Tuning Optical and Structural Properties of Lead Halide Perovskites via Organic Molecules

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- A. Lang,[‡] M. Kurashvili,[‡] J. Sklar, I. Polishchuk, A. Fada'os, I. Sessa, A. Buyan-Arivjikh, A. Katsman, J. Feldmann, and B. Pokroy *Exploring Lysine Incorporation as a Strategy to Mitigate Postsynthetic Halide Exchange in Lead-Halide Hybrid Perovskites*ACS Applied Materials & Interfaces 2025, 17 (6), 9485-9493
- M. Kurashvili,[‡] L. S. Stickel,[‡] J. Llusar, C. Wilhelm, F. Felixberger, I. Ivanović-Burmazović, I. Infante, J. Feldmann, Q. A. Akkerman Charge Transfer from Perovskite Quantum Dots to Multifunctional Ligands with Tethered Molecular Species
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Zusammenfassung

Bleihalogenid-Perowskite (BHP) sind Halbleiter mit der allgemeinen Formel APbX₃ (A = Cs^+ , $CH_3NH_3^+$ (MA⁺); X = Cl^- , Br^- , I^-). Ihre außergewöhnlichen optischen und strukturellen Eigenschaften, wie hohe Defekt-Toleranz und starke Lichtabsorption, machen BHP vielversprechend für optoelektronische und photokatalytische Anwendungen. Besonders kolloidale BHP-Quantenpunkte (QP) - Nanokristalle, die in allen drei Dimensionen eingeschränkt sind - haben großes Potenzial.

Die Entwicklung von Multi-Perowskit-Bauelementen (MPB) bleibt herausfordernd, da Halogeniddiffusion zu irreversiblem Verlust der spektralen Merkmale führt, was ihre Nutzung in lichtemittierenden Bauelementen begrenzt und gleichzeitig die Bildung scharfer Grenzflächen verhindert, die für Solarzellen essenziell sind. Eine vielversprechende Alternative für MPB und andere Anwendungen sind QP-Donor und Molekül-Akzeptor Hybride mit effizientem Energietransfer (ET) oder Ladungstransfer. Sie sind aber weniger erforscht als solche mit konventionellen QP (z. B. CdSe). Eine weitere Strategie zur Unterdrückung der Halogeniddiffusion ist die partielle Substitution nativer A-Kationen durch organische Moleküle, was weitere Forschung erfordert.

Darauf basierend konzentriert sich diese Arbeit auf zwei zentrale Forschungsbereiche:

CsPbBr₃-QP und organische Molekül-Hybride. ATTO610-Farbstoffe mit einer Dimethyliminium-Bindungsgruppe, die eine starke Affinität zu BHP-Oberflächen hat, werden an CsPbBr₃ QP gebunden, um ein Donor-Akzeptor-System zu bilden. Stationäre und zeitaufgelöste Photolumineszenz (PL) Spektroskopie zeigen, dass der ET von QP zu ATTO610 über den Dexter-Austauschmechanismus erfolgt. Die enge Bindung der Farbstoffe an die QP minimiert den Donor-Akzeptor-Abstand und ermöglicht die räumliche Überlappung der Wellenfunktionen von isoenergetischen Zuständen, was wichtig für diesen Mechanismus ist. Aufbauend darauf werden multifunktionale Liganden entwickelt, die starke Bindung, kolloidale Stabilität und funktionale Ferrocen Moleküle (Lochfänger) kombinieren. Optische Spektroskopie an CsPbBr₃-QP, die mit multifunktionalen Liganden stabilisiert sind, bestätigt die Bedeutung des Donor-Akzeptor-Abstands für ihre Wechselwirkungseffizienz. Ferrocen ermöglicht eine effiziente Dissoziation der QP-Exzitonen durch Löchereinfang, wobei die strukturelle Reorganisation von Ferrocen nach der Ladungsaufnahme die Ladungstrennungseffizienz beeinflusst.

Volumen-BHP MAPbBr₃-Lysin Kompositkristalle. Der Einfluss des Einbaus der Aminosäure Lysin auf den postsynthetischen Halogenidaustausch in MAPbBr₃-Kristallen wird untersucht. Ionenchromatographie, Röntgenbeugung und PL Spektroskopie zeigen, dass das eingebaute Lysin die postsynthetische Halogenid-Diffusion in MAPbBr₃ stark reduziert.

Diese Studie bietet ein Rahmenkonzept zur Entwicklung effizienter BHP-Molekül-Hybride und zeigt ihr Potenzial als Alternative oder Weiterentwicklung von MPB sowie für andere optoelektronische und photokatalytische Anwendungen.

Abstract

Lead halide perovskites (LHPs) are semiconductors with the general chemical formula APbX₃ (A = Cs⁺, CH₃NH₃⁺ (MA⁺); X = Cl⁻, Br⁻, Γ). Their remarkable optical and structural properties, such as strong light absorption and high defect tolerance, make them highly promising candidates for optoelectronic and photocatalytic devices. In particular, LHP colloidal quantum dots (QDs), which are nanocrystals confined in all three dimensions, have emerged as promising materials for many applications.

Multi-perovskite devices containing LHPs with different halides face challenges due to halide diffusion, which leads to an irreversible loss of distinct spectral features and limits their use in light-emitting devices. Rapid halide diffusion in multi-perovskite devices also prevents the formation of sharp interfaces needed for optimal device operation, such as in solar cells. QD-molecule donor-acceptor hybrids that exhibit efficient excited-state interactions via energy transfer (ET) or charge transfer (CT), present a promising alternative for both multiperovskite devices and other applications. However, they remain less explored compared to those containing conventional QDs (e.g. CdSe). Another promising strategy to suppress halide diffusion involves partial replacement of native A-site cations via organic molecules, necessitating further research.

Based on these considerations, this study focuses on two key areas of interest:

CsPbBr₃ QD-organic molecule hybrids. ATTO610 organic dyes with a dimethyl iminium binding group, which strongly bind to LHP surfaces, are attached to CsPbBr₃ QDs to form a hybrid donor-acceptor system. Steady-state and time-resolved photoluminescence (PL) spectroscopy demonstrate that efficient ET from QDs to dyes occurs via the Dexter exchange-type mechanism, due to close binding of ATTO610 dyes to the QD surfaces, which facilitates spatial wavefunction overlap of donor and acceptor isoenergetic states, an important prerequisite for this mechanism. Building on this, multi-functional ligands are designed which combine strong binding, colloidal stability, and functional ferrocene molecules (hole scavenger). Optical spectroscopy measurements performed on CsPbBr₃ QDs exclusively capped with these multi-functional ligands confirm that minimizing the donor-acceptor distance enhances their interaction efficiency. The results show that ferrocene efficiently dissociates excitons on QDs by capturing holes and a molecular structure reorganization of ferrocene upon charge acquisition impacts the charge separation efficiency.

Bulk MAPbBr₃-lysine composite crystals. The effect of the amino acid lysine (Lys) incorporation into bulk MAPbBr₃ on post-synthetic halide exchange is investigated. Ion chromatography, X-ray diffraction and steady-state PL spectroscopy unanimously reveal that incorporated Lys strongly reduces post-synthetic Cl⁻ and I⁻ diffusion into MAPbBr₃.

These findings provide a framework for designing efficient LHP-molecule hybrid systems and highlights their potential as alternatives or improvements to multi-perovskite devices, as well as in other optoelectronic and photocatalytic applications.

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Chapter 1

Introduction

Lead halide perovskites (LHPs) are semiconductors with the general chemical formula APbX₃ (A e.g. cesium cation (Cs⁺), methylammonium cation (CH₃NH₃⁺, MA⁺); X - a halide ion, e.g. chloride (Cl⁻), bromide (Br⁻), iodide (I⁻)). LHPs have been known for over a century,¹ with some of their key properties investigated as early as the second half of the 20th century.^{2–6} However, these materials remained largely unnoticed by the scientific community until their revival in the early 2010s by the photovoltaic community. This renewed interest led to the establishment of LHPs as highly efficient sunlight-absorbing materials for photovoltaic devices,^{7–9} followed by rapid advancements in LHP-based light-emitting diodes (LEDs) in recent years.¹⁰ This drastic rise in the success of LHPs can be attributed to their ease of synthesis, their ability to form high-quality, defect-poor crystals, strong light absorption, and the tunability of their optical properties via chemical composition and crystal size or dimensional engineering.^{11,12} In particular, LHP colloidal quantum dots (QDs), nanocrystals confined in all three dimensions, have emerged as promising materials for photocatalysis.^{18–22}

Despite their tremendous potential in optoelectronic and photocatalytic applications, certain challenges still exist. One significant issue is the difficulty in engineering multi-perovskite devices containing LHPs with different halides. For example, mixing colloidal QDs with different halide compositions results in an irreversible loss of distinct spectral features due to halide diffusion,²³ which is detrimental to multi-perovskite-based light-emitting devices. Similarly, rapid halide diffusion between two LHP layers with different halide compositions prevents the formation of sharp interfaces, which are essential for optimal device operation, such as in solar cells.^{24–27} QD-molecule donor-acceptor hybrids that exhibit efficient excited-state interactions via energy transfer (ET) or charge transfer (CT) are a promising alternative for both multiperovskite devices and other applications. However, the design of efficient LHP QD-molecular systems is less explored compared to those containing conventional QDs (e.g. CdSe). Another promising strategy involves supressing post-synthetic halide exchange by partial replacement of native A-site cations via organic molecules,^{28–30} warranting further research.

Based on these considerations, this work investigates two key areas of interest:

1. CsPbBr₃ QD-organic molecule hybrid systems.

QD-molecular hybrid systems have been proposed for various applications, including sensing,^{31,32} solar light harvesting,^{33,34} microscopy,³⁵ and as platforms for studying excited-state interactions.^{36–38} Conventional bright-emitting QDs, such as CdSe and InP, typically require a shell of a wide band gap material to passivate detrimental surface defects for efficient emission and ligands to maintain colloidal stability. This shell strongly limits the extent of interactions between QDs and surface-bound organic molecules. In contrast, LHP QDs can be effectively passivated by ligands alone,^{39,40} making their surfaces more accessible for the direct attachment of molecules. This is crucial for efficient interaction. ET from QDs to dye molecules is of particular interest, because optically excited QDs act as sensitizers, enabling excitation of dyes at energies or to states that otherwise would not be accessible through direct optical excitation.^{41,42} In addition, QD-molecular systems exhibiting efficient CT hold promise for photocatalysis and solar cells.^{21,33,43} In this work, CsPbBr₃ QD-molecular hybrids are designed, which exhibit ET and CT, positioning them as strong contenders for multi-perovskite devices.

2. Bulk MAPbBr₃-amino acid composite crystals.

Recently, a unique approach has emerged in which individual amino acids can be incorporated into bulk semiconductor crystals.^{44–49} This approach draws inspiration from biomineralization in nature, where organic molecules become incorporated into brittle crystalline minerals. A study led by the Pokroy lab at the Technion - Israel Institute of Technology demonstrated that individual amino acids, such as lysine (Lys), can be incorporated into MAPbBr₃ bulk crystals, significantly altering the host's structural properties.⁴⁴ In collaboration with the Pokroy Lab, funded by the German-Israeli foundation, this work investigates the effect of Lys incorporation into MAPbBr₃ crystals as a potential strategy for suppressing post-synthetic halide exchange in bulk LHPs.

A deep understanding of the physical processes occurring in LHP-molecular systems is crucial for their successful integration into different optoelectronic and photocatalytic devices. This work examines donor-acceptor CsPbBr₃ QD-molecule hybrids, where molecules are attached to QD surfaces, as well as bio-inspired bulk MAPbBr₃-Lys composites, in which Lys molecules are incorporated inside the crystals. This study is divided into five chapters: **Chapter 2** introduces the fundamental physical concepts necessary for understanding the results presented in this work, assuming a basic knowledge of semiconductor and organic molecule physics on the reader's part. **Chapter 3** describes the experimental techniques used for structural and optical characterization, including the chemical synthesis of the studied materials. In **Chapter 4**, the excited-state interactions in two different CsPbBr₃ QD-molecular donoracceptor hybrids, exhibiting efficient ET and CT, respectively, are investigated. **Chapter 5** explores the effect of Lys incorporation into bulk MAPbBr₃ crystals on post-synthetic halide diffusion. Finally, **Chapter 6** provides a summary of the key findings of this work.

Chapter 2

Fundamentals

This chapter is divided into three main sections. The first section provides a general overview of the structural and optical properties of bulk and nanocrystalline LHPs. It highlights the effects of post-synthetic halide exchange on their photophysical properties, as well as the role and binding mechanisms of surface ligands in LHP QDs.

The second section offers a brief overview of the structural and optical properties of organic molecules, with a particular focus on dye molecules and amino acids.

The third section explores LHPs and organic molecules as unified systems. It begins with a general discussion of donor-acceptor systems, with an emphasis on the interaction between LHP QD donors and molecular acceptors. The mechanisms of ET and CT in donoracceptor systems are discussed in more detail. Additionally, an overview on the amino acid incorporation into bulk inorganic semiconductors is provided, discussing its effects on the structural and optical properties of the host material. Special emphasis is placed on lysine incorporation into bulk hybrid organic-inorganic LHPs.

2.1 Lead Halide Perovskites

2.1.1 What is a Lead Halide Perovskite?

The term perovskite was originally coined in 1839 for the naturally occurring mineral CaTiO₃. Since then, the name has grown to encompass a wide range of compounds with various chemical compositions and formulas.⁵⁰ In particular, LHPs studied in this work have the general chemical formula ABX₃, where A is a monovalent cation, B is a divalent lead cation (Pb²⁺) and X is a monovalent halide anion such as chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), or a combination of these. The crystal structure of LHPs consists of corner-sharing BX₆ octahedra surrounding an A-cation, as illustrated in **Figure 2.1a**, **b**. LHPs are classified as either hybrid organic—inorganic perovskites (HOIPs) or fully inorganic perovskites, depending on whether the A-cation is organic or inorganic. Inorganic perovskites typically have cesium (Cs⁺) or rubidium cations (Rb⁺) as the A-cation, while HOIPs generally have small organic molecules such as methylammonium (CH₃NH₃⁺, MA⁺) or formamidinium (CH₅N₂⁺, FA⁺). LHPs are predominantly held together by ionic bonds, which is also a reason why they can be easily synthesized at ambient conditions, unlike conventional semiconductor crystals, such as GaAs, with highly covalent lattices.^{11,12,50}

Whether a given perovskite composition ABX₃ is stable and capable of forming a perovskite crystal structure with corner-sharing octahedra shown in **Figure 2.1a** can be assessed using the Goldschmidt tolerance factor t and the octahedral factor δ , defined by **Equations 2.1** and **2.2**, respectively.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$
(2.1)

$$\delta = \frac{r_B}{r_X} \tag{2.2}$$

Here, r_A , r_B and r_X represent the ionic radii of the cations and anions comprising the perovskite crystal. A stable perovskite structure is expected for $0.8 < t < 1^{51}$ and $0.44 < \delta < 0.9$.⁵² Outside of these ranges, other structures are generally more energetically favorable.⁵⁰ In addition, the structural stability of LHPs also depends on temperature and pressure.⁵³

At room temperature, Cs-based LHPs typically adopt an orthorhombic phase and transition to tetragonal and cubic phases at higher temperatures.⁵⁴ MA-based LHPs are found in cubic or tetragonal phases and undergo phase transitions upon cooling.^{3,55,56} The smaller ionic radius of Cs⁺, compared to the larger MA⁺ molecule, results in Cs⁺ occupying less space between octahedra than MA⁺. This size difference significantly influences the octahedral tilt angle. Tilting of octahedra against each other alters the arrangement of ions within the unit cell, causing phase transition, that in turn influences optical properties such as the band gap of the crystal.^{57,58} LHPs are direct band gap semiconductors that possess a unique electronic band structure.^{59–61} In LHP, the valence band (VB) originates from the strong σ anti-bonding interaction between outermost Pb *s*- and halide X *p*-atomic orbitals, giving it an overall *s*-like character. The conduction band (CB) is mainly formed by the σ anti-bonding coupling of empty outermost Pb *p* atomic orbitals, giving it a *p*-like character (**Figure 2.1c**).^{12,61,62} This is an inverse arrangement, compared to conventional semiconductors such as GaAs.⁶³ The VB and CB in LHPs have similar curvature, meaning that the effective masses of holes m_h^* and electrons m_e^* , are comparable, implying that their response to external electromagnetic forces is similar.⁶²



Figure 2.1: LHP crystal structure and electronic band structure. a) Illustration of the cubic perovskite crystal structure with a chemical formula ABX₃ with monovalent A-cation, a divalent B-cation and a monovalent X-anion. The corner-sharing BX₆ octahedra surround an A-cation. b) A unit cell of a cubic perovskite. c) Schematic illustration of the electronic band structure of LHPs. In LHPs, the VB originates from the σ anti-bonding (σ^*) interaction between Pb s and halide X p atomic orbitals (red), giving it an overall s-like character. The conduction band (CB) is mainly formed by the σ anti-bonding coupling of empty outermost Pb p atomic orbitals (blue), giving it a p-like character. E_g is the band gap. Adapted from [12].

The unique electronic band structure of LHP has many interesting consequences. One striking example is their unusual temperature dependence of the band gap, which decreases with decreasing temperature, a behavior opposite to that observed in GaAs.^{58,63}

Unlike conventional semiconductors, LHP are characterized by high defect tolerance, meaning their functional properties remain relatively unaffected by crystal defects. In conventional semiconductors, defect states associated with point defects or dangling bonds form deep trap states within the band gap, which can be detrimental to their performance in optoelectronic and photocatalytic devices.¹² In LHPs, defects associated with deep trap states have high formation energies and are therefore, uncommon. More common defects include A-site and X-site vacancies, which typically form shallow trap states within or near the VB and CB edges.^{12,39,59,64} Thermal energy is usually sufficient to efficiently de-trap photoexcited electrons and holes trapped in shallow defect states back to the CB and VB, respectively. As a result, even LHP synthesized at ambient conditions and technical-grade chemicals can be bright emitters.¹²

One of the key aspects responsible for the superior performance of LHP-based devices is their strong interband optical absorption. Since bulk semiconductors exhibit a continuous range of energy states within their VB and CB, interband transitions occur over a broad range of energies, giving rise to a continuous absorption spectrum starting at the band gap energy. In quantum mechanics, the transition rate $k_{i\to f}$ from an initial state *i* to a final state *f* as a result of weak perturbation is given the by Fermi's Golden rule:

$$k_{i \to f} = \frac{2\pi}{\hbar} \sum_{i,f} |\langle \Psi_f | H' | \Psi_i \rangle|^2 \rho(E_f, E_i)$$
(2.3)

where \hbar is the reduced Planck's constant, H' is the perturbing Hamiltonian, and the term $|\langle \Psi_f | H' | \Psi_i \rangle|^2$ is the matrix element that determines the transition probability between the initial Ψ_i and final Ψ_f states. $\rho(E_f, E_i)$ corresponds to the joint density of states (jDOS), which depends on the initial and final state energies, E_i and E_f , respectively. It can be shown that the perturbing Hamiltonian governing the process of photon absorption by a semiconductor can be described in the so-called electric-dipole approximation as $H' \approx -erE_0$, with -er the electron dipole moment and E_0 the perturbing electric field amplitude of light. The term $\langle \Psi_f | er | \Psi_i \rangle$ is called the transition dipole moment μ and the corresponding matrix element is directly proportional to the oscillator strength of the transition.⁶⁵ In the electric-dipole approximation, the transitions in the momentum space involving photons can be visualized as vertical lines given that the photon momentum compared to the electron momentum is negligible. Most importantly, the transition rate depends on the jDOS. LHPs have a high DOS near the VB and CB, as a result, they show strong optical absorption.⁶²

The attractive Coulomb force between a photoexcited e-h pair may lead to the formation of a bound state called exciton, a bosonic quasi-particle. In inorganic bulk semiconductors, an interacting electron and hole can be described in analogy to the quantum-mechanical description of a hydrogen atom. The Hamiltonian of an exciton can be separated into two components: relative motion, describing a particle with reduced mass $m_{\rm red} = (m_e^* m_h^*)/(m_e^* + m_h^*)$ and center-of-mass motion, describing the exciton as a free particle with a mass $M = m_e^* + m_h^*$. This yields the exciton's dispersion relation:

$$E_n(\mathbf{K}) = E_g - \frac{1}{n^2} R y_{\mathbf{X}} + \frac{\hbar^2 \mathbf{K}^2}{2M} = E_g - \frac{1}{n^2} \left(\frac{e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \frac{m_{\text{red}}}{\epsilon^2} \right) + \frac{\hbar^2 \mathbf{K}^2}{2M}$$
(2.4)

where E_g is the band gap, $\mathbf{K} = \mathbf{k}_e + \mathbf{k}_h$ is the exciton wavevector, with \mathbf{k}_e and \mathbf{k}_h representing the electron and hole wavevectors, respectively, and $n \in \mathbb{Z}^+$ is the principal quantum number. Ry_X is the exciton binding energy, e is the elementary charge, ϵ_0 is the vacuum permitivity, and ϵ is the dielectric constant of the material. **Equation 2.4** shows that single photons with energies slightly below the semiconductor band gap E_g can excite the material by creating bound e-h pairs. In addition, the Coulomb potential between a photoexcited free e-h pair enhances photon absorption probability, a phenomenon known as the Sommerfeld enhancement.⁶⁶ The exciton ground state (n = 1) is characterized by the exciton Bohr radius r_X , which represents the preferred electron-hole (e-h) separation distance:

$$r_{\rm X} = \frac{4\pi\epsilon_0\hbar^2}{e^2} \frac{\epsilon}{m_{\rm red}}$$
(2.5)

Excitons in inorganic semiconductors, also known as Wannier-Mott excitons, typically extend across several unit cells and remain delocalized. In addition to the discrete exciton energy states given in **Equation 2.4**, the Schrödinger equation for excitons also has continuum state solutions, where unbound e-h pairs can exist. Wannier-Mott excitons can be visualized using a two-particle picture, as shown in **Figure 2.2**, where the excited e-h pair energy $E(\mathbf{K})$ is plotted as a function of the exciton wavevector $\mathbf{k}_{e} + \mathbf{k}_{h}$. Excitons remain stable as long as the total thermal energy stored as phonons, quasiparticles describing the collective vibrational excitation of the atoms or molecules within a crystal, is smaller than the exciton binding energy Ry_{X} .^{65,67-69}



Figure 2.2: Bulk excitons. a) Illustration of a Wannier-Mott exciton with Bohr radius r_X in a bulk inorganic semiconductor crystal lattice. Energetic states of a bulk exciton with its bound states n = 1, 2 and the continuum states ∞ are shown in a two-particle picture as a function of the exciton wavevector **K**. Ry_X is the exciton binding energy and E_g is the band gap. b) Schematic illustration of an absorbance spectrum of bulk excitons at ambient conditions.

Despite various experimental techniques being available, the exact determination of exciton binding energies in LHPs remains challenging. For example, in bulk and bulk-like MAPbBr₃ reported values in literature span a wide range of values from 15 to 80 meV.^{58,70–74} Several factors complicate the determination of the exciton binding energy in LHPs such as the strong electron-phonon coupling due to the polar nature of these materials.⁷³ Some reported band gaps, exciton binding energies and Bohr radii of LHPs at room temperature are listed in **Table 2.1**.

2.1.2 Quantum Confinement: from Bulk Crystals to Quantum Dots

Reducing the crystal size, even in a single dimension, such that the motion of excitons is significantly restricted in that spatial dimension, can have significant consequences on the Table 2.1: Band gaps, exciton binding energies and exciton Bohr radii of LHPs at ambient conditions. These selected values provide a reference for the properties of different LHPs. Reported values may vary from a study to a study, as discussed in the main text for exciton binding energies in MAPbBr₃ crystals.

	$CsPbCl_3$	CsPbBr_3	CsPbI_3
Band gap E_g (eV) ⁷⁵	2.8	2.3	1.3
Exciton binding energy $Ry_{\rm X}$ (meV)	64^{76}	20^{77}	25^{78}
Exciton Bohr radius $r_{\rm X}$ (Å)	17^{79}	31^{79}	46^{79}

	MAPbCl_3	$MAPbBr_3$	$MAPbI_3$
Band gap $(eV)^{62}$	3.1	2.3	1.5
Exciton binding energy $Ry_{\rm X}$ (meV)	41^{80}	41^{58}	32^{58}
Exciton Bohr radius $r_{\rm X}$ (Å)	n/a	20^{73}	22^{73}

optical properties of the crystal. This effect is called quantum confinement and it happens because electrons and holes in the confined dimension behave similar to a particle in a box.

Reducing the crystal size in all three dimensions to the point that it becomes comparable to twice the exciton Bohr radius $2r_X$, the crystal can be considered as a quantum box. In inorganic semiconductors exciton Bohr radii typically range up to tens of nanometers,^{73,81} meaning that crystals exhibiting quantum confinement effects have dimensions on this scale. Crystals confined in all three dimensions are called QDs or nanocrystals (NCs). QDs come in many shapes and forms, but treating them as ideal cubic or spherical particles simplifies modeling and allows for easier description of confinement effects.⁶⁹

The LHP QDs investigated in this work have a nearly spherical shape.⁸² In quantummechanics a spherical QD can be treated as a three-dimensional spherical potential box with an infinite potential well, confining electrons and holes with isotropic effective masses. If the QD radius $r_{\rm QD}$ is a few times larger than the exciton Bohr radius $r_{\rm X}$, the exciton Hamiltonian can be described in analogy to a hydrogen atom model, as was done for bulk excitons, but now with an additional potential energy term representing the spherical confining potential. This regime is known as weak confinement. Here, the exciton's center-of-mass motion becomes quantized and the exciton spectrum is modified.

