carrier, and trapmediated recombination. In Figure 3, we have depicted the photoluminescence process (emission), the free carrier and trap mediated recombination pathways for the recombination processes in p-NCs. Those recombination processes compete with the energy and carrier transfer. For devices such as solar cells, converting the absorbed photon energy into the photocurrent is the ultimate goal. Therefore, no recombination process is desired during such a conversion; instead, after light excitation, an energy transfer or carrier transport process is required to separate the photogenerated electrons and holes and direct them to the conductor material. For LED devices, on the other hand. the radiative recombination of the charge carriers is required to trigger the PL emission. All the non-radiative decay mechanisms are considered as unwanted competition in this case. The PLQY measures the efficiency of the radiative process. A 100% PLQY implies that all photons absorbed can be converted into charge carriers and are emitted radiatively afterward.

The trapping process accounts for the most common nonradiative recombination in perovskite NCs. The existence of both surface and bulk traps in perovskite materials is widely reported.⁵¹ The surface traps are induced by surface dangling bonds or unsaturated atoms, while the vacancies or interstitials can generate the traps in the bulk volume (e.g., Br- ions).⁵¹ The trap states in

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perovskites can also be tuned by the morphology and geometry of materials. Smaller dimensions induce more trap states.⁵² In other QDs such as CdSe traps generate localized electronic states with a long lifetime. In these cases, the electron trapped can no longer be harvested before the non-radiative recombination. However, in lead halide perovskites, the bandgap is formed between two sets of antibonding orbitals, so the vacancies form states residing within the VB and CB are only shallow defects. Dangling bonds at the surface of CsPbX₃ NCs have similar scenarios, leading to localized, nonbonding states. The formation of benign vacancies suggests the existence of relatively delicate surfaces, which was subsequently confirmed for CsPbBr₃ by computational studies.^{53,54} The above factors render a significant defect tolerance in lead halide perovskites where the charge carrier transport is not significantly inhabited by the trapping, which is one reason for high performing properties such as high PLQY in perovskites.

In Auger recombination, an excited electron recombines with a hole and the energy released excites another charge carrier is also an important pathway for excited state depopulation. Auger recombination is mainly observed when high carrier density is triggered with high energy excitation sources or high fluence.²⁴

Several factors, especially the material structure, influence the three main processes presented in this chapter. The next section will discuss the intrinsic and extrinsic properties regarding the material structures affecting this material photophysics.

STRUCTURAL FACTORS INFLUENCING PHOTOPHYSICS BEHAVIOR IN CSPBX₃ NCs

CHEMICAL COMPOSITION:

The light absorption in p-NCs is mainly determined by the orbitals defining the VB and CB. The nature of the electronic structure of halide perovskites is depicted in Figure 5. The conduction band forms from the antibonding orbitals of the hybridization of the Pb 6p orbitals and the outer p orbitals of the halide (5p for I, 4p for Br, and 3p for Cl), and it is p-type of orbital due to the high density of states (DOS) from the lead contribution. On the other hand, the valence band forms from the antibonding states of the hybridization of the Pb 6s and the same halide p-orbitals.^{55,56}



Figure 5. Energetic bands of lead iodide perovskite from the orbitals hybridization of lead and iodide.⁵⁵

As illustrated above, the VB and CB of perovskites are only affected by PbX. The cation orbitals exhibit little contribution to the band structures, although they are influenced by electrostatic interactions.⁵⁷ Common A sites from the ABX₃ structure are MA, FA, and Cs. However, the change of those cations can indirectly change the bandgap due to modifications in the lattice constant. As the size of the A-cation decreases (from FA > MA > Cs), the bandgap increases. The underlying mechanism is an increased tilting angle of Pb-X-Pb bonds and the concomitant distortion of the cubic crystal structure.⁵⁸ The A site also influences the metal halide overlap, directly impacting VB and CB positions.^{59,56}

Furthermore, the B-site cation can also dictate the final optical properties of perovskite NCs. Substituting Pb with Sn in the halide perovskites is a widely reported strategy to achieve the green transition of perovskite materials by removing the heavy metals in the composites. The resultant Sn-based perovskites exhibit a narrower bandgap of 1.2–1.4 eV, intensely red shifting the absorbance of the NC. ⁶⁰ This is most likely due to the higher electronegativity of the Sn²⁺ in respect to Pb²⁺.⁶¹ Ge-based perovskite has also been studied.⁶² However, the stability of both Ge and Sn-based perovskites is inferior due to a reduced inert electron pair effect, which corresponds to a decrease in the stability of the divalent oxidation state.

Changing the halide composition in CsPbX₃ makes it possible to significantly tune their optical band gap to cover the visible spectrum. In Figure 6, optical properties of different NCs of CsPbX₃, including mixed halide NCs. All of them show narrow emission spectra. Figure 6D also demonstrates the change in composition leads to changes in the photoluminescence lifetime, which is attributed to the different trap densities present in the NCs. ²⁹

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Figure 6. Colloidal perovskite CsPbX₃ NCs (X = Cl, Br, I) composition-tunable bandgap energies with narrow and bright emission: (a) colloidal solutions in toluene under UV lamp (λ = 365 nm); (b) representative PL spectra (λ_{exc} = 400 nm for all but 350 nm for CsPbCl₃ samples); (c) typical optical absorption and PL spectra. d) time-resolved PL decays for all samples shown in (c) except CsPbCl₃. Reproduced with permission of Ref.²⁹

The electronic influence structure can also the Experimental⁶³ recombination process. and theoretical⁵⁷ calculations agree that perovskite containing larger A site cations favors a longer excited-state lifetime following the trend FA > MA > Cs. The longer lifetime corresponds to low recombination rates, which leads to higher PLQY and power conversion efficiency of the solar cells.

As discussed above, APbX₃ NCs typically exhibit high values of PLQY even without electronic surface passivation with wider-gap epitaxial shells. Cs and MA-based lead halide perovskites have been reported to have PLQY values of up to 80–95% for bromides and iodides.^{14,64,65} These high values signify the strong defect tolerance of halide perovskite materials, which arises due to their electronic structure and the bandgap that forms between two antibonding orbitals. Indeed, this characteristic, coupled with the fact that interstitial and antisite defects require very high formation energies, leads to the predominant formation of shallow traps. ^{56,66}

A recent theoretical study shows that halide vacancies in the NCs are the major contributor to the defect energy levels, which are shallow for CsPbBr₃ and CsPbI₃ but deep in the case of CsPbCl₃. ^{67,68} The high trap density in large bandgap CsPbCl₃ NCs accounts for its weak luminescence (PLQY <10%), and ultrafast spectroscopic studies show multiple carrier trapping channels with time constants ranging from 3 to 64 ps.⁶⁹⁻⁷²

SURFACE CHEMISTRY:

The interactions presented on the surface of NCs vary from the bulk due to incomplete crystal structure and the pronounced effect of defects and substitutions. Surface chemistry has a significant influence on the photophysics of nanostructures due to the dominant surface area of these materials in contrast to their bulk counterparts.

The low-dimensional perovskites typically feature different cuts from the 3-D structure along the (100), (110), and (111) directions on the surface, which present different reactivity. In Figure 7, the different facets of the perovskite structure are depicted. (100)- Oriented perovskites are obtained by removing the inorganic framework's metal (Pb) component. In contrast to the common (100)-oriented perovskite, the (110)- and (111)-oriented perovskites have rarely been reported for CsPbBr₃ NCs. ⁷³



Figure 7 Different Facets of Perovskite structure. Purple balls are the Cs; blue balls the Pb and red balls the halogen atoms. Reproduced with permission from ref ⁷³.

Sunjib et al. showed the different facets significantly changed the PLQY and fluorescence lifetime of CsPbBr₃ NCs. More defects tend to form on the facets with less stability, i.e. high surface energy, which serve as quenchers for photoluminescence (PL). On the other hand, those defect states also help to trap photogenerated charge carriers to trigger chemical reactions. In this scenario, the facets with lower PLQY showed higher photocatalytic reactivity.⁷⁴

CAPPING AGENT:

The capping agents are in general ligands bonded to the NCs surface. They have the role of passivating surface defects, avoiding trapping, and enhancing the stability of the NCs. They also influence the morphology of as-synthesized NCs since it defines the boundary conditions during the particle nucleation and growth during the wet chemical synthesis. The ligands that attached to the surface of the perovskite NCs are highly dynamic and labile and can be easily debonded during the isolation and purification process. Consequently, when shifting the solvent polarity (a necessary protocol for NC isolation and purification), the capping agents detachment in CsPbX₃ NCs often leads to loss of their bright luminescence properties, colloidal stability, and, occasionally, structural integrity.^{75,76}

The most common ligands used in CsPbX₃ NCs are longchain alkylamines oleylamine (OLA) and oleic acid (OA).⁷⁷ To overcome the labile nature of this capping agent, bidentate ligands (or chelating ligands) are utilized for enhanced stability and to retain high PLQY even after purification of NCs.²³ Among the new alternatives for developing stable NCs are zwitterionic surfactants and quaternary alkyl ammonium compunds. These strategies have proven that the structural lability of CsPbBr₃ NCs can be mitigated. Zwitterionic surfactants render high PL QYs of above 90% after four rounds of precipitation/redispersion. The binding of zwitterionic ligands to the NC surface is kinetically stabilized by the chelate effect. Densely packed films of these NCs exhibit high PLQY values and effective charge transport.⁷⁸

One of the quaternary alkylammonium compounds that have stood out is the halide ion pair didodecyl dimethylammonium bromide (DDAB, which is relatively shorter than OLA). DDAB capped CsPbX₃ NCs films have shown high stability.²⁴ In addition, DDAB binds stronger to CsPbX₃ NCs than OLA and OA, offering higher stability of the devices. The charged state of DDA cations, like other quaternary ammonium salts, are pH independent (unlike OLA and OA). The two hydrocarbon chains are known to form stable monolayers due to a good match between the molecule cross section and the typical densities of negatively charged surface sites.⁷⁹ In addition, the size of DDAB is shorter than conventional OLA and OA, which allows better inter-dot electron or energy transport, which is usually demanded in LED applications where the NC compacted solid is the main building block.

Compared to NCs decorated by conventional OA /OLA ligands, passivation with the quaternary ammonium or zwitterionic surfactants increases the NC solid-state emission yield by up to 40% by halving the average trap depth and increasing by 1.5 times the exciton binding energy. Furthermore, the aforementioned ligands better preserve the size of NCs in thin films, as shown by the absence of significant NC aggregation.⁸⁰

The post-synthetic chemical treatment of NCs has been proved another effective strategy to increase the stability of the NCs. Potassium-oleate (K-oleate) has also been introduced to protect and passivate the surface of CsPbBr₃ NCs, which enhances the optical properties.⁸¹ The post-synthetic treatment with a PbBr₂ligand solution showed that the poor blue emission PLQY of CsPbBr₃ NPLs could be boosted from ~7 to ~70 %.⁸² By carefully limiting the number of surface defects (such as the Pb and Br vacancies) in HP NPLs, it is possible to obtain efficient blue-emitting nanostructures which can be integrated into electroluminescent devices.^{82,83}

MORPHOLOGY FACTORS AND THEIR INFLUENCE ON

PHOTOPHYSICS BEHAVIOR IN CSPBX₃ NCs

Morphology of the NCs mainly includes their size and shapes. In bulk semiconductors, the morphology does not play a significant role in its optical properties. Both elements of morphology determine the properties of NCs since both significantly modulate the degree of quantum confinement. Only recently (2017) has it been possible to achieve the size and shape control for CsPbX₃ NCs thanks to the development of novel synthetic methods, enabling the preparation of QDs,⁸⁴ nanoplatelet (NPL),⁸⁵ nanosheets⁸⁶, and nanowires (NW)⁸⁷ of different sizes. Those structures are shown in Figure 8 and classified into 0D, 1D and 2D, referring to the number of dimensions free from confinement. We will discuss the influence of shape and size on the photophysical properties of NCs separately.



Nanocubes/ Quantum Dots / Nanoplatelets / Nanowires Figure 8. Different morphology of CsPbX₃ NCs

NC SIZES:

Size tuning causes variations in the bandgap of NCs, creating a direct change in the spectral response of light absorption and emission. Such effect is dominated by the degree of quantum

confinement. The smaller the size, the greater the quantum confinement causing a wider bandgap. This induced the blue shift of absorption and emission band. The size can also impact the efficiency of the light absorption, measured in terms of absorption cross-section. Studies in NCs of different sizes report a linear relationship of OPLA to the NC volume.⁵ Such linearity is only due to the increased DOS with size, and hence is independent of the shape of the NC. ⁶ In Article I, we confirm such relationship in perovskite NCs with different shapes (NPL and NW).

The variation of quantum confinement by size also affects the exciton binding energy. The exciton binding energy is vital for optoelectronic applications, since it governs the dominant photoexcited species, i.e. excitons or free charges. The exciton binding energy of CsPbBr₃ QD has been reported to be 40 meV for an 8 nm QD.^{29,30} According to theoretical studies on the effect of quantum confinement in the exciton binding energy of CsPbBr₃ QDs, the values can increase to 60 meV in a 3.33 nm lattice and to 128 meV for a 2.62 nm lattice.⁸⁸ In Article I, we calculated the exciton binding energy for a 0D NPL (dimensions: 2.1± 0.4 thickness and 16.3 ± 3.7 average length), and obtained 57 ± 3 meV E_b, which is consistent with the theoretical estimation.

The size also impacts the carrier diffusion by affecting the exciton binding energy. Free electrons have a higher probability of propagating. Another size-dependent aspect is the formation of traps states. Smaller dimensions yield more trap states due to the larger surface area.^{52,23} As a result, the trapping process would suppress the carrier diffusion after photoexcitation. In addition, with reduced sizes, the structural stability of NCs are easy to be broken, making them more prone to generate deep and shallow trap state.