A weakly confined exciton is characterized by the quantum number $n \in \mathbb{Z}^+$ describing the internal exciton states arising from the Coulomb interaction, in analogy to the Wannier-Mott excitons, and by two additional quantum numbers, $\tilde{n} \in \mathbb{Z}^+$ and an angular momentum $\tilde{l} \in \mathbb{N}$, describing the quantized center-of-mass motion in the presence of the spherical confinement potential. Since photon absorption can only create an exciton with zero angular momentum, the exciton absorption spectrum consist of a discrete transitions corresponding to states with $\tilde{l} = 0$, governed by the expression

$$E_{n\tilde{n}0} = E_g - \frac{1}{n^2} Ry_{\rm X} + \frac{\hbar^2 \pi^2 \tilde{n}^2}{2M r_{\rm OD}^2},$$
(2.6)

The lowest weakly confined exciton state in **Equation 2.6** is shifted upwards in energy compared to the lowest bulk exciton state in **Equation 2.4** by

$$\Delta E = \frac{m_{\rm red}}{M} \left(\frac{\pi r_{\rm X}}{r_{\rm QD}}\right)^2 R y_{\rm X} \tag{2.7}$$

Therefore, quantum confinement shifts exciton energies upwards. Weakly confined excitons in QDs are vizualized in **Figure 2.3**. The lowest exciton states of weakly confined excitons are labeled as $(n = 1, \tilde{n} = 1, \tilde{l} = 0) \equiv X1, (n = 1, \tilde{n} = 2, \tilde{l} = 0) \equiv X2$, etc.



Figure 2.3: Weakly confined excitons. a) Illustration of a weakly confined exciton with Bohr radius r_X in a spherical QD of radius r_{QD} . Quantized energetic states of a confined exciton X1 and X2 are shown (green dots) as a function of the exciton wavevector $\mathbf{K}_{\tilde{n}}$. The lowest weakly confined exciton is shifted upwards in energy compared to the lowest bulk exciton (grey solid line) by ΔE . b) Schematic illustration of an absorbance spectrum of weakly confined excitons in a QD ensemble at ambient conditions.

If the QD radius $r_{\rm QD}$ is much smaller than the exciton Bohr radius $r_{\rm X}$, the system is said to be in a strong confinement regime. In this case, the Hamiltonian can no longer be separated into center-of-mass motion and relative motion of the e-h pair. Instead, the behavior of electrons and holes is better described by considering their uncorrelated motion, neglecting the Coulomb interaction between them in the first approximation. Spatial confinement of electrons and holes restricts them to quantized energy states, allowing optical transitions only between specific levels, reducing the absorption spectrum to a set of discrete bands. Therefore, QDs in the strong confinement regime are sometimes referred to as "artificial atoms". It should be noted that Coulomb interaction does not vanish in small QDs and it can be treated as a weak perturbation to improve the quantum mechanical description of the strong confinement regime.

In short, the optical properties of QDs can be systematically tuned by altering their size.^{83–85} Generally, quantum confinement blue-shifts not only optical transitions, but also alters DOS, and increases exciton binding energy.^{67,69,86}

These idealized models of bulk and confined excitons do not account for the contribution

of electron and hole spins or the influence of crystal symmetry on exciton energy levels. Effects such as the spin-orbit coupling and e-h exchange interactions can lead to exciton fine-structure splitting, significantly impacting the optical properties of a material.^{87–90} However, these considerations fall beyond the scope of this work, and therefore, only the idealized exciton model will be considered.

2.1.3 Exciton Recombination Dynamics

Following the generation of (bound) e-h pairs with energies significantly above the band gap, they rapidly relax to the lowest excited state within several femtoseconds through multiple scattering events with phonons, forming a thermal distribution. From this state, excitons recombine after an average lifetime, typically in the nanosecond range, in accordance with energy and momentum conservation laws.

Excitons can recombine either radiatively or non-radiatively, returning the semiconductor to its ground state. In a radiative recombination, a photon is spontaneously emitted. In a non-radiative recombination, the energy is dissipated without photon emission, often through heat generation, trapping in defect states at lower energies, ET to other charge carriers or excitons, ET or CT to other species, such as molecules. PL intensity of a material is influenced by the radiative and non-radiative recombination rates.

In the simplest model, the change in the exciton density in a bulk semiconductor crystal as a function of time $\dot{n}(t)$ is proportional to the exciton density $k_1n(t)$, where $k_1 = \kappa_{\rm rad}$ is the radiative recombination rate. In case of non-radiative recombination involving defect states, the dependence of the exciton density can be expressed as $k_2n_{\rm defect}n(t)$ with a proportionality factor k_2 and a constant defect density $n_{\rm defect}$, where $k_2n_{\rm defect} = \kappa_{\rm defect}$ is a non-radiative recombination rate due to defects. This type of recombination dominates at high defect densities. Different types of defects can have different recombination rates, which can be taken into account by adding up different contributions. In case of exciton-exciton annihilation, the exciton density is proportional to $k_3n(t)^2$, with a proportionality factor k_3 and the recombination rate $\kappa_{\rm ee} = k_3n(t)$. This process requires high exciton densities to be efficient and is neglected for low excitation powers. These processes can all be combined into one differential equation

$$\dot{n}(t) = -k_1 n(t) - \sum_m k_m n_{\text{defect, m}} n(t) = -\kappa_{\text{rad}} n(t) - \kappa_{\text{non-rad}} n(t)$$
(2.8)

where $\kappa_{\text{non-rad}}$ is the sum of all non-radiative recombination rates. Equation 2.8 can be solved for n(t), which is proportional to the time-resolved PL (TRPL) intensity $I_{\text{PL}}(t) \sim n(t) =$ $n(0)\exp(-(\kappa_{\text{rad}} + \kappa_{\text{non-rad}})t)$ at any given time t. In this simple case TRPL is represented by a single exponential function. Measuring the TRPL intensity experimentally, the PL lifetime of excitons $\tau_{\text{PL}} = (\kappa_{\text{rad}} + \kappa_{\text{non-rad}})^{-1}$ can be extracted.^{60,91,92}

In contrast, when describing exciton dynamics in QDs, each QDs must first be modeled

individually. This is because exciton capture and recombination are random processes, independent on the average occupation number of that state within a QD ensemble. Only after considering individual QDs can an ensemble average be performed. In QDs, charge carriers populate discrete energy levels, which are either occupied or not. To account for this, microstates describing all possible occupation scenarios of a single QD are introduced. Transitions between different microstates are governed by master equations, which describe all possible exciton relaxation and recombination pathways.^{93,94} This microstate-based description of QDs differs from the ensemble description of bulk excitons using differential equations as in **Equation 2.8**. However, the ensemble approach provides a reasonable first approximation of time-resolved e-h pair dynamics in a QD ensemble, as demonstrated in different studies.^{36,95–97} In this case n(t) represents the number of excited QDs in the measured ensemble, assuming only one exciton per QD is present. Therefore, in this work, exciton and QD ensemble dynamics are analyzed using simple ensemble differential equations as an initial framework to gain insights into their behavior.

All optical transitions, including absorption and emission, possess a finite linewidth in energy due to homogeneous and inhomogeneous broadening mechanisms. Homogeneous broadening affects all emitters in the same way. The natural linewidth is a type of homogeneous broadening, which is an intrinsic characteristic of an emission from a single emitter at 0 K and is related to the finite lifetime of the excited state by the Heisenberg's uncertainty principle.⁹⁸ Additionally, homogeneous broadening can be caused by exciton-phonon scattering, which is temperature dependent.⁹⁹ Scattering from ionized impurities and carrier-carrier scattering can also contribute to homogeneous broadening. Homogeneous broadening leads to a Lorentzian line shape of an optical transition. Inhomogeneous broadening does not affect all emitters equally. It may originate from variations in the sample, such as differences in the local dielectric constant, electronic band structure, or size distribution of QDs (dependence of **Equation 2.6** on the QD radius $r_{\rm QD}$). These are intrinsic properties of any material and, hence, do not strongly change with temperature. Inhomogeneous broadening leads to a Gaussian line shape of an optical transition.

2.1.4 Surface Ligands for LHP QDs

Colloidal QDs generally consist of a semiconductor core capped with a surfactant-like organic molecule shell - ligands, as shown in **Figure 2.4a**. Typically, a ligand is an organic molecule containing a head group that binds to the QD surface and a long alkene or alkane tail group. Ligands play an important role in the synthesis, colloidal stability, and surface defect passivation of QDs.

During synthesis, ligands can help regulate the solubility and availability of precursors and control the size and shape of QDs.^{82,86,101} After synthesis, ligands minimize the surface energy of QDs by binding to their surfaces, securing QDs' colloidal stability in various solvents.¹⁰² Purposeful engineering of ligand tail groups can significantly enhance QD colloidal stability

for target solvents.¹⁰³ By binding to QD surfaces, ligands can passivate deleterious surface defects, significantly improving the QD's PL quantum yield (PLQY) and, consequently, their suitability for devices such as LEDs.¹⁰⁴ This is especially important for conventional QDs, such as CdSe, where surface defects usually form deep trap states that increase non-radiative recombination rates, significantly quenching QD emission and decreasing charge carrier mobilities in these materials.^{12,40} Additionally, ligand tail groups can be purposefully engineered to include special functional groups that can interact with the QD and shape the optical properties of the QD-ligand system.¹⁰⁵

The way ligands bind to QD surfaces depends on the type of ligand and the QD surface. Ligand binding to LHP surfaces is highly dynamic, with ligands in constant and rapid exchange between free and surface-bound states. Ligands tend to desorb from LHP due to aging, dilution, or purification, leading to the formation of surface defects and a reduction in NCs colloidal stability.¹⁰⁶ This can be combated by choosing ligands that have high binding affinity to LHP surfaces, contain more than one head group, or have a purposefully engineered tail group.^{103,107–109}

Typical head groups of ligands suitable for LHP surfaces include ammonium-carboxylate pairs (e.g. NH_3^+ and COO⁻), ammonium-phosphonate or ammonium-sulfonate pairs (e.g. $N(CH_3)_3^+$ and PO_3^- , or $N(CH_3)_3$ and SO_3^- ,), and ammonium salts (e.g. $N(CH_3)_2^+$ and X^-), as schematically illustrated in Figure 2.4b.^{39,40} One of the most commonly used ligand pairs for LHP QDs from the first group is oleylamine (OLA) and oleic acid (OA) (Figure 2.4c). It is believed, that in the presence of excess OLA a proton is exchanged from the acid to the amine, leading to the formation of base-acid oleylammonium-oleate pair, where the former can bind at the A-site and the latter at the X-site of the LHP surface.^{39,40,106} From the second group, neutral zwitterionic lecithin ligands containing two head groups, positively charged quaternary ammonium and a negatively charged phosphonic acid, are very popular (Figure **2.4c**).⁸² From the third group, didodecyldimethylammonium bromide (DDAB) ligands are the most prominent example (Figure 2.4c). Both of these ligands have been shown to significantly improve the PLQY and colloidal stability of LHP QDs due to their tight binding to their surfaces.^{82,108} It has been suggested that ammonium head groups substitute A-site vacancies or displace A-site cations, whereas head groups containing sulfonic or phosphonic acid substitute X-site vacancies or possibly displace X-site anion and bind to undercoordinated lead on the surfaces of LHP NCs.^{39,40,106}

2.1.5 Post-Synthetic Compositional Variation

LHPs have the unique ability to rapidly undergo post-synthetic halide exchange.¹¹⁰ Immersing a LHP ABX₃ in a solution containing a high concentration of Y⁻ halides different than the native halide X⁻ in the original crystal, results in a solid solution in the form ABX_zY_{3-z} with the stoichiometric coefficient $0 \le z \le 3$. Depending on the reaction time and the new halide concentration, native halides can be partially or completely replaced by the new halide.



Figure 2.4: Ligand capping of LHP QD surfaces. a) Schematic illustration of a ligand capped QD. b) Schematic illustration of LHP QD surface with attached ligands featuring different head groups. c) Chemical formulas of common LHP QD ligands, including OA and OLA pair, lecithin, and DDAB ligands. Red head groups have binding affinities to an A-site, whereas green head groups have binding affinities to an X-site at QD surfaces.

The halide exchange reaction can be described by new halides entering the original crystal while the native halides diffuse out:

$$ABX_3 + Y_{sol} \xrightarrow{Time} ABX_zY_{3-z} + X_{sol} + Y_{sol}$$
 (2.9)

Halide exchange reaction in LHPs is diffusion governed, where the diffusion process is kinetically driven by the halide concentration gradient between the crystal and its surrounding environment.^{111,112} The full process of the halide exchange involves the exchange between halides in the solution and native halides in the crystal at the crystal-solution interface and subsequent migration of the new halides inside the crystal. Generally, halide diffusion can be described by Fick's first law, which states that a solute will move from a region of high concentration to a region of low concentration across a concentration gradient.¹¹²

Following the exchange at the interface, the new halides diffuse and migrate inside the crystal. Halide migration inside the LHP lattice involves predominantly vacancy and interstitial diffusion mechanisms.¹¹² In a vacancy diffusion mechanism an atom on an adjacent site hops into the vacant site. The efficiency of this mechanism depends on the vacancy density

in the crystal. In case of the interstitial diffusion mechanism, an atom hops from one interstitial site to one of its nearest-neighbor interstitial sites without permanently displacing any of the matrix atoms. Solute atoms which can occupy interstitial sites are usually appreciably smaller than the matrix atoms. For atoms to hop via these mechanisms, the lattice must dilate and distort locally at an appreciable magnitude, which constitute an energetic barrier for the hopping. The energetic barrier can be overcome if, for example, sufficient thermal energy is present. Other less common diffusion mechanisms may involve translocation and ring mechanisms. In the former two atoms of the same type exchange places, in the latter nearest-neighbor atoms rotate in a ring to exchange places (**Figure 2.5**).^{112,113}



Figure 2.5: Post-synthetic halide exchange. A simplified illustration of post-synthetic halide exchange and diffusion in a LHP crystal with native halide species (green) immersed in a highly concentrated solution containing new halide species (orange). (i) New halides diffuse to the crystal interface and exchange native halides. New halides diffuse inside the crystal via (ii) vacancy diffusion, (iii) translocation, (iv) ring or (v) interstitial mechanisms away from the interface.

Important thermodynamic factors affecting halide diffusion efficiency include changes in the lattice and surface energies as well as disorder. For example, substitution of native halides with new halides can induce lattice strain due to differences in atomic sizes, and influence the diffusion process. Factors such as temperature and halide type also play an important role, since the diffusion coefficient is temperature- and halide-type dependent. Solubility of the new and native halides in the solution will affect the diffusion kinetics, too.^{20,112,114}

One important consequence of halide exchange in LHPs is a change in the lattice constant. In solid solutions, the change in the lattice constant with respect to the unalloyed lattice constant a(0) generally varies linearly with the amount of the alloyed species:

$$\Delta a(\tilde{z}) = a(\tilde{z}) - a(0) = (a(1) - a(0))\tilde{z}$$
(2.10)

Here \tilde{z} is a normalized stoichiometric coefficient, $\tilde{z} \in [0, 1]$, and $a(\tilde{z})$ is the corresponding lattice constant.^{115,116} This change is primarily due to differences in sizes of the alloyed and alloying atoms, as well as the nature of atomic interactions, and can be easily measured

using X-ray diffraction (XRD) technique. In LHPs, exchanging Br⁻ with Cl⁻ reduces the lattice constant due to the ionic radius of Cl⁻ being smaller than that of Br⁻. Conversely, substituting Br⁻ with I⁻ increases the lattice constant due to the larger ionic radius of I⁻ (**Figure 2.6**).^{23,52,117–119} Deviation from this linear trend may occur if alloying induces a phase change or if the difference in ionic radii of the alloyed and alloying atoms is too large.¹²⁰

Another important consequence of halide exchange in LHPs is a change in their band gap. Empirically, the change in the band gap of an alloy with respect to unalloyed band gap $E_g(0)$ as a function of its composition is described by a second-order polynomial

$$\Delta E_q(\tilde{z}) = E_q(\tilde{z}) - E_q(0) = (E_q(1) - E_q(0))((1 - b)\tilde{z} + b\tilde{z}^2), \qquad (2.11)$$

where $E_g(\tilde{z})$ is the band gap of alloy, *b* is the bowing parameter quantifying the deviation from a linear band gap dependence. These nonlinear effects arise from local variations in the crystal structure due to differences in size of alloyed and alloying atoms, inhomogeneous alloying, and electronic interactions between alloying atoms.^{67,121} Because the VB in LHPs has a significant contribution from the halide orbitals, exchanging native halides with new halides affects the band structure and ultimately, the band gap. Adjusting the halide ratio Y⁻/X⁻ (i.e., the stoichiometric coefficient z) allows precise tuning of the LHPs' band gap across the entire visible spectrum. Substituting Br⁻ with Cl⁻ in MAPbBr₃ increases the band gap (blue-shift) despite lattice contraction, because higher electronegativity of Cl⁻ compared to Br⁻ causes a significant downward shift in VB. For the opposite reason, substituting Br⁻ with I⁻ decreases the band gap (red-shift) (**Figure 2.6**).^{23,52,117–119,122,123} Properties such as PL emission, PLQY, and exciton binding energy (**Table 2.1**) may also be affected by the chemical composition.



Figure 2.6: Effect of halide composition on LHP crystal lattice and band gap. Schematic representations of (top) the cubic unit cell and (bottom) the band gap of MAPbX₃ crystals. Lattice constant reduces and band gap increases from I⁻ to Cl⁻. For clarity, the cubic structure of MAPbI₃, which is stable at high temperatures, is depicted.

Post-synthetic compositional changes in LHPs are not limited to halide exchange only. Post-synthetic A-site and B-site ion exchange are both possible. A-site cation migration occurs through the unit cell face consisting of four X-site ions. This leads to a higher activation energy compared to an X-site anion migration. In addition, A-site cations, especially in HOIPs, tend to have a larger ionic radius compared to X-site anions, making their migration detrimental for the crystalline stability. B-site ion migration is even more restricted, as B-site cations occupy the central position in the cation sublattice structure and have the highest migration energy barrier.¹¹² The types of species that can replace native ions in LHPs are limited by the Goldschmidt tolerance and octahedral factors shown in **Equations 2.1** and **2.2**.

2.2 Organic Molecules

Organic molecules are composed of carbon atoms bonded with hydrogen, oxygen, nitrogen, or carbon itself. Carbon atoms have a very high affinity for forming strong covalent bonds with other elements. Carbon's ability to form four equivalent hybrid atomic orbitals from its singly occupied outermost s and p atomic orbitals allows it to establish four covalent bonds. In a covalent bond, electrons can no longer be assigned to the atomic orbitals of individual atoms that make up a molecule but to joint molecular orbitals instead.

In the ground state of a molecule, the energetically highest occupied molecular orbital is called the HOMO, and the energetically lowest unoccupied molecular orbital is called the LUMO. In the simplest picture, when a molecule absorbs a photon, an electron is promoted from the HOMO to the LUMO, leaving a hole behind in the HOMO. The Coulomb interaction between excited electrons and holes, as well as electron spin, cannot be adequately described using the single-electron HOMO-LUMO picture. Instead, in analogy to a two-particle picture for excitons in inorganic semiconductors, a many-electron state picture should be used. In the state picture, the ground state energy of the molecule is arbitrarily set to zero. The excited state energies are positioned above and relative to it.

In the majority of molecules, the HOMO is fully filled, and hence, the ground state has a total spin of zero. Therefore, it is sufficient to consider the spins of the unpaired electrons in an excited state configuration. A state with a total spin of 0 is called a singlet state, while a state with a total spin of 1 - a triplet state. Typically, in molecules, the energy of the lowest triplet state T_1 is lower than that of the lowest excited singlet state S_1 due to the exchange interaction.

To obtain a potential energy surface of a molecular state, the total energy of a molecule is calculated for different configuration coordinates of atoms, Q_i . The potential energy surface describes how the total energy of the molecular state changes when the configuration coordinates of atoms are varied. The configuration coordinates Q_i describe the collective vibrational motion of atoms in a molecule as coupled harmonic oscillators. Q_i are expressed as linear combinations of each individual atom's displacement from its equilibrium coordinates. In the i^{th} normal mode, the entire system oscillates with a single vibrational frequency ω_i and the vibrational energy is given by $E_n = (n + \frac{1}{2})\hbar\omega_i$, where $n \in \mathbb{N}$ denotes the number of excited quanta.

In a real molecule, there are many normal modes present at different energies. Taking a slice through the potential energy surface of a certain molecular state along a configuration coordinate Q_i , the energies of the corresponding vibrational levels can be visualized as horizontal lines, labeled as n = 0, 1, 2, ... as shown in **Figure 2.7a**. Because of the large energetic difference between consecutive vibrational levels (100-300 meV), at room temperature, $\hbar \omega \gg k_B T$ (k_B is the Boltzmann constant) only the lowest vibrational levels (n = 0) are occupied. The potential energy curves corresponding to an excited state of a molecule are displaced to greater equilibrium bond lengths, corresponding to a larger value of the configuration coordinate Q_i , because electronically excited states usually have a more anti-bonding character than the electronic ground state. The magnitude of the displacement depends on factors such as the rigidity of the bonds in the molecule and its immediate environment. In the state picture, the optical transitions between initial and final states can be visualized by vertical lines as illustrated in **Figure 2.7a**.^{124,125}

At room temperature, absorption happens from the 0th vibrational level of the ground state to the mth vibration level of the final excited state of the molecule, shown in **Figure 2.7b**, with the transition probability given by the Franck-Condon factor, which describes the spatial overlap of vibrational wavefunctions. Photon absorption involves different vibrational levels of different normal modes. Hence, the resulting spectrum is a superposition of the transitions between different vibrational modes.

Immediately following optical excitation, the molecule is initially in the ground state configuration and has excess potential energy relative to the excited state configuration S_i . This excess energy is quickly dissipated via vibrational relaxation and intersystem crossing, as the atoms adapt to the change in electronic distribution in the excited state. This process, referred to as geometric reorganization, leads to the relaxation of the excited molecule to it's lowest singlet excited state S_1 within a few tens to hundreds of femtoseconds. Vibrational relaxation refers to dissipation of energy within a single molecular state by emission of vibrational quanta. Internal conversion refers to "energy transfer" from an excited state S_i to an isoenergetic vibrational level of the next lower excited state S_{i-1} of the same molecule (**Figure 2.8**).

From the lowest excited singlet state S_1 , the molecule can relax radiatively to the singlet ground state S_0 via fluorescence, usually on the nanosecond timescale. Due to internal conversion and vibrational relaxation rates being several orders of magnitudes faster than the fluorescence rate, emission in molecules occurs from the lowest vibrational level of the lowest excited state of a spin manifold, known as Kasha's rule. Photon emission from the excited state of molecule can be described in a similar manner as photon absorption, including the Franck-Condon factor. Therefore, emission spectra in molecules typically appear as a mirror image of the corresponding absorption spectra (**Figure 2.7b**). The emission and absorption spectra of molecules at room temperature are affected by homogeneous and inhomogeneous broadening, just as is the case for inorganic semiconductors.¹²⁵

Alternatively, non-radiative relaxation to the ground state via internal conversion is also possible. The efficiency of this pathway is determined by the energy difference between the S_1 and S_0 states. Intersystem crossing is another non-radiative relaxation pathway, where transfer from a singlet excited state S_1 to an isoenergetic vibrational level of the lower triplet excited state T_1 of the same molecule takes place. The intersystem crossing efficiency is dictated not only by the energy difference between the S_1 and T_1 states, but most importantly, by the spin-orbit coupling magnitude in the molecule. Spin-orbit coupling can obtain a con-



Figure 2.7: Absorption and emission in organic molecules. a) Potential energy curves of the singlet ground state S_0 and the lowest excited singlet state S_1 of a molecule as a function of configuration coordinates Q_i . The excited state curve is displaced to a larger configuration coordinates Q_1 compared to the ground state Q_0 . Vibrational levels are separated by an energy difference $\hbar \omega_i$, with their corresponding wavefunctions depicted as grey shaded areas. b) Illustration of absorption and emission spectra of a molecule ensemble at ambient conditions, highlighting different vibrational transitions.

siderable magnitude if the molecule contains heavy atoms or if heavy atoms are placed in its vicinity. Ultimately, the molecule in the T_1 state can relax to the singlet ground state S_0 radiatively via phosphorescence. Since the transition from the T_1 state to the S_0 state is spin-forbidden, phosphorescence occurs on very long timescales, with its efficiency dictated by the spin-orbit coupling. Intersystem crossing can also occur in the reverse direction, from the triplet excited state to the singlet ground state. Various radiative and non-radiative relaxation pathways are depicted in a Jablonski diagram in **Figure 2.8**.



Figure 2.8: Jablonski diagram. The diagram shows singlet and triplet states of a molecule, along with their vibrational levels. Various radiative and non-radiative relaxation pathways are indicated and color-coded.

Dye Molecules

Dye molecules are organic compounds, that absorb light in the UV, visible, and NIR regions. The part of the dye molecule responsible for light absorption is called a chromophore, which consists of a π -conjugated system: a hydrocarbon chain with alternating double and single bonds. In a single bond, a carbon atom forms a σ bond with another atom. A σ bond is symmetric around the internuclear axis. A double bond is formed when a carbon atom bonds with another atom through both a σ bond and a π bond. In a π bond electrons more likely to be found above or below the internuclear axis. In a π -conjugated system, electrons are delocalized in the interconnected p atomic orbitals, which lowers the overall energy of the molecule and stabilizes it. Typically, as the number of conjugated double bonds increases, optical transitions shifts towards lower energies, resulting in absorption at longer wavelengths.^{124,126} An exemplary dye molecule, rhodamine 110 chloride, along with its representative absorption and emission spectra, is shown in **Figure 2.9**.



Figure 2.9: Rhodamine 110 chloride dye. a) Chemical structure of rhodamine 110 chloride dye, highlighting the xanthene core (chromophore) in green. Single bonds are depicted with solid lines, and double bonds with two parallel lines. b) Representative absorption and emission spectra of rhodamine 110 chloride adapted from [127], exhibiting absorption and emission maxima at 500 and 520 nm, respectively.

Chromophores carry an electric dipole moment, caused by temporal fluctuations of the electron density in the ground state and redistribution of the molecule's electron density in response to the excitation in their excited state. When a dye molecule is closely surrounded by other molecules, its dipole moment can induce polarization in the surrounding molecules, leading to van-der-Waals dipole-dipole interaction. This interaction lowers the potential energy of the dye-adjacent-environment system by the interaction energy, which is mirrored as a shift in the dye's absorption and emission spectra. In molecules dissolved in a solvent, this effect leads to a photon emission at slightly lower energies compared to the the photon absorption, a phenomenon known as Stokes' shift.¹²⁵

Interactions between adjacent molecules play an important role not only for dyes in solvents but in condensed-phase such as disordered undiluted films, where dye molecules are arranged close to each other. Van-der-Waals and electronic coupling between neighboring dye molecules can lead to the formation of dimers or excimers, which exhibit optical properties different from those of an isolated monomer.¹²⁵ Therefore, optical properties of dyes are very sensitive to their immediate environment.

Amino Acids

Another important subgroup of organic molecules is amino acids. So far, hundreds of different amino acids have been synthesized, but the most important ones are the so-called α -amino acids, which are the building blocks of peptides and proteins in biological systems.¹²⁸ α -amino acids contain amino (NH₂) and carboxyl acid (COOH) functional groups, a central α -carbon atom bonded to a hydrogen atom and a side chain R. The side chain can be polar, charged, or hydrophobic and significantly influence the physical and chemical properties of amino acids.¹²⁹ α -amino acids include molecules such as cysteine, serine, lysine (**Figure 2.10**), and glycine.

All α -amino acids are intrinsically chiral, meaning they cannot be superimposed on their mirror image by any combination of rotations, translations, or some conformational changes, except for glycine. In nature only L-amino acids exist in abundance, their stereoisomers, D-amino acids, being more rare.¹²⁸ L and D notation is used to distinguish between two molecules that are mirror images of each other, also called enantiomers.



Figure 2.10: Amino acid L-lysine. Chemical structure of the amino acid L-Lys. The α -carbon is highlighted in blue, the side chain in green, the amino group in orange, and the carboxyl group in red.

2.3 Organic Molecules on LHP QD Surfaces

Donor-acceptor systems consisting of a QD donor and a molecular acceptor, exhibiting efficient interaction have emerged as crucial elements in diverse fields such as sensing,^{31,32} solar light harvesting,^{33,34} microscopy,³⁵ quantum information,¹³⁰ and photocatalysis,^{21,43} or simply as platforms for investigating excited-state interactions.^{36–38} Especially, LHP QDs have garnered significant attention due to their unique properties compared to conventional QDs like CdSe. Conventional QDs typically need a wide band gap thick inorganic shell to passivate surface defects and ligands to ensure colloidal stability. This shell strongly limits the extent of interactions between QDs and surface-bound organic molecules. In contrast, LHP QDs can achieve high PLQYs by ligands alone due to their high defect tolerance,¹¹⁹ making their surfaces more accessible for the direct attachment of molecules, which is crucial for efficient interaction.

In a typical donor-acceptor system, energy or charge is transferred from an excited-state donor to a ground-state acceptor. Depending on the desired application, a donor-acceptor system must be optimized either for energy or charge transfer to achieve the desired functionality. **Figure 2.11** illustrates energy band alignment between two bulk semiconductors. In a so-called type I band alignment, the smaller band gap material provides the lowest energy states for both electrons and holes, facilitating ET. In a type II band alignment, minimum energies for electrons and holes are in the different materials, promoting CT.¹³¹



Figure 2.11: Energy band alignment between two semiconductors. a) In a type I band alignment, the smaller band gap material provides the lowest energy states for both electrons and holes, facilitating ET. b) In a type II band alignment minimum energies for electrons and holes are in the different materials, facilitating CT. χ_i represents electron affinity relative to the vacuum energy level E_{vac} . In case of molecules, their oxidation and reduction energies need to be considered with respect to E_{vac} . Adapted from [131].

2.3.1 Energy Transfer

ET from QDs to molecules can occur via two main pathways: radiatively by emission and reabsorption of light or non-radiatively by quantum-mechanical coupling. Far-field radiative
ET is a two-step process involving photon emission by the donor, followed by its reabsorption by the acceptor. This long-range interaction, extending over hundreds of nanometers, depends on the spectral overlap between donor emission and acceptor absorption, and their respective concentrations.¹³² If the donor and acceptor are of the same species with significant spectral overlap, radiative ET can lead to excited state trapping, appearing to increase its lifetime.¹²⁵ This process reduces the total PLQY of the system.

In a non-radiative ET via quantum-mechanical coupling the excited donor relaxes to the ground state while the ground state acceptor is excited through quantum-mechanical coupling. The ET rate from a donor D to an acceptor A is given by the Fermi's golden rule in **Equation 2.3**, which is a sum of all possible initial and final donor-acceptor transition probabilities. For conceptual understanding of ET, let's consider initial and final states, where the electronic wavefunctions with spin wavefunctions written out explicitly, are given by **Equations 2.12** and **2.13**, respectively, involving only two electrons.^{125,132}

$$\Psi_{i} = \frac{1}{\sqrt{2}} (\psi_{\mathrm{D}^{*}}(\mathbf{r}_{1})\chi_{\mathrm{D}^{*},1}\psi_{\mathrm{A}}(\mathbf{r}_{2})\chi_{\mathrm{A},2} - \psi_{\mathrm{D}^{*}}(\mathbf{r}_{2})\chi_{\mathrm{D}^{*},2}\psi_{\mathrm{A}}(\mathbf{r}_{1})\chi_{\mathrm{A},2})$$
(2.12)

$$\Psi_f = \frac{1}{\sqrt{2}} (\psi_{\rm D}(\mathbf{r}_1) \chi_{\rm D,1} \psi_{\rm A*}(\mathbf{r}_2) \chi_{\rm A*,2} - \psi_{\rm D}(\mathbf{r}_2) \chi_{\rm D,2} \psi_{\rm A*}(\mathbf{r}_1) \chi_{\rm A*,2})$$
(2.13)

Here, the vector \mathbf{r} refers to the electron spatial coordinates, and the numbers 1 and 2 refer to the electrons involved. $\psi(\mathbf{r})$ and χ represent spatial and spin wavefunctions of electrons, respectively. * denotes an excited state.

To evaluate the ET probability, the interaction matrix element $|\langle \Psi_f | H' | \Psi_i \rangle|^2$ must be computed, where H' is the coupling perturbation, that is the sum of all Coulomb interactions of the outer-shell electrons and cores of the donor with those of the acceptor, accounting for the dielectric constant of the surrounding medium. Upon evaluating the interaction matrix element, we find that it can be divided into two parts: a Coulomb term $\beta_{\rm C}$, as shown in **Equation 2.14**, and an exchange term $\beta_{\rm ex}$, as shown in **Equation 2.15**, assuming the interaction is spin-independent.

$$\beta_{C} = |\langle \psi_{\rm D}(\mathbf{r}_{1})\psi_{\rm A}*(\mathbf{r}_{2})|H'|\psi_{\rm D}*(\mathbf{r}_{1})\psi_{\rm A}(\mathbf{r}_{2})\rangle|^{2}|\langle \chi_{\rm D,1}\chi_{\rm A}*,_{2}|\chi_{\rm D}*,_{1}\chi_{\rm A,2}\rangle|^{2}$$
(2.14)

$$\beta_{\rm ex} = |\langle \psi_{\rm D}(\mathbf{r}_1)\psi_{\rm A*}(\mathbf{r}_2)|H'|\psi_{\rm D*}(\mathbf{r}_2)\psi_{\rm A}(\mathbf{r}_1)\rangle|^2|\langle \chi_{\rm D,1}\chi_{\rm A*,2}|\chi_{\rm D*,2}\chi_{\rm A,1}\rangle|^2$$
(2.15)

The Coulomb term describes the process, in which the initially excited electron on donor returns to the ground state while an electron on acceptor is simultaneously excited. The exchange term is a purely quantum mechanical effect and describes an exchange of electron between donor and acceptor.^{125,132,133}

Förster Resonance Energy Transfer

If the distance between the donor and acceptor is much larger than their size, such that they can be considered point-like, the Coulomb term can be approximated by the dominant dipole-dipole interaction, as shown in **Equation 2.16**, which gives rise to so-called Förster resonance energy transfer (FRET).^{133,134}

$$\beta_C \sim \frac{\mu_{\rm D}\mu_{\rm A}}{R^3} (\cos\theta_{\rm DA} - 3\cos\theta_{\rm D}\cos\theta_{\rm A})$$
(2.16)

Here, $\mu_{\rm D}$ and $\mu_{\rm A}$ are the donor and acceptor transition dipole moments. $\theta_{\rm DA}$ is the angle between the transition dipole moments, and $\theta_{\rm D}$ and $\theta_{\rm A}$ are the angles between each transition dipole moment and the distance vector connecting them. By evaluating the total transition probability from Fermi's golden rule, including all possible initial and final donor-acceptor transition possibilities, we obtain the FRET rate $\kappa_{\rm FRET}$

$$\kappa_{\rm FRET} \sim \frac{1}{n^4} \frac{\eta_{\rm D}}{\tau_{\rm D}} \frac{\kappa^2}{R^6} \int \tilde{I}_{\rm D}(\lambda) \epsilon_{\rm A}(\lambda) \lambda^4 d\lambda \sim \frac{1}{\tau_{\rm D}} \left(\frac{R_0}{R}\right)^6.$$
(2.17)

Here *n* is the refractive index of the medium surrounding the donor and acceptor. $\eta_{\rm D}$ and $\tau_{\rm D}$ are the PLQY and PL lifetime of the donor, respectively. $\kappa^2 = (\cos\theta_{\rm DA} - 3\cos\theta_{\rm D}\cos\theta_{\rm A})^2$ is the dipole orientation factor, *R* is the donor-acceptor distance, $\tilde{I}_{\rm D}(\lambda)$ is the normalized donor emission, such that $\int \tilde{I}_{\rm D}(\lambda) d\lambda = 1$, and $\epsilon_{\rm A}(\lambda)$ is the extinction coefficient of the acceptor, λ is the wavelength. The integral $J = \int \tilde{I}_{\rm D}(\lambda)\epsilon_{\rm A}(\lambda)\lambda^4 d\lambda$ is referred to as the spectral overlap integral. The Förster radius R_0 is the distance at which FRET and emission from the donor are equally likely. Knowing the Förster radius, FRET can be used as a "molecular ruler" to estimate intermolecular distances.¹³⁵

From Equation 2.17, three main requirements for efficient FRET can be deduced:

- 1. The $1/R^6$ dependence of the FRET rate shows that the dipole-dipole interaction is highly sensitive to the interparticle distance. As a result, the FRET range typically extends over distances up to 10 nm (**Figure 2.12**).
- 2. For the integral $\eta_{\rm D} \int I_{\rm D}(\lambda) \epsilon_{\rm A}(\lambda) \lambda^4 d\lambda$ to be large, both the donor emission and acceptor absorption must have large oscillator strengths and large spectral overlap.
- 3. The transition dipole moments of the donor and acceptor need to be aligned to maximize κ^2 . For isotropic arrangement of dipoles, $\kappa^2=2/3$, but for perpendicular dipoles, $\kappa^2=0$.

Inspecting the spin part of **Equation 2.14**, it is nonzero only if the spin wavefunctions of the donor and acceptor in their ground and excited states have the same spin multiplicities. Hence, FRET can occur between two singlet states. ET from a singlet-excited donor with a triplet ground state to an acceptor in a singlet ground state transitioning to its triplet excited state is spin-forbidden in FRET. In addition, since the absorption and emission oscillator strengths of singlet-triplet transitions are very small, FRET between these states is highly unlikely.^{125,132–134,136,137}

Equation 2.17 holds only at distances where donor and acceptor can be considered pointlike. If a donor is positioned in front of a thin, large semiconductor nanoplatelet acceptor,



Figure 2.12: Förster resonance ET. a) Simplified illustration of FRET, which arises from dipole-dipole interactions between a point-like donor and acceptor. FRET efficiency depends on the donor-acceptor distance, their transition dipole orientations (not shown), and b) the spectral overlap between donor emission and acceptor absorption. VB and CB stand for valence band and conduction band, respectively.

the FRET rate scales as $1/R^4$. If the acceptor is a bulk semiconductor layer, the FRET rate follows a $1/R^3$ dependence. As the donor-acceptor distance decreases, the dipole-dipole approximation is no longer sufficient to accurately describe the donor-acceptor interaction. Higher order terms, such as electric dipole-quadrupole interactions, must be considered. At even smaller distances, the exchange term becomes significant, leading to Dexter exchange ET.^{133,138}

Dexter Exchange Energy Transfer

The exchange term β_{ex} in **Equation 2.15** represents the electrostatic interaction between the charge clouds of the donor and acceptor. Since wavefunctions $\psi(\mathbf{r})$ decay exponentially with increasing donor-acceptor distance, their interaction will be insignificant throughout most of the space except when the donor-acceptor distance is very small, such that significant charge cloud overlap occurs. This is why Dexter exchange ET is also referred to as through-bond ET.¹²⁵ The ET rate of the Dexter exchange mechanism can be written as:

$$\kappa_{\text{Dexter}} \sim e^{-2\frac{R}{L}},$$
(2.18)

where L is an effective orbital radius of the excited donor and ground-state acceptor states and R is the donor-acceptor distance.

For efficient Dexter exchange ET following requirements can be identified:

- 1. The donor-acceptor distance R must be kept as short as possible, because the interaction efficiency decreases exponentially with increasing distance due to the decreasing spatial wavefunction overlap, as illustrated in **Figure 2.13**. Dexter exchange ET typically occurs at distances of 1 nm or less.
- 2. Isoenergetic states in donor and acceptor for energy "donation" and "acceptance" must

be available. Unlike FRET, optical transitions to and from these states with respect to the ground state do not necessarily need to have large oscillator strengths. This means that Dexter exchange ET can also occur between optically inactive states.¹³² Therefore, compared to FRET, for the Dexter exchange ET the spectral overlap requirement is fully lifted.



Figure 2.13: Dexter exchange ET. Simplified illustration of a) efficient and b) inefficient Dexter exchange ET. This process occurs through interaction between the charge clouds of the donor and acceptor. The spatial wavefunctions of the donor, $\psi_{\rm D}(\mathbf{r})$, and acceptor, $\psi_{\rm A}(\mathbf{r})$, depicted in grey, decay exponentially with increasing donor-acceptor distance. Consequently, significant interaction occurs only at short distances where substantial spatial wavefunction overlap is present (dark grey area in (a)). VB and CB stand for valence band and conduction band, respectively.

Examining the spin part of **Equation 2.15** reveals that ET between states of different spin multiplicities is allowed. For example, Dexter exchange ET can convert an initially excited-state triplet donor and a ground-state singlet acceptor into a ground-state singlet donor and an excited-state triplet acceptor. This ET process is known as triplet-triplet ET. Thus, in contrast to FRET, Dexter exchange ET allows not only singlet-singlet but also triplet-triplet ET processes.^{132,133,136}

From this discussion, it becomes clear that Dexter exchange ET is more versatile than FRET. Unlike FRET, where spectral overlap is a limiting factor, Dexter exchange ET allows a wider selection of possible donor-acceptor pairs. In addition, its spin selection rules permit ET between states that cannot interact via the FRET mechanism.

Both the Coulomb and exchange terms together determine the total ET rate. Which term will dominate depends on the donor-acceptor distance. At large distances, given that all the requirements for the dipole-dipole interaction are fulfilled, ET occurs primarily via FRET. However, at shorter distances below 1 nm, the exchange interaction becomes the dominant mechanism.¹²⁵ At even smaller distances, wavefunctions start to overlap significantly, causing the donor and acceptor to no longer behave as separate entities but as a single material with electronic properties distinct from those of its individual components.^{139–141}

2.3.2 Charge Transfer

Charge carrier injection or extraction in donor-acceptor systems is important for the successful operation of LEDs or solar cells. For successful CT, charges must overcome the CT barrier. CT from a photoexcited donor to a ground state acceptor can be described by Marcus' theory, which has been experimentally verified for molecular donors and acceptors,¹⁴² as well as, extensively applied to describe CT in QD donor-molecular acceptor systems at ambient conditions.^{105,143–145}

In Marcus' theory, the donor, acceptor and solvent are treated as a unified system. The potential energy curve of this system, as a function of the generalized configuration coordinate Q, is approximated as a parabola. The potential energy minimum of the system, consisting of the excited donor and ground state acceptor, occurs at a different configuration coordinate than that of the final state, in which a charge has transferred to the acceptor. The energy needed to rearrange the initial system to match the final geometry is called the reorganization energy λ_g . However, CT does not require the full value of λ_g . Rather, CT can happen via thermal activation to the point where the initial and final state potential energy curves cross. In cases when the energy of the vibrational and phonon modes is small compared to the thermal energy of the environment, $\hbar \omega \ll k_B T$, and the initial and final potential parabola are equivalent, the CT rate can be expressed as:

$$\kappa_{\text{Marcus}} \sim H_{DA}^2 \sqrt{\frac{1}{\lambda_g k_B T}} e^{\frac{(\lambda_g + \Delta G_0)^2}{4\lambda_g k_B T}}$$
(2.19)

Here, ΔG_0 is the potential energy difference between the initial and final states, also known as the driving force, H_{DA} is the electronic coupling term between donor and acceptor states. Therefore, the CT rate depends on the probability of the initial system distorting to reach the intersection, giving rise to the exponential factor in **Equation 2.19**, and the electronic coupling between donor and acceptor states. Schematically, Marcus' theory of CT is illustrated in **Figure 2.14**. **Equation 2.19** predicts that the CT rate first increases with increasing ΔG_0 and then decreases, a phenomenen known as the Marcus inverted regime.¹²⁵ The term H_{DA}^2 usually decreases exponentially with increasing donor-acceptor separation and can be expressed as

$$H_{DA}^2 \sim e^{-2\beta R} \tag{2.20}$$

where β describes the extent of donor-acceptor electronic coupling through the energy barrier, and R is the donor-acceptor distance.^{146,147} Additionally, λ_g has also been found to be distance dependent. Typically, the term H_{DA}^2 limits CT to distances up to 1 nm. However, thermal activation can enable efficient CT at distances beyond 1 nm. Regardless, the CT rate generally decreases with increasing donor-acceptor separation.¹⁴⁷

Equation 2.19 is no longer suitable for large energy differences between the initial and



Figure 2.14: Marcus' theory of CT. a) Simplified schematic illustration of electron transfer from an excited donor D^* to a ground state acceptor A, resulting in a positively charged donor D^+ and a negatively charged acceptor A^- . b) Potential energy curves of the initial and final donor-acceptor-environment systems with equal parabolas, depicting electron transfer from D^* to A, forming a final state D^+A^- . VB and CB stand for valence band and conduction band, respectively.

final states, and particularly, for electron transfer at low temperatures, where tunneling between the initial and final states needs to be taken into account. In that case, the vibrational wavefunction overlap between the initial and final states needs to be explicitly considered and treated quantum mechanically.^{125,147}

Energy conservation is an absolute requirement for ET or CT. Consider a QD donor where the energy difference between the excited and ground states is larger than that of an acceptor molecule. ET or CT occurs isoenergetically, meaning that energy is transferred from the excited donor level to a vibrationally excited state of the acceptor. The excess potential energy of the acceptor is quickly dissipated within less than a picosecond via internal conversion and vibrational relaxation, leaving the acceptor in the lowest vibrational state of its first excited state. The energy dissipation step is usually much faster than the typical time scale of the resonant ET or CT and therefore, ET and CT become a "one way" process. If the energetic difference between the donor and acceptor following the transfer is larger than the thermal energy, energy or charge back transfer is unlikely.

2.3.3 Characterizing Donor-Acceptor Systems

If the donor is emissive, ET or CT in a donor-acceptor system quenches the donor's emission and may alter its PL lifetime, both of which can be used to monitor donor-acceptor interaction efficiency. Here, we focus on QD-donor and molecule-acceptor systems.

A common measure of the donor-acceptor interaction efficiency in a donor-acceptor ensemble is the donor PL quenching, defined as

$$\Phi = \left(1 - \frac{I_{\rm DA}}{I_{\rm D}}\right) \cdot 100\% \tag{2.21}$$

where I_{DA} is the (integrated) PL intensity of the donors in the donor-acceptor ensemble, and I_{D} is the (integrated) PL intensity of the same donor ensemble without the acceptors.^{31,91}

To estimate the ET or CT rates in QD-donor molecule-acceptor systems, the TRPL of such donor-acceptor ensemble can be modeled based on following assumptions:

1. In an ensemble, where several acceptor moleculess can interact with a single donor QD, the portion of QDs interacting with exactly N molecules is given by the Poisson distribution:¹⁴⁸

$$P(\langle N \rangle, N) = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}.$$
(2.22)

where $\langle N \rangle$ is the average number of molecules per QDs in the ensemble, and $\langle N \rangle$ is small.

- 2. Throughout a measurement cycle at any given time, each QD is interacting with a fixed constant number of molecules. All molecules are interacting with QDs at a fixed constant distance, with no free-floating molecules in the solution. This condition can be assumed to be fulfilled for acceptor molecules that have high binding affinity to QD surfaces.
- 3. The ET or CT transfer rate from a single QD to a single acceptor, κ_{transfer} , is constant, regardless of the number of acceptors a single donor is interacting with. The total transfer rate for a QD interacting with N molecules is $N \cdot \kappa_{\text{transfer}}$. There is no interaction between molecules, between QDs, or excitation back-transfer from acceptors to donors.
- 4. A pulsed excitation at t = 0 excites at most one exciton per donor QD. This assumption is valid at low excitation powers.

Under these assumptions, the TRPL of QD ensemble in the QD-molecule system can be described by the differential equation: $^{149-152}$

$$\dot{n}_{\rm D}(t) = -\kappa_{\rm D} n_{\rm D}(t) - N \kappa_{\rm transfer} n_{\rm D}(t), \qquad (2.23)$$

Here, $n_{\rm D}(t)$ is the time-dependent excited-state population of QDs interacting with exactly N molecules. The PL decay rate of the pure donor $\kappa_{\rm D} = \tau_{\rm D}^{-1}$ can be determined experimentally. Solving this equation, considering the Poisson distribution of acceptors across donors, assuming no direct excitation of molecules is possible, and incorporating instrument response function (IRF) via convolution with a Gaussian function $G(t, \mu, \sigma)$, with the mean μ and full width at hald maximum (FWHM) σ , **Equation 2.24** is obtained.

$$I_{\rm D}(\langle N \rangle, t) = A \cdot \theta(t) \sum_{N=0}^{N_{\rm max}} P(\langle N \rangle, N) \cdot e^{-(\kappa_{\rm D} + N\kappa_{\rm transfer})} * {\rm IRF},$$
(2.24)

Here, A is the proportionality factor. $\theta(t)$ is zero for t < 0 and 1 for $t \ge 0$. * represents convolution and N_{max} is the maximum number of molecules a QD can interact with.

Integrating Equation 2.24 with respect to time and disregarding the convolution with the Gaussian IRF, it can be shown that the quenching efficiency Φ introduced in Equation 2.21 can be expressed as:^{60,91,153,154}

$$\Phi = \left(1 - \sum_{N=0}^{N_{\text{max}}} P(\langle N \rangle, N) (1 + N \kappa_{\text{transfer}} \tau_{\text{D}})^{-1}\right) \cdot 100\% \approx$$

$$\approx \frac{\langle N \rangle \kappa_{\text{transfer}}}{\kappa_{\text{D}} + \langle N \rangle \kappa_{\text{transfer}}} \cdot 100\%,$$
(2.25)

which can be used as an alternative measure to assess the donor-acceptor interaction efficiency.

2.3.4 Designing LHP QD-Molecule Hybrid System

To design QD-molecule hybrids exhibiting efficient Dexter exchange ET or CT, the distance between donor QDs and acceptor molecules needs to be minimized, as interaction efficiency decreases with separation. QD-molecule donor-acceptor hybrids exhibiting efficient excited-state interactions are promising alternatives for multi-perovskite QD based devices, such as white-light emitters or photocatalytic systems. Despite their potential, the design of efficient LHP QD-molecular systems is underexplored compared to the systems containing conventional QDs, such as CdSe.

One common design method of QD-molecule hybrids involves directly mixing QDs with desired molecules that do not necessarily possess high binding affinity to the QD surface.^{149,155–157} This approach is mainly suited for systems interacting via FRET but is not very efficient for Dexter exchange-type ET or CT because the minimum achievable donor-acceptor distance is restricted by capping ligands. For instance, the length of the commonly used OA and OLA ligands for QDs is around 2 nanometers,¹⁵⁸ which is larger than the recommended 1 nm separation required for efficient Dexter exchange-type ET or CT.^{132,133,146}

A more widespread way to designing QD-molecule hybrids involves anchoring functional molecules with suitable binding groups, often through a ligand exchange procedure, to achieve a minimum donor-acceptor separation.^{19,22,42,105,139,140,144,146,159–165} However, most studies use molecules with amino or carboxylic acid binding groups,^{19,159,161,164,166–169} which are more commonly used in conventional QD chemistry.^{140,165,170} While these molecules (e.g., anthracene-9-carboxylic acid, perylene diimide) can bind to LHP surfaces, the binding is generally weak. Molecules with quaternary amine group or those closely resembling it would offer stronger binding.