NC SHAPES:

The shape of NCs, which can also be noticed as dimensionality, varies the number of confined dimensions. Various shapes of CsPbX₃ NCs are shown in Figure 8. 0D NCs represent NCs with all dimensions within the quantum confinement regime, e.g. q QD, NPL, NWs, and nanocubes. 1D NCs have two dimensions in the confinement regime as nanowires NW. 2D NCs have only one dimension in the confinement regime: NPL and Nanosheets.⁸⁹

Enhancement of quantum confinement is usually observed with the increment of confined dimensions, i.e. from 3D, to 2D, 1D, and 0D. In general, the compound's bandgap increases accordingly. This has been verified by the blue shift of absorption and emission band and changes in the photo-induced carrier recombination and cooling dynamics. ⁵⁶

The localization of photogenerated species, i.e excitons or carriers, in HPs is also strongly affected by the polarizability of the surrounding polar perovskite lattice, which is associated with the dimensionality of the NCs. Dielectric inhomogeneities enhance self-energy contributions in low dimensional perovskite structures and nanostructures. The latter also influences electron-hole pair interactions, giving strong excitonic resonances and high exciton binding energies.⁹⁰

Most research on CsPbBr₃ NCs and their relationship to morphology has been based on the properties in the solution. Since the material applications are in a solid film, assessing its properties on film is very important. In the next section, we will discuss the effect of the micro-assembly in a multi-sized film, which resembles the typical configuration in the LED device.

MACROSCOPIC ASSEMBLY OF THE NCS:

A macro assembly reported for CsPbBr₃ NCs is their organization in superlattices. Thanks to post-synthesis techniques, it is possible to induce self-assembly of as-prepared NCs in which individual components arrange themselves into an ordered structure.⁹¹ Various methods lead to 1D or 3D p-NC superlattices, such as solvent/ligand-assisted,^{92,93} templated,⁹⁴, and dryingmediated^{95,96} self-assembly. The superlattices show a redshift compared to the PL emission of the starting NCs. This phenomenon is observed due to the cooperative emission of CsPbX₃ NCs. Significant features of the cooperative emission in such superlattices are the modification of the radiative lifetime (e.g., from 148 to 400 ps for 3D superstructures of CsPbBr₃ NCs) and their superfluorescence (short, intense bursts of light).⁹⁶

Another example is the formation of CsPbX₃ Cuboid NCs from the stacking of NPLs. The stacking of the NPLs creates the overlap of wave functions of neighboring NPLs. Leading to electronic coupling and the formation of minibands, provided that the inorganic spacer layer is thin enough (in the order of 1.5 nm), which could significantly promote the charge transport.⁵⁶


Figure 9. Superlattice of CsPbBr₃ Quantum Dots. Adapted by permission from Springer Nature, Superfluorescence from lead halide perovskite quantum dot superlattices by Gabriele Rainò et al. Copyright © 2018.⁹⁶

Recent studies have found NPLs that can self-assemble and transform on solid substrates in the shape of mosaic nanotiles. Such structures undergo oriented attachment, a process by which the NCs achieve a lattice match and eventually connect and build larger single objects under the combined effects of short- and long-range interactions. Adjacent NCs with identical crystal facets that face one another undergo continuous rotation and rearrange their atoms through the formation of a neck in the region of contact until they become a single structure.^{97,98,99}

Most reports on these nanotiles from CsPbX₃ are on the synthesis and mechanism of attachment. Their optoelectronic properties are still to be explored further. However, other types of semiconductor NCs oriented films show properties superior to

those of the disoriented films. Such as directional charge-carrier transport, high carrier diffusion lengths, and high carrier mobility.¹⁰⁰



Figure 10. TEM image of nanotiles 100 nm scalebar. Depiction of mosaic nanotiles formation from CsPbX₃ NPLs. Reproduced with permission.⁹⁷ Copyright 2020, American Chemical Society.

From the above introduction, we see how the nano and micro morphology of CsPbX₃ perovskite NCs have a significant impact on the photophysical behavior. However, there are still several questions left to answer. We tackle the task of understanding how the nanoscale morphology affects the same fundamental optical parameters of asymmetric NCs with different aspect ratios AR. Furthermore, we study the carrier diffusion properties of a QD solid with macroscopic assemble of the QDs. The methodologies used in those studies are first explained in the next chapter.

SYNTHESIS OF NANOCRYSTALS

MULTI-SIZED CSPBBR3 QDS SYNTHESIS

The synthesis method of CsPbBr₃ QDs is based on the famous synthesis elaborated by Protescue et al.²⁹ This is a hot injection method that uses different temperatures 140 °C (4 nm QD) and 180 °C (10 nm QD) of injection of Cs-Oleate composite to a PbBr₂ solution with OA and OLA. ¹⁰ If we analyze the process from the hydrosol theory developed by the La Mer model for particle formation.^{101,102} The timing of nucleation and growth phases governs the particle size and dispersity. The nucleation phase governs the particle concentration, and the growth phase governs the size. If we consider this, the 140 °C has less energy available for the growth phase causing a smaller size than the 180 °C. To avoid a broad size distribution, controlling the injection temperature is crucial, and a quick quench of the reaction by a cold water bath right after injection. The 10 nm nanoparticles are very stable and easy to make. although the 4 nm samples are more unstable than the 10 nm ones. Their small size makes them more reactive and less stable due to increased surface chemistry. For the experiments, we required a superb optical quality. So we discarded any sample with broad size distribution observed mainly in the FWHM of the UV-Vis spectra and the PL. It was often encountered in the 4 nm size sample that two sizes were made. Reproducibility in this 4 nm sample is difficult. It requires expert hands, minor changes such as the local

environment (humidity), change of laboratories where causes of failed samples.

After the synthesis, a surface ligand exchange to DDAB is performed on the QDs. The ligand exchange follows the method described elsewhere.²⁹ The detailed synthesis procedure for QDs is provided in **Article II.** In Figure 11 A we observe the CsPbBr₃ QD film, in 11 B) the solution of mixed QDs excited by 395 nm laser.



Figure 11. A) CsPbBr₃ 10 nm QD film B) CsPbBr₃ 10 nm and 4 nm mixture solutions. Excited with 395 nm laser light.

CSPBBR3 THIN NANOCRYSTALS

The synthesis method for NPLs and NW is based on the method for NPL synthesis.¹⁰³ It is very similar to the procedure for QDs with some changes. The injection temperature utilized is between 90 and 100 oC to keep a smaller size, and an increase of Br is added in the form of the (OLA-HBr).

These ions typically replace surface Cs⁺ ions and act as integrated bonded ions on the surface of perovskite crystals as shown in Figure 12. Accordingly, with an increase of their density or concentration on the reaction mixture, the dimension of the NCs became smaller because of instant capping.¹⁰³ With the increase of its concentration, the size of the cubes and width of sheets were reduced. Our conditions resulted in a thin thickness between 2 and 3 nm.



Figure 12. Schematics of capping agent in the structure of CsPbBr₃

CHARACTERIZATION METHODS

TRANSMISSION ELECTRON MICROSCOPY TEM

Transmission electron microscopy (TEM) has been used to examine the morphology and measure the dimensions of the synthesized CsPbBr₃ NCs. In TEM, a beam of high-energy electrons produces an image of the sample. The images can achieve the magnification of features on the nanometer scale. TEM can magnify objects up to 2 million times. The electrons are generated by heating a tungsten filament, accelerated by a potential difference, and then focused into a coherent beam by a set of electromagnetic lenses. When the beam hits the sample, some of the electrons are transmitted. The transmission of electrons depends on the thickness and electron density of the sample. The transmitted electrons are focused onto a detector, which correlates local electron densities with sample thickness to create a 2D projection of the sample, with the dark areas of the image representing denser parts of the sample and bright areas representing less dense parts. The instrument is operated in a vacuum to prevent the electrons from interacting with particles in the air.^{22, 23}

For the imaging of NCs, we use a carbon substrate. The sample is drop-casted and left under vacuum for 2 hours before analyzing. Imaging was conducted on Tecnai G2 T20 TEM and FEI Titan Analytical 80-300ST TEM from FEI Company. The obtained TEM images were processed with Image J. To obtain a statistically significant analysis of the dimensions. The images are taken from different spots on the substrate and at least 300 measurements are collected for each dimension.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface technique used to determine the electronic states' overall electronic structure and density of a material, including the elemental composition and chemical state. It involves the bombardment of monochromatic X-rays into the sample, followed by the release of photoelectrons from the sample. The detection depth of this technique depends on the escape depth of the photoelectrons ranging from 5 to 10 nm. We use this technique mainly to determine the VB energy. XPS (ThermoScientific) was performed to analyze the VB and compositions of samples, with Al K α (1486 eV) as the excitation X-ray source. C (1s) peak at about 284.8eV was used to calibrate the energy scale. The pressure of the analysis chamber was maintained at 2×10⁻¹⁰ mbar during measurement.

SPECTROSCOPY CHARACTERIZATION METHODS

STEADY-STATE UV-VIS AND THE DETERMINATION OF BANDGAP ENERGY

Steady-state Uv-Vis was performed to investigate the light absorption features of the NCs. The absorption spectra are also used to estimate the size of the NC after synthesis. The maximum absorption peak refers to the 1S exciton transition, which also refers to the energy of band-edge excitation. The peak position indicates the NC's size since the size of NCs alters the bandgap. The narrower the FWHM indicates a narrow size distribution. The presence of more than one peak indicates more than one dominant size or different shape of NCs. Figure 13A shows two different quantum dots of CsPbBr₃ QD-4 (4 nm) and QD-10 (10 nm). 8 B shows absorption spectra of different mixtures of size 4 nm with 10 nm CsPbBr₃ QD. We confirmed the mixture of the two sizes QDs in **Article II**. from the spectrum.



Figure 13. A) Absorption Spectra of QD-4 and QD-10 B)spectrum of mixtures with ascending concentration of acceptor QD C) Tauc plot of QD-4 and QD-10

We also use the UV-Vis data to calculate the bandgap of the NCs by generating a Tauc plot. The Tauc plot is constructed by plotting $(A x hv)^2$ against hv. The quadratic dependence corresponds to direct bandgap materials. hv is obtained from the following equation $E = \frac{hc}{\lambda}$ Where λ is the wavelength axis from a UV-Vis spectrum, h is Planck's constant (4.14 x10⁻¹⁵ eVs), and c is the speed of light (2.99 x 10¹⁷nm/s)). The region showing a steep, linear increase of light absorption with increasing energy is characteristic of semiconductor materials. The x-axis intersection point of the linear fit of the Tauc plot gives an estimate of the bandgap energy.

This approach can be applied for all semiconducting materials that do not absorb light of the sub-bandgap energy (or show a negligible absorbance), as exemplified in Figure 14C. ¹⁰⁴

TRANSIENT ABSORPTION SPECTROSCOPY (TAS)

Time resolution is crucial to follow ultra-fast events. In other words, the equipment needs a faster time response (or at least as quick) than the process under investigation. Carrier dynamics, electron or energy transport happen in the ultrafast domain, fs to ps timescale. In TAS, the NCs are excited by an intense quasimonochromatic laser pulse (the pump), and the absorbance spectrum is measured by a second pulse (the probe). A basic scheme of a pump-probe technique is shown in Figure 15. By varying the delay time of the second pulse concerning the first one, the time-dependence of the absorption change can be measured.^{105,106}



Figure 15. General scheme of a pump-probe technique.

A differential spectrum is then obtained by subtracting the pump-on spectrum from the pump-off spectrum at a specific time

delay. The resulting transient differential spectra characterize the excited-state dynamics of the system under study. The kinetics of the excited-state dynamics can also be determined for the system by changing the delay time between probe and pump, done by directing one of the beams through an optical delay line. The delay line merely changes the path length without any effect on the direction and position of the beam. ¹⁰⁷ The final result combines the absorption differential spectrum as a function of time.

Depending on the target system, different spectrum ranges can be used as pump and probe pulses. In this project, TAS experiments were performed using a femtosecond pump-probe setup. The probe pulse is white light through CaF₂ crystal, which gives the Visible spectrum to near IR. Laser pulses (800 nm, 150 fs pulse length, and 3 kHz repetition rate) were generated by a Ti:sapphire amplifier with an integrated oscillator and pump lasers (Libra LHE, Coherent Inc.) and a transient absorption spectrometer (Newport Corp.). Briefly, the output of a Ti:sapphire amplifier with an integrated oscillator and pump lasers (800 nm, 150 fs, 3 kHz, Libra LHE, Coherent Inc.) was split into two beams that were used to generate 400 nm light through the doubling crystal as a pump beam and to generate white light through the CaF_2 crystal as a probe. The probe beam was split to two beams: one going through the sample and another as a reference. The generated supercontinuum was then focused onto the sample and overlapped with the pump beam. The transient spectra were detected with a fiber-coupled CCD-based monochromator (Oriel, Newport).

Transient absorption spectroscopy is an excellent tool for characterizing the fundamental photophysical parameters of CsPbBr₃NCs. In **Article I,** we obtain the exciton and biexciton lifetime at different excitation wavelengths. In addition, using TAS with different excitation intensities, we can quantify the excitation

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population on each NC. From these quantifications, OPLA and TPA cross-sections can be obtained. The calculation methods are discussed in detail in each article. In **Article II**, we combine the global analysis of the transient absorption spectra and the kinetic trances modeling to determine the lifetime of the recombination processes and the electron transfer process. A more detailed description of global analysis will be described in the following part.

GLOBAL ANALYSIS

The global analysis combines a kinetics model and the spectra components, becoming a spectro-temporal model. Global refers to simultaneous analysis of all measurements. The model parameters like rate-constant and spectra can be estimated from the data providing a concise description of the complex system dynamics.¹⁰⁸ It is a unified separable nonlinear model that describes all measurements collected over multiple independent variables.

The goal is to fit the data with a sufficient number of exponential decays and their amplitudes (i.e. the lifetimes of the components), where the feature and timescale of specific dynamic processes can be assigned and analyzed from a singular value decomposition (SVD) on the data matrix. The starting values for the amplitudes of the components are often based on a rough guess based on the assumed dynamic processes under study.

SVD represents a dataset by eliminating the less important parts and generating an accurate approximation of the original dataset. In this regard, SVD is a method of data reduction.SVD will take a matrix as an input and decompose it into a product of three simpler matrices.

An m by n matrix M can be represented as a product of three other matrices as follows:

$$M = U * S * V^{T}$$
 (2)

Where U is an m by r matrix, V is an n by r matrix, and S is an r by r matrix; where r is the rank of the matrix M. The * represents matrix multiplication. T indicates matrix transposition.

The Global analysis gives out several results. The one we focus on is the decay associated spectra (DAS). Each DAS represents a spectral component in the dataset associated to a specific lifetime, in the DAS modality, the processes are independent of one another. This detail is essential because as we expressed earlier, carrier recombination competes with other processes, so several processes can be happening simultaneously. We discuss in **Article II** the DAS of two samples, as seen in Figure 16. The spectral component represents processes happening which are described by the diagram for 1.1% and 2.1% samples. The lifetime of each spectral component is present on the left. The interpretation of the spectral component is described in detail in **Article II**.



Figure 16. Example of DAS extracted from global analysis from *Article II.* DAS components of mixture films with the corresponding diagram of the process. Each DAS represents a dataset associated with a specific lifetime of A) 1.1% B) 2.1 % mixture films.

3 MORPHOLOGY EFFECT ON OPLA AND TPA PROPERTIES CSPBBr₃ NCs (Article I)

In this research, we investigate the effect of the NC morphology on the optical properties of $CsPbBr_3$ NCs. The NCs studied are asymmetric shapes: NPLs and NW with various aspect ratios from 0.13 to 19.4. The optical properties under characterization are the OPLA and TPA cross-sections (σ), which demonstrate the basic parameters for the optical response.

Our NCs all have a dimension in the strong quantum confinement regime. The NPLs have a thickness below 3 nm and the NW has a diameter of 2.6 nm. Such dimension in the strong quantum confinement could induce a clear blue-shifted emissions. Compared with typical green emission of perovskite QDs.

The OPLA cross-section (σ^1) of those NCs presents a linear volume dependence of all the samples, which agrees with the previous behavior in CsPbBr₃ QDs,³⁶ and independent of the NC morphology.

The TPA cross-sections (σ^2) of the NCs are in the range (1.3-2.3×10⁶ GM), values higher than previously reported nanocubes.³⁶ The σ^2 values do not exhibit conventional power dependency of the crystal volume as observed in nanocubes. Instead, we confirmed that the shape-dependent local field factors also modulate them. The local field arises as a response to the external applied field, and is dependent on the morphology of the NCs. As a representation of the shape, the aspect ratio (AR) of the NCs is the dominant parameter that modulates σ^2 . We found that asymmetric shapes with smaller and bigger ARs than QDs exhibit higher TPA coefficients (β) following the local field theory model observed in other semiconductor NCs¹⁰⁹.



Figure 17. Dependence of TPA coefficient β to AR of different-shaped NCs blue are NPLs, and light blue are NW. The green dots are reported values of QDs, and the light green dotted lines are calculated from local field theory at different AR for the different shapes. The AR is defined as AR_{NW}= L/d for NW, with L=length and d= diameter, AR_{NPL}= t/L for NPL with t= thickness and L average length, and AR_{QD}= lx/ly for QD.

We also investigated the excited state dynamics of those samples at both OPLA and TPA regimes. No clear morphology dependence of excited state lifetime has been found in both cases.

This chapter is a submitted article: Morphology-dependent one-photon and two-photon absorption properties in Blue Emitting

CsPbBr₃ Nanocrystals. With authors Sol Gutiérrez Álvarez, Christina Basse Riel, Mahtab Madani, Mohamed Abdellah, Qian Zhao, Xianshao Zou, Tõnu Pullerits and Kaibo Zheng

Find the article below.

Morphology dependent one-photon and two-photon absorption properties in Blue Emitting CsPbBr₃ nanocrystals

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ABSTRACT:

The outstanding optical properties of CsPbBr₃ Nanocrystals (NCs) facilitate their application for optoelectronic devices. Their basic linear and non-linear optical parameters and morphologic

dependence are crucial for device engineering. Although size-dependence of one photon linear absorption (OPLA) and two-photon absorption (TPA) in symmetric nanocubes have been widely discussed, such information in asymmetric nanocrystals is still insufficient. To understand the influence of shape or dimensionality in the above optical parameters, we characterized the OPLA cross-sections (σ^1) and TPA cross-sections (σ^2) of a series CsPbBr₃ nanocrystals with various aspect ratios using femtosecond transient absorption spectroscopy (TAS). The σ^1 presents a linear volume dependence of all the samples, which agrees with the previous behavior in CsPbBr₃ QDs¹. However, the σ^2 values do not exhibit conventional power dependency of the crystal volume as observed in nanocubes. Instead, we confirmed that the shape-dependent local field factors also modulate them. In addition, we revealed that the photo-generated exciton and biexciton lifetime of those nanocrystals feature identical size dependence in both OPLA and TPA.

INTRODUCTION

Colloidal all-inorganic CsPbBr₃ perovskite nanocrystals (NCs) keep attracting the interest of researchers due to their superior optical properties that benefit their application in solar cells, LEDs, and other optoelectronic devices. ^{2,3,4} Aside from their well-known optical properties in one linear photon absorption (OPLA) regime, these NCs also present desirable features after two-photon absorptions (TPA). In the TPA regime, the two photons with lower energy than the optical bandgap of the materials are utilized to excite them to an excited state. The use of lower energy photons renders advantageous features in the optoelectronic application, including less phototoxicity, better three-dimensional spatial localization, deeper penetration depth, and lower self-absorption.¹ The typical applications related to TPA features include non-linear photonic

devices for information and communication technologies,⁵ three-dimensional material microfabrication, information technology, and bioimaging.⁶

TPA cross-sections (σ^2) is the most fundamental parameter to determine the capability of two photon absorption transitions in the materials. Compared to standard TPA materials such as organic dves, semiconductor NCs can reach TPA cross-sections (σ^2) as high as ~10⁶ GM and higher photostability.⁷ In general, both σ^1 and σ^2 exhibit a strong size dependence in semiconductor NCs. Our previous results revealed congruency with literature reports on the linear relationship of σ^1 to the dimension of CsPbBr₃ ODs arising from the extension of the density of states.^{1,8} However, most previous studies only focus on the CsPbBr3 nanocubes with symmetric dimensionalities. The facile solution synthesis process enables the preparation of perovskite NCs with other morphologies, including 0D quantum dot (QD) structures, 1D Nanowires (NW), and 2D nanoplatelets (NPL).⁹ The asymmetry in dimensionality renders them unique superiority in the fundamental research and device applications where optical anisotropy is highly concerned. 10 In this scenario, whether such dimensional asymmetry influences TPA properties is vital for material and device engineering. Previous reports on CdSe NCs indicated that such influence exists due to the local field effect on the optical transition of the NCs.¹¹ When an object is placed in a vacuum and is exposed to a uniform static electric field, a uniform internal electric field arises, known as the local field. The local field amplitude varies depending on the object's shape, simplified by the aspect ratio (AR). ¹² Since colloidal NCs are conceptually embedded in a homogenous nonabsorbing dielectric medium, the classic local field theory applies.¹³ As a result, the TPA cross-section is modulated by the AR of the NCs.¹¹

This paper tried to confirm whether such morphologic dependence in the two-photon absorption regime occurs in CsPbBr₃ perovskite NCs, which usually exhibit less quantum confinement than conventional semiconductor quantum dots. We targeted four NCs featuring the morphology of NPLs and NWs with a wide range of aspect ratios from 0.13 to 19.4. Those NCs present blue emissions due to the low dimensionality instead of the traditional perovskite nanocubes.¹⁴ We first characterized the one-photon linear absorption (OPLA) and two-photon absorption (TPA) crosssection of all the samples extracted from the transient absorption spectroscopic measurement. The same linear relationship of OPLA cross-section (σ^1) to volume was observed consistent with our previous study¹. The obtained TPA cross-sections (σ^2) of our NCs (1.3- 2.3×10⁶ GM) are higher than previously reported nanocubes.¹ However, the TPA coefficients (β) exhibit a typical relationship to the ARs of the samples following the local field theory model observed in other semiconductor QDs¹¹. In addition, we investigated the excited state dynamics of those samples at both OPLA and TPA regimes. No clear morphology dependence of excited state lifetime has been found in both cases. The above results provide a basic overview of linear and non-linear optical properties of perovskite NCs with various dimensionality, which can serve as guidance for materials engineering and device application.

RESULTS AND DISCUSSION:

We synthesized colloidal CsPbBr3 Nanocrystals (NCs) with different aspect ratios (AR). They are prepared by the hot-injection method described previously in the literature with modifications on temperature and reactant concentration to form nanoplatelets (NPLs) morphology.¹⁵ To obtain various ARs, different amounts of precursors HBr-OLA (0,8 mL, 1,0 mL, 1,2 mL) were used for the growth at 90°C and 100°C, as summarized in Table S1. In order to obtain a more contrasting AR while keeping a comparable dimension of the NCs, a nanowire (NW)-shaped sample was also synthesized. Details of the procedure are presented in the supporting information. The thickness/diameters of the as-obtained NPLs/NWs range from 1.9 to 3 nm, confirmed by the TEM characterization (Figure 1B). NPLs tend to stack face-to-face in the TEM images, as illustrated in Figure 1C. Therefore the top view of the NPLs exhibits a rectangle shape with its dimension representing the lateral length of the NPLs (Figure 1D top). In contrast, the side view presents parallel stacking of the NPLs where the thickness can be extracted. (Figure 1D bottom). On the other hand, NWs only exhibit one type of view in the TEM image where both their lengths and diameters are determined (Figure 1D). Table 1 summarizes all the dimensional parameters of the samples.

Since the modification on the NC dimensionality will first influence their quantum confinement dominating the electronic structure and optical transition, we first overview the degree of quantum confinement in all those samples. It can be quantified by comparing the critical thickness (t) to the Bohr radius of bulk CsPbBr₃ ($a_0 = 7 \text{ nm}$) ¹⁶ as t/2 a_0 to be between 0.2 and 0.4, which corresponds to the strong quantum confinement regime.¹⁷ Such a strong quantum confinement also accounts for the blue-shifted exciton absorption and emission bands compared with the bulk

phase. ¹⁸ The absorption band edge of the NPLs ranges from 425 to 450 nm, with the corresponding emission peak ranging from 450-475 nm at 385 nm excitation, as shown in Figure 1A. Figure 1E demonstrates the blue emission of the colloidal sample excited with 385 nm CW laser light. We can also confirm the strong quantum confinement by the large exciton binding energy (E_b) calculated from a temperature-dependent PL measurement.^{19,20,21} The E_b of NPL-2 is 57 ± 3 meV (see S.I. for more details), which is larger than the value for 8 nm CsPbBr₃ QDs (40 meV) and within the range of strongly confined CsPbBr₃ QDs from the theoretical calculation. ^{16,22} ²³



Figure 1 A) Normalized Uv-Vis and PL of samples B) Histograms of Nanoplatelets thicknesses and sample images C) Diagram of Nanoplatelets D) TEM Top and side view of NCs E) picture of an excited sample with 395 nm lightTEM top view of N D

Next, we extract the OPLA cross-section of those quantum-confined NCs via ultrafast transient absorption spectroscopy (TAS) as performed in previously reported studies. ^{1, 8} All the samples

are excited at 400 nm, varying the excitation fluence from $(0.2 \text{ to } 6) \times 10^{13} \text{ photons} \times \text{pulse}^{-1} \text{ cm}^{-2}$. The recovery of band-edge ground state bleach (GSB) represents the evolution of the excited state population in the NCs. According to the classic assumption, the initial excited exciton population in NCs follows the Poissonian distribution^{24, 25}

$$\mathbf{P}_N = \frac{\mathbf{e}^{-\langle \mathbf{N} \rangle \cdot \langle \mathbf{N} \rangle^N}}{\mathbf{N}!} \tag{1}$$

where $\langle N \rangle$ is the average number of excitons per NCs, N is the number of excitons, and P_N is the fraction of NCs with N excitons. We can present the average number of excitons per NCs by multiply absorption cross-section σ with excitation intensity I as $\langle N \rangle = \sigma \cdot I$. From equation 1, we can then calculate the fraction of excited NCs, P_{exc} , as:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 = 1 - e^{-\sigma \cdot I}$$
(2)

In reverse, if P_{exc} is given, σ can then be calculated from (2). In TA measurement of NCs, the band edge ground state bleach (GSB) represents the lowest exciton state population after excitation. We can obtain P_{exc} by modeling the excitation intensity dependence of the late-time region signal at GSB maximum (t > 1 ns), which corresponds to the last remaining exciton population after the Auger process. (Detailed description of the calculation is presented in the S.I.). The analysis provides σ^1 values of (1.6 to 5.7)×10⁻¹⁴ cm² for all the samples. The values are within the same order of magnitude as previously reported QDs¹, as summarized in Table 1.

We implement the fluence-dependent TAS measurement with 800 nm excitation (Figure S5). The TPA cross-section σ^2 can be calculated by relating the one- and two-photon absorption coefficients to experimental fitted parameters C1 and C2 in TAS measurement.¹ The excitation population in the NCs depends on the excitation fluence linearly for the OPLA and quadratically for the TPA (Figure S6)²⁶

$$\frac{-\Delta A}{A} = C_1 * \emptyset_{400} \tag{4}$$

$$\frac{-\Delta A}{A} = C_2 * \emptyset_{800}^2$$
 (5)

Here, the ratio between $-\Delta A$ (i.e., GSB signal amplitude at t₀) and the linear absorbance of NCs (A) at exciton transition energy ($-\Delta A/A$) quantifies the number of photo-generated excitons in QDs within the excitation optical path. \emptyset_{400} and \emptyset_{800} denote the excitation fluences at 400 and 800 nm. C1 and C2 are the fitting parameters from the experimental fluence dependence. The quadratic fluence dependence to $-\Delta A/A$ is direct evidence of simultaneous TPA at 800-nm excitation of our NCs. At the weak excitation-intensity limit (i.e., the average number of excitons per NC <N><1), the exciton density can be related to the excitation intensity as well as the OPLA coefficient (α^{1}) and TPA coefficient (α^{2}) as follows: ²⁶

$$\alpha^{2} = \frac{c_{2}\sqrt{2\tau}}{c_{1}}\left(1 - e^{-\alpha^{1}L}\right) \tag{6}$$

where τ is the excitation pulse duration (150 fs), and L is the sample thickness (1 mm). The TPA cross-section (σ^2) coefficient can then be obtained from the α^2 from the following:

$$\sigma^2 = \frac{h v_{800} \alpha^2}{(f_{\omega})^4 N}$$
(7)

Where *h* is the Plank constant, *v* frequency at 800 nm, N concentration in particles per cm³ and $(f_{\omega})^4$ the local field factor corresponding to the aspect ratio of each sample (for details of the calculation, see SI).