The most efficient approach to designing QD-molecule hybrids involves developing multifunctional ligands that combine strong binding to the QDs, colloidal stability, and the desired functionality. This design allows to control the loading of the functional groups on the QD surfaces and their distance from the QDs and to tune the number of acceptors that a donor can interact with. This increases the probability of donor-acceptor interactions without compromising the colloidal stability of QDs. This approach is more challenging to realize, as it requires precursor molecules with special properties, as discussed later in **Section 3.1**. So far, the design of LHP capping ligands has primarily focused on ligand engineering to improve the stability of LHP QDs in various solvents¹⁰³ and the exploration of multi-functional ligands capable to colloidally stabilizing and interacting with QDs has been lacking.

Regardless of the design method employed, in the majority of studies, a significant excess of molecular acceptors is needed to achieve high ET and CT efficiencies from QD donors,^{18,42,159,167,171,172} complicating the investigation of their excited-state interactions and potentially compromising long-term colloidal stability of the QDs. Many QD-molecule systems desiged to achieve ET from QDs to molecules still follow a conventional FRET-based route,^{42,156,167,171,173} with very few studies addressing non-FRET interactions.^{171,174}

In **Chapter 4** of this work, two different $CsPbBr_3$ QD-molecular hybrids using two different ways are designed and investigated:

- In Section 4.1, ATTO610 organic dyes with a dimethyl iminium binding group, are attached to CsPbBr₃ QDs to form a hybrid donor-acceptor system. Dimethyl iminium binding group has a strong binding affinity to LHP surfaces, which ensures close binding of ATTO610 dyes to the QD surfaces, minimizing the donor-acceptor distance. CsPbBr₃ QDs and ATTO610 exhibit negligible spectral overlap, but close binding of ATTO610 dyes to the QD surfaces allows for the spatial wavefunction overlap of donor and acceptor isoenergetic states. Steady-state and time-resolved PL spectroscopy is used to thoroughly investigate and characterize the excited state interactions between the two species not only from the donor but also from the acceptor perspective.
- Based on these findings, in Section 4.2 multi-functional ligands for LHP QDs are designed which combine three key aspects: strong binding, colloidal stability, and functional ferrocene (hole-scavenger) molecules. Steady-state and time-resolved PL, and transient absorption spectroscopy measurements are performed on CsPbBr₃ QDs exclusively capped with these multi-functional ligands to investigate and characterize the excite state interactions between QDs and ferrocene.

2.4 Amino Acids Inside Bulk LHP Crystals

2.4.1 Bioinspired Incorporation of Amino Acids into Inorganic Semiconductors

Recently, a unique approach of incorporating individual amino acids into single crystalline minerals, mimicking the process of biomineralization, has emerged. In a biomineralization process organic molecules become incorporated in brittle crystalline minerals. For example, mollusk shells, composed of brittle calcium carbonate, gain remarkable hardness and toughness due to intra- and intercrystalline organic inclusions.¹⁷⁵ One clear sign of the incorporation of organic molecules within a host matrix is the appearance of lattice distortions, which can be measured by XRD techniques and has been extensively studied.^{176–181} The Pokroy lab has explored the effect of molecular inclusions on the crystalline host in depth, demonstrating that individual amino acids become incorporated into the lattice of calcite, inducing significant lattice distortions.^{182,183} They also showed that the mechanical properties of the host calcite are enhanced when large amounts of amino acids are incorporated.¹⁸²

Building on this work, the Pokroy lab successfully incorporated individual amino acids into bulk inorganic semiconductors such as zinc oxide (ZnO) and copper oxide (Cu_2O) .^{44–49} The ZnO-amino acid composites not only showed anisotropic lattice distortions, a well-known effect for calcium carbonate crystals with incorporated intercrystalline organic molecules 177,180,182 but also experienced a significant increase in the band gap, up to 4% in the case of cysteine incorporation, as revealed by diffuse reflectance and PL spectroscopy experiments.^{46,47} The blue-shift in the band gap of ZnO upon amino acid incorporation was not a result of the physical size reduction of the host crystals, which were bulk crystals ranging from hundreds of nanometers to microns in size. The amino acid-induced lattice expansion was an order of magnitude too small to explain the blue-shift. Similarly, for Cu₂O, the observed lattice contraction upon amino acid incorporation, measured by powder XRD, predicted band gap widening,^{45,184} yet diffuse reflectance and PL excitation (PLE) spectroscopy experiments showed a blue-shift in the band gap.^{48,184} Combining experimental results with theoretical calculations, it was shown that the amount of incorporated amino acids was sufficient to induce quantum confinement-like effects within the micron-sized crystals. Amino acids can be assumed to act as voids forming energetic barriers to electrons and holes, confining them akin to the particle-in-a-box concept, where the confining size is the average distance between amino acids in the host.⁴⁶ The void-induced quantum confinement, along with compositional disorder of the composite crystals, significantly influenced the optical properties, leading to a shift in their band gaps.^{46,48}

2.4.2 Lysine Molecular Bridge Inside MAPbBr₃

The possibility to engineer novel MAPbX₃-molecular composite systems could prove to be a viable way for tuning the properties of HOIPs. A recent study by Lang et al. showed that individual amino acids can be incorporated into MAPbBr₃ bulk crystals.⁴⁴ Amino acid analysis performed on these novel composite crystals confirmed successful lysine (Lys, $C_6H_{14}N_2O_2$) incorporation, showing that the Lys concentration inside the crystals was proportional to its concentration during synthesis of the composite material. The study focused on examining the effects of Lys incorporation, which has two amino groups, on the structural properties of HOIP MAPbBr₃ bulk crystals.

Similar to calcium carbonate crystals with intercrystalline organic molecules, Lys incorporation into the MAPbBr₃ crystals induced change in the host's lattice constant, as analyzed using XRD. Specifically, the amount of incorporated Lys positively correlated with the magnitude of observed lattice contraction. XRD analysis combined with in-situ cooling revealed that Lys incorporation lowered the thermal expansion coefficient, enhancing their thermal stability. In addition, using differential callorimetry experiments Lang et. al. also demonstrated that the cubic-to-tetragonal phase transition temperature of the composite crystals was shifted, likely due to the inhibition of octahedral tilting by incorporated Lys molecules. MAPbBr₃-Lys crystals proved to be more stable in water and humid conditions compared to pure MAPbBr₃ crystals. Impedance measurements of water containing the crystals indicated a slower dissolution rate of Lys-incorporated samples. XRD analysis further revealed that, under identical humid conditions, the crystals with incorporated Lys showed reduced formation of PbBr₂, a sign of perovskite degradation.

The authors assessed the most probable way Lys molecules are incorporated into MAPbBr₃ crystals. Given possible ionization states of Lys - ranging from one ionized NH_3^+ cation group to two ionized NH_3^+ cation groups or two ionized NH_3^+ cation and one carboxyl COO⁻ anion - it is reasonable to assume that the amino groups of Lys can replace A-site MA⁺ cations (Section 2.1.4). Lang et. al. proposed that the significant lattice contraction observed upon Lys incorporation suggests a bridging effect, in which Lys pulls the lattice together. If Lys replaced only one MA⁺ cation by its amino group, the lattice contraction would be less pronounced, as evidenced by the modest changes in the lattice constant of MAPbBr₃ crystals with incorporated amino acids containing a single amino group, such as glycine (C₂H₅NO₂) or histidine (C₆H₉N₃O₂). In addition, the reduction in the thermal expansion coefficient, along with decreased water dissolution and degradation rates under humid conditions, further supports the Lys bridging hypothesis.

Based on these considerations, the authors developed a model to determine possible crystallographic positions of Lys inside MAPbBr₃ crystals and the induced lattice distortion levels. The model compared the distance between the two amino groups in Lys to the spacing between MA⁺ molecules in the host HOIP MAPbBr₃ unit cell, along with the estimated stiffness coefficient ratio of Lys and MAPbBr₃. Using this model, Lang et. al. identified two main modes of Lys incorporation into MAPbBr₃:

 Lys incorporation via its two NH₃⁺ amino groups substituting two adjacent MA⁺ ions, either creating a Br⁻ vacancy or, more probably, bending around it, illustrated in Figure 2.15a and b. 2. Lys incorporation via its two NH₃⁺ amino groups substituting two neighboring MA⁺ ions in a unit cell and the ionized carboxyl COO⁻ group substituting an X-site halide Br⁻, illustrated in **Figure 2.15c**.

The second incorporation mode induces less lattice contraction than the first. The first type of incorporation was expected for MAPbBr₃-Lys crystals grown at room temperature and investigated in this work, whereas the second type of incorporation was expected for MAPbBr₃-Lys crystals grown at elevated temperatures, as inferred from the observed lattice contraction magnitudes.



Figure 2.15: Different modes of Lys incorporation in MAPbBr₃. Two NH_3^+ amino groups of Lys substitute two adjacent MA⁺ ions, a) most probably bending around Br⁻ or b) creating a Br⁻ vacancy. These incorporation types are most likely for MAPbBr₃-Lys crystals grown at room temperature and investigated in this work. c) Two NH_3^+ amino groups of Lys can also substitute two neighboring MA⁺ ions in a unit cell and the ionized carboxyl COO⁻ group can substitute a Br⁻ vacancy. H atoms are not shown. Adapted from [44].

In **Chapter 5** of this work the effect of Lys incorporation on the post-synthetic Cl^- and I^- exchange in MAPbBr₃ crystals is investigated. Various complementary structural and optical characterization techniques, including ion chromatography, XRD analysis, and steady-state PL spectroscopy are used to reveal the role of Lys incorporation on post-synthetic halide diffusion.

Chapter 3

Materials and Methods

The first section of this chapter describes the synthesis procedures used to produce LHP QDs and hybrid organic-inorganic perovskite bulk crystals investigated in this work. It also provides a protocol for synthesizing multi-functional ligands for LHP QDs.

The second section outlines the chemical and structural characterization techniques used to analyze mixed-halide hybrid organic-inorganic perovskite MAPbBr₃-Lys composites. These include ion chromatography and high resolution powder X-day diffraction experiments.

The third section describes the optical characterization tools used for both LHP QDs and hybrid organic-inorganic perovskite bulk crystals. Steady-state techniques, such as UV-Vis absorption, PL, and PL excitation spectroscopy experiments, with an emphasis on their specific applications in this work, are introduced. Time-resolved techniques, including time-resolved PL and transient absorption spectroscopy experiments, are also discussed, highlighting their role in the research presented.

3.1 Synthesis of Lead Halide Perovskites

As discussed previously, optical and electronic properties of QDs and bulk crystals strongly depend on inhomogeneities within the crystal structure, such as defects. In addition, size of QDs is an important parameter in shaping their optoelectronic properties.^{83–85} Therefore, obtaining a defect-poor QD ensemble with a narrow size distribution and homogeneous bulk crystals is essential for achieving samples with uniform and well-defined optical and electronic properties. Choosing the right synthesis procedure is important for fabricating samples with desired properties.

One popular approach for crystal growth is the so-called bottom-up approach, that is based on particle-by-particle construction of a crystal from its smallest constituents. Nucleation and growth can be categorized into this approach. In general, in order to obtain monodisperse QD samples, it is important to separate nucleation and growth, such that during the growth phase no new nuclei are formed and all the previously formed nuclei grow with the same rate.^{185,186} Care must be taken to terminate the QD growth before the Ostwald ripening starts, which entails growth of the large particles on the expense of dissolution of small particles, consequently broadening the particle size distribution. Therefore, timely termination of the QD growth is crucial for obtaining monodisperse QD samples.^{185,187} Separating nucleation and growth is also important in obtaining homogeneous high quality bulk LHP crystals.

3.1.1 Ligand-Assisted Synthesis of Monodisperse CsPbBr₃ QDs

Recently, a ligand assisted approach was developed that allows to synthesize monodisperse LHP QDs at ambient conditions,⁸² as opposed to the traditional hot injection method.^{85,188–190} CsPbBr₃ QDs investigated in this thesis were synthesized by slightly modifying this method.

Preparation of Stock Solutions

Precursor stock solutions were prepared as follows:

- PbBr₂-TOPO: 1 mmol of lead bromide (PbBr₂) and 4 mmol trioctylphosphine oxide (TOPO) were dissolved in 5 mL octane at 120°C, followed by cooling to room temperature and dilution with 20 mL hexane.
- Cs-DOPA: 100 mg cesium carbonate (CsCO₃) and 1 mL diisooctylphosphinic acid (DOPA) were dissolved in 2 mL octane at 120°C, followed by cooling to room temperature and dilution with 27 mL hexane.
- 0.1 M OA-OLA: 1 mmol of oleic acid (OA) and 1 mmol of oleylamine (OLA) were dissolved in 10 mL chloroform.
- 0.1 M DDAB: 1 mmol of didodecyldimethylammonium bromide (DDAB) was dissolved in 10 mL chloroform.

- 0.1 M Lecithin: 1 mmol of lecithin was dissolved in 10 mL chloroform.
- 0.2 M TOPO: 4 mmol of TOPO was dissolved in 20 mL hexane.
- ZnCl₂-TOPO: 1 mmol of zinc chloride (ZnCl₂) and 4 mmol of TOPO were dissolved into 5 mL octane at 120°C, followed by cooling to room temperature and dilution with 20 mL of hexane. 20 μL of ZnCl₂-TOPO stock solution was diluted with 1 mL toluene and aliquots of this were used for halide exchange experiments.
- ZnI₂-TOPO: 1 mmol of zinc iodide (ZnI₂) and 4 mmol of TOPO were dissolved into 5 mL octane at 120°C, followed by cooling to room temperature and dilution with 20 mL hexane. 20 μL of ZnI₂-TOPO stock solution was diluted with 1 mL toluene and aliquots of this were used for halide exchange experiments.
- ATTO610: 0.63 μ mol ATTO610 was dissolved in 13.5 mL chloroform.
- Pyronin Y: 3.80 μ mol pyronin y was dissolved in 50 mL acetonitrile and 20 mL toluene.
- Crystal violet: 2.50 μ mol crystal violet was dissolved in 55 mL chloroform.
- IR895: 1.94 μ mol IR895 was dissolved in 43 mL chloroform.
- Ferrocene: 7 $\mu \rm{mol}$ ferrocene was dissolved in 14 mL chloroform.

Synthesis of Multi-Functional Ligands

Multi-functional ligands containing ferrocene functional group were synthesized following the Menshutkin reaction at 100°C.^{191–193} 1 mmol of 1-bromododecane and 1 mmol of dimethylaminomethyl ferrocene were reacted at 100°C under ambient conditions for 1 hour under mild stirring, yielding (ferrocenylmethyl) dodecyldimethylammonium bromide (FeDDAB). After cooling to room temperature, FeDDAB ligands were diluted with 10 ml chloroform, yielding 0.1 M FeDDAB stock soltuion.

Synthesis of QDs

For preparation of QDs with approximately 6 nm in diameter, 1 mL heptane was loaded with 300 μ L PbBr₂-TOPO stock solution. Under heavy stirring, 150 μ L Cs-DOPA stock solution was rapidly injected. 2 minutes after the injection of the Cs-DOPA stock solution, 1 mL of chloroform was added. After 1 minute, 150 μ L of 0.1 M ligand stock solution (OL-OLA, DDAB, lecithin, or multi-functional ligands) in chloroform was injected. Finally, 2 mL acetonitrile was added to the QD solution. The solution was then centrifuged at 6,000 rpm for 2 minutes. The supernatant containing unreacted precursors was disposed. The precipitate containing the QDs was dispersed in toluene and centrifuged again for another 2 minutes at 14,500 rpm. This time the precipitate was disposed and the supernatant containing the QDs was retained for further experiments (for transmission electron microscopy (TEM) images of various QDs see **Figure 3.1**).

To synthesize spherical-like QDs with approximately 10 nm in diameter, 100 μ L of 0.2 M TOPO stock solution in hexane was added in the first step of the synthesis, together with the PbBr₂-TOPO stock solution. The rest of the synthesis proceeded as described above.

Mixed halide QDs were prepared by adding a small aliquot of diluted ZnI₂-TOPO or ZnCl₂-TOPO stock solutions to a CsPbBr₃ QD solution in toluene containing a known amount of QDs. It was assumed that halide exchange does not change the size of the QDs.⁸³

a) OA-OLA-capped CsPbBr₃ QDs (ø 6nm) b) OA-OLA-capped CsPbBr₃ QDs (ø 10nm)



c) DDAB-capped CsPbBr₂ QDs (ø 6nm)





d) FeDDAB-capped CsPbBr₃ QDs (ø 6nm)



Figure 3.1: Transmission electron microscope images of CsPbBr₃ QDs. OA-OLAcapped CsPbBr₃ QDs with an average diameter of approximately **a**) 6 nm and **b**) 10 nm (courtesy of David Ederle). Additionally, 6 nm-sized CsPbBr₃ QDs capped with **c**) DDAB and **d**) FeDDAB ligands are also shown (courtesy of Quinten Akkerman).

QD-Molecule Sample Preparation

QD-ATTO610 samples were dispersed in a mixture of 90% toluene and 10% chloroform, since the addition of chloroform facilitates the dispersion of dye molecules, which generally are not soluble in non-polar solvents. A mixed QD-ATTO610 solution was prepared by replacing a portion of chloroform with an equal volume of the ATTO610 stock solution, followed by vigorous shaking and used without any further purification. Due to the low solubility of the dyes in the chosen solvent used and their high binding affinity to the QD surface it was assumed that all dyes were attached to a QD and the amount of free-floating dyes in the solution can be neglected. Throughout all experiments the total volume of the solution containing both QDs and ATTO610, as well as the volumetric ratio between toluene and chloroform, was kept

constant, if not mentioned otherwise. The samples containing other molecules were prepared in a similar manner.

In the titration experiments shown in **Figure 4.18**, molecules were added drop-wise to a 2 mL toluene solution containing DDAB-capped QDs. Simultaneously, an identical volume of solvent not containing any molecules was added to a separate control solution containing the same concentration of DDAB-capped QDs. The PL intensity of the control solution was monitored to account for dilution-related decrease in the PL intensity, allowing to correct its effect in the experimental solution accordingly.

The concentration of molecules was calculated by dissolving the known quantity of molecules in the known volume of solvent. The concentration of QDs was determined from their absorbance spectra.

3.1.2 Incorporating Lysine into Bulk MAPbBr₃ Crystals

Bulk MAPbBr₃ crystals, both with and without incorporated Lys, as well as mixed-halide hybrid organic-inorganic perovskite (HOIP) samples, were synthesized by a collaborator from the Pokroy Lab in Technion, Arad Lang.

4 g of lead acetate (Pb(CH₃COO)₂) was dissolved in 20 mL concentrated hydrobromic acid (48% HBr). Afterwards, 0, 1, or 2 mg of L-Lys was added to the solution and stirred until Lys was fully dissolved, forming the PbBr₂-Lys stock solution. Methylammonium bromide (MABr, CH₆N⁺Br⁻) stock solution was prepared by adding methylammonium hydroxide (CH₆NOH, MAOH) dropwise to a concentrated hydrobromic acid in a 1:1 volumetric ratio while stirring, with the reaction vessel kept in an ice water bath. An equimolar amount of the MABr stock solution was injected into the PbBr₂-Lys solution, which was heated in an oil bath at 95°C. The mixture was allowed to naturally cool to room temperature. The resulting micron-sized orange crystals were filtered, washed with acetone, and air-dried.⁴⁴ Throughout this work, these samples are labeled as MAPbBr₃ Lys- α , with $\alpha = 0, 1, 2$, respectively.

Post-Synthetic Halide Exchange

The MAPbBr₃ crystals were used to prepare mixed halide perovskites. MA⁺Z⁻ (Z = Cl, I) was dissolved in isopropanol to obtain a 0.1 M MAZ stock solution. Approximately 500 mg of L-Lys was added to each solution, causing it to become slightly turbid due to Lys exceeding its solubility limit in isopropanol. Approximately 500 mg of each MAPbBr₃ crystals were placed into a 15 mL centrifuge tube. Then, 10 mL of the MAZ stock solution containing Lys was added using a syringe and a 0.45 μ m cellulose filter to ensure saturation with Lys without any undissolved aggregates. The tubes were sealed and placed on a rocking stage in the dark for different time durations (t = 0, 1, 6, and 24 hours). Subsequently, the samples were filtered using *Whatman* No. 5 filter paper, washed three times with acetone, and air-dried.

3.2 Chemical and Structural Characterization of Mixed Halide Perovskites

Ion Chromatography

Liquid ion chromatography (IC) measurements were performed by a collaborator from the Pokroy Lab in Technion, Arad Lang. 881 Compact IC pro – Anion-MCS, with chemical suppression by the Metrohm Suppressor Module, equipped with 836 Compact Autosampler by Metrohm AG was used to assess the amounts of post-synthetically exchanged Cl⁻ and I⁻ into bulk MAPbBr₃ crystals. Anion separation was done on Shodex column IC-SI-52 4E (4.0 mmID x 250 mmL). 3.6 mM sodium carbonate solution was applied as an eluent.

10 mg of each sample were transferred to a polypropylene tube, followed by the addition of 10 mL of DI water. The tubes were sealed and placed on a rocking stage for 48 hours, until complete dissolution. Then, the samples were diluted by taking 1 mL of each and adding 9 mL of DI water. Since the amount of I⁻ in the solution is small, its determination was performed without the final dilution step.

High-Resolution Powder X-Ray Diffraction

High resolution powder X-ray diffraction (HR-PXRD) measurements on bulk MAPbBr₃ crystals were performed at beamline ID22 of the European Synchrotron Radiation Facility in Grenoble, France, by a collaborator from the Pokroy Lab in Technion, Arad Lang. X-rays with a wavelength $\lambda_{X-ray} = 0.3542$ Å were used. To avoid beam damage, each sample underwent three fast scans, which were later averaged.

MAPbBr₃ and MAPbCl₃ crystals are known to adopt a cubic unit cell at room temperature.^{3,55,56,194} On the other hand, pure MAPbI₃ adopts a tetragonal unit cell at room temperature,⁵⁸ however, the Γ -exchanged samples in this study exhibit a cubic structure,¹⁹⁵ probably due to the low incorporated Γ levels. Therefore, the lattice constant of each sample was calculated assuming a cubic unit cell. The (100) reflection in the HR-PXRD spectrum was identified and fitted to a Voigt function to extract the diffraction peak position, $2\theta_{(100)}$. The lattice constant *a* of the samples, assuming a cubic unit cell, was calculated using Bragg's relation:

$$a = d_{(100)} = \frac{\lambda_{\text{X-ray}}}{2\text{sin}(\theta_{(100)})},$$
(3.1)

where $d_{(100)}$ is the interplanar spacing between two neighboring (100) planes.

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) measurements were performed on selected samples with a Zeiss Ultra+ scanning electron microscope (SEM) together with a collaborator from the Pokory Lab in Technion, Arad Lang. EDS measurements provide a qualitative picture of a sample's surface composition. The samples were glued to a stainless-steel stub holder using carbon tape, and coated with a few nanometers of carbon to improve electrical conductivity. The primary electron beam energy in the SEM was set to 10 keV.

Electron microscopy offers significantly higher resolution than the traditional light microscopy. According to Abbe's diffraction limit, the minimum resolvable distance between two structures is given by $d = \lambda/(2 \cdot n \cdot \sin(\alpha))$, where λ is the wavelength used for the observing radiation, n is the refractive index of the medium, and α is the half angle of the lens aperture. Since electrons have much shorter wavelength than that visible light, electron microscopes can resolve much smaller structures, achieving resolution down to nanometers.

EDS is an analytical technique used to analyze the elemental composition of a sample. In EDS, a high-energy electron beam, such as in a SEM, ejects an inner-shell electron of an atom in the sample creating an electron vacancy. Higher-energy outer-shell electrons quickly fill the vacancy, during which they emit X-rays with characteristic energies for each element. Detecting and measuring these X-rays can be used to identify which elements are present in a sample and at what quantity.

3.3 Optical Characterization of Lead Halide Perovskites

3.3.1 Steady-State Absorption

The first step in the optical characterization of any sample is measuring its linear absorbance spectrum. A simple and effective method to do so is via the transmission-mode UV-Vis spectroscopy, which is a quantitative ensemble technique, probing only optically allowed transitions. All absorbance spectra reported in this thesis were recorded with a *Cary* 60 UV-Vis Spectrophotometer from Agilent Technologies and plotted as a function of energy, $h\nu$.

The absorbance spectrum of a sample can be related to the incoming and transmitted light intensities through the Beer-Lambert law, which assumes that the attenuation of the incoming light is only due to absorption by the sample. For this assumption to be valid, intensities of back-reflected and scattered light must be negligible. These conditions are well satisfied by a low-concentration colloidal QD dispersions (**Figure 3.2a**).