Table 1. Dimensions of samples and OPLA and TPA calculated cross-sections, compared to previously reported data in a study with different size QDs (dSize-QDs¹) and a study with different NCs (dMorph⁸).

Sample	Shape	Thickness (nm)	Length (nm)	Volume (nm ³)	AR	σ^1 (cm ²)	σ^2 (GM)
NPL-1	NPL	1.9 ± 0.4	13.9 ± 4.1	367 ± 171	0.14	$(4 \pm 1)x10^{-14}$	$\begin{array}{c} (1.98\pm 0.09) \\ x10^6 \end{array}$
NPL-2	NPL	2.1 ± 0.4	16.3 ± 3.7	557 ± 208	0.13	$(5.7 \pm 1)_{14} x 10^{-1}$	$\begin{array}{c} (2.35\pm 0.07) \\ x10^6 \end{array}$
NPL-3	NPL	2.4 ± 0.5	11.0 ± 2.7	290 ± 117	0.22	$(1.6 \pm 1)_{14} x 10^{-1}$	$(1.32\pm 0.08) \\ x10^6$
NPL-4	NPL	2.9 ± 0.9	10.5 ± 2.1	320 ± 134	0.28	$(2.2 \pm 0.6) x 10^{-14}$	
NW-1	NW	2.6 ± 05	49.5 ± 15.9	334 ± 140	19.04	$(2.8 \pm 0.9) x 10^{-14}$	$(1.72\pm 0.06) \\ x10^6$
dSize-QDs ¹	QD	10.5 ± 0.5	12.2 ± 0.5	1345 ± 101	1.16	$(12 \pm 2)_{14} x 10^{-14}$	$(4.5 \pm 0.5) x 10^5$
	QD	8.7 ± 0.4	10 ± 0.5	760 ± 64	1.15	$(8 \pm 1)x10^{-14}$	$(1.8 \pm 0.2) x 10^5$
	QD	6.4 ± 0.4	7.4 ± 0.5	300 ± 40	1.16	$\begin{array}{c} (3.1 \pm \\ 0.7) x 10^{-14} \end{array}$	$\begin{array}{c} (0.61 \pm \\ 0.04) x 10^5 \end{array}$
	QD	4.5 ± 0.5	5.8 ± 0.6	120 ± 22	1.29	$(1.3 \pm 0.4) \times 10^{-14}$	$\begin{array}{c} (0.29 \pm \\ 0.07) x 10^5 \end{array}$
	QD	3.9 ± 0.5	5.2 ± 0.6	80 ± 16	1.33	$(9\pm3)x10^{-15}$	$\begin{array}{c} (0.16 \pm \\ 0.03) x 10^5 \end{array}$
dMorph ⁸	QD	6.2	6.2	240.0	1.00	1.87x10 ⁻¹⁴	
	NPL	3.1	9.8	300.0	0.32	2.68x10 ⁻¹⁴	NA
	NW	2.2	36.6	180.0	16.64	1.67x10 ⁻¹⁴	

The calculated OPLA and TPA cross-sections (σ^1 and σ^2 respectively) are summarized in Table 1, accompanied by the dimension information of each sample. The relevant results for CsPbBr₃ NCs in our previous work and literature are also included for broader comparison. We first study

the dependence of the cross-sections on the NCs volume and critical dimension (i.e., the length of the smallest dimension, also noted as thickness) as illustrated in Fig. 2. The σ^1 shows a linear relationship with the NC volume as shown in Figure 2A, consistent with previous results,⁸ which indicates the identical optical transition mode to the bulk material.²⁷ In addition, the volume-normalized cross-section values (i.e., σ^1/V) are fixed to be (8.5 ± 0.3)x10⁻¹⁷ cm²/nm³ independent of the NC thickness as observed in Figure 2B. The volume independence implies the negligible effect of quantum confinement on the optical absorption transition. We have argued in our previous study that such linear size-dependence of OPLA cross-section should still be valid if the excitation energies are far above the band-edge (~400 nm in this case) since the density of states in this region resembled that of the bulk material.²⁸

On the contrary, σ^2 of all the NCs exhibit no clear dependence on the volumes of NCs, as seen in **Figure 2C**. The volume-normalized σ^2 (also well-known as TPA coefficient β) are also independent of the NC thickness as shown in **Figure 2D**:

$$\frac{\sigma^{(2)}}{V_{NC}} = \beta \tag{8}$$

Previously research demonstrated a simple TPA cross-section power dependence on the NC dimension. ¹ Apparently, such a model cannot interpret the significant deviation among NCs with different morphologies. In other words, there should be other morphological-related parameters that play a critical role in the optical transition.²⁹



Figure 2. A) OPLA cross-section (σ^1) at 400 nm vs. volume. B) Volume normalized OPLA cross-section (σ^1/V) vs. thickness. C) TPA cross-section (σ^2) at 800 nm vs volume. D) TPA coefficient β vs. thickness. Comparison of calculated results (This work) with reported results from (dSize-QDs)¹ (dMorph)⁸.

A previous study on the TPA process in CdSe NCs demonstrates the influence of the local field on the absorption transition when asymmetric dimensionality occurs in the NCs.¹¹ This is mainly due to variation in the polarization of the NCs concerning the external electromagnetic field, known as local field, ^{11, 29}. Such local field varies depending on the shape of the object. ¹², The local field factor is known as $f_{(w)}$ for a simplified sphere can be expressed as:

$$f_{(w)} = \frac{3\epsilon_m}{2\epsilon_m + \epsilon_s} \tag{9}$$

Where ϵ_m is the dielectric constant of the surrounding medium and ϵ_s is the dielectric constant of the object. Such a model applies very well to QD NCs with symmetric shapes. However, for asymmetric objects like our NPLs and NW, the local permittivity of the object is modulated by a particular shape parameter, the so-called depolarization factor related to the AR. The depolarization factors along the long semiaxis (L_z) and perpendicular to the long semiaxis ($L_{x,y}$) of various morphologies have been previously calculated by Osborn.³⁰ (see further details SI). Here we can apply a prolate spheroid model to NW and an oblate spheroid model for NPLs.^{7, 13} In those spheroids models, the local field can be expressed as a function of depolarization factors ($L_i = L_x$, L_y and L_z):⁷

$$f_{(w)} = \frac{1}{1 + L_i \left(\frac{\epsilon_s}{\epsilon_m} - 1\right)} \tag{10}$$

Now that we have the local field extracted, the TPA coefficient β can then be expressed by the modification of the absorption coefficient of bulk β_{bulk} as shown in eq 11.³¹

$$\beta = \frac{(f_w)^4 N \frac{h\omega}{n_c} \beta_{bulk}}{V_{NC}} \tag{11}$$

Where n_c = density of unit cells in bulk, N is the number of cells in the NC, ω = the frequency of the incident radiation, β_{bulk} value is 3.7 cm/GW CsPbBr3³², and $f_{(w)}$ can be calculated from eq 10. Figure 3 shows the dependence of ARs in β for all the NCs in the study while the dashed line refer to the theoretical modeling based on eq 10 and 11. The experimental values agree with the local field theory model where the lowest β value occurs in the objects with AR close to 1 (i.e. QDs) while our NPLs with AR<1 and NW with AR>1 are expected to have higher β values. This is because the symmetric sphere has three identical depolarization factors. However, in ellipsoids that spherical symmetry is broken, causing the polarizabilities to be different in all the 3 dimensions.¹² Such deviations can significantly alter spectroscopic characteristics.²⁹ The pronounced effect we observed in the TPA coefficients is attributed to their quartet dependence of the field factor compared with quadratic dependence for OPLA absorption cross-section. ³³ As a result, the TPA absorption efficiency can be significantly enhanced due to local field effects.



$$\sigma^{1} = \frac{2\omega}{n_{m}} V_{QD} \left| f(\omega)_{QD} \right|^{2} n_{s} k_{s}$$
(12)

Figure 3 Dependence of TPA coefficient β to AR of different-shaped NCs blue are NPLs, and light blue are NW. The green dots are reported values of QDs, and the light green dotted lines are calculated from local field theory at different AR for the different shapes. The AR is defined as AR_{NW}= L/d for NW, with L=length and d= diameter, AR_{NPL}= t/L for NPL with t= thickness and L average length, and AR_{OD}= lx/ly for QD.

One step further, we studied whether the asymmetric dimensionality would influence the excitedstate dynamics of the NCs by characterizing the OPLA and TPA induced exciton (τ^1) and biexciton (τ^2) lifetime, respectively. The exciton lifetime can be extracted from the exponential decay fitting of the GSB decay at the lowest fluence (2*10¹² photons pulse⁻¹ cm⁻²) corresponding to the average excitation density <N> from 0.04 to 0.10, where no multi-exciton recombination can exist (See S8 in SI). The exciton lifetime τ_1 is shown in Figure 4C with various NCs thicknesses. The biexciton Auger recombination lifetime can be calculated from GSB decays with higher excitation intensity.²⁴ We first subtract the GSB kinetics at high fluence (2>N>1) with one exciton GSB decay from low fluence measurements (N<<1)) with their amplitude normalized at the long time delay > 200 ps (Figure 4A). As shown in Figure 4b, the residual decays feature merely a two-exciton Auger recombination process. The biexciton lifetime (τ^2) can then be confirmed as the average lifetime from the mono-exponential fitting of all the kinetics at various fluences measured for one sample. Such a strategy has been applied in the analysis of our samples for both TPA and OPLA conditions. As summarized in Figure 4D, the biexciton lifetimes for all samples are identical between OPLA and TPA conditions, about five times longer than the single exciton lifetime. The results obtained for biexciton lifetime agree with 9 ± 1 ps biexciton-lifetime obtained by previously reported CsPbBr₃ NPL with dimensions 4 ± 2 nm thickness and 23 ± 7 nm length.³⁴

As illustrated in Figures 4C 4D, it is clear that both τ^1 and τ^2 exhibit independence on NC morphology and TPA/OPLA conditions. The identical excited-state dynamics between OPLA and TPA conditions should be attributed to the narrow size distribution of the NCs and especially the very similar and narrow thickness distribution. Our previous study shows that the deviation between OPLA and TPA-induced excited-state lifetime is mainly induced by the change of excitation distribution among various sized QDs between the two cases.³⁵ The morphology or size-dependent exciton or biexciton dynamics have been widely observed in nanostructures following a universal volume scaling law.^{36,37,38} However, such monotonous scaling could be significantly suppressed by the quantum confinement.³⁹ This could explain our observation as all the samples are in a strong confinement regime as evaluated above.



Figure 4 A) Tail normalized GSB decay for NPL-1 excited at 400 nm B) Subtraction of one exciton decay from Tail normalized GSB decay for NPL-1 excited at 400 nm C) Exciton lifetime at 400 nm excitation and 800 nm excitation in different thickness NCs. D) Bi-exciton lifetime at 400 nm excitation and 800 nm excitation in different thickness NCs.

CONCLUSION

We have successfully synthesized low-dimensional CsPbBr₃ blue-emitting NPL and NW with various aspect ratios. The TPA and OPLA cross-sections have been characterized from the TAS study. The results show that the σ^1 shows a linear dependency to the volume of all the NCs as expected. However, their TPA cross-sections are dependent on the NC aspect ratios following the local field theory model, where QDs with AR=1 exhibit the lowest values. Nevertheless, we demonstrated that the excited-state lifetimes of all the NCs are independent of the morphologic

both at OPLA and TPA conditions, which can be due to their strong quantum confinement that suppresses the classic size scaling law. Our findings provide clear guidance for materials engineering in TPA-related applications: Nanostructures with high aspect ratios such as NW and NPLs potentials perform better due to the higher absorption cross-section and identical excited state dynamics.

ASSOCIATED CONTENT:

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Morphology dependent one-photon and two-photon absorption properties in Blue Emitting CsPbBr₃ nanocrystals

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(S1) Sample preparation

Synthesis Method:

CsPbBr₃ NPs of different morphologies are synthesized following a variation of the previously published procedure.¹

Materials: PbBr₂, Cs₂CO₃, Oleic Acid (OA 90%), Oleylamine (OLA 70%), 1-Octadecene (ODE for synthesis), HBr (48%), and Methyl Acetate (for synthesis) were purchased from Sigma Aldrich. Hexane (GC grade) was purchased from Supelco. ODE, HBr, and Hexane are dehydrated for 24 hours using molecular sieves and degassed at 120°C before any reaction. OA and OLA are degassed at 120°C before any reaction.

Cesium oleate synthesis: In a 50 mL pear-shaped flask, 0.163 g of Cs₂CO₃ was added with 9 mL ODE and 1 mL of OA. This mixture is degassed for 1 hour at 120°C. Then it is set under argon for 10 min at 150°C. Afterward, it is preheated to 100°C for nanoparticle synthesis.

HBr-OLA synthesis: In a 100 mL round bottom flask, 1 mL HBr was added with 10 mL OLA. This mixture is degassed for 1 hour at 120°C. Then it is set under argon for 1 hour at 150°C. This is preheated to 80°C for nanoparticle synthesis.

Synthesis of nanoparticles: In a 100 mL three-neck round bottom flask, add 0.14 g of PbBr₂, 20 mL ODE, and degas under vacuum for 1 hour at 120°C. Then set under inert conditions (Ar) afterward, and 1 mL of OLA and 1 mL OA are injected. HBr-OLA is injected (0.8 mL or 1.0 mL for NPLs, 1.2 mL for NW). The mixture reached to injection temperature (90°C or 100°C). When the temperature is reached, 0.8 mL of cesium oleate is added swiftly, and the flask is immediately put in an ice bath.

Purification of nanoparticles:

When the reaction mixture is below 50°C, it is centrifuged 15 min 6500 rpm, and the supernatant is collected and precipitated within a mixture 2:1 methyl acetate: supernatant. This is centrifuged for 15 min at 6500 rpm. An excess of methyl acetate is added to the supernatant and is centrifuged for 20 min at 10000 rpm. The precipitate is dissolved in 6 mL hexane.

Name	Injection temperature (°C)	Amount HBr-OLA (mL)	Thickness (nm)	FWHM thickness	Length (nm)	FWHM length
NPL-1	90	0.8	1.9 ± 0.4	0.9	13.9 ± 4.1	4.4
NPL-2	90	1.0	2.1 ± 0.4	0.7	16.3 ± 3.7	6.6
NPL-3	100	1.0	2.4 ± 0.5	1.0	11.0 ± 2.7	3.1
NPL-4	90	1.0	2.9 ± 0.9	2.7	10.5 ± 2.1	4.1
NW-1	90	1.2	2.6 ± 0.5	0.9	49.5 ± 15.9	34.5

Table SI. Sample synthesis conditions and TEM characterization.

(S2) TEM Characterization



Figure S1 TEM images of samples previously presented left top view right side view.



Figure S2 TEM histograms of samples

(S3) Temperature dependent PL and calculation of exciton binding energy.

We calculated the exciton binding energy of our NCs samples using temperature-dependent photoluminescence. PL spectra of NCs were measured at temperatures ranging from 78~300K in a cryostat, and the integrated PL intensities I(T) were calculated. Here the PL intensity decreased with increased temperatures due to the thermal dissociation of excitons at higher temperatures, see Fig S3 A. The temperature-dependent PL intensity can then be expressed as follows ^{2,3}:

$$I(T) = \frac{I_0}{1 + Ae^{(\frac{-E_b}{k_B T})}}$$
(S1)

 I_0 is the PL intensity at low temperature, and k_B is the Boltzmann constant. From the linear fitting of Ln($I_0/I(T)$ -1) vs. 1/k_BT plot in Fig. S3B, we can obtain the Eb as the slope of 57 ± 3 meV.



Figure S3 A) Temperature-dependent PL of NPL-2 sample B) ln(I₀/I(T)-1) vs. 1/k_BT plot of temperature-dependent photoluminescence of NCs at temperatures from 78-300 K.

(S4) Transient absorption (TA)

TA experiments were performed by using a femtosecond pump-probe setup. Laser pulses (800 nm, 150 fs pulse length, 3 kHz repetition rate) were generated by Ti:sapphire amplifier with

integrated oscillator and pump lasers (Libra LHE, Coherent Inc.) and Transient Absorption Spectrometer (TAS, Newport Corp.). Briefly, the output of a Ti:sapphire amplifier with integrated oscillator and pump lasers (800 nm, 150 fs, 3 kHz, Libra LHE, Coherent Inc.) was split into two beams which were used to generate 400 nm light through the doubling crystal as a pump beam and to generate the white light through CaF₂ crystal as a probe. The two-photon absorption experiments obtained the 800 nm pump pulses directly from the amplifier. The probe beam was split into two beams, one through the sample and another as a reference. The generated supercontinuum was then focused onto the sample and overlapped with the pump beam. The transient spectra were detected with a fiber-coupled CCD-based monochromator (Oriel, Newport). Samples for transient absorption experiments were kept in the dark between each measurement.

(S5) OPLA Cross-section calculation

The OPLA cross-section can be calculated from a pump-probe experiment previously reported. ^{4,5} The samples are excited with a 400 nm pump with fluence ranging from (0.2 to 6)x10¹³ photons x pulse⁻¹ cm⁻² and probed by white light through CaF₂ crystal. The GSB decay of the NCs represents the exciton population decay in the NCs. Assuming a behavior of the exciton population as a Poissonian distribution^{6,7} we obtain:

$$P_N = \frac{e^{-\langle N \rangle} \langle N \rangle^N}{N!}$$
 (S2)

where P_N is the fraction of NCs with N excitons, N denotes the number of excitons, and $\langle N \rangle$ the average exciton number per NC. When the optical density of the sample is low, the excitation intensity does not vary in the sample volume, and $\langle N \rangle$ can be expressed as:

$$\langle N \rangle = \sigma^1 * I \tag{S3}$$

where *I* is the pump intensity corresponding to the excitation fluence (photons per pulse per excitation area) and σ^1 is the OPLA cross-section at a specific excitation wavelength (400 nm). The method combines equations (1) and (2), and the fraction of excited NCs (P_{exc}) can be calculated as follows:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 - e^{-\sigma^1 I}$$
(S4)

To avoid the effect of multiple excitation decay, the pump intensity dependence is measured from 1 ns signal up to 8 ns. Multiple excitations in a NC decays through the Auger process, which is significantly faster than the radiative decay of the single excitation. This means that once the Auger process is completed, the signal amplitude is proportional to P_{exc} . All excited CsPbBr3 NCs contain only a single exciton at a long timescale. In this scenario, ΔA (I, t ≥ 1 ns) is proportional to P_{exc} and decays mono-exponentially. We can rescale it to the corresponding signal at t=0, named $\Delta A_0(I)$. ΔA_{0max} represents the highest single exciton signal (all NPLs excited) rescaled to t=0.

$$\Delta A_0(I) = \frac{\Delta A(I, t \ge 1 ns)}{e^{-t/\tau}} = \Delta A_{0,max} \left(1 - e^{-\left(\frac{I}{I_0}\right)\langle N \rangle_0}\right)$$
(S5)

Here the lowest pump intensity (lowest fluence) utilized in TA measurement was defined as I_0 . We used an intensity low enough that multiple excitons in one NC can be neglected. Clearly, $\langle N \rangle_0$ can be obtained from the performed exponential fit of the $\Delta A_0(I)$ vs. (I/I₀) plots as described in equation (S5), and σ^1 can be calculated according to equation (S3). Figure S4 shows the GSB decays with ascending pump intensity for each NC and in the insert the exponential relationship of $\Delta A_0(I)$ vs. (I/I₀) with the result for each σ^1 . In table S2, the values of σ^1 are summarized and the concentration and extinction coefficient.



Figure S4. Pump-intensity dependence of TA dynamics for CsPbBr3 NPLs, and NW, excited at 400 nm. With the calculation of absorption cross-section from OPLA.

The extinction coefficient can be calculated from the following relationship

$$\sigma(in\ cm^2) = \frac{1000 \cdot \ln(10)}{N_a} \cdot \varepsilon = 3.825 \cdot 10^{-21} \varepsilon \left(in\ \frac{L}{mol \cdot cm}\right)$$
(S6)

The concentration is calculated from Beer-Lambert law.

Table S2 OPLA cross-section, concentration, and extinction coefficient.

Sample	σ^1 (cm ²)	^{ε400 nm} (L cm ⁻¹ mol ⁻¹)	C (µM/L)
NPL-1	$(4.1 \pm 1.1) \times 10^{-14}$	$(1.1 \pm 0.3) \times 10^7$	1.1 ± 0.3
NPL-2	$(5.7 \pm 1.0) \times 10^{-14}$	$(1.5 \pm 0.3) \times 10^7$	0.6 ± 0.1
NPL-3	$(1.6 \pm 1.0) \times 10^{-14}$	$(4.1 \pm 0.1) \times 10^6$	3.4 ± 0.9
NPL-4	$(2.2 \pm 0.6) \times 10^{-14}$	$(5.7 \pm 0.1) \times 10^{6}$	1.5 ± 0.4
NW-1	$(2.8 \pm 0.9) x 10^{-14}$	$(7.3 \pm 2.3) \times 10^{6}$	1.9 ± 0.6

(S6) TPA coefficient calculation

The two-photon absorption cross-section (σ^2) is calculated from the TAS method, reported previously.^{4,8} The TAS is performed in the samples with an excitation pump of 800 nm, the fluence of the excitation pulse is performed in an increasing manner from (4.3 to 38.5)x10¹⁴ photons*pulse⁻¹ cm⁻² (Figure S5). The extrapolated amplitude at t=0 from the long timescale of each GSB decay is plotted against the fluence at 800 nm excitation and the 400 nm excitation performed previously for the OPLA. The ratio between extrapolated GSB signal amplitude ($-\Delta A$) and the linear absorbance of QDs (A) at exciton transition energy ($-\Delta A/A$) quantifies the number of photogenerated excitons in QDs within the excitation optical path. The signal amplitude is proportional to the exciton population in the QDs. The population depends on the excitation fluence linearly for the OPLA (Figure S6, left) and quadratically for the TPA (Figure S6, right) ⁸:

$$\frac{-\Delta A}{A} = C_1 * \phi_{400}$$
(S7)
$$\frac{-\Delta A}{A} = C_2 * \phi_{800}^2$$
(S8)

Here, C1 and C2 are the fitting parameters from the experimental fluence dependence reported in Figure 6 and summarized in Table S3.



Figure S5 Pump-intensity dependence of TA dynamics for CsPbBr3 NPLs, and NW, pumped at 800 nm.



Figure S6. Excitation fluence dependence to ground state bleaching signal (extrapolated to t=0) normalized with absorbance at first exciton transition energy (- $\Delta A/A$) for CsPbBr₃ NCs with different dimensions. Left panel: 400 nm excitation; Right panel: 800 nm excitation.

Table S3. Summary of factors C1 C2

Sample	C1 (cm ² /mJ)	$C2 (cm^4/mJ^2)$
NPL1	1.81 ± 0.09	$(7.9 \pm 0.3)^* 10^{-2}$
NPL2	1.32 ± 0.08	$(4.5 \pm 0.3)^* 10^{-2}$
NPL3	0.61 ± 0.02	$(3.99 \pm 0.08)*10^{-2}$
NPL4	0.86 ± 0.05	
NW-1	1.06 ± 0.04	$(6.1 \pm 0.3)^* 10^{-2}$

The OPLA and TPA induced excitation density (ρ) is related to OPLA and TPA coefficients at weak excitation fluence (the average number of excitons per NC $\langle N \rangle < 1$):

$$\rho = \frac{\int_{-\infty}^{+\infty} I_{400}(t) dt \left(1 - e^{-\alpha^{1}L}\right)}{h v_{400}} = \frac{I_{400}^{peak} \tau \left(1 - e^{-\alpha^{1}L}\right)}{h v_{400}}$$
(S9)
$$\rho = \frac{\int_{-\infty}^{+\infty} (I_{800}(t))^{2} dt \, \alpha^{2}L}{2h v_{800}} = \frac{(I_{400}^{peak})^{2} \tau \alpha^{2}L}{2\sqrt{2}h v_{800}}$$
(S10)

 $I_{400}(t)$ is the intensity of the 400 nm laser pulse, and $I_{800}(t)$ is the intensity of the 800 nm laser pulse, α^1 is the OPLA coefficient, α^2 is the TPA coefficient, L is the sample thickness (1 mm), v₄₀₀ and v₈₀₀ is the frequency of the 400 nm laser pulse and 800 nm respectively, *h* is plank constant. Factor 2 in Eq.S4 considers the requirement of two photons to generate one exciton. We assume the 400 nm and 800 nm pulses are Gaussian. Hence, we can carry the integration and express it via the peak intensity (I_{400}^{peak} , I_{800}^{peak}) at 400 nm and 800 nm respectively, and pulse duration (τ =150 fs). With the equations S7 to S10, we can correlate the OPLA and TPA coefficients to the experimentally fitted parameters C₁ and C₂ found in table S3:

$$C_1 \propto \frac{(1-e^{-\alpha^1 L})}{hv_{400}}$$
 (S11)
 $C_2 \propto \frac{\alpha^2 L}{2\sqrt{2}hv_{800}\tau}$ (S12)

We have assumed that the intensity change of the 800 nm laser beam due to the TPA while passing the sample is negligible. Then the TPA coefficient can be calculated as:

$$\alpha^{2} = \frac{c_{2}}{c_{1}} \frac{\sqrt{2}\tau}{L} (1 - e^{-\alpha^{1}L})$$
(S13)

(S7) TPA Cross-section calculation

Then the TPA cross-section can be calculated from

$$\sigma^2 = \frac{h v_{800} \alpha^2}{(f_{\omega})^4 N}$$
 (S14)

Where *h* plank constant, *v* frequency at 800 nm, N concentration in particles per cm³ and $(f_{\omega})^4$ the corresponding local field factor to the aspect ratio of each sample. The local field factor is explained in the next section. Lastly, we calculate the TPA cross-section divided by the NC volume, a factor mostly known as the TPA coefficient β .

$$\frac{\sigma^{(2)}}{V_{NC}} = \beta \quad (S15)$$

(S8) Local field Calculation

As mentioned in the main article, geometry is a determinant factor that modulates the local field. The case of a sphere is shown in the main article. As previously said, the sphere is the model used to describe the local field of a cube shape. For NW, the best geometry to describe its dielectric response is the prolate spheroid and for NPL is an oblate spheroid. In Fig S7, the NC structure corresponding to its model for local field calculation is shown.



Figure S7 Nanostructure and its corresponding model for local field factor.

We will now discuss the calculation of the local field factor for the oblate and prolate spheroids. For a prolate and oblate spheroid the local field factor is:⁹

$$f_{(w)} = \frac{1}{1 + L_i \left(\frac{\epsilon_s}{\epsilon_m} - 1\right)}$$
(S16)

 ϵ_m = dielectric constant of the surrounding medium (toluene 2.38) and ϵ_s =dielectric constant of the semiconductor CsPbBr₃ (7.3).¹⁰ L_i are the depolarization factors L_x, L_y, and L_z. Osborn¹¹ has previously calculated these factors.