UV-Vis spectroscopy is a powerful tool for characterizing LHP QDs. In this thesis, the concentration of colloidal CsPbBr₃ QDs in a given solution, $c_{\rm QD}$, was determined from their absorbance spectra using the relation:¹⁹⁶

$$c_{\rm QD} = \frac{\ln 10 \mathcal{A}(\lambda)}{\mu_i(\lambda)L} \cdot \frac{1}{N_{\rm Av}V_{\rm QD}}$$
(3.2)

Here, the absorbance $A(\lambda)$, also known as the optical density (OD), is the measured absorbance of QDs at wavelength λ , $\mu_i(\lambda)$ is the intrinsic absorption coefficient of the QDs in a given solvent, L is the thickness of the cuvette used, $V_{\rm QD}$ is the volume of a single QD calculated assuming a spherical shape with an average QD diameter estimated via TEM, and $N_{\rm Av}$ is Avogadro's constant. The intrinsic absorption coefficients of CsPbBr₃ QDs in toluene and hexane have been previously reported in literature and are listed in **Table 3.1**.¹⁹⁷ The QD concentration was calculated for $\lambda = 335$ and 400 nm, and the average was taken as the value for $c_{\rm QD}$ (**Figure 3.2b**). For mixed-halide QDs, their concentration was determined from CsPbBr₃ QDs before halide-exchange and it was assumed that halide-exchange process does not alter their size and shape.⁸³

Table 3.1: Intrinsic absorption coefficient of CsPbBr₃ QDs. Experimental values of intrinsic absorption coefficient $\mu_i(\lambda)$ of CsPbBr₃ QDs at wavelengths $\lambda = 335$ and 400 nm in hexane and toluene.¹⁹⁷

Solvent	$335 \mathrm{~nm}$	400 nm
hexane	$(1.59 \pm 0.05) \cdot 10^5 \text{ (cm}^{-1})$	$(7.7 \pm 0.8) \cdot 10^4 \text{ (cm}^{-1})$
toluene	$(1.79 \pm 0.06) \cdot 10^5 \text{ (cm}^{-1})$	$(8.7 \pm 0.9) \cdot 10^4 \text{ (cm}^{-1})$

For thick bulk solid crystals such as MAPbBr₃ crystals investigated in Chapter 5 of this



Figure 3.2: UV-Vis absorbance. a) Illustration of light transmission through a lowconcentration colloidal QD dispersion. b) An exemplary absorbance spectrum of CsPbBr₃ QDs. The QD absorbance spectrum can be used to determine the QD concentration in the solution.

work, which tend to scatter incoming light even as fine powders, transmission-mode UV-Vis spectroscopy is not suitable for absorbance measurements. Instead, their absorbance spectra can be qualitatively assessed via diffuse reflectance measurements with an integrating sphere (also known as Ulbricht sphere) or via PL excitation (PLE) spectroscopy, which is introduced in the next section.

3.3.2 Steady-State Photoluminescence

PL spectroscopy is another method for optically probing the electronic band structure of a material. It is an ensemble technique, though single-particle measurements are also possible. In this thesis, only ensemble measurements on LHP QDs and molecules were performed. In the case of MAPbBr₃ crystals, the performed measurements could technically be classified under the single-particle measurement umbrella due to the large size of the crystals (several tens of micrometers) and the small size of the focused excitation light (focused beam diameter around 1 μ m).

In this thesis, the PL spectra were recorded using either a *Fluorolog-3 FL3-22* from *Horiba* or a home-built μ -PL setup. The *Fluorolog-3 FL3-22* is a simple setup for measuring PL spectra and is suitable for dilute and moderately high to highly luminescent samples. In case of very dense samples, undesired processes such as self-absorption can considerably distort the measured PL spectra, and for samples with very low luminescence, no PL signal is detected at all. In such cases, the μ -PL setup is very useful, as it allows for better focusing of the excitation light on the sample and more efficient collection of the emission, helping reduce self-absorption artifacts and enabling the detection of signals even from very weakly luminescent samples.

A simplified scheme of the home-built μ -PL setup is sketched in **Figure 3.3**. The excitation light source is a pulsed white light laser, the *SuperK EXTREME EXR-20* from *NKT Photonics*. Here, a 1064 nm high-power pulsed ytterbium-doped fiber laser is coupled into a photonic crystal fiber, where it generates a broad white light spectrum ranging from 475 to 2400 nm, while maintaining the fundamental Gaussian mode. The light is then directed into an acousto-optic tunable filter in the SuperK SELECT unit from NKT Photonics, which is used to select a single wavelength in the visible (470-640 nm) or infrared (690-1100 nm) range as the final laser output. Wavelength in the ultraviolet region (330-480 nm) can be generated using the SuperK EXTEND-UV from NKT Photonics, which is based on second harmonic generation (SHG). A built-in pulse picker in both of these units allows adjustments of the repetition rate of the excitation light within the range of 0.152 - 78 MHz, which is favorable for time-correlated single photon counting (TCSPC) measurements introduced in Section 3.3.5. The excitation laser pulse width varies from 20 to 100 ps, depending on the selected wavelength. The excitation laser light is directed towards the sample with an appropriate dichroic mirror and focused on the sample by an air objective, SLCPlanH 40x/0.55from *Olympus*, to a spot with a diameter around 1 μ m. The PL emitted by the sample is collected by the objective, separated from the scattered excitation light by the dichroic mirror, and focused on the entrance slit of an Acton SpectraPro 2300 spectrograph from Princeton Instruments. In the spectrograph, either a grating or a mirror can be selected to direct the PL on a charge-coupled device (CCD), the Pixis400 from Princeton Instruments, for recording the PL spectrum in one go, or on a multimode fiber from AMS Technologies connected to an avalanche photodiode (APD), SPCM-AQRH-16-FC from Excelitas Technologies, for TC-SPC measurements. The adjustments to the recorded PL spectrum need to be performed to account for different sensitivities of the CCD at different wavelengths.



Figure 3.3: Schematic illustration of the μ -PL setup. The SuperK EXTREME, combined with the SuperK SELECT and SuperK EXTEND-UV units, allows selection of pulsed excitation laser light across a broad wavelength range. The excitation laser light is directed towards the sample and focused using an an objective lens. A movable neutral density gradient filter in the beam path allows tuning the pulse power. The PL emitted by the sample is collected by the objective, separated from the scattered excitation light, and focused on the entrance slit of a spectrograph. In the spectrograph, either a grating (depicted) or a mirror (not depicted) can be selected to direct the PL signal either on a CCD for PL spectrum acquisition or on a fiber connected to an APD for TCSPC measurements.

By default, PL spectra recorded with any of the above-mentioned devices are displayed as functions of wavelength. However, presentation of data as a function of energy provides better physical insight, especially when multiple peaks are present over a broad wavelength range in a spectrum. When plotting PL spectra on an energy scale, the PL intensity $I(\lambda)$ needs to be correctly converted into $I(h\nu)$ using the relation $I(h\nu) = I(\lambda) \frac{\lambda^2}{hc}$.¹⁹⁸

In this study, steady-state PL spectra shown in **Figures 5.1**, **5.6** and **5.7** were recorded using the μ -PL setup. The excitation energies and corresponding powers used to acquire the spectra in **Figures 5.6** and **5.7** were 3.26 eV and P < 19.1 μ J/cm², and 2.56 eV and P < 31.3 μ J/cm², respectively. All the other steady-state PL spectra reported in this study were measured using the *Fluorolog-3 FL3-22* device.

3.3.3 Photoluminescence Excitation Spectroscopy

PLE spectroscopy is a versatile steady-state PL technique that allows to gain insight into various properties of a sample, such as its electronic energy levels. In a typical PLE experiment, the PL intensity of a sample at a fixed wavelength is monitored as a function of different excitation wavelengths. In this thesis, PLE measurements were performed using either the *Fluorolog-3 FL3-22* device or the home-built μ -PL setup.

In general, the PLE intensity of any sample can be written as:

$$I_{\rm PLE}(\lambda_{\rm ex}, \lambda_{\rm PLE}) = \rho_{\rm abs}(\lambda_{\rm ex}) \cdot \rho_{\rm relax}(\lambda_{\rm ex}, \lambda_{\rm PLE}) \cdot \rho_{\rm emit}(\lambda_{\rm PLE}) \cdot I_{\rm ex}(\lambda_{\rm ex}) \sim N_{\rm emit}.$$
 (3.3)

Here, λ_{ex} is the excitation wavelength, and λ_{PLE} is the detection (or emission) wavelength. The terms ρ_{abs} , ρ_{relax} , and ρ_{emit} denote, respectively, the probability that an incident photon at λ_{ex} is absorbed by the sample, the probability that the photoexcited e-h pair relaxes to the emissive state, and the probability of radiative recombination leading to photon emission at the monitored wavelength of λ_{PLE} .⁶⁸ $I_{\text{ex}}(\lambda_{\text{ex}})$ is the excitation light intensity, proportional to the number of incident photons N_{in} . The PLE intensity $I_{\text{PLE}}(\lambda_{\text{ex}}, \lambda_{\text{PLE}})$ is proportional to the number of emitted photons, N_{emit} . An illustration of the processes involved in a PLE experiment are shown in **Figure 3.4** using a molecular state picture as an example.

The absorption probability is given by the ratio of photons absorbed $N_{\rm abs}$ to incident photons $N_{\rm in}$, expressed as $\rho_{\rm abs} = N_{\rm abs}/N_{\rm in}$, which is related to the absorbance spectrum of the sample at a given wavelength, i.e., $\rho_{\rm abs}(\lambda) \sim A(\lambda)$.

The relaxation probability ρ_{relax} generally depends on both the excitation λ_{ex} and the detection λ_{PLE} wavelengths. For example, in a PLE spectrum of a bulk semiconductor, the PLE intensity may decreas with decreasing excitation wavelength, even though the absorbance of the sample increases. This occurs because, at shorter wavelengths, the light penetration depth into the sample decreases. As a result, more e-h pairs are created near the crystal surface, where they are more likely to get trapped in surface defects and recombine non-radiatively, reducing the PL intensity.

The emission probability ρ_{emit} depends only on the emission wavelength λ_{PLE} and can be assumed to be constant throughout the chosen excitation wavelength range, as e-h pairs have no memory of how they were excited. Excitation trapping in defect states, ET or CT



Figure 3.4: Illustration of a PL excitation experiment using a molecular state picture. The absorption probability ρ_{abs} is the ratio of absorbed photons to incident photons and depends on the excitation wavelength λ_{ex} . The relaxation probability ρ_{relax} depends on both the excitation and the detection λ_{PLE} wavelengths. The emission probability ρ_{emit} depends only on the emission wavelength λ_{PLE} . Excitation trapping in defect states, ET or CT processes can influence the values ρ_{relax} and ρ_{emit} , affecting the overall PLE intensity.

processes can influence the values ρ_{relax} and ρ_{emit} , affecting the overall PLE intensity.

In the excitation wavelength range were the the product $\rho_{\text{relax}} \cdot \rho_{\text{emit}}$ can be assumed to be constant and non-zero, the PLE spectrum becomes proportional to the absorbance spectrum of the investigated sample. This relation allows PLE spectroscopy to be used as an alternative way to assess the absorbance spectra of emissive samples for which transmission-mode UV-Vis spectroscopy is not feasible.

PLE spectroscopy is also an excellent tool for investigating ET in donor-acceptor systems where the acceptor is emissive. The PLE spectrum of a donor-acceptor system, selectively detected at the emission wavelength of the acceptor, can be used to quantify the likelihood of a photoexcited e-h pair on the donor relaxing and emitting from an excited acceptor state relative to the direct photoexcitation of the acceptor state. Assume that an e-h pair excited directly on the acceptor at $\lambda_{ex, A}$ has a 100% relaxation and emission probability at the monitored wavelength $\lambda_{PLE, A}$ (**Figure 3.5a**). What is the relative likelihood of an e-h pair excited on the donor at $\lambda_{ex, D}$ to relax and emit at $\lambda_{PLE, A}$ (**Figure 3.5b**)? The relative relaxation and emission probability Φ_{rel} is defined as:

$$\Phi_{\rm rel}(\lambda_{\rm ex, D}; \lambda_{\rm ex, A}; \lambda_{\rm PLE, A}) = \frac{\rho_{\rm relax}(\lambda_{\rm ex, D}; \lambda_{\rm PLE, A}) \cdot \rho_{\rm emit}(\lambda_{\rm PLE, A})}{\rho_{\rm relax}(\lambda_{\rm ex, A}; \lambda_{\rm PLE, A}) \cdot \rho_{\rm emit}(\lambda_{\rm PLE, A})} \cdot 100\% =$$

$$= \frac{I_{\rm PLE}(\lambda_{\rm ex, D}; \lambda_{\rm PLE, A})}{A(\lambda_{\rm ex, D})} \cdot \frac{A(\lambda_{\rm ex, A}; \lambda_{\rm PLE, A})}{I_{\rm PLE}(\lambda_{\rm ex, A}; \lambda_{\rm PLE, A})} \cdot 100\%.$$
(3.4)

Using Equation 3.4, the relative relaxation and emission probability can easily be calculated using the measured PLE intensities $I_{PL}(\lambda_{ex}; \lambda_{PLE})$ and the absorbance spectra $A(\lambda_{ex})$.

In this work, the PLE spectra shown in Figure 5.1 were measured using the μ -PL setup with appropriate longpass and shortpass filters used. All the other PLE spectra were measured



Figure 3.5: Selective excitation of a donor and acceptor. a) An e-h pair is selectively excited on the acceptor at $\lambda_{\text{ex, A}}$. The pair relaxes energetically, and recombines and emits at $\lambda_{\text{PLE, A}}$. b) An e-h pair is selectively excited on the donor at $\lambda_{\text{ex, D}}$. The energetic relaxation of the e-h pair is followed by isoenergetic ET to the acceptor, where the pair further relaxes energetically, and recombines and emits at $\lambda_{\text{PLE, A}}$. VB and CB stand for valence band and conduction band, respectively.

using the Fluorolog-3 FL3-22 device.

3.3.4 Photoluminescence Quantum Yield

From the above discussion, it is evident that the product of the relaxation and emission probabilities, $\rho_{\text{relax}} \cdot \rho_{\text{emit}}$, is proportional to the ratio of $\frac{N_{\text{emit}}}{N_{\text{abs}}}$. This ratio is known as the photoluminescence quantum yield (PLQY) and measures the efficiency with which a sample re-emits absorbed photons. PLQY is an ensemble technique that provides an average PLQY value for a given sample ensemble.

In this work, absolute PLQY measurements were performed using the *Fluorolog-3 FL3-22* device in combination with an integrating sphere. The sample concentration was kept very low (e.g., $OD\approx0.1$ at the excitation wavelength) to avoid artifacts due to self-absorption or excessive sample scattering, which could distort the measurement.

PLQY depends on both radiative and non-radiative recombination rates. For a homogeneous sample, it can be expressed as:

$$PLQY = \frac{N_{emit}}{N_{abs}} = \frac{\kappa_{rad}}{\kappa_{rad} + \kappa_{non-rad}},$$
(3.5)

where κ_{rad} is the radiative recombination rate, and $\kappa_{\text{non-rad}} = \sum_{i} \kappa_{\text{non-rad},i}$ is the sum of all non-radiative recombination rates. However, for non-homogeneous ensemble of particles, a more generalized definition of the PLQY should be used:

$$PLQY = \sum_{m=1}^{m_{total}} P(m) \frac{\kappa_{rad}}{\kappa_{rad} + \kappa_{non-rad} + \kappa_m}.$$
(3.6)

Here, P(m) is the fraction of particles in the measured ensemble where the photoexcited e-h pairs experience an additional non-radiative decay pathway with a unique rate κ_m , in addition

to the usual radiative and non-radiative recombination channels. Summing over all PLQYs of m_{total} particles, weighted by P(m), the PLQY of the ensemble is obtained.¹⁴⁶

3.3.5 Time-Resolved Photoluminescence

So far the discussion has focused on time-integrated measurements. However, some characteristics of a material or processes happening in the material can only be uncovered by time-resolved measurements. For example, an average lifetime of excited e-h pairs is an important characteristic of any semiconductor and can be easily extracted from the time-resolved PL (TRPL) measurements. Moreover, the shape and profile of the TRPL can provide an important insight into the processes that e-h pairs undergo following the excitation.

In a typical TRPL experiment a time-dependent PL intensity profile of a sample ensemble is recorded following a pulsed light excitation. Similar to the PLQY measurements, the recorded TRPL is a weighted sum of TRPL profiles of individual particles in the ensemble. Since PL involves both electrons and holes, the measured PL intensity at any given time is proportional to the number of surviving excited e-h pairs. If the measured particle ensemble is homogeneous, that is all particles have similar radiative and non-radiative recombination rates, the recorded TRPL can be described by a single-exponential function, as explained in **Section 2.1.3**. If the particle ensemble is inhomogeneous, where each individual particle has a unique radiative or non-radiative recombination rate, the TRPL will be best represented by a multi-exponential function.

3.3.6 Time Correlated Single Photon Counting

A widely used and easy-to-implement time-resolved PL technique is TCSPC. In a typical TCSPC measurement, data is collected over multiple excitation and emission cycles, ensuring that, on average, less than one emission photon is detected per TCSPC cycle. In this work, TCSPC experiments were conducted using the μ -PL setup shown in **Figure 3.3**. PL light was directed towards the spectrograph. In the spectrograph, the light was directed on the fiber connected to the APD using the mirror instead of the grating, and the signal was subsequently analyzed with a TCSPC unit (*PicoQuant*). For samples exhibiting dual emission, appropriate longpass or shortpass filters were placed in front of the spectrograph entrance to isolate the desired spectrum region. Before recording TRPL profile, the PL signals were verified for spectral purity. The repetition rate of the excitation light was set to $f_{\rm rep} = 1.22$ MHz, and the TCSPC setup achieved a time resolution of approximately 1.3 ns. For improved time-resolution over the TCSPC setup, time-resolved PL spectra were recorded using a streak camera.

3.3.7 Streak Camera Setup

The main components of the streak camera setup are depicted in **Figure 3.6**. The *MIRA* 900 Kerr-lens mode-locked titanium-sapphire laser, pumped by a Verdi V12 CW laser, serves as the source of femtosecond excitation pulses. These pulses have a repetition rate of $f_{\rm rep} =$ 75.6 MHz and a temporal width of approximately $\tau_{pulse} = 150$ fs. A birefringent filter allows selection of the excitation wavelengths in the range of 740-920 nm. The pulses are frequency doubled via SHG in a barium borate (BBO) crystal using Harmonics unit, all from Coherent. Depending on the desired application, the repetition rate of the pulsed excitation light can be reduced using the *PulseSelect* pulse picker from A.P.E., which is based on the acoustooptic effect, where light is scattered by traveling acoustic waves in a transparent medium.¹⁹⁹ The power of the excitation pulses can be adjusted by a tunable grey filter. The pulses are directed towards and focused on the sample (focused beam diameter estimated to be around 1 mm). The PL emitted by the sample is focused on the entrance slit of a SpectraPro HRS-300 spectrograph from *Princeton Instruments*, which resolves individual PL wavelengths. The wavelength-resolved PL is focused on the entrance slit of a Universal Streak Camera C10910 from Hamamatsu, which "sorts" PL photons according to their arrival times with respect to the excitation pulse, allowing to capture light emission phenomena occurring in extremely short time periods. Finally, the wavelength- and time-resolved PL is detected by an ORCAFlash 4.0 V3 CMOS sensor from Hamamatsu and displayed on a computer. A PIN photodiode (PD) creates trigger signals needed to synchronize the operation of the streak camera with the excitation pulses.



Figure 3.6: Schematic illustration of the streak camera setup. The *MIRA 900* laser, pumped by the *Verdi V12* CW laser, generates femtosecond excitation pulses, which are frequency doubled via SHG in a BBO crystal. The repetition rate of the pulsed excitation can be optionally reduced using a pulse picker. The PL emitted by the sample is focused on the entrance slit of a spectrograph. The wavelength-resolved PL leaving the spectrograph is focused on the entrance slit of the streak unit, which allows to capture light emission phenomena occurring in extremely short time periods. The wavelength- and time-resolved PL is detected by a camera and displayed on a computer. The PD creates trigger signals needed to synchronize the operation of the streak camera with the excitation pulses. The excitation pulse power is adjusted using a tunable grey filter. An appropriate longpass filter (LP) in front of the spectrograph filters out residual excitation light.

The TRPL profiles of OA-OLA-capped CsPbBr₃ QDs and CsPbBr₃ QD-ATTO610 systems, depicted in **Figures 4.1b**, **4.7**, and **4.9**, were recorded using the streak camera setup equipped with the *Single Sweep unit M10913-11*, in combination with the *Synchronous Delay Generator C10647* and the *Delay Unit C1097-05*, all from *Hamamatsu*. In addition, the repetition rate of the excitation pulses was reduced by a factor 1/3 using the pulse picker. The average power of the excitation pulses was $P < 227 \text{ pJ/cm}^3$. The samples were dispersed in a mixture of 10% chloroform and 90% toluene in a 10 mm cuvette. The TRPL spectra were measured under constant stirring with OD of 0.2 at the absorption wavelength of the first exciton peak X1 of the QDs. The time-resolved PL spectra of the QDs were averaged over 2.48-2.50 eV, whereas the time-resolved PL of the ATTO610 molecules were averaged over 1.86-1.99 eV and in **Figure 4.7b** smoothed for clarity additionally.

The TRPL profiles of DDAB- and FeDDAB-capped CsPbBr₃ QDs, depicted in **Figure 4.20**, were recorded using the streak camera setup equipped with the Synchroscan unit M10911-01, in combination with the Delay Unit C12270, all from Hamamatsu. The repetition rate of the excitation pulses was $f_{\rm rep} = 75.6$ MHz, and the average power of the excitation pulses was P < 1.3 nJ/cm³. The samples were dispersed in a 2 mm cuvette in toluene, with OD of 0.2 at the absorption wavelength of the first exciton peak X1 of the QDs. The time-resolved PL spectra of the DDAB-capped QDs were averaged over 2.49-2.50 eV and FeDDAB-capped QDs - 2.47-2.48 eV.

An important characteristic of any instrument used for time-resolved measurements is the instrument response function (IRF). In an ideal measurement, a homogeneous particle ensemble is excited by a pulse with an infinitely narrow temporal linewidth, and each emitted photon's arrival time at the detector is precisely detected. However, in reality, a laser pulse has a finite temporal linewidth, meaning that different regions of the sample are excited at slightly different times and intensities. As a result, the emitted photon arrival times at the detector will have at least the same linewidth as the excitation laser pulse. In addition, the recorded photon arrival times are further broadened by the response of the electronics and optics involved in the detection process. This broadening dictates the precision with which the instrument can measure time-resolved processes. All these effects affecting the time-resolution precision of the instrument are collectively summed up as the IRF. Hence, the IRF essentially defines the shortest time-resolved profile the measurement device can measure. The full width half maximum (FWHM) of the IRF is a measure of the best time resolution the instrument can achieve. The measured TRPL profile is a convolution of the true decay signal with the IRF. For a precise determination of the PL lifetime, a re-convolution of the measured TRPL signal from the IRF is done.

3.3.8 Time-Resolved Transient Absorption Spectroscopy

Time-resolved transient absoprtion spectroscopy (TAS) is a pump-probe technique used to investigate the charge carrier dynamics in the excited state of a material. Here, a femtosecond pump pulse excites the sample. After a certain time delay, a probe pulse assesses the state of the sample. The transmitted intensity of the probe pulse is recorded as a function of the delay time between the pump and probe pulses. The presence of the excited e-h pairs following the pump affects the transmission of the probe. The difference between the sample's transmission with pump and without pump conditions is calculated, which can easily be related to the change in the sample's absorbance, $\Delta A(\Delta t) = A_{pump}(\Delta t) - A_{no pump}$, where Δt is the time delay between pump and probe pulses. This change in absorbance, $\Delta A(\Delta t)$, is used to investigate charge carrier dynamics. A more precise way to refer to this technique is Differential Transmission Spectroscopy, since it measures changes in the sample's transmission.

The transient absorption setup used in this work is shown in **Figure 3.7**. Ultrashort excitation pulses with a temporal width of $\tau_{\text{pulse}} \sim 100$ fs, a repetition rate of $f_{\text{rep}} = 1$ kHz, and a wavelength of 800 nm are generated by the *Libra HE+* amplifier laser system by *Coherent*. Using a 98:2 laser beam splitter, the 800 nm pulse is divided into two beams.



Figure 3.7: Schematic illustration of the transient absorption setup. The *Libra* HE+ amplifier laser creates laser pulses at 800 nm, which are split into two beams. The first beam is frequency-doubled to a 400 nm pump pulse by a BBO crystal. LP removes residual 800 nm light. A chopper in the beam path blocks every second pump pulse. The second 800 nm beam is directed towards a variable delay stage, which allows precise control over the time delay between the pump and probe pulses. This beam is then focused on a CaF₂ crystal, where it is converted via self-phase modulation into the white-light spectrum probe pulse . The probe pulses are focused onto the sample, and the transmitted probe intensity is recorded by a spectrograph for both, pump and no-pump conditions at different time delays.

The first 800 nm beam is directed onto a BBO crystal and frequency-doubled via SHG to produce 400 nm pump pulses, which are used to excite the sample (focused beam diameter approximately 0.65 mm at the sample position). A chopper placed in the beam path, operating at a frequency of 0.5 kHz and synchronized with the laser repetition rate, transmits every second pump pulse. This allows the transmitted intensity of the probe pulse to be recorded for both ground and excited states of the sample. An adjustable grey filter in the pump path is used to control the excitation power.

The second 800 nm beam is directed towards a retroreflector mounted on a variable delay stage, which allows control of the time delay between pump and probe pulses. The beam

is then focused on a CaF₂ crystal, where, via self-phase modulation, it is converted into a white-light spectrum probe pulse spanning from 350 to 900 nm. The probe pulses are then focused on the sample by a parabolic mirror, and their transmitted intensity is collected by an optical fiber connected to a MS260i spectrograph from Newport for wavelength and spectral intensity read-out. The size of the probe beam at the sample position is much smaller than that of the pump beam, ensuring that the probed sample volume is uniformly excited. The samples were dispersed in a 2 mm cuvette in toluene, with OD at the excitation wavelength of around 0.2. It is important to select the cuvette with a narrow width and keep the sample OD low, to ensure that the excitation density remains virtually constant throughout the probed sample volume. The excitation power was around 15 μ J/cm³.

Chapter 4

Efficient Excited-State Interactions Between CsPbBr₃ QDs and Closely-Bound Organic Molecules

This chapter investigates and discusses the design of a CsPbBr₃ QD-molecule hybrid system exhibiting efficient excited-state donor-acceptor interactions.