For a prolate spheroid a >b=c, AR=m=a/c. the a, b, c coordinates are as seen in figure S7

$$L_{z} = \frac{1}{m^{2}-1} \left(\frac{m}{2\sqrt{(m^{2}-1)}} * ln\left(\frac{m+\sqrt{m^{2}+1}}{m-\sqrt{m^{2}-1}}\right) - 1 \right)$$
(S17)
$$L_{x/y} = \frac{m}{2(m^{2}-1)} \left(m - \frac{1}{2\sqrt{(m^{2}-1)}} * ln\left(\frac{m+\sqrt{m^{2}+1}}{m-\sqrt{m^{2}-1}}\right) \right)$$
(S18)

And for an oblate spheroid a = b > c, AR = m = a/c

$$L_{z} = \frac{m^{2}}{m^{2}-1} \left(1 - \frac{m1}{\sqrt{(m^{2}-1)}} \arcsin\left(\frac{\sqrt{m^{2}+1}}{m}\right) \right)$$
(S19)
$$L_{x/y} = \frac{1}{2(m^{2}-1)} \left(m^{2}\sqrt{(m^{2}-1)} \arcsin\left(\frac{\sqrt{m^{2}+1}}{m} - 1\right) \right)$$
(S20)

(S9) Exciton and Biexciton lifetime

With the exponential decay fitting of the GSB-decay, the exciton lifetime can be extracted at 400 nm (OPLA) and 800 nm (TPA) excitation.



Figure S8. A) GSB decay at 400 nm excitation (OPLA) B) GSB decay with 800 nm excitation (TPA).

Table S4.	Summary of	of calculated	exciton an	d bi-exciton	lifetimes	at 400 nn	n excitation	and
800 nm ex	citation.							

Sample	Excitor	ı lifetime	Biexcitor	n lifetime
		Excitation wa	velength	
	400 nm	800 nm	400 nm	800 nm
NPL-1	2404 ± 292	2714 ± 936	13.2 ± 2.4	11.2 ± 1.4
NPL-2	3811 ± 585	3272 ± 573	10.3 ± 2.3	9.1 ± 1.3
NPL-3	2034 ± 225	3629 ± 1346		12.5 ± 2.2
NPL-4	1705 ± 95		9.2 ± 2.7	
NW-1	2901 ± 750	2457 ± 205	$7.8\ \pm 0.1$	12.5 ± 2.0
Average	2571 ± 471	3018 ± 293	10.1 ± 1.3	11.3 ± 0.9

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4 CsPbBr₃ Nanocrystal Micro-Assembly: EFFECTS ON PHOTOPHYSICS (Article II)

Besides the morphology of individual NC, as we discussed in the previous chapter, the macroscopic morphology of NCs, i.e. microassemblies in a superlattice or mosaic nanotile solids film, give the assembly different properties than the NCs alone. An essential issue to tackle is how micro-assembly or NCs arrangement in a film alter their photophysics.

We investigated the charge carrier transport dynamics in benchmark DDAB capped CsPbBr₃ QD solids by constructing a bisized QDs mixture film. As we mentioned before, DDAB is a short capping agent that may promote the NC stability and inter-dot charge transfer. The carrier transport dynamics are then determined using a Zhitomirsky 3D modeling, where carrier diffusion mean free path is controlled by the mixture's population of acceptors (i.e. one size of QDs).

Our results confirm higher carrier transport efficiency by obtaining diffusion lengths of charge carriers to be \sim 239 ± 16 nm in 10 nm CsPbBr₃ QDs and the mobility values of electrons and holes to be 2.1 (± 0.1) and 0.69 (± 0.03) cm2/V s, respectively in comparison to 71 nm reported for OA/OLA capping agent.

We also discover the effect of NC size on carrier diffusion. Excited-state dynamics of the QDs solids obtained from ultrafast transient absorption spectroscopy reveal that photogenerated electrons and holes are difficult to diffuse among small-sized QDs (4 nm) due to the strong quantum confinement. On the other hand, photo-induced electrons and holes in large-sized QDs (10 nm) would diffuse towards the interface with the small-sized QD, followed by a recombination process.

The synthesis of NCs always generates a size distribution, with the solid film unavoidable involving the mixtures of NCs with various sizes. Modeling the arrangement of the NCs in a film and demonstrating their modification on the actual photophysics can become a crucial step for the development of efficient devices.

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Charge Carrier Diffusion Dynamics in Multisized Quaternary Alkylammonium-Capped CsPbBr₃ Perovskite Nanocrystal Solids

Sol Gutiérrez Álvarez, Weihua Lin, Mohamed Abdellah, Jie Meng, Karel Žídek, Tõnu Pullerits, and Kaibo Zheng*



investigated the charge carrier transport dynamics in DDAB-capped CsPbBr₃ QD solids by constructing a bi-sized QD mixture film. Charge carrier diffusion can be monitored by quantitatively varying the ratio between two sizes of QDs, which varies the mean free path of the carriers in each QD cluster. Excited-state dynamics of the QD solids obtained from ultrafast transient absorption spectroscopy reveals that the photogenerated electrons and holes are difficult to diffuse among small-sized QDs (4 nm) due to the strong quantum confinement. On the other hand, both photoinduced electrons and holes in large-sized QDs (10 nm) would diffuse toward the interface with the small-sized QDs, followed by a recombination process. Combining the carrier diffusion study with a Monte Carlo simulation on the QD assembly in the mixture films, we can calculate the diffusion lengths of charge carriers to be $\sim 239 \pm 16$ nm in 10 nm CsPbBr₃ QDs and the mobility values of electrons and holes to be $2.1 (\pm 0.1)$ and $0.69 (\pm 0.03) \text{ cm}^2/\text{V s}$, respectively. Both parameters indicate an efficient charge carrier transport in DDAB-capped QD films, which rationalized the perfect performance of their LED device application.

KEYWORDS: ultrafast spectroscopy, diffusion lengths, CsPbBr3, DDAB, quantum dot photovoltaics, carrier transport, charge transfer

INTRODUCTION

CsPbBr₃ colloidal perovskite quantum dots (QDs) have recently attracted great interest to the research community due to their outstanding optoelectronic properties.^{1,2} The facile solution-processed synthesis, size-tunable optical bandgap, and near-unity photoluminescence quantum yields (PLQYs), together with narrow emission bandwidth, render these materials great potential in different applications such as photodetectors, solar cells, and especially light-emitting diodes (LEDs).^{1,3–6}

(DDAB) in LED devices. The device performance significantly

depends on both the diffusion length and the mobility of photoexcited charge carriers in QD solids. Therefore, we

Despite substantial materials and device engineering, the transport of charge carriers in QD solids remains a challenge for LED applications.⁶ The conventional capping agents for CsPbBr₃ QDs such as oleylamine (OLA) and oleic acid (OA) stabilize the QDs but prevent the carrier from hopping across the QDs in the solid. One promising solution is to replace them with smaller capping ligands, which has been done with molecules like octylamine' or di-dodecyl dimethyl ammonium bromide (DDAB).^{8,9} DDAB is a quaternary alkylammonium with a halide ion pair that provides strong anchoring to the QD surface. This leads to superior surface passivation with an enhanced PLQY.^{10,11} In addition, shorter alkyl chains of

DDAB compared with OA and OLA are believed to facilitate the charge carrier transport.^{12,13} Significant improvement in LED external quantum efficiency (EQE) using DDAB-capped QDs has been reported recently, with the recording value reaching 13.4%.^{14,15} However, the enhancement of the charge carrier transport by the DDAB capping agent has not been confirmed, with the important parameters including carrier mobility and diffusion coefficient.^{4,16,17} Furthermore, the assembly of the QDs in the solid plays a vital role in the charge transport in the solid, which should also be influenced by the surface capping agents. Therefore, a systematic characterization of the charge carrier transport dynamics in a DDAB-capping QD solid film is of great importance to rationalize the underlying mechanism of the optoelectronic devices.

μ _{h+}~ 0.69 cm²/Vs

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Figure 1. (A) Absorption (straight line) and photoluminescence (dotted line) spectra of pure QDs with sizes of 4 and 10 nm. (B) TEM images and size distribution of two sizes of QDs. (C) Absorption spectra of the mixture film with ascending percentage of 10 nm QD bandgap (BG) extracted from the Tauc plot in Figure S3. (D) Energy band alignment.

There are several techniques to study charge carrier transport in QD solids. The electrical methods (e.g., field effect transistor and Hall effect measurements) are highly sensitive to electrode contact and device configuration.¹ Instead, the optical methods focus more on the intrinsic features of the QD solid materials.^{21–23} Those methods usually introduce an acceptor to terminate the charge carrier diffusion and probe the lifetime of the charge carriers by ultrafast spectroscopies before they get trapped by the acceptors. In most cases, the target film is coated onto the acceptor layer, and different charge carrier lifetimes are obtained by varying the thickness of the target layer, which is defined as a 1D model.²⁴ In the 3D model, donors and acceptors are intermixed and the diffusion path of the charge carrier is controlled by the inter-ratio between the donors and acceptors.^{4,25} Such a 3D model is closer to the functioning status in a real device.

In this paper, we use this 3D model to analyze the charge carrier transport dynamics in randomly mixed two-sized DDAB-capped CsPbBr₃ QD solids (4 nm QD (QD-4) and 10 nm QD (QD-10)) by fs-TA. The ratio between two QDs varies to control the mean free path of the photogenerated charge carriers. Singular value decomposition (SVD) analysis first revealed that the carriers in QD-10 diffuse and get recombined with the carriers in QD-4. This means smaller QDs can be considered as acceptors in the bi-sized QD solid. We then vary the ratio between QD-10 and QD-4 and measure the mean diffusion time of electrons and holes in QD-10 clusters from the SVD fitting components of TA. In the next step, a Monte Carlo simulation was employed to model the assembly of the QDs and provided the average distance

between the donor (QD-10) and the acceptor (QD-4). The diffusion coefficient and electron/hole mobility for QD-10 in the solids were then calculated using the 3D mixture diffusion model. The electron mobility obtained is (2.1 ± 0.1) cm²/Vs and the hole mobility is (0.69 ± 0.03) cm²/Vs. The diffusion length of the photoinduced charge carriers in the QD-10 obtained is 239 ± 16 nm. In contrast, a previous report shows that only energy transfer can occur in OA-capped QD solids with much lower $L_{\rm D}$ of exciton migration (50 nm).²⁶ This confirms the improved charge carrier separation and transportation in DDAB-capped QD solids, which rationalize the enhanced device performance. Also, the Monte Carlo simulation shows how the concentration of the different sizes of QDs in the solid influences the average QD-QD distance and determines the interdot charge transfer efficiency. We believe that our results can be a useful guide of the film preparation as building blocks in the perovskite QD LED devices.

RESULTS AND DISCUSSION

Two sizes of DDAB-capped CsPbBr₃ quantum dots (QDs) were employed in our study (i.e., 4 nm (QD-4) and 10 nm (QD-10)). They were synthesized by a previously reported hot injection method initially capped by OA and OLA and afterward underwent a surface ligand exchange to DDAB.²⁷ The detailed synthesis procedure for QDs is provided in the Supporting Information.

Figure 1A shows the UV-Vis absorption and photoluminescence spectra of each size of QDs in the colloidal solution form. The absorption band edges for QD-10 and QD-



Figure 2. (A–D) TA spectrodiagram of QD-4, QD-10, and 1.1 and 2.1% mixture samples. Excitation pump at 400 nm. (E, F) TA kinetics of GSB B1 for QD-4 and 1.1 and 2.1% mixture samples. (G, H) TA kinetics of GSB for 10 nm QD and 1.1 and 2.1% mixture samples.

4 are located at 497 and 440 nm, respectively. The narrow emission bandwidth of both samples (i.e., 12.3 ± 0.3 nm for QD-4 and 21.6 \pm 0.2 nm for QD-10) indicates their narrow size distribution. The mean sizes of 3.9 ± 0.6 and 9.9 ± 1.2 nm are further confirmed by HR-TEM measurements as seen in Figure 1B and Figure S1. To study the carrier diffusion dynamics, two quantum dots are used in the mixture film. It is commonly believed that larger QDs with a narrower bandgap can be considered as an acceptor to terminate the electron or hole transport due to the energetically favorable charge transfer from big QDs to small QDs.²⁴ The photoexcited charge carriers in donor QDs (i.e., the smaller QDs) change their lifetime when the concentration of the acceptor varies. However, in our system, the situation is different where the big QDs serve as acceptors, which will be discussed later.

To fabricate the QD mixture films, we first mixed two QDs directly in the solution phase with the concentration ratio ($R_{\rm QD} = \frac{C_{\rm QD-10}}{C_{\rm QD-10}+C_{\rm QD-4}} \times 100$) varying from 0.3 to 5.1%. The solid films are then prepared by spin-coating 50 μ L of the mixture onto quartz substrates. In the following text, all the multisized QD films are referred to by these $R_{\rm QD}$ percentage values.

The absorption spectra (Figure 1C) further confirm the mixture between QD-4 and QD-10 in those films with various ratios. The bandgap (BG) change is also depicted in Figure 1C and extracted from the Tauc plot in Figure S3, and the values of BG for each film are reported in Table S4. The redshift of the QD-4 exciton absorption band can also be observed in the film, with the increment of the QD-10 ratio attributed to the enhanced light scattering from the larger QDs. The energy band alignment between two QDs (Figure 1D) is confirmed by the XPS measurement to probe the valence band maximum (VBM) position (Figure S7) as well as Tauc plots of the absorption spectra (Figure S2) to determine the optical bandgap. The in-band state at 0.82 eV refers to a trap state located in QD-4, which will be explained later. The band alignment indicates that both electron transfer and hole transfer are energetically favorable from QD-4 to QD-10.

The photoinduced charge carrier dynamics in multisized QD films was investigated by transient absorption (TA) spectroscopy. A similar investigation has been implemented in PbS QD solids where one size of QDs is utilized as traps.²⁴ The method is based on the concept that diffusing charge carriers are captured by those traps, determining the diffusion length and lifetime.⁴ Therefore, by introducing a fixed number of traps, the diffusion coefficient can be calculated by tracking the charge carrier lifetimes at various trap densities accordingly.