Section 4.1 of this chapter is based on the publication [200]. It focuses on designing $CsPbBr_3$ QD-dye hybrids exhibiting efficient Dexter exchange ET from QD to dyes at low dyeper-QD ratios, relying on substantial donor-acceptor spatial wavefunction overlap rather than the conventional prerequisite of large spectral overlap. Dyes containing a dimethyl iminium binding group, which exhibit a very strong binding affinity to LHP surfaces, are used. It is demonstrated that close binding of the dyes to the QDs facilitates spatial wavefunction overlap of donor and acceptor isoenergetic states - an important prerequisite for efficient Dexter exchange ET. A wide range of QD-bound dimethyl iminium dyes exhibit efficient excited-state donor-acceptor interactions between QDs and dyes. This opens up new avenues for using LHP QD-molecule hybrids in various applications such as light emission.

Section 4.2 of this chapter is based on the reference [201]. Here multi-functional ligands featuring a quaternary ammonium binding group with high affinity for LHP QD surfaces, a long tail group for colloidal stability, and a functional group capable of interacting with QDs are designed. Ferrocene, a well-known hole scavenger, is chosen as the functional group. CsPbBr₃ QDs exclusively capped with these multi-functional ligands are synthesized. The hybrid system exhibits efficient photoexcited hole transfer from QDs to ferrocene. It is revealed that structural reorganization of ferrocene due to positive charge acquisition alters energetic positions of molecular orbitals, affecting charge separation efficiency. This facile approach of multi-functional ligand engineering for QDs provides a blueprint for designing efficient QD-molecular hybrids for different optoelectronic and photocatalytic applications.

4.1 Dexter Exchange Energy Transfer from QDs to Dimethyl-Iminium-Based ATTO610 Dyes

4.1.1 Optical Characterization of QDs and ATTO610 Dyes

Colloidal CsPbBr₃ QDs with a spherical-like shape and an average diameter 6 nm were synthesized as described in **Section 3.1.1**. The QDs were capped with oleic acid (OA) and oleylamine (OLA) ligands, chosen for their highly dynamic binding to the QD surfaces,¹⁰⁶ which should facilitate the attachment of dye molecules to QDs via ligand exchange. The absorbance, PL (excited at 2.95 eV), and PL excitation (PLE) (detected at 2.52 eV) spectra of QDs dispersed in a 90% toluene and 10% chloroform solution are shown in **Figure 4.1a**. In the absorbance spectrum of the QDs, several sharp excitonic resonances labeled as X1, X2 can be observed,²⁰² pointing towards a narrow size distribution of the synthesized particles (see transmission electron microscopy (TEM) image in **Figure 3.1a**).⁸³ The PL emission of the QDs peaks at 2.50 eV and the PL quantum yield (PLQY) of the QDs is approximately 33%. The time-resolved PL (TRPL) of these QDs measured with a streak camera (excited at 2.95 eV) exhibits a nearly single-exponential profile, indicating relatively homogeneous QD population (experimental details in **Section 3.3.7**). Fitting a single-exponential function to the TRPL yields the PL lifetime $\tau_{QD} \approx 1.3$ ns of QDs (**Figure 4.1b**).



Figure 4.1: Optical characterization of CsPbBr₃ QDs. a) Absorbance (dashed line), PL (solid line) and PLE (colored area) spectra of colloidal OA-OLA-capped CsPbBr₃ QDs with a spherical-like shape and an average diameter 6 nm, dispersed in 90% toluene and 10% chloroform solution. The inset shows a schematic representation of an excited QD. b) TRPL of OA-OLA-capped CsPbBr₃ QDs. The inset shows the data on a logarithmic y-axis. Solid colored line is the single-exponential fit to the TRPL data.

ATTO610 dyes were selected as a suitable dye for designing a QD-dye hybrid system. This dye has a cationic dimethyl iminium group containing a carbon-nitrogen double bond $(RC=N^+(CH_3)_2)$, which closely resembles a dimethyl ammonium group $(R^1R^2N^+(CH_3)_2)$ of didodecyldimethylammonium bromide (DDAB) ligands, which bind strongly to the A-site of the LHP surfaces,^{39,40} as discussed in **Section 2.1.4**. In addition, the dimethyl iminium group is part of the dye's conjugated system, with no additional alkane groups between the

choromophore and the binding group. This feature should facilitate wavefunction overlap between the dyes and the QDs, which is crucial for excited-state interactions between the two species. ATTO610 also contains a carboxyl acid (COOH) group, known to bind to the LHP surfaces at the X-site.^{39,40} However, as demonstrated by the density functional theory (DFT) calculations of absolute binding energies of these binding groups, the binding affinity of the carboxyl group to the LHP surfaces is significantly weaker compared to that of the dimethyl iminium group.²⁰⁰ Hence, ATTO610 dyes are expected to predominantly bind to the QD surface via their dimethyl iminium group.

Due to their high PLQY, up to 70%, ATTO610 dyes are commonly used as laser dyes or luminescent markers.²⁰³ In a solution of 90% toluene and 10% chloroform, ATTO610 molecules have a PLQY of approximately 48%. As shown in **Figure 4.2a**, ATTO610 molecules in their monomeric state exhibit strong absorption in the 1.90-2.30 eV energy range, corresponding to the transition from the ground state, S_0 , to the first excited state, S_1 . The PL emission of ATTO610 dyes peaks at 1.98 eV (excited at 2.10 eV), and the PLE spectrum (detected at 1.91 eV) closely follows the shape of the absorbance spectrum. The TRPL of ATTO610 dyes measured via TCSPC is characterized by single-exponential profile. Fitting a singleexponential function to the TRPL yields the PL lifetime of ~ 3.5 ns (**Figure 4.2b**).



Figure 4.2: Optical characterization of ATTO610 molecules. a) Absorbance (dashed line), PL (solid line) and PLE (colored area) spectra of ATTO610 molecules in 90% toluene and 10% chloroform solution. The inset shows a chemical structure of the ATTO610 dye. b) TRPL of ATTO610 molecules. The inset shows the same data on a logarithmic y-axis. Solid colored line is the single-exponential fit to the TRPL data.

4.1.2 Energy Transfer from QDs to ATTO610 Dyes

To study the interactions between QDs and ATTO610 dyes, several samples were prepared, each containing a fixed concentration of QDs while varying the ATTO610 concentration (experimental details in **Section 3.1.1**). It was assumed that ATTO610 molecules either displace the relatively weak binding OLA ligands or attach to an A-site surface vacancy on the QDs through the dimethyl iminium binding group. Due to the low solubility of the dyes in the chosen solvent and their high binding affinity to the QD surface, it was assumed that all dyes were attached to QDs, and the presence of free-floating dyes in the solution could be neglected. The concentration of ATTO610 in the QD-ATTO610 solution was varied to obtain an average of 0 to 12 dye molecules per QD. This ratio is the maximum possible average number of dyes bound to each QD, denoted as $\langle N \rangle$.

As shown in **Figure 4.3a**, the absorbance of ATTO610 molecules appears in the 1.90 - 2.30 eV energy range as their concentration increases in the solution containing QDs. The absorbance of the QDs in the range 2.50 - 3.20 eV energy range remains unchanged, and the excitonic resonances remain clearly visible.

While the absorbance spectrum of the QDs remains unchanged, their PL is significantly affected, as shown in **Figure 4.3b**. Here, the QDs are excited at 2.95 eV, avoiding direct excitation of ATTO610 molecules. A significant quenching of QD PL at 2.50 eV is observed after the addition of a few ATTO610 molecules per QD. This quenching is accompanied by the emergence of a distinct emission in the 1.90 - 2.30 eV energy range, which increases with the amount of dye molecules added. This emission is assigned to the ATTO610 monomer. The PL excitation (PLE) spectra of the QD-ATTO610 system at different dye concentrations, detected at the spectral position of the ATTO610 monomer ($h\nu_{PLE, Atto} = 1.91 \text{ eV}$), are shown in **Figure 4.3c**. In the excitation range of 1.95 - 2.40 eV, the PLE spectra closely resemble that of pure ATTO610 molecules (**Figure 4.2a**). This is not surprising, as in this excitation range, the dye molecules are excited directly. For excitation energies above 2.50 eV, the PLE spectra resemble that of pure QDs (**Figure 4.1a**), meaning that the product of the relaxation and emission probabilities, $\rho_{relax}(h\nu_{ex}, QD; h\nu_{PLE, Atto}) \cdot \rho_{emit}(h\nu_{PLE, Atto})$, is greater than zero (**Section 3.3.3**). In contrast, for pure ATTO610 molecules, this product is nearly zero in the excitation range above 2.50 eV (**Figure 4.2a**).



Figure 4.3: Optical characterization of the QD-ATTO610 system. a) Absorbance spectra of the QD-ATTO610 system at various ATTO610/QD ratios. b) PL spectra of the QD-ATTO610 systems, excited at 2.95 eV. c) PLE spectra of the QD-ATTO610 systems, detected at 1.91 eV.

The significant quenching of QD PL and the concomitant appearance of ATTO610 monomer emission, which has negligible absorbance at 2.95 eV, strongly suggest that ET from QDs to ATTO610 molecules is occurring, despite minimal spectral overlap between QD emission and ATTO610 absorbance (**Figure 4.4a**). This conclusion is further supported by

4.1. Dexter Exchange Energy Transfer from QDs to Dimethyl-Iminium-Based ATTO610 Dyes

the PLE measurements. Excitation of ATTO610 molecules at 2.95 eV in the absence of QDs results in negligible emission due to extremely low absorption at this energy (black curve in **Figure 4.4b**). In contrast, in the QD-ATTO610 system with a 10 ATTO610-per-QD ratio, the maximum PL intensity of ATTO610 molecules excited at 2.95 eV increases by a factor of 300 (red curve in **Figure 4.4b**). The enhancement factor is defined as the ratio between the integrated PL intensities of ATTO610 molecules in the absence and in the presence of QDs. This dramatic increase in PL clearly demonstrates an efficient interaction between QDs and ATTO610 molecules, where QDs effectively extend the absorption range of ATTO610 molecules in the high-energy region. Here, QDs act as an "antenna" for the incoming excitation light, efficiently funneling the excitation energy to the dye molecules (**Figure 4.4c**). Efficient ET from QDs to closely bound dye molecules at low dye-per-QD ratio despite the negligible spectral overlap suggests that ET proceeds via the Dexter exchange mechanism.



Figure 4.4: ET from QDs to ATTO610. a) Illustration of spectral overlap between 6 nm sized CsPbBr₃ QDs and ATTO610 dyes. b) PL spectra of ATTO610 molecules excited at 2.95 eV, in the absence (black solid line, multiplied by a factor of 50) and presence (red solid line) of QDs. The PL intensity of ATTO610 molecules increases by a factor of 300 in the presence of QDs. c) Schematic representation of the excitation of ATTO610 molecules via ET from QDs.

The absorbance of the QD-ATTO610 hybrid system closely resembles the sum of the individual absorbance spectra of QDs and ATTO610 molecules (**Figure 4.5a**). This shows that there is no formation of a charge-transfer state, and ATTO610 does not alter the QD size, electronic band structure, or excitonic energy levels. A minor red-shift in the absorbance of ATTO610 molecules in the QD-ATTO610 system, compared to that of ATTO610 in the abscence of QDs, can be attributed to an energetic shift in the $S_0 \rightarrow S_1$ transition, which likely results due to changes in the dielectric environment of the dye molecules upon attachment to the QD surface (Section 2.2), and can be interpreted as evidence that ATTO610 dyes are indeed attaching to the QD surface. No H- or J-aggregate formation-related spectral shifts in the absorbance of ATTO610 molecules in QD-ATTO610 system are observed.²⁰⁴ In addition, no excimer-related broad, red-shifted emission is observed.²⁰⁵ The overall shape of the PL spectra of ATTO610 dyes in the absorbance and presence of QDs in Figure 4.5a. The PLQY of ATTO610

molecules, following direct excitation at 2.12 eV, decreases from 48% for pure ATTO610 to 37% in the QD-ATTO610 system (ATTO610/QD = 10). The integrated PL intensities of both QDs and ATTO610 molecules in QD-ATTO610 system at ATTO610-per-QD ratio of 10 exhibit linear dependence on power (**Figure 4.5c**).



Figure 4.5: The QD-ATTO610 system at 10 ATTO610-per-QD. a) Comparison of the QD-ATTO610 system absorbance spectrum (light green) with the sum of the individual absorbance spectra of QDs and ATTO610 molecules (dark green). b) PL spectra of ATTO610 molecules in the abscence (light green) and in the presence of QDs (dark green), excited at 2.12 eV. c) Excitation power dependent PL of the QD-ATTO610 system excited at 2.95 eV. Grey solid lines represent fits to a linear function ($R^2 = 0.99$).

Efficiency

A common quantitative measure of ET efficiency is the quenching efficiency of donor QD PL by acceptor ATTO610 molecules, as explained in **Section 2.3.3**. This is defined as

$$\Phi_{\rm ET} = \left(1 - \frac{I_{\rm QD}}{I_{\rm QD,0}}\right) \cdot 100\%, \tag{4.1}$$

where $I_{\rm QD}$ is the integrated PL intensity of the QDs at a given ATTO610/QD ratio, and $I_{\rm QD,0}$ is the integrated PL intensity of QDs in the absence of ATTO610. As shown in **Figure 4.6a**, even at low dye concentrations, such as 10 ATTO610 molecules per QD, a quenching efficiency of almost 90% is achieved (dark green dots). This efficiency stays almost constant with further increase in ATTO610 concentration. This observation aligns with the apparent saturation of ET-related ATTO610 PL in **Figure 4.3b**, suggesting that the QD-ATTO610 system is approaching its efficiency limit.

Such a high ET efficiency at such low dye concentrations is in contrast with LHP QD-dye systems reported in the literature, which generally require several orders of magnitude more dye molecules compared to the number of QDs to achieve similar ET efficiencies.^{42,168,171,206} For example, in a system consisting of CsPbI₃ QDs and cyanine dyes (IR125), almost a 40-fold excess of dye molecules was required to achieve an ET efficiency of 94%.⁴² In another example, in a CsPbBr₃ QDs-rhodamine B system, an approximately 1000-fold excess of dyes was
necessary to achieve an ET efficiency of 88%.¹⁷¹ However, a Förster resonance ET (FRET)based CsPbBr₃ QD-cyanine-3-NHS-ester system achieved an ET efficiency of 70% just with 13 molecules per QD.¹⁵⁶ These comparisons highlight a significant improvement in the excitedstate interactions in the CsPbBr₃ QD-ATTO610 system compared to other reported LHP QD-dye systems.

Moderate to high ET efficiencies have been observed in conventional QD-dye hybrid systems at low dye/QD concentrations. For instance, a CdSe-ZnS core-shell QD donor and cyanine 3 dye acceptor system showed a maximum FRET efficiency of 75% for 3 dye molecules per QD,³¹ whereas a CdSe/CdS/ZnS QDs and rhodamine 6G system exhibited a maximum FRET efficiency of 60% with 3 dye molecules per QD.³⁷

An alternative and more accurate method for quantifying ET efficiency involves a combination of PLE and absorbance spectra, as explained in **Section 3.3.3**. Assuming that ATTO610 molecules selectively excited at $h\nu_{\text{ex, Atto}} = 2.12$ eV have a 100% relaxation and emission probability at the energy $h\nu_{\text{PLE, Atto}} = 1.91$ eV, then the relative relaxation and emission probability at $h\nu_{\text{PLE, Atto}}$ when exciting the QD-ATTO610 system at $h\nu_{\text{ex, QD}}$ can be found using the relation:

$$\Phi_{\rm rel} = \frac{I_{\rm PL}(h\nu_{\rm ex, QD}; h\nu_{\rm PLE, Atto})}{A(h\nu_{\rm ex, QD})} \cdot \frac{A(h\nu_{\rm ex, Atto})}{I_{\rm PL}(h\nu_{\rm ex, Atto}; h\nu_{\rm PLE, Atto})} \cdot 100\%.$$
(4.2)

The relative relaxation and emission probability can be easily calculated using the measured PLE intensities $I_{PL}(h\nu_{ex}; h\nu_{PLE, Atto})$ and the absorbance spectra $A(h\nu_{ex})$. Figure 4.6b depicts the relative relaxation and emission probability for different concentrations of ATTO610 and at various excitation energies $h\nu_{ex, QD}$. The relative relaxation and emission probability Φ_{rel} appears independent of the QD excitation energy $h\nu_{ex, QD}$, suggesting that exciton relaxation to the energetically lowest excited state occurs on a much faster timescale than ET from QD to ATTO610. For 10 ATTO610/QD, Φ_{rel} is approximately 17%. If direct excitation of ATTO610 molecules to their S_1 excited state at $h\nu_{ex, Atto} = 2.12$ eV were to yield a 100% relaxation and emission probability, equivalent to a PLQY of 100%, then relative to that, PLQY of ATTO610 excited indirectly via ET in the QD-ATTO610 system would be 17%. Since the PLQY of ATTO610 in the QD-ATTO610 system following direct excitation is approximately 37%, this analysis suggests its PLQY when excited indirectly through ET from QDs should be around 6.5%.

The last statement of the previous paragraph can be easily tested, as ATTO610 is an emissive dye, and its PLQY in the QD-ATTO610 system can be measured experimentally. **Figure 4.6c** shows the PLQY of ATTO610 molecules in the QD-ATTO610 system excited at 2.95 eV. Importantly, the PLQY peaks at approximately 7.5% for a 10 ATTO610/QD, consistent with the previous analysis based on PLE and absorbance spectra.

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Figure 4.6: ET efficiency in the QD-ATTO610 system. a) Quenching efficiency $(\Phi_{\rm ET})$ of the QD PL in the QD-ATTO610 system as a function of the ATTO610/QD ratio, excited at 2.95 eV (dark green dots). Light green dots represent modeled $\Phi_{\rm ET}$ according to Equation 4.4. b) Relaxation and emission probability ($\Phi_{\rm rel}$) at $h\nu_{\rm PLE, Atto} = 1.91$ eV, following excitation of the QD-ATTO610 system at $h\nu_{\rm ex, QD}$, relative to direct excitation of ATTO610 molecules at $h\nu_{\rm ex, Atto} = 2.12$ eV. c) ET-related PLQY of ATTO610 molecules in the QD-ATTO610 system, excited at 2.95 eV.

Dynamics

Key characteristic of ET from QDs to dye molecules is the modification of the TRPL kinetics of both species. Figure 4.7a shows the normalized TRPL of the QD ensemble in the QD-ATTO610 system, excited at 2.95 eV and recorded using a streak camera (experimental details in Section 3.3.7). The PL decay profile of QDs becomes predominantly multi-exponential with increasing ATTO610 concentration, as compared to a nearly single-exponential PL decay profile of pure QDs. This is accompanied by the increase in the PL decay rate. This change implies that different QDs have varying PL lifetimes, suggesting a statistical distribution of ATTO610 molecules across the QD population,^{95,153,207-209} with ET introducing an additional exciton decay pathway along intrinsic radiative and non-radiative processes.

Figure 4.7b shows the corresponding TRPL of ATTO610 dyes in the QD-ATTO610 system, normalized and smoothed for clarity (experimental details in Section 3.3.7). The TRPL shows a concentration-dependent rise time, with faster rise time at higher ATTO610 concentrations. This rise indicates that the excited state of the dyes is gradually populated via ET from QDs. Shorter rise times reflect increased ET efficiency, as more ATTO610 molecules are attached to a single QD.

The PL lifetime of ATTO610 molecules in the QD-ATTO610 system, when excited indirectly at 2.95 eV, is lengthened compared to that of ATTO610 molecules in the absence of QDs ($\tau_{\text{Atto}} \approx 4.9$ ns, **Figure 4.8**). This is because ET from the QDs to the dyes continues beyond the effective lifetime of the dyes.^{149,210}

To estimate the ET rate from QDs to ATTO610 molecules, the multi-exponential function

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Figure 4.7: Time-resolved PL of the QD-ATTO610 system. TRPL of a) QDs and the corresponding TRPL of b) ATTO610 molecules in the QD-ATTO610 system, excited at 2.95 eV, normalized to maximum intensity.



Figure 4.8: Time-resolved PL of ATTO610 at ATTO610-per-QD ratio of 10. a) The TRPL profile of ATTO610 molecules normalized to maximum intensity, following direct excitation at 1.98 eV (light green). The TRPL of ATTO610 molecules, excited indirectly at 2.95 eV has the PL lifetime $\tau_{\text{Atto}} \approx 4.9$ ns (dark green) and shows a distinct PL rise. b) The same data as in (a) shown on a logarithmic y-axis. Single-exponential fits are shown as black solid lines.

in Equation 4.3, which describes the time-resolved dynamics of donor PL as explained in Section 2.3.3, was fitted to the TRPL data of the QD ensemble in the QD-ATTO610 system.

$$I_{\rm QD}(\langle N \rangle, t) = A \cdot \theta(t) \sum_{N=0}^{N_{\rm max}} P(\langle N \rangle, N) \cdot e^{-(\kappa_{\rm QD} + N\kappa_{\rm ET})} * \mathcal{G}(\mu, \sigma)$$
(4.3)

Here, $\langle N \rangle$ is the average number of ATTO610 molecules per QD (ATTO610/QD ratio), A is the proportionality factor, and $\theta(t)$ is zero for t < 0 and 1 for $t \ge 0$. The Poisson distribution $P(\langle N \rangle, N)$ describes the fraction of QDs with N attached ATTO610 molecules. $\kappa_{\rm QD} = \tau_{\rm QD}^{-1}$ is the PL decay rate of pure QDs and $\kappa_{\rm ET}$ is the ET rate from a single QD to a single ATTO610 molecule. The Gaussian instrument response function (IRF), $G(\mu, \sigma)$, has a mean μ and full width at half maximum (FWHM) σ , and convolution is denoted by *. During fitting, A, $\kappa_{\rm ET}$, μ , and σ were varied, with σ constrained by the experimentally measured IRF FWHM. The maximum number of attached ATTO610 molecules per QD was assumed to be $N_{\text{max}} = 25$.

The TRPL spectra of the QD-ATTO610 systems at various ATTO610/QD ratios, measured with a streak camera, along with the QD TRPL (green dots) and corresponding fits (dark green line) are depicted in **Figure 4.9**. The extracted ET rates are summarized in **Table 4.1**, and an average ET rate from a QD to a single ATTO610 molecule is $\kappa_{\rm ET} \approx 0.4$ ns⁻¹. Since exciton Bohr diameter in CsPbBr₃ QDs, $2a_{\rm ex} \approx 6$ nm, is comparable to the QD size, it can be assumed that excitons do not need to diffuse to the donor surface to interact with an acceptor. Thus, $\kappa_{\rm ET}$ describes intrinsic ET transfer rate, including subsequent internal conversion and vibrational relaxation in the acceptor. For comparison, ET rates in FRET-based LHP QD-multiple-dye systems typically range from 1 to 100 ns⁻¹, making the QD-ATTO610 system at least an order of magnitude slower.^{42,171,206}

Table 4.1: Fitted ET rates. The ET rates from a single QD to a single ATTO610 molecule obtained by fitting Equation 4.3 to the TRPL profiles of QDs for a given ATTO610/QD ratio.

$\langle N \rangle = Atto/QD$	Fitted ET rate (ns^{-1})	\mathbf{R}^2
5	0.37	0.95
10	0.44	0.97
15	0.43	0.98

The ET rate of 0.4 ns^{-1} is consistent with the observed QD PL quenching efficiency. As detailed in **Section 2.3.3**, the donor PL quenching efficiency in **Equation 4.1** can also be written as^{146,153,154,211}

$$\Phi_{\rm ET} = \left(1 - \sum_{N=0}^{N_{\rm max}} P(\langle N \rangle, N) (1 + N \kappa_{\rm ET} \tau_{\rm QD})^{-1}\right) \cdot 100\%.$$
(4.4)

Inserting the fitted ET rate $\kappa_{\rm ET} \approx 0.4 \text{ ns}^{-1}$ in this equation and calculating the QD PL quenching efficiency $\Phi_{\rm ET}$, excellently predicts the experimentally measured data shown in **Figure 4.6a**. This implies that a single ATTO610 molecule attached to a QD can achieve a quenching efficiency of up to $\Phi_{\rm ET,\ single} = (1 - (1 + \kappa_{\rm ET}\tau_{\rm QD})^{-1}) \cdot 100\% = 35\%$. The highest reported single-dye quenching efficiency for an LHP QD-dye systems is 12%,¹⁵⁶ highlighting high ET efficiency of the QD-ATTO610 system.

To check that the estimated ET rate is consistent with the PL rise of ATTO610 molecules, the TRPL of the ATTO610 ensemble in the QD-ATTO610 system was modeled using the differential equation $\dot{n}_{\text{Atto}}(t) = N\kappa_{\text{ET}}n_{\text{QD}}(t) - \kappa_{\text{Atto}}n_{\text{Atto}}(t)$. Solving this equation, considering the Poisson distribution of molecules across QDs, assuming no direct excitation of molecules at 2.95 eV, **Equation 4.5** is obtained: 4.1. Dexter Exchange Energy Transfer from QDs to Dimethyl-Iminium-Based ATTO610 Dyes

$$I_{\text{Atto}}(\langle N \rangle, t) = B \cdot \theta(t) \sum_{N=0}^{N_{max}} P(\langle N \rangle, N) \cdot \frac{N\kappa_{\text{ET}}}{\kappa_{\text{Atto}} - N\kappa_{\text{ET}} - \kappa_{\text{QD}}} \cdot (e^{-(\kappa_{\text{QD}} - \kappa_{\text{Atto}} + N\kappa_{\text{ET}})t} - 1) \cdot e^{-\kappa_{\text{Atto}}t} * \mathcal{G}(\mu, \sigma).$$
(4.5)

Here, B is the proportionality factor. All parameters were determined experimentally or obtained from the previous multi-exponential fit to QD TRPL. The only parameter allowed to vary was B.

In Figure 4.9, red dots represent the experimentally measured TRPL of the ATTO610 ensemble in the QD-ATTO610 system at various ATTO610/QD ratios, and the dark red line is the modeled curve. The good agreement between the model and measured ATTO610 PL rise indicates that ET process has a single-step character.



Figure 4.9: Modeling time-resolved PL of the QD-ATTO610 system. 3D maps (*top*) and individual TRPL profiles (*bottom*) of QDs (green dots) and ATTO610 molecules (red dots) for a) 5, b) 10, and c) 15 ATTO610-per-QD ratios. The dark green solid line represents Equation 4.3 fitted to the experimentally measured TRPL of the QDs, and the dark red solid line represents the model of the TRPL of the ATTO610 molecules in the QD-ATTO610 system given by Equation 4.5.

The PLQY of ATTO610 dyes in the QD-ATTO610 system, following excitation at 2.95 eV, is lower than expected given high ET efficiency (~90%) and the directly excited dye PLQY of 37%. Several factors may contribute to this discrepancy. First, the presence of heavy atoms such as Pb and Br near the attached ATTO610 dyes could enhance spin-orbit coupling through so called external heavy atom effect, promoting intersystem crossing to molecular triplet states.¹²⁵ Second, attachment of ATTO610 to the QD surface might introduce new trap states that compete with ET. Third, despite the Coulomb attraction between electron

and hole in an exciton, they may transfer to separate but neighboring ATTO610 molecules rather than the same one. These factors could collectively reduce the ET-related PLQY of ATTO610 dyes in the QD-ATTO610 system. This underscores the importance of analyzing ET not only through the donor PL quenching perspective but also via the ET-related acceptor PL enhancement, providing a more complete understanding of donor-acceptor interactions.

Mechanism

An ET process through FRET requires significant spectral overlap between donor emission and acceptor absorption^{125,133,134,155,156} and is strongly dependent on the oscillator strengths of these transitions, as discussed in **Section 2.3.1**.^{133,134} A quantitative measure of donoracceptor spectral overlap is the spectral overlap integral J, defined as

$$J = \int \tilde{I}_{\rm QD}(\lambda) \epsilon_{\rm Atto}(\lambda) \lambda^4 d\lambda, \qquad (4.6)$$

where $I_{\rm QD}$ is the normalized PL intensity of pure QDs, such that $\int I_{\rm QD}(\lambda)d\lambda = 1$, and λ is the wavelength. $\epsilon_{\rm Atto}$ is the extinction coefficient of ATTO610 molecules, obtained from its experimental absorbance spectrum.

In the QD-ATTO610 system with 6 nm QDs and 10 ATTO610 molecules per QD, J is $3.10 \cdot 10^{12} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$. This value is at least two orders of magnitude smaller than the values of J reported for comparable FRET-based CsPbBr₃ QD-dye¹⁷¹ and CdSe-ZnS core-shell dye systems.³⁸ Despite this, the QD-ATTO610 system exhibits QD PL quenching efficiency of nearly 90% (**Figure 4.6a**). This suggests that large spectral overlap may not be relevant for efficient ET in this system.

To test this hypothesis, the composition of the CsPbBr₃ QDs was modified to CsPbCl_xBr_{3-x} and CsPbI_yBr_{3-y} via post-synthetic halide exchange (**Figure 4.10a**), allowing spectral tuning between QD emission and ATTO610 absorption. In this experiment, 10 nm spherical-like CsPbBr₃ QDs (see TEM image in **Figure 3.1b**) were selected as the starting point (**Figure 4.10b**, $J = 5.01 \cdot 10^{12} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$). The spectral overlap was reduced by blue-shifting the QD emission via changing halide composition from CsPbBr₃ to CsPbCl_xBr_{3-x}, while keeping QD size and quantum confinement effects unaltered (**Figure 4.10c**, $J = 2.12 \cdot 10^{12} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$).^{23,212} Even in this extreme case, exciting the QD-ATTO610 system at 2.95 eV resulted in dual emission, confirming ET from QDs to dye molecules (**Figure 4.10d**, **e**), with QD PL quenching efficiency remaining high (~81% for 10 ATTO610/QD, **Figure 4.10d**). Conversely, increasing spectral overlap by alloying the CsPbBr₃ QDs with iodide to form CsPbI_yBr_{3-y} QDs did not enhance the PL quenching efficiency (~64% for 10 ATTO610/QD, **Figure 4.10d**). This shows that the ET in the QD-ATTO610 system cannot be adequately described by conventional FRET theory.

A recent study reported significant ET from single FAPbBr₃ QDs to single cyanine 5 NHS-ester dyes despite the lack of substantial donor-acceptor spectral overlap. The authors



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Figure 4.10: ET and spectral overlap. a) Absorbance spectra of 10 nm-sized QDs with different halide compositions. b) Spectral overlap between QD emission and ATTO610 absorbance (red), which can be tuned by modifying the halide composition of the QDs. c) Absorbance spectra of QD-ATTO610 systems including QDs with different halide compositions at 10 ATTO610-per-QD ratio. d) PL spectra of QD-ATTO610 systems shown in (c), excited at 2.95 eV, and normalized to the maximum QD PL intensity. Despite a significant reduction in spectral overlap upon Cl⁻ alloying, exciting the QD-ATTO610 system at 2.95 eV still results in dual emission, confirming ET from QDs to dye molecules. e) PLE spectra of QD-ATTO610 systems shown in (d), further confirming ET from QDs to ATTO610 in all three cases.

proposed that the energetic difference between the initial and final states involved in the ET was bridged by strong electron-phonon coupling in the donor, enabling non-resonant $\rm ET.^{174}$ However, in the QD-ATTO610 system, bridging the large donor-acceptor energetic difference (~700 meV for CsPbCl_xBr_{3-x} QDs) via phonon-assisted non-resonant ET would require exciton coupling to a large number of phonon modes, making the transition highly unlikely. This is clearly not the case, as ET remains relatively efficient even when the energetic difference nearly doubles upon changing from CsPbBr₃ to CsPbCl_xBr_{3-x}. Therefore, exciton-phonon coupling cannot explain the observed efficient ET in this system.

A recent study has reported that ET between small CdSe QDs and surface-bound squaraine dyes proceeds via the Dexter exchange ET mechanism.²¹³ Similarly, triplet-triplet ET from confined CsPbBr₃ QDs to surface-bound 1-pyrenecarboxylic acid molecules has also been attributed to this mechanism.¹⁶⁶ Therefore, ET in the QD-ATTO610 system most likely follows the same Dexter exchange pathway.

As detailed in Section 2.3.1, efficient Dexter exchange ET requires two conditions: 1. a donor-acceptor distance below ~ 1 nm to facilitate donor-acceptor spatial wavefunction overlap, and 2. the presence of isoenergetic states available for energy "donation" and "acceptance".^{125,132,133} Given that ATTO610 molecules are closely bound to the QD surface by a special binding group, it is reasonable to assume that some degree of spatial wavefunction overlap exists between the highly quantum-confined exciton state in QDs and isoenergetic vibrational states of the dye's excited state. Unlike in FRET, optical transitions to and from these states with respect to the ground state do not necessarily need to have large oscillator strength, meaning that Dexter exchange ET can also occur even between optically inactive states.

Upon excitation, quantum-mechanical coupling between QDs and surface-bound ATTO610 molecules forms hybrid donor-acceptor coupled states. ET then occurs isoenergetically from the QD's excited X1 state to a vibrationally excited state of the acceptor. The excess potential energy in the acceptor is quickly dissipated within sub-picosecond timescales via vibrational relaxation and internal conversion, leaving the dye in the lowest vibrational level of its first excited state. Since this energy dissipation is much faster than the typical ET timescale, ET essentially becomes a "one way" process. Additionally, the energetic difference between QD and ATTO610 molecules is larger than thermal energy, making energy back transfer highly unlikely. After ET, ATTO610 molecules can subsequently emit red light. The Dexter exchange ET mechanism is illustrated in **Figure 4.11**.



Figure 4.11: Dexter exchange ET from a QD to a surface-bound ATTO610 molecule. The close proximity of ATTO610 to the QD surface allows for spatial wavefunction overlap between the highly quantum-confined exciton state in the QDs and isoenergetic vibrational states of the dye's excited state. Upon excitation, quantum-mechanical coupling between QDs and surface-bound ATTO610 molecules forms hybrid donor-acceptor states. ET occurs isoenergetically from the QD's excited X1 state to a vibrationally excited state of the acceptor. The excess energy in the acceptor is quickly dissipated via vibrational relaxation within sub-picosecond timescales, leaving ATTO610 in its lowest vibrational level of the first excited state. Since this energy dissipation is faster than the typical ET timescale, ET becomes a "one way" process. Subsequently, ATTO610 can emit red light.

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Furthermore, efficient through-bond ET has been demonstrated in covalently linked donorbridge-acceptor systems, where the bridge is a conjugated molecule.^{214–221} This suggests that the binding group of the dyes, as part of its conjugated system, might further facilitate efficient excitation funneling from QDs to the chromophore.

The efficient ET observed in the QD-ATTO610 system is not limited to OA-OLA-capped QDs. QDs capped with state-of-art ligands such as DDAB and lecithin also exhibit efficient ET to ATTO610 molecules, achieving an ET-related PLQY up to 11% of ATTO610 dyes (**Figure 4.12**). This is not surprising, since the binding affinity of the dimethyl iminium group to the QD surface's A-site is similar to that of the A-site binding quaternary ammonium group found in both DDAB and lecithin ligands (**Figure 2.4c**)), as demonstrated by DFT calculations of absolute binding energies of these binding groups.²⁰⁰



Figure 4.12: Optical characterization of DDAB- and lecithin-capped QD-ATTO610 systems. Absorbance, PL, and PLE spectra of a-c) the DDAB-capped QD-ATTO610 system in a 90% toluene, 7.5% chloroform, and 2.5% ethanol and d-f) the lecithin-capped QD-ATTO610 system in a 92.4% toluene, 3.8% chloroform, and 3.8% ethanol, both at ATTO610-per-QD ratio of 10.

4.1.3 Down-Conversion White Light Emitter

QD-molecule hybrid systems have a great potential in various optoelectronic and photocatalytic applications. For example, a down-conversion white light emitter can be engineered by combining blue excitation light with the dual emission of the QD-ATTO610 system. Here, red (R) green (G) emissions originate from the QD-dye hybrid system, with ATTO610 molecules providing red and QDs giving green in the spectrum. The blue (B) part of the spectrum is supplied by the transmitted excitation light. By adjusting the relative intensities of the three RGB components, down-conversion white-light emission can be achieved.

As a proof-of-concept, a highly concentrated sample of OA-OLA-capped CsPbBr₃ QDs (\sim 10 nm diameter) and ATTO610 molecules was prepared in a 2 mm cuvette in a solvent composed of 54% chloroform and 46% toluene. An LED source with a 460 nm central wavelength was used as excitation light, predominantly exciting QDs (**Figure 4.13a**). By optimizing the ATTO610/QD ratio and optical density, the relative intensities of transmitted excitation light and the PL of QDs and dyes could be tuned.

The recorded spectra are shown in **Figure 4.13b**, where the transmitted intensity of the excitation light (460 nm) is shown alongside QD (518 nm) and ATTO610 (664 nm) PL. The chromaticity output of the total spectrum in the CIE 1931 color space is shown in (**Figure 4.13c**), marked with a green rectangle at coordinates (0.26, 0.36), illustrating near-white light emission with a greenish hue. Such synergistic QD-dye systems present a viable alternative to multi-perovskite-based white-light emitters, where halide diffusion-related loss of spectral features poses a great challenge.²³



Figure 4.13: White light emission from the blue-LED-CsPbBr₃ QD-ATTO610 system. a) Schematic illustration of the experimental setup used to measure the spectra shown in (b). b) PL spectra of the highly concentrated QD-ATTO610 sample recorded together with the transmitted excitation light of the blue LED source. The inset shows a photo of the sample under blue LED excitation. c) CIE 1931 color space diagram. The green rectangle at coordinates (0.26, 0.36) marks the chromaticity position of the spectra depicted in (b). The orange circle in the center marks the ideal white-light coordinates.

4.1.4 Efficient QD-Dye Hybrids Beyond ATTO610

The example of OA-OLA capped CsPbBr₃ QDs and ATTO610 dyes, which contain the dimethyl iminium binding group demonstrates the significance of choosing dyes with the appropriate binding group. These groups facilitate dye attachment to the QD surface, enabling donor-acceptor spatial wavefunction overlap, which is an essential prerequisite for efficient Dexter exchange ET. This approach can also be extended to other dimethyl iminium-based dyes, such as pyronin y (PY), crystal violet (CV), and IR895. In all cases, strong QD PL

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intensity quenching, even at low dye concentrations, is observed, indicative of efficient excited state interactions between QDs and dye molecules.

For example, **Figure 4.14a**, **d** shows the QD-PY system, where the luminescent PY dye strongly quenches QD PL at below 10 dye molecules per QD. Selective excitation of QDs at 2.95 eV, where PY absorbance is negligible, results in dual emission from both QDs and PY dyes, demonstrating efficient ET. Similarly, as shown in **Figure 4.14b**, **e**, CV strongly quenches QD PL, with over 50% loss of the initial PL intensity at only 2 dye molecules per QDs. Finally, **Figure 4.14c**, **f** shows the case of IR895, which has little spectral overlap with QD emission and a large energetic difference (~1.4 eV) between the lowest exciton level and the dye's $S_0 \rightarrow S_1$ 0-0 transition. Despite this, significant QD PL quenching at low dye concentrations is observed, further supporting efficient excited state interaction between LHP QDs and dimethyl iminium-based dyes.



Figure 4.14: CsPbBr₃ QDs with various dimethyl iminium-based dyes. Absorbance (*top*) and PL spectra (*bottom*) of OA-OLA-capped CsPbBr₃ QDs together with a,d) pyronin y (PY), b,e) crystal violet (CV), and c,f) IR895 dyes. For comparison, the absorbance and, if applicable, PL spectra of the dyes alone are shown as dashed orange lines. The spectra with PY were recorded in a 90% toluene and 10% acetonitrile solution, with CV and IR895 - in a 90% toluene and 10% chloroform solution. The dimethyl iminium binding group of the dyes is highlighted in red.

All these examples clearly demonstrate that the dyes containing the dimethyl iminium binding group as part of their conjugated system exhibit excellent excited state interaction with QDs and are highly promising candidates for designing efficient LHP QD-dye systems. 4.1. Dexter Exchange Energy Transfer from QDs to Dimethyl-Iminium-Based ATTO610 Dyes

4.2 Charge Transfer from QDs to Ligands Functionalized with Ferrocene

4.2.1 Multi-Functional Ligands

The previous section demonstrated how to design efficient QD-molecular hybrid systems. It showed that the efficient interactions between LHP QDs and the molecules require selecting acceptor molecules with right binding groups. Close binding of these molecules on QD surfaces minimizes the donor-acceptor distance, which is essential for efficient Dexter exchange ET or CT processes. Based on these insights, this strategy can be further improved by purpose-fully designing molecules that combine three key attributes: binding group tailored for LHP surfaces, long alkyl tail group for colloidal stability, and the desired functional group. Such molecules are also known as multi-functional ligands. These ligands allow for more precise control over the spacing between QDs and functional molecules. They also allow tuning of the number of acceptors a donor can interact with, thus increasing their interaction probability (**Figure 4.15**).



Figure 4.15: Different approaches for designing a QD-molecule hybrid system. a) In the simplest approach QDs are directly mixed with molecules that do not necessarily possess high binding affinity to the QD surfaces. b) In a more widespread approach, functional molecules with suitable binding groups are anchored to QD surfaces, often through a ligand exchange procedure. c) The third approach involves developing multi-functional ligands that combine strong binding to the QDs, colloidal stability, and the desired functionality.

Multi-functional ligands with a dimethylammonium bromide binding group $((CH_3)_2N^+Br^-)$ were synthesized following the exothermic Menshutkin reaction described in **Section 3.1.1**.^{191–193} A wide range of multi-functional ligands with varying tail group lengths and functional groups can be designed using different combinations of tertiary dimethylamines and alkyl halides. These multi-functional ligands are similar to DDAB ligands but with one tail group replaced by a functional group R, which imparts the desired functionality onto the ligands. The DDAB-like quaternary ammonium binding group ensures strong binding affinity of these ligands to the QD surfaces and passivation of surface defect states, which is important for achieving high PLQY in QDs.¹⁰⁸ In this

work, ferrocene, a well-known hole scavenger for QDs,^{144,222} was chosen as the functional group, resulting in multi-functional (ferrocenylmethyl) dodecyldimethylammonium bromide (FeDDAB) multi-functional ligands (**Figure 4.16**).



Figure 4.16: Synthesis of multi-functional ligands. a) Schematic illustration of multi-functional ligands (*left*), alongside a chemical structure of the multi-functional ligand FeD-DAB, featuring a ferrocene functional group and a dodecyl tail group (*right*). b) General single-step chemical reaction used in this work to synthesize multi-functional ligands.

4.2.2 Optical Characterization of QDs Capped with Multi-Functional Ligands

DDAB- and FeDDAB-capped CsPbBr₃ QDs with an average diameter of approximately 6 nm were synthesized as described in **Section 3.1.1** (see TEM images in **Figure 3.1c**, **d**). **Figure 4.17a** shows the absorbance and PL (excited at 3.10 eV) spectra of DDAB-capped QDs dispersed in toluene. The absorbance spectra display characteristic excitonic resonances of weakly confied CsPbBr₃ QDs (labeled as X1, X2).²⁰² As expected, DDAB-capped QDs display bright PL with a PLQY of up to 80%. They exhibit a single-exponential PL profile with a PL lifetime of $\kappa_{\text{OD-DDAB}}^{-1} = 3.5$ ns (**Figure 4.17b**).



Figure 4.17: Optical characterization of DDAB-capped CsPbBr₃ QDs. a) Absorbance and PL (excited at 3.10 eV) spectra of DDAB-capped QDs. Inset: schematic of a DDAB-capped QD and DDAB ligand structure. b) TRPL of DDAB-capped QDs measured via TCSPC, excited at 3.10 eV. The inset shows the spectra on a logarithmic y-axis. The red line represents the single-exponential fit to the data.

The absorbance and PL spectra of FeDDAB-capped QDs dispersed in toluene are shown

in Figure 4.18a. Their absorbance spectrum is identical to that of the DDAB-capped QDs, indicating that even at 100% FeDDAB ligand coverage and after purification, the QDs remain monodisperse and colloidally stable.⁸³ An excitation energy of 3.10 eV was chosen, close to the absorbance minimum of FeDDAB ligands. The absorbance of FeDDAB-capped QDs shows no detectable signal from FeDDAB ligands, which absorb light very weakly (Figure 4.18b). Therefore, following excitation at 3.10 eV, it can be assumed that predominantly the QDs are excited, while FeDDAB ligands remain in their ground state. Unlike DDAB-capped QDs, FeDDAB-capped QDs emit very weakly, with a low PLQY of less than 0.1%, close to the detection limit. The shape and energetic position of both absorbance and PL spectra is unchanged regardless of FeDDAB ligand concentration, indicating weak coupling between QDs and ferrocene molecules.^{139,140}

Because DDAB and FeDDAB ligands share the same binding group, the ratio of FeDDAB to DDAB ligands can be precisely controlled. **Figure 4.18c**, **d** shows that by varying the percentage of FeDDAB in the total ligand amount during synthesis, the QD PLQY can be finely tuned across the entire range from 80% to 0.1%.

Titration experiments using ferrocene and FeDDAB on DDAB-capped QDs highlight the significance of multi-functional ligands specifically designed for QD surfaces. When ferrocene, which lacks the dimethyl ammonium group, is added to a toluene solution of DDAB-capped QDs, it has little effect on QD PL quenching, even at high ferrocene-to-QD ratios. This is because ferrocene molecules do not bind to QD surfaces; the strongly bound DDAB ligands prevent their access. As a result, ferrocene molecules are too far away to engage in efficient excited-state interactions with QDs (**Figure 4.18e**). This finding aligns with previous reports in literature.^{18,19} In contrast, titrating FeDDAB ligands leads to clear and efficient quenching of QD PL, even at low FeDDAB-to-QD ratios. This highlights the importance of donor-acceptor distance for efficient interactions and emphasizes the necessity of acceptor molecules binding to QD donor surfaces.

Furthermore, the PL intensity of FeDDAB-capped QDs exhibits linear dependence on the excitation power (**Figure 4.19a**). The FeDDAB-capped QDs remain stable for at least a month, showing no notable changes in absorbance, maintaining low PLQY, further supporting the strong binding of these ligands to the QD surfaces (**Figure 4.19b**).

4.2.3 Photoexcited Charge Transfer from QDs to Ferrocene Functionalized Ligands

To investigate why QD PL is quenched following FeDDAB capping, TRPL measurements were performed. **Figure 4.20a**, **b** show time-resolved 3D spectra of DDAB- and FeDDABcapped QDs, following excitation at 3.10 eV, measured using a streak camera. In contrast to DDAB-capped QDs, the PL lifetime of FeDDAB-capped QDs is dramatically shortened to $\kappa_{\rm QD-FeDDAB}^{-1} = 6.1$ ps, which is three orders of magnitude smaller than that of DDAB-capped QDs. In addition, as illustrated in **Figure 4.20c**, the maximum PL intensity is reduced



Figure 4.18: Optical characterization of FeDDAB-capped CsPbBr₃ QDs. a) Absorbance and PL (excited at 3.10 eV) spectra of FeDDAB-capped QDs. Inset: schematic of a FeDDAB-capped QD and FeDDAB ligand structure. b) Absorbance spectra of highly concentrated FeDDAB ligands and commercial ferrocene molecules in chloroform. c) PL spectra of QDs synthesized with varying amounts of FeDDAB and DDAB ligands (excited at 3.10 eV). The percentage (%) refers to the portion of FeDDAB ligands in the total ligand solution, which is a mixture of FeDDAB and DDAB ligands. Slight variations in the energetic position of each individual PL spectrum arise from batch-to-batch differences in QD size. d) Integrated PL intensity of QDs from (c), normalized to the integrated PL intensity of purely DDAB-capped QDs. e) Post-synthetic titration of ferrocene and FeDDAB molecules into a toluene solution of DDAB-capped QDs.

despite identical experimental conditions for both samples. No CT exciton- or exciplex-related red-shifted emission can be identified in the measured spectra.²²³

According to the literature, ferrocene molecules have a type II energetic band alignment relative to CsPbBr₃ QDs, which facilitates photoexcited hole transfer from QDs to ferrocene.^{19,224} This is further confirmed by the DFT calculations.²⁰¹ This mechanism may explain the observed quenching of PL in FeDDAB-capped QDs. As explained in **Section 2.1.3**, the experimentally measured PL decay rate κ_{PL} is the sum of all radiative and non-radiative decay rates. Assuming that in FeDDAB-capped QDs, ferrocene molecules introduce an additional non-radiative relaxation pathway for excitons through dissociation by hole transfer to ferrocene - alongside the intrinsic non-radiative mechanisms, which can be assessed from TRPL measurements of DDAB-capped QDs, - this, allows the hole transfer rate to be estimated



Figure 4.19: Power dependence and stability. a) Integrated PL intensity of DDABand FeDDAB-capped QDs as a function of excitation power. Grey lines represent linear fits to the data (R^2 =0.99). b) Absorbance spectra of FeDDAB-capped QDs measured directly after synthesis (0 days) and after 28 days.

as $\kappa_{\rm ht} \approx 0.16 \text{ ps}^{-1}$. Given that the exciton Bohr diameter in CsPbBr₃ QDs is approximately 6 nm, comparable to the QD size, it can be assumed that the exciton does not need to diffuse to the QD surface to interact with a ferrocene molecule. Thus, $\kappa_{\rm ht}$ represents the intrinsic hole transfer rate.



Figure 4.20: Time-resolved PL of DDAB- and FeDDAB-capped QDs. 3D streak spectra of a) DDAB- and b) FeDDAB-capped QDs, excited at 3.10 eV. c) TRPL profiles of DDAB- (light green) and FeDDAB-capped (dark green) QDs. The red line represents the single-exponential fit to the data ($R^2 = 0.99$).

To confirm that the rapid PL quenching in FeDDAB-capped QDs is due to hole transfer from QDs to ferrocene, femtosecond transient absorption (TA) experiments were performed. Samples were pumped at 3.10 eV, and pump-induced changes in absorption (ΔA , experimental details in **Section 3.3.8**) were monitored using a broad white light probe pulse. **Figure 4.21a** shows TA spectra of DDAB-capped QDs. The negative feature at 2.55 eV can be predominately attributed to the phase-space filling of the energetically lowest X1 exciton state.²⁰² DDAB-capped QDs exhibit a long-lived single exponential recovery of ΔA signal at the X1 position, consistent with their TRPL lifetime. **Figure 4.21b** shows the TA spectra of FeDDAB-capped QDs, which have a comparable shape to those of DDAB-capped QDs but exhibit a significantly shorter recovery time. Notably, the ΔA signal at the X1 position of FeDDAB-capped QDs recovers on a slower timescale compared to their TRPL, and its maximum intensity relative to the ΔA signal of DDAB-capped QDs is also reduced (**Figure 4.21c**).

The different behaviors of TRPL and ΔA signal of the lowest exciton state in FeDDABcapped QDs provide clear evidence of hole transfer from QDs to ferrocene molecules. In TRPL measurements, PL is detected only if an exciton on a QD recombines radiatively. If CT dissociates the exciton, radiative recombination of the separated e-h pair, emitting a photon of the same energy as the pristine exciton, is not possible. However, in TA experiments, the ΔA signal can be assumed to be proportional to the sum of the excited electron and hole population densities, given that phase-space-filling is the dominant origin of this signal. In this case, the presence of both charge carriers or either one of them on a QD will generate a signal. Therefore, during CT, the TRPL decays on a faster timescale than the ΔA signal.^{159,161,162,225,226}

A positive ΔA signal around 2.00 eV, which would indicate the appearance of charged ferrocene species,¹⁸ is absent, likely due to ferrocene's low absorbance. The ΔA signal at the X1 position exhibits a nearly single exponential profile and fully recovers within ~60 ps. This suggests that hole transfer is soon followed by a subsequent electron transfer to the positively charged ferrocene.