However, in the following, we will demonstrate that the charge carrier diffusion dynamics in multisized DDAB-capped CsPbBr₃ QD solids is more complicated. Figure 2A,B shows the TA spectra of single-sized QD-4 and QD-10 films. Pronounced ground-state bleach (GB) at the band edge absorption regions B1 and B3 for QD- 4 and QD-10, respectively, can be attributed to the population of the lowest excited-state carriers. In addition, the TA spectrum of QD-4 presents an additional bleach at 470 nm (B2). It could be related to either the GBs of larger-sized QDs with a lower optical bandgap or a sub-bandgap trap state with optical strength for absorption. The TEM analysis of QD-4 can exclude the existence of another distinct size of QDs. Therefore, the B2 band should be attributed to the trap state filling. This can be further verified by the observable absorption tail after the excitonic absorption band edge from 460 to 480 nm in Figure 1A. Such absorptive sub-bandgap trap states have been widely reported in lead halide bulk materials.28,29

In the mixture films, both QD-4 and QD-10 are excited by a 400 nm excitation laser pulse. Therefore, the GB of the band edge exciton transition of the two QDs, i.e. B1, B2, and B3, occurs concurrently as shown in Figure 2C,D. Figure 2C,D demonstrates the TA spectra of mixture films with two typical $R_{\rm QD}$ values of 1.1 and 2.1%.

To reveal the charge transport dynamics, we first compared the TA kinetic traces at B1 and B3 in both mixed films with the neat QD-4 and QD-10 films (Figure 2E–H). The kinetic traces at B1 exhibit a negligible difference between the mixed and neat QD films (Figure 2E,F). On the contrary, TA kinetic

ACS Applied Materials & Interfaces www.acsami.org A 1.1% В 2 1% Δ3 18 ps 1590 ps 0 B1 B2 B3 Energy ₹0 B2 ≮ 1035 ps nergy B3 B1 4315 ps 0 5226 ps 5226 ps 4315 ps . 1035 ps 18 ps 1590 ps 450 500 450 500 Wavelength (nm) Wavelength (nm)

Figure 3. SVD components of mixture films and the diagram of the process of decay-associated spectra (DAS) at (A) 1.1% and (B) 2.1%.

traces at B3 corresponding to the excited-state population of QD-10 exhibit a difference between the mixed films and the neat QD-10 film as shown in Figure 2G,H. At the early timescale, the B3 kinetics in the 1.1% film shows a slow rising component up to 14 ps compared with the instantaneous rise of the signal in the pure QD-10 film in Figure 2G. Such a slow rise is less pronounced in the 2.1% film as well as in other mixed films as shown in Figure 2H and Figure S4B. In general, the slower buildup of the TA GB in the mixture system compared with the single components indicates the charge injection from the donor to the acceptor. Unique early time rising kinetics in the 1.1% film suggests different charge transfer dynamics from the other mixed film, which will be discussed later. At the longer timescale, the TA kinetics of B3 decays slower in mixed films than the neat QD-10 film, with the decay rate increasing with the decrease in QD-10 concentration. This can be attributed to the delayed charge transfer after the charge carrier diffusion in the donor observed in the multisized QD film system.²

The above single-wavelength kinetics manifests the diffusion-assisted interfacial charge transfer in our multisized QD films. To unambitiously assign each photoinduced process in the mixture film, we carried out the singular value decomposition (SVD) of the TA dynamics where the decay-associated spectra (DAS) have been extracted. Figure 3 summarizes the different behaviors for the 1.1% mixture and 2.1% mixture from the SVD analysis.

In the 1.1% film, we can extract three DAS components: one short-lived component with a lifetime of 18 ps and two longlived components with lifetimes of 950 and 5022 ps. The lifetime of the fastest component (18 ps) resembles the slow rising time of B3 kinetics in the mixture film, as shown in Figure 2G. The negative bands at 450 and 480 nm represent the decay of B1 and B2. The positive band at 508 nm together with the negative band at 495 nm mirrors the excited-state absorption (A3), representing the rise of A3 and GB of QD-10 (B3), respectively. Therefore, they refer to the appearance of A3 and B3 in QD-10, which can be further confirmed by the TA kinetics at these wavelengths (more details in Figure S5). Such simultaneous excited-state depopulation in QD-4 with the population in QD-10 is a fingerprint of interdot electron injection or energy transfer³⁰ from QD-4 to QD-10. However, since the exciton binding energy of CsPbBr₃ QDs is in the

order of thermal energy at room temperature, the majority of the photoexcited species should be free carriers in the solids.¹⁶ In addition, electron transfer should be more reasonable at the rates that are observed.³¹

The second component with a lifetime of 1035 ps shows the negative bands at B1, B2, and B3 corresponding to the decay of three GBs at the same time. The excited-state depopulation dynamics within such a lifetime is absent in both individual QD-4 and QD-10 (for details, see Figure S6). Therefore, such simultaneous depopulation of the excited state in two QDs can only be attributed to the interdot charge recombination. Since this recombination also induces the decay of the trap state bleach B2, it must be the recombination of the excited electrons in QD-10 with the excited holes in QD-4. This is because the hole population at VB in QD-4 would also block absorption transition to the trap states, whereas the electron population at CB is independent of such a process. On the other hand, the component with the longest lifetime of 5 ns featured only a negative band of B1 and B3. Therefore, it should be attributed to the recombination of the excited electrons in QD-4 and the excited holes in QD-10 instead. The above recombination process takes into account the time for photogenerated carriers in one size of QD to diffuse to the interface with the other size of QDs. Therefore, the DAS component's lifetime can be utilized to analyze the charge carrier diffusion with various $R_{\rm QD}$ values. The 2.1% mixed film, for instance, exhibits the same two interfacial charge recombination components in SVD fitting but with different lifetimes (Figure 3B). This phenomenon applies to the rest of the mixed films, indicating an R_{QD}-dependent charge carrier diffusion in the mixture film given that the interfacial charge recombination time is independent of the QD assembly. However, we did not observe the ultrafast electron injection component from small QDs to large QDs in the other mixture film. The detailed reason needs to be further explored. The trap state denoted by B2 can either be an electron trap or a hole trap. However, if B2 refers to the hole trapping, we should obtain a 1000 ps hole diffusion time and 5000 ps electron diffusion time from the SVD signal. Despite the similar effective mass of the electron and hole in CsPbBr₃ perovskites, the mobility of the electron in such a perovskite should still be expected to be larger than the hole due to polaron formation.³² According to a previous study, excitation in CsPbBr₃ would

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Figure 4. (A) DAS of the electron recombination process for ascending R_{QDi} (B) SVD-associated kinetic trace for the DAS of the electron recombination process with ascending R_{QDi} ; (C) % trap vs trapping time plot describing the electron diffusion process; (D) DAS of the hole recombination process for ascending R_{QDi} ; (E) SVD-associated kinetic trace for the DAS of the hole recombination process with ascending R_{QDi} ; (F) % trap vs trapping time plot describing the hole diffusion process.



Figure 5. (A) Schematic of the diffusion in 4 and 10 nm QD mixtures in our system. (B) Schematic of the excited-state dynamics between 4 and 10 nm QDs.

generate large electron polarons and small hole polarons, which should lead to a larger electron mobility than the hole.³² In this scenario, we believe that the overall electron diffusion should be more efficient than the hole diffusion, and thus, the above situation to assign B2 as hole traps can be excluded.¹⁰

In the next step, we aim to reveal the dependence of QD-10 concentration on charge diffusion dynamics. We observed that the lifetime of the two long-lived components is increasing with the increment of QD-10 concentration in the mixture film but keeping the primary spectral feature shown in Figure 4A,D with the corresponding SVD fitted component decay trace plotted in Figure 4B,E. This indicates the prolongation of the

charge carrier diffusion as discussed above. Figure 4C,F shows the N_t^{-1} vs τ_{trap} , which will be used for the diffusion parameter calculation later. Interestingly, we notice the same trend in the single-wavelength TA kinetics at B3, but the TA kinetics at B1 almost remains constant as shown in Figure S4A. It occurs together with the reduction of the relative amplitude ratio between B1 and B3 bands in the DAS component, as shown in Figure 4A. All the above phenomena denote that changes in TA dynamics should be dominated by the photophysical processes in QD-10 rather than in QD-4. According to the literature reports, the exciton binding energy (E_b) of large-sized CsPbBr₃ QDs (i.e., 8 nm) is about 40 meV,^{3,33} meaning

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Figure 6. (A) Monte Carlo simulation for two 1.1% R_{QD} layers of 100 nm² set for a minimum deposit of 1000 QDs and a maximum of 5000 QDs. (B) Histogram of the average distance of the first 20 nearest QD-10 to QD-4.

that the major excited species should be dissociated free carriers according to the Saha–Langmuir model.³⁴ On the other hand, a larger E_b as well as numerous surface trap states in smaller QDs is expected to largely hinder the carrier diffusion.³⁵

In addition, the charge recombination at the QD-4 and QD-10 interface is mainly decided by the interdot spacing as well as the energetic driving force extracted from the energy band alignment between two QDs. All those factors are independent of the QD-10 ratio. Consequently, the variation on the overall charge recombination time extracted from the TA dynamics can only be induced by the different charge carrier diffusion time prior to the interfacial recombination, as illustrated in Figure 5A,B.

When more QD-10 are integrated into the mixture film, the average distance between QD-4 and QD-10 would increase as the aggregated domain of the QD-10 cluster starts to expand. This should prolong the diffusion path length for the charge carrier in QD-10 to the interface of QD-4. We can evaluate the average QD center-to-center distance between QD-4 and QD-10 in the random mixture film using a Monte Carlo simulation on the internal assembly of the QD.^{5,7} The initial input for the simulation includes the total amount of quantum dots, the geometry, and the size of both quantum dots QD-4 (4 nm) and QD-10 (10 nm) (Figure 6A) (for details of the simulation, see the Supporting Information). The histograms of the first 20 nearest neighbors of QD-10 to QD-4 were summed to provide the overall statistics for different $R_{\rm QD}$ values (Figure 6B). The simulated distribution of the R_{QD} represents the packaging capacity of the QD assembly. As observed in Figure 6B, the average D-A distance varies little from 0.3 to 1.1% sample, followed by a pronounced distance increasing with the increment in the Q-10 concentration above 1.1%. Such a trend can also be observed in the full width half maximum (FWHM) as summarized in Table S3, where the QD centerto-center distance distribution broadens with the increase of QD-10 (Figure 6B).

After knowing the average diffusion path length in the mixture film, we can determine the diffusion coefficient of electrons and holes by applying a modified version of the Zhitomirsky 3D model for carrier diffusion.⁴ This model modulates the carrier diffusion by controlling the population of

acceptors (i.e., traps) in the mixture. However, unlike in the conventional case where the narrow bandgap QDs can be considered as charge carrier acceptors, in our CsPbBr₃ QD mixture film, QD-4 serves as an acceptor for larger-sized QD-10 since the interfacial Z-scheme charge recombination is more dominant than charge injection within the CB or VB.

To implement the Zhitomirsky 3D modeling, we need to establish the relationship between the lifetimes of diffused charge carriers in the QD solid extracted from the SVD component and the calculated trap percentage. As discussed above, we simplify the hole and electron recombination lifetimes obtained in two SVD components to be the diffusion time of two species to the acceptor's interface (i.e., QD-4).

The capture rate of carriers into traps (k_{trap}) is the inverse of the trapping lifetime τ_{trap}^{-1} and, in the Shockley–Read–Hall recombination model, can be expressed as²⁴

$$k_{\rm trap} = \tau_{\rm trap}^{-1} = V_{\rm th} \sigma N_{\rm t} \tag{1}$$

where $V_{\rm th}$ is the thermal velocity in the hopping regime, also expressed as $V_{\rm th} = d/\tau_{\rm hop}$ with the interdot distance d and the interdot hopping time $\tau_{\rm hop}$. $N_{\rm t}$ is the density of traps. σ is the capture cross section, which for the 3D model is assumed to be $\frac{1}{\tau}\pi d^{2}$.⁴ Mobility μ is expressed as

$$\mu = \frac{qd^2}{6\tau_{\rm hop}kT} \tag{2}$$

where k is the Boltzmann distribution, T is the temperature, and q is the charge of the carrier.

D is related to carrier mobility via the Einstein relation

$$D = \frac{kT\mu}{q}$$
(3)

From the Einstein equation relating diffusion D and μ

$$V_{\rm th} = \frac{6D}{d} \tag{4}$$

D can be obtained as

1

$$D = \frac{dV_{\rm th}}{6} = \frac{d}{6\sigma\tau_{\rm trap}N_{\rm t}}$$
⁽⁵⁾

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Table 1. Transport Properties for the QDs Obtained from the Diffusion Model and Comparison of Diffusion Measurements for the CsPbBr₃ QD

Method	Sample	State	Capping agent	Acceptor	μ	L_d	(cm ² /s)	Slope (% $trap^{-1} ps^{-1}$)
TPLQ* ²⁶	halide-treated CsPbBr ₃ QDs	solid film	OA	Au Np	I ⁻ : 0.009 Cl ⁻ : 0.018 cm^2/s	I ⁻ : 52 and Cl ⁻ : 71 nm		
T-THz** ¹⁶	11 nm CsPbBr ₃ QDs	sls (HMN)"	OA	N.A.	$4500 \text{ cm}^2/\text{V} \text{ s}$	(>9.2 µm)		
TAS (this study)	10 nm CsPbBr ₃ QDs	solid film	DDAB	4 nm CsPbBr ₃	$\begin{array}{c} e^{-:} \left(2.1\pm0.1\right)h^{+}\!$	239 ± 15 nm	$\begin{array}{l} e^{-:} (5.3 \pm 0.4) \times 10^{-2}; h^{+}: \\ (1.76 \pm 0.07) \times 10^{-2} \end{array}$	$\begin{array}{l} e^{-:} \left(\begin{array}{c} 1.16 \pm 0.08 \right) \times 10^{-5}; \\ h^{+:} \left(3.8 \pm 0.1 \right) \times 10^{-6} \end{array}$

^a2,2,4,4,6,8,8-Heptamethylnonane. *Time resolved fluorescence quenching. **Time resolved THz.

By rearranging this formula, we obtain

1

$$D = \frac{d}{6\sigma\left(\frac{\tau_{mp}}{N_{c}^{-1}}\right)}$$
(6)

Therefore, we can obtain D from the slope in the plot of $N_{\rm t}^{-1}$ vs $\tau_{\rm trap}$ (Figure 4C,F). Since the diffusion process in both cases occurs in QD-10, $N_{\rm t}^{-1}$ refers to the percentage of QD-4. The interdot distance (12 nm) and QD density (3.8 \times 10¹⁷ cm^{-3}) of the pure QD-10 film are obtained from the Monte Carlo simulation (for details of these parameters, see the Supporting Information). Table 1 summarizes the calculated diffusion parameters.

The diffusion length (L_d) was calculated from the diffusion coefficient D of the carriers and their lifetime by the following formula: $L_d=\sqrt{D\tau}$. The diffusion length relies on the density of acceptors in our QD system. Using the carrier lifetime of the neat QD-10 film (10.7 ns), we can obtain an L_d of 239 \pm 16 nm. The diffusion coefficient and corresponding mobility of the electrons are higher than those of the holes, which is consistent with the argumentation above.

As summarized in Table 1, the carrier diffusion length for the DDAB-capped CsPbBr₃ samples in our study is significantly longer than the values in the OA-capped CsPbBr₃ solid samples. On the other hand, we notice that the diffusion length obtained by the THz method shows a very high value in comparison with our result. This is because the THz measurement only reflects the intrinsic capabilities of the charge transport dominated by the local acoustic phonon or optical phonon scattering and is less capable of tracking the scattering with defects or interfacial boundaries, which can dominate in the QD solid film.³⁶

CONCLUSIONS

We studied the electron and hole transport dynamics in densely packed QD films using two different sizes of quaternary alkylammonium-capped CsPbBr3 QD mixtures via the TA spectroscopy analysis. The excited-state dynamics in the TA measurement exhibits strong dependence on the QD ratio. Using the SVD analysis, we reveal that the photoinduced electrons and holes are less mobile in small-sized QD-4, whereas they are more freely diffused within QD-10 clusters and recombine with charges in QD-4 at the interface. The lifetimes of such diffused charge carriers are decided by the ratio of QD-10 (i.e., the mean path length between QD-10 and QD-4). After simulating such a mean path length using a Monte Carlo simulation with different QD-10 ratios in the mixture film, we conduct Zhitomirsky 3D modeling for carrier diffusion, which provided the charge carrier diffusion coefficients of electrons and holes in QD-10 of (5.3 \pm 0.4)

 $\times 10^{-2}$ and $(1.76 \pm 0.07) \times 10^{-2} \text{ cm}^2/\text{s}$, respectively. The calculated charge carrier diffusion length is longer than the reported value for OA/OLA-capped QD films by a factor of 5, suggesting enhanced charge carrier transport dynamics. We argue that perovskite QD solid-based optoelectronic devices can highly benefit from such an understanding of the relationship between charge transport dynamics and film configuration as well as QD surface ligands. The characterization methodology in this paper can be also applied to optoelectronic devices constructed by the mixture of different nanocrystals or even plasmonic nanoparticles in the photoactive layers where the mean free path of the excited charge carriers plays a critical role for the device performance.

EXPERIMENTAL SECTION

Synthesis Method. CsPbBr₃ QDs of two different band gaps and sizes were synthesized following a previously published procedure.¹ The ligand exchange follows a method described elsewhere.²

Materials. CsCO₃ (99.9%), octadecene (ODE; for synthesis), oleic acid (OA; technical grade, 70%), PbBr₂ (99.999%), oleylamine (OLA; technical grade, 70%), toluene (99.8%), hexane (95%), and didodecyl dimethyl ammonium bromide (DDAB; 98%) were purchased from Sigma-Aldrich. ODE, OA, and OLA were degassed at 120 °C before any reaction.

Cesium Oleate Synthesis. In a 50 mL round-bottom flask, 0.407 g of CsCO₃ was added to 20 mL of ODE and 1.25 mL of OA. This mixture was degassed for 1 h at 120 °C and then set under argon for 30 min at 150 °C. This was preheated to 100 °C for the quantum dot synthesis.

Synthesis of Quantum Dots. In a 50 mL three-necked roundbottom flask, 0.1378 g of PbBr₂ was added to 20 mL of ODE and degassed under vacuum for 1 h. The mixture was then set under inert conditions (Ar) at 120 °C; afterward, 1 mL of OLA and 1 mL of OA were injected, and the temperature was changed to 150 °C until PbBr₂ was completely soluble. The injection temperature of the mixture was then increased for different sizes (140 °C for 4 nm and 180 °C for 10 nm). When the temperature was reached, 0.8 mL of cesium oleate was added swiftly, and the mixture was immediately put on an ice bath.

Purification for QD-4. The reaction mixture was centrifuged for 10 min at 6500 rpm, and the supernatant was collected and precipitated within a 3:1 methyl acetate/supernatant mixture. This was centrifuged for 10 min at 6500 rpm, and the precipitate was collected and dissolved in 10 mL of toluene. This is the QD-4 solution in OA.

Purification for QD-10. The reaction mixture was centrifuged for 10 min at 6500 rpm, and the precipitate was collected and redissolved in 10 mL of toluene. The mixture was then centrifuged for 15 min at 5000 rpm, and the supernatant was than collected. This is the QD-10 solution in OA.

Ligand Exchange. This procedure was based on a reported method elsewhere. We added 500 μ L of OA and 1000 μ L of 0.05 M solution of DDAB in hexane. This was shaken and then precipitated

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with methyl acetate. The precipitate was redissolved in 5 mL of hexane. This is the stock solution.

Film Preparation. Quartz slides $(1 \times 1 \text{ cm})$ were cleaned with sequential sonication in acetone and isopropanol each for 20 min and then ozone-cleaned with plasma. QD films were deposited by spincoating 50 μ L of the QD mixtures with $R_{\rm QD}$ values ranging from 0.32 to 7.44% at 1000 rpm onto the cleaned quartz substrates.

Absorption Spectroscopy. UV–Vis absorption spectra for colloidal solutions and films were collected using a spectrophotometer from Agilent Technologies (Santa Clara, USA).

Photoluminescence Spectroscopy. The emission spectra steady-state photoluminescence was measured using a FluoroMax(@ -4 spectrofluorometer (HORIBA JOBIN YVON, Inc., Edison, NJ) with the excitation at 400 nm.

Transmission Electron Microscopy. Imaging was conducted on a Tecnai G2 T20 TEM and FEI Titan Analytical 80-300ST TEM from FEI Company.

The obtained TEM images were processed with Gatan Microscopy Suite software.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS; Thermo Scientific) was performed to analyze the valence and composition of the samples, with Al K α (1486 eV) as the excitation X-ray source. The peak of C 1s at about 284.8 eV was used to calibrate the energy scale. The pressure of the analysis chamber was maintained at 2×10^{-10} mbar during measurement.

Transient Absorption. TA experiments were performed by using a femtosecond pump-probe setup. Laser pulses (800 nm, 150 fs pulse length, and 3 kHz repetition rate) were generated by a Ti:sapphire amplifier with an integrated oscillator and pump lasers (Libra LHE, Coherent Inc.) and a transient absorption spectrometer (Newport Corp.). Briefly, the output of a Ti:sapphire amplifier with an integrated oscillator and pump lasers (800 nm, 150 fs, 3 kHz, Libra LHE, Coherent Inc.) was split into two beams that were used to generate 400 nm light through the doubling crystal as a pump beam and to generate white light through a CaF2 crystal as a probe. The probe beam was split to two beams: one going through the sample and another as a reference. The generated supercontinuum was then focused onto the sample and overlapped with the pump beam. The transient spectra were detected with a fiber-coupled CCD-based monochromator (Oriel, Newport). Samples for transient absorption experiments were kept in the dark between each measurement. Global SVD analysis was performed with the Glotaran software package (http://glotaran.org).

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c11676.

Calculations of the QD concentration, simulation details, TEM images, Tauc plot, kinetic traces at B1 and B3 at different $R_{\rm QD}$ values, decay-associated spectra and kinetic traces of pure QD films with sizes of 4 and 10 nm, and XPS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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Charge carrier diffusion dynamics in multi-sized Quaternary Alkylammonium-capped CsPbBr₃ perovskite nanocrystal solids

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Calculation of CsPbBr₃ QDs Concentration:

The concentration of the QDs in the stock solutions (SS) were calculated using Beer's Law, $A = \varepsilon bc$. The absorbance of the solutions was measured at 400 nm using UV-Vis spectrometer and a 1 mm path length cuvette. The molar absorptivity of the sample at 400 nm (ε_{400nm}) was calculated using the formula^{3,4}:

$$\varepsilon_{400nm} \left(M^{-1} cm^{-1} \right) = \frac{N_A \sigma(cm^2)}{1000 \ln 10} \tag{S1}$$

 N_A = Avogadro's constant and σ = absorption cross-section at 400 nm obtained from ref ⁵ for 2 sizes

Table S1. Calculation of stock solutions concentration.

Sample	σ 400 nm (cm ²)	ε400nm	OD _{400 nm} (A.U.)	Concentration (mol/L)
QD-4 SS	4.6 nm $(8.97 \pm 3.53) \times 10^{-15}$	$(2.3 \pm 0.9) \ge 10^6$	0.456 ± 0.004	$(10 \pm 4) \ge 10^{-7}$
QD-10 SS	9.4 nm (7.87±1.29) x10 ⁻¹⁴	$(2.0 \pm 0.3) \ge 10^7$	0.428 ± 0.004	$(1.0 \pm 0.2) \ge 10^{-7}$

Table S2 Preparation of Mixture solutions of films and R_{OD}

Volume QD-10 (µL)	Volume QD-4 (µL)	Volume Toluene (µL)	R _{QD}
0.25	100	99.75	0.03
3	100	97	0.32
5	100	95	0.53
10	100	85	1.06
15	100	80	1.58
20	100	50	2.10
50	100	0	5.09
75	100	0	7.44

The R_{OD} is calculated by

$$R_{QD} = \frac{C_{QD-10}}{C_{QD-10} + C_{QD-4}} * 100$$
(S2)

 $C_{\text{QD-10}}$ and $C_{\text{QD-4}}$ are calculated by multiplying the volume with the stock solution concentration reported in table S1.

Distribution of QD-QD distance in the random films.

Monte Carlo simulations of random QD layers were carried out for each R_{QD} . In each case we obtain a histogram of the QD-4 to QD-10 centre-to-centre distance for the 1st, 2nd, n-closest neighbor. The histogram results are taken until the 20th neighbor and are summed and the result is fitted to a Gaussian as observed in figure 6B. The results of the center of the Gaussian peak (mean free path) and full width half maximum (FWHM) of the Gaussian fitting are presented in table S3.

R _{QD} (%)	Mean free path (nm)	FWHM (nm)
0.3	9.68 ± 0.04	5.14 ± 0.09
0.5	9.55 ± 0.03	5.38 ± 0.07
1.1	9.58 ± 0.05	5.3 ± 0.1
1.6	10.31 ± 0.04	6.38 ± 0.1
2.1	10.24 ± 0.03	6.06 ± 0.07
5.1	11.03 ± 0.07	7.3 ± 0.2

Table S3 Results of mean free path

Calculation of QD density:

QD density (3.8x10¹⁷ cm⁻³) of the pure QD-10 film is obtained from the Monte-Carlo simulation.



Figure S1 TEM images of A) QD-4 and B) QD-10



Figure S2 Tauc Plot QD-4 and QD-10

S-4



Figure S3. Tauc Plot Mixed films increasing R_{QD} .

Table C4	Commence	of Dond	~~~	main a d	filme	***** 1 6	in ana aim (~ D
1 able 54	Summarv	of Band	gad m	mixed	mms	with	increasing	2 KOD
	,		0.1					J QD.

R _{QD} (%)	Band Gap (eV)
0.3	2.73
0.5	2.72
1.1	2.71
1.6	2.7
2.1	2.69
7.4	2.44/ 2.66
13.8	2.43
17.7	2.42



Figure S4 A)-B1 and B)-B3 kinetic traces at different percentages of R_{QD} .



Figure S5 R_{QD} 1.1% kinetic trace and fitting at 495nm and 508nm QD-4



Figure S6 Associated kinetic traces of A) QD-4 and C) QD-10, and decay associated spectra of B) QD-4 and D) QD-10.




Figure S7 XPS spectra of the valance band CsPbBr₃

We first performed the XPS measurement of the valance band of QD-10 to confirm valance band maximum VBM position. The VBM position of QD-4 is estimated by subtracting 35 meV as previously reported in a size-dependent VB energy study.⁶

Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, *15* (6), 3692–3696.

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The tunability of perovskite NCs covers aspects from the possible chemical structure, the morphology, the capping agents, and the final micro-arrangement of the NCs. All of these components contribute to the photophysical characteristics the NCs will exhibit. An in-depth understanding of their fundamental properties is essential to improve and optimize p-NCs for optoelectronics. As we see in chapters 3 and 4, each part's role can significantly improve the material's performance in the different applications. Our experiments provided fundamental guidance on how to view the nanoscopic and microscopic morphologies as determining factors for the device application.

In particular, we are beginning to understand the intricacies quantum confinement has on CsPbX₃ NCs, from an ideal model (i.e., symmetric individual NC), to a more realistic scenario in an actual device (i.e. imperfect shaped NC assembled in a compacted solid film). However, how various parameters interact and result in a collective influence on photophysics remains investigated. In addition, the effects of dielectric confinement have not yet been separated from quantum confinement, which is even more relevant in the solid film where the interfacial chemistry among NCs is complicated.

In addition, there are fundamental questions that still need an answer for designing materials for new applications. Parameters such as Auger recombination rates and exciton versus biexciton formation rates will need to be determined if these NCs are used in high-power LEDs and lasers with various microscopic and nanoscopic morphologies. With the excitons playing such a prominent role in lead halide perovskites NCs, especially at high excitation intensity regimes, future work needs to focus on understanding the corresponding exciton dynamics in the nonlinear regime and their correlation with NC morphologies. Developing a Ph.D. project has brought multiple experiences in my life, from the laser lab adventures in Japan and Germany, the Chinese conference, and day-to-day life in the office. I treasure the moments shared with all the people who have accompanied me in this process.

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