To support this claim, the ΔA signal of FeDDAB-capped QDs was modeled as discussed below. In a simplified approach, given that $\kappa_{\rm ht} \gg \kappa_{QD-DDAB}$, the differential equation for the photoexcited hole population density $n_{\rm h}(t)$ at time t in the measured QD ensemble after the pulsed excitation can be approximated as $\dot{n}_{\rm h}(t) \approx -\kappa_{\rm ht}n_{\rm h}(t)$. Here, it is assumed that ferrocene molecules remain in the ground state during the excitation process. The differential equation for the electron population density $n_{\rm e}(t)$ can be approximated as $\dot{n}_{\rm e}(t) \approx -(1-\exp(-\kappa_{\rm ht}t))\kappa_{\rm et}n_{\rm e}(t)$, where the intrinsic electron transfer rate $\kappa_{\rm et} \gg \kappa_{QD-DDAB}$. Since electrons and holes in LHPs have comparable effective masses,⁶² the ΔA signal at the X1 position can be assumed to be proportional to the sum of electron and hole population densities in the measured QD ensemble: $\Delta A \sim n_{\rm e} + n_{\rm h}$.^{225,226} Solving the differential equations, and assuming that $n_{\rm h}(0) = n_{\rm e}(0)$, the ΔA signal can be modeled with the equation

$$\Delta A = \alpha(\exp(-\kappa_{\rm ht}t) + \exp(-\kappa_{\rm et}t - \frac{\kappa_{\rm et}}{\kappa_{\rm ht}}(\exp(\kappa_{\rm ht}t) - 1)), \qquad (4.7)$$

where α is a proportionality factor. Fitting this expression to the experimentally measured ΔA signal at the X1 position, with α and κ_{et} as fitting parameters, yields an electron transfer rate $\kappa_{et} = 0.067 \text{ ps}^{-1}$, corresponding to an electron transfer time of ~15 ps. This is about three times slower than the hole transfer time. These results align well with a previous study showing that positively charged ferrocene molecules have a favorable band alignment with CsPbBr₃ QDs, facilitating photoexcited electron transfer from QDs. Note that the hole transfer rate κ_{ht} depends on the number of ferrocene molecules attached to and interacting with a single QD,^{146,200} as discussed earlier in this chapter. In contrast, electron transfer can



only occur to the single photooxidized ferrocene molecule attached to the same QD.

Figure 4.21: Transient absorption spectra of DDAB- and FeDDAB-capped QDs. TA spectra of a) DDAB- and b) FeDDAB-capped QDs, excited at 3.10 eV. Grey shaded areas represent steady-state absorbance spectra of the samples as guides. c) $\Delta A/A_0$ signal of X1 excitons in DDAB- (light green) and FeDDAB-capped (dark green) QDs. A_0 is the steady-state absorbance of the sample at the X1 energy. The red line represents fit to the model as discussed in the main text ($R^2 = 0.99$). The grey spectra represent TRPL of FeDDAB-capped QDs, appropriately normalized.

Based on these results, the excited-state interaction between closely bound ferrocene molecules and QDs can be described as follows: QD and ferrocene molecules attached via multi-functional FeDDAB ligands are separated by a single carbon bond, resulting in a minimal donor-acceptor distance that facilitates their spatial wavefunction overlap, important for CT. Following photoexcitation of the QDs, the entire QD-FeDDAB hybrid system enters an excitad state: $(QD^*-FeDDAB) \rightarrow (QD-FeDDAB)^*$, where * denotes the excited state. Due to the substantial energetic driving force for a hole to localize on a ferrocene molecule, charge separation happens on an average timescale of 6 ps. As a result, a negatively charged QD and a positively charged ferrocene hybrid system is formed $(QD^*-FeDDAB^+)$. The hole transfer efficiency in the QD-FeDDAB hybrid is remarkably high, calculated as $\Phi_{\rm CT} = \kappa_{\rm ht}/(\kappa_{\rm QD-DDAB} + \kappa_{\rm ht}) \cdot 100\% = 99.9 \%$.¹⁴⁶ The high efficiency is attributed to the fact that a single QD can interact with a multiple attached ferrocene molecules, which increases the interaction probability.

Following the acquisition of the positive charge, ferrocene molecules undergo structural reorganization on femtosecond timescales, a behaviour typical of organic molecules, which are sensitive to their oxidation state. The molecular structure and energetic position molecular orbitals are closely related (Section 2.2).¹²⁵ Consequently, the molecular orbitals of ferrocene and their alignment relative to CsPbBr₃ QDs change, creating a significant driving force for electrons to localize on the charged ferrocene molecule (QD-FeDDAB^{*}). This is supported by reports in the literature¹⁸ and further confirmed by DFT calculations.²⁰¹ As a result, electron transfer happens on an average timescale of 15 ps. Ultimately, the electron and hole on the ferrocene molecule recombine non-radiatively. All in all, it results in step-wise ET from QDs to ferrocene molecules (Figure 4.22).



Figure 4.22: CT from QDs to ferrocene. Illustration of step-wise CT from FeDDABcapped CsPbBr₃ QDs to functionalized ferrocene molecules.

This study emphasizes the significance of the donor-acceptor distance for efficient CT, as demonstrated through steady-state PL measurements. It is shown that ferrocene molecules engage in efficient excited-state interactions with QDs only when incorporated as part of multi-functional FeDDAB ligands. Additionally, this work highlights, using the time-resolved spectroscopy experiments, the importance of molecular structure reorganization following CT, which affects the energetic position of molecular orbitals of the acceptor molecule and, ultimately, influences charge separation efficiency. This straightforward approach of multifunctional ligand engineering for LHP QDs provides a blueprint for designing efficient QDmolecular hybrids for various photocatalytic and optoelectronic applications.

Chapter 5

Mitigating Post-Synthetic Halide Exchange in Bulk MAPbBr₃ via Lysine Inclusions

This chapter is based on the publication [195] and investigates the effect of Lys incorporation in MAPbBr₃ crystals on the host's propensity to undergo post-synthetic halide exchange. The findings unanimously indicate that incorporated Lys hinders post-synthetic Cl⁻ and I⁻ diffusion into the bulk MAPbBr₃, underscoring the significance of molecular inclusions and A-site cation engineering for the physical properties of crystalline hosts. Although this study focuses on MAPbBr₃, the underlying mechanism by which Lys inclusions hinder halide diffusion is likely applicable to other LHPs as well. Additionally, molecular inclusions within bulk LHP crystals hold potential for addressing photoinduced halide segregation.

5.1 Lysine Does Not Influence Optical Properties of MAPbBr₃

Bulk MAPbBr₃ LHPs with incorporated Lys at three different concentrations were prepared as described in **Section 3.1.2**. The synthesis yielded micron-sized orange crystals, with Lys incorporation proportional to its concentration in the precursor solution.⁴⁴ These samples are labeled as MAPbBr₃ Lys- α , where $\alpha = 0$, 1, 2 corresponds to 0, 1, and 2 mg of Lys added to the precursor solutions, respectively. MAPbBr₃ Lys-0 is also referred to as pure MAPbBr₃.

As discussed in **Section 2.4.1**, amino acid incorporation at sufficient concentrations can alter the optical properties of bulk inorganic host semiconductors. For example, in ZnO and Cu₂O, incorporated amino acids induced quantum confinement-like effects within micronsized crystals. Amino acids acted as voids, forming energetic barriers to electrons and holes, confining them akin to the particle-in-a-box concept. The confining size was assumed to be the average distance between amino acids, which was estimated via wavelength-dispersive X-ray spectroscopy, and found to be comparable to the exciton Bohr diameter of these materials.⁴⁶ The void-induced quantum confinement, along with compositional disorder, significantly influenced optical properties.^{46,48} Therefore, the key question is whether amino acid incorporation similarly affects the optical properties of bulk MAPbBr₃.

To explore this, PL and PLE spectroscopy experiments were performed using the μ -PL setup described in **Section 3.3.2**. Generally, the first step in optical characterization of any material is measuring its absorbance spectrum with UV-Vis spectroscopy. However, since the bulk crystals studied here are not transparent and strongly scatter light, this method was not applicable. Fortunately, the electronic band structure of bulk LHP, including MAPbBr₃, has been extensively researched (**Section 2.1**).^{57,58,71,72,227,228} Based on this, PL spectra of Lys-incorporated MAPbBr₃ crystals were recorded following the above-band-gap excitation at 2.56 eV.

The PL spectra of all three MAPbBr₃ Lys- α crystals are shown in **Figure 5.1**. The spectra peak around 2.30 eV and have a slight asymmetric shape with low-energy tail, which in the literature has been attributed to bromide surface vacancy trap state recombination.⁵⁶ The FWHM of Lys-incorporated MAPbBr₃ crystals (88 and 89 meV for MAPbBr₃ Lys-1 and Lys-2, respectively) is slightly broader compared to that of MAPbBr₃ (81 meV).

The dots in **Figure 5.1** represent PLE spectra detected at 2.19 eV. Assuming the product of relaxation and emission probabilities $\rho_{\text{relax}} \cdot \rho_{\text{emit}}$ remains constant and non-zero over the chosen excitation energy range, PLE spectra can be correlated with absorbance spectra, as detailed in **Section 3.3.3**. Onset and shape of the PLE spectra align with what would be expected for a direct band gap excitonic semiconductor. A weak peak slightly above 2.30 eV in the PLE spectra could be interpreted as a signature of the energetically lowest excitonic transition.

As shown in Figure 5.1, Lys incorporation does not significantly alter the optical proper-



Figure 5.1: Optical characterization of bulk MAPbBr₃ with varying Lys incorporation. PL (solid line) and PLE (dots) spectra of bulk MAPbBr₃ with different Lys concentrations: a) Lys-0, b) Lys-1, and c) Lys-2. Dashed grey lines are visual guides.

ties of bulk MAPbBr₃ crystals, unlike ZnO and Cu₂O. No void-induced quantum-confinement effects are observed in the PL and PLE spectra of the Lys-incorporated MAPbBr₃ crystals. The absence of this effect is potentially related to factors such as the actual amount and manner of Lys incorporation. A subtle broadening in the PLE onset is observed, likely due to sample-to-sample variations.

Alternatively, Lys incorporation could influence the optical properties of the MAPbBr₃ through changes in the chemical composition and induced strain, altering their electronic band structure.^{118,229,230} As explained in **Section 2.4.2**, Lys forms a "molecular bridge" in MAPbBr₃ by replacing two adjacent A-site MA⁺ cations by its two amine groups, leading to lattice contraction.⁴⁴ However, since A-site cation orbitals do not directly contribute to formation of VB and CB in LHPs (**Section 2.1**),²³⁰ effect of chemical compositional changes due to amino group substitution on the electronic band structure are expected to be insignificant. Moreover, the lattice contraction induced by Lys incorporation appears insufficient to significantly alter the host's electronic band structure.

5.2 Lysine Mitigates Post-Synthetic Halide Exchange in MAPbBr₃

Mixed halide perovskites were prepared by immersing MAPbBr₃ Lys- α crystals in 0.1 M MAZ (Z = Cl⁻ or l⁻) isopropanol solution, as described in **Section 3.1.2**. The sealed sample containers were gently shaken in the dark for t = 0, 1, 6, or 12 hours to allow the halide Z to diffuse into and replace native Br⁻ in the MAPbBr₃ Lys- α matrix. Afterwards, the samples were washed with acetone and air-dried, resulting in mixed halide MAPbCl_xBr_{3-x} and MAPbI_yBr_{3-y} crystals. Here, x and y represent the stoichiometric coefficients of the exchanged Cl⁻ and I⁻, respectively ($0 \le x, y \le 3$). Figure 5.2 shows scannin electron microscope (SEM) secondary electron (SE) images and false color energy-dispersive X-ray spectroscopy (EDS) elemental maps of single MAPbBr₃ Lys-0 and Lys-2 crystals after 24 hours of Cl⁻ (Figure

5.2a, b) and I⁻ (**Figure 5.2c, d**) diffusion, respectively. The elemental maps clearly demonstrate that both, Cl⁻ and I⁻ treatments of MAPbBr₃ crystals result in the formation of mixed halide perovskites.



Figure 5.2: SEM-EDS maps of MAPbBr₃ crystals after 24 hours of Cl⁻ and I⁻ diffusion. SEM-SE images and false color EDS elemental maps of single MAPbBr₃ Lys-0 and Lys-2 crystals after 24 hours of Cl⁻ (\mathbf{a} , \mathbf{b}) and I⁻ (\mathbf{c} , \mathbf{d}) diffusion, respectively.

To evaluate the impact of incorporated Lys on post-synthetic halide diffusion into MAPbBr₃ crystals, the stoichiometric coefficients x and y were determined using ion chromatography (IC). **Figure 5.3** shows the values of x and y plotted as a function of halide diffusion time t. As expected, longer diffusion times for both Cl⁻ and l⁻ result in higher x and y values. In addition, for the same diffusion time, x is consistently higher than y. This difference is attributed to the higher diffusion coefficient of Cl⁻ compared to l⁻, because of the smaller ionic radius of Cl⁻ relative to Γ .^{52,111} Importantly, the MAPbBr₃ samples with incorporated Lys consistently show lower x and y values compared to the sample with no incorporated Lys. For example, **Figure 5.3** demonstrates that after 24 hours of post-synthetic halide diffusion, MAPbBr₃ crystals with the highest Lys content (Lys-2) exhibit 62% smaller stoichiometric coefficients compared to the MAPbBr₃ with no incorporated lysine (Lys-0). This strongly suggests that incorporated Lys hinders post-synthetic halide exchange in MAPbBr₃ crystals.

To assess halide exchange-related structural changes in the investigated crystals, highresolution powder X-ray diffraction (XRD) experiments were performed. Figure 5.4a-c shows the XRD patters of MAPbBr₃ crystals with different Lys incorporations after halide diffusion time of 24 hours. The XRD patterns exhibit typical halide-exchange related shifts, but no diffraction peaks appear, disappear, or change intensity significantly, which would indicate a phase change in the crystal structure. This suggests that all crystals retain the



Figure 5.3: Chemical analysis via ion chromatography. Stoichiometric coefficients a) x in MAPbCl_xBr_{3-x} and b) y in MAPbI_yBr_{3-y} as functions of halide diffusion time and different levels of incorporated Lys. Grey dashed lines serve as a guide for the eye.

cubic perovskite structure of the initial MAPbBr₃ crystals.

For better comparison, **Figure 5.4d-f** shows zoom-in view of the (100) XRD reflections. For Cl⁻ exchange, a diffraction peak shift towards higher 2θ values is observed, while for l⁻ exchange, the peak shifts towards lower angles. This can be attributed to lattice contraction in the case of Cl⁻ and lattice expansion in the case of l⁻, a direct consequence of the differing ionic radii of the three halides (**Section 2.1.5**).^{111,117,231} In the sample with no incorporated Lys (Lys-0), the Cl⁻-related shift in the XRD pattern (**Figure 5.4d**) is much stronger than that in the sample with the highest incorporated Lys (Lys-2, **Figure 5.4f**), indicating reduction in Cl⁻ diffusion in the presence of incorporated Lys. In the case of l⁻, the trend is not as clear.

A closer investigation of the XRD patterns in **Figure 5.4** reveals that halide exchange results not only in shifts in the XRD peaks but also their shape becomes broader and more asymmetric. This asymmetric broadening is most prominent in the sample with no incorporated Lys (Lys-0) after Cl⁻ diffusion. Such broadening indicates crystal inhomogeneity, also observed in the EDS maps in **Figure 5.2**. The inhomogeneity stems from the diffusioncontrolled halide exchange process, which results in a halide concentration gradient from the surface of the host crystals towards the center.¹¹¹ Consequently, this variation is reflected in the crystal structure. Since XRD measurements probe an ensemble of thousands of unit cells, the recorded signal represents a superposition of individual XRD signals from regions with varying Cl⁻ concentrations. For example, XRD intensities at higher 2θ values in the Cl⁻-exchanged sample in **Figure 5.4d** will stem from the crystal regions with higher Cl⁻ content compared to the XRD intensities at lower 2θ . Due to the nonuniform halide distribution within the MAPbBr₃ host, XRD patterns are expected to exhibit inhomogeneous broadening.

To further investigate the effect of Lys incorporation on halide exchange-induced structural changes in MAPbBr₃ crystals, the change in the lattice constant, assuming a cubic unit cell, was calculated using the relation $\Delta a(z) = a(0) - a(z)$, where a(0) is the lattice constant of a MAPbBr₃ crystal with a given Lys incorporation, and a(z) is the lattice constant of the mixed halide LHP with the stoichiometric coefficient z. The lattice constants were calculated



Figure 5.4: Structural analysis via X-ray diffraction. Enlarged view of the XRD patterns of MAPbBr₃ crystals with different Lys incorporations: **a**) Lys-0, **b**) Lys-1, and **c**) Lys-2 (middle, green). Also shown are the XRD patterns after 24 hours Cl⁻ (bottom, blue) and I⁻ (top, orange) diffusion. Panels **d-f**) show (100) XRD reflection of MAPbBr₃, and after 24 hours of Cl⁻ and I⁻ diffusion for different Lys incorporation levels: **d**) Lys-0, **e**) Lys-1, and **f**) Lys-2.

as detailed in Section 3.2. The results are illustrated in Figure 5.5.

For Cl⁻ exchange, the change in lattice constant is negative, indicating lattice contraction. The magnitude of the lattice change Δa is negatively correlated with both the amount of alloyed Cl⁻ and also the incorporated Lys. The sample with no incorporated Lys (Lys-0) exhibits the strongest Cl⁻-exchange related reduction in the lattice constant, whereas the sample with the highest incorporated Lys (Lys-2) shows the smallest reduction. The experimentally determined Δa was fitted to the expression $\Delta a(\tilde{x}) = (a(1) - a(0))\tilde{x}$, introduced in Section **2.1.5**, which described the change in the lattice constant of a solid solution. Here the parameter a(1) is the lattice constant of cubic MAPbCl₃, and \tilde{x} is the normalized stoichiometric coefficient x, where $\tilde{x} \in [0,1]$. The fit is shown as a grey line in **Figure 5.5a**. Estimating a(1) from the experimentally determined lattice constant of MAPbBr₃ Lys-0 crystal $a(0) \approx$ 5.9496 Å and the slope obtained via fitting ($s \approx 0.1465$), it is found $a(1) \approx 5.8031$ Å, which is reasonably close to the experimentally measured lattice constant of MAPbCl₃, 5.7 Å, reported in the literature.⁶² This confirms, that the lattice change Δa is a function of the alloyed Cl⁻ amount and varies linearly with it in a uniform manner, as expected for a solid solution,^{116,117,232} which further confirms the hindrance of post-synthetic Cl⁻ diffusion by Lys inclusions in MAPbBr₃ crystals.

In the case of Γ exchange (**Figure 5.5b**), the change in the lattice constant is positive, indicating lattice expansion. The lattice expansion in Γ -exchanged samples is linear in y. However, unlike Cl⁻-exchanged samples, different linear trends with varying slopes are observed for different Lys concentrations. This behavior likely results from the opposing effects of Γ and Lys on the MAPbBr₃ crystal structure: while Lys incorporation in MAPbBr₃ crystals induces lattice contraction,^{44,111} exchanging Br⁻ with Γ causes lattice expansion.¹¹⁷ In addition, the magnitudes of the Lys-related lattice contraction and Γ exchange-induced lattice expansion are comparable.⁴⁴ As a result, the Γ -related lattice expansion appears to depend on the extent of pre-existing lattice contraction of MAPbBr₃ crystals caused by the incorporated Lys. This suggests that the lattice contraction Δa is not only a function of the alloyed Γ amount but also the amount of incorporated Lys. **Figure 5.5b** also reveals that the magnitude of Γ exchange-induced lattice expansion is less significant than that of Cl⁻-induced lattice contraction, consistent with IC measurements, which show that y < x, (**Figure 5.3**).



Figure 5.5: Halide-exchange related change in the lattice constant. Lattice constant variation as a function of the stoichiometric coefficients x and y for a) MAPbCl_xBr_{3-x} and b) MAPbI_yBr_{3-y}. Grey lines represent a linear fit to the function $\Delta a(\tilde{z}) = (a(1)-a(0))\tilde{z}$, where a(0) is the experimentally determined lattice constant of MAPbBr₃ Lys- α . The parameter a(1) is the lattice constant of MAPbCl₃ or MAPbI₃, and \tilde{z} is the normalized stoichiometric coefficient, where $\tilde{z} \in [0, 1]$.

To further evaluate the influence of incorporated Lys on post-synthetic exchange of native Br⁻ with Cl⁻ or I⁻ in MAPbBr₃ crystals, steady-state PL spectroscopy experiments were conducted. As explained in **Section 2.1.5**, exchanging one halide with another changes the electronic band structure of LHPs, as a result, modifying their band gap.^{23,117} For example, substituting Br⁻ with Cl⁻ in MAPbBr₃ crystals increases the band gap (blue-shift), whereas I⁻ substitution decreases the band gap (red-shift). The magnitude of the band gap shift is directly proportional to the amount of exchanged halide.^{23,118}

A straightforward method to assess halide exchange-related change in the band gap is by UV-Vis spectroscopy experiments. However, since this technique is not applicable to bulk MAPbBr₃ crystals, PL spectroscopy can provide insights into halide exchange-related changes in the electronic band structure of MAPbBr₃ crystals, since it has been demonstrated that the halide-exchange related changes in the PL spectra follow a nearly identical trend as the changes in the band gap.^{117,118}

The PL spectra of MAPbBr₃ with different incorporated Lys concentrations after various Cl⁻ diffusion times, measured at multiple spots, are shown in **Figure 5.6**. The PL spectra were detected immediately following excitation at 3.26 eV with very low power (P < 19.1 μ J/cm²) to prevent any effects due to light-induced halide segregation.^{233,234} For better comparison, the spectra are normalized to maximum intensity. As shown in **Figure 5.6a**, longer Cl⁻ diffusion times result in a stronger blue-shift of the PL spectra towards the energetic position of the PL peak of pure MAPbCl₃ (marked with a grey arrow in **Figure 5.6**).^{227,235} The magnitude of the PL shift at any given diffusion time decreases with increasing Lys incorporation, pointing towards a reduced Cl⁻ exchange rate (**Figure 5.6a-c**).



Figure 5.6: Change in PL spectra due to Cl⁻ exchange. PL spectra of MAPbBr₃ following Cl⁻ exchange, excited at 3.26 eV, for different Lys incorporation: a) Lys-0, b) Lys-1, c) Lys-2. In each panel, peaks with the same color represent measurements performed on different spots of the respective sample. The arrow near 2.9 eV denotes an approximate energetic position of the PL peak of bulk MAPbCl₃.

Similarly, Figure 5.7 shows the PL spectra of MAPbBr₃ with different incorporated Lys concentrations after various Γ diffusion times, measured at multiple spots and excited at 2.56 eV with very low power (P < 31.3 μ J/cm²). Longer Γ diffusion translates into a stronger red-shift of the PL spectra towards the energetic position of the PL peak of pure MAPbI₃ (marked with a grey arrow in Figure 5.7).^{227,232} For the same diffusion time, the magnitude of the Γ -exchange related PL shift is significantly smaller compared to the magnitude of Cl⁻exchange induced PL shift, suggesting that less Γ is exchanged compared to Cl⁻ under identical conditions. This observation is consistent with the IC results shown in Figure 5.3. Additionally, a decrease in the magnitude of the halide-exchange related PL shift with higher incorporated Lys concentration is evident. In the sample with the highest Lys incorporation (Lys-2), Figure 5.7c the shift is nearly absent. These findings clearly indicate that incorporated Lys mitigates both Cl⁻ and Γ exchange and are consistent with previous IC and XRD measurement results.

The energetic position and shape of the PL spectra of the mixed-halide samples are highly spot-dependent, especially for Cl⁻-exchanged samples. This is because each spectrum represents a small section of the crystal, as PL spectroscopy probes only a fraction of the micron-



Figure 5.7: Change in PL spectra due to I[−] exchange. PL spectra of MAPbBr₃ following I[−] exchange, excited at 2.56 eV, at different Lys incorporation: a) Lys-0, b) Lys-1, c) Lys-2. In each panel, peaks with the same color represent measurements performed on different spots of the respective sample. The arrow near 1.7 eV denotes an approximate energetic position of the PL peak of bulk MAPbI₃.

sized crystals. The focused beam diameter is approximately 1 μ m, and the light penetration depth in MAPbBr₃ crystals for the chosen excitation energy is relatively short, ranging from a few tens to hundreds of nanometers.²²⁷ The broadening of the PL spectra upon halide exchange can be traced back to compositional inhomogeneities within the measured spot of a mixed LHP crystal. As demonstrated by XRD measurements (**Figure 5.4**), different regions of the mixed crystal have varying amounts of exchanged-to-native halide ratios. This variation leads to local band gap differences within the crystal as a function of locally alloyed halide content. Excitons that can diffuse towards energetically favorable low band gap regions within their lifetime, can emit lower-energy photons. However, excitons that get trapped in relatively high band gap regions and cannot diffuse to lower-energy band gap regions within their lifetime will emit higher-energy photons. As a result, the PL spectra of alloyed sample exhibit more inhomogeneous broadening compared to pure MAPbBr₃ samples.

To quantify the halide exchange-related changes in the PL spectra, the mean change in the PL peak energy $\langle \Delta h \nu_{\rm PL peak} \rangle$ of the halide-exchanged crystals relative to the PL peak energy of the respective Lys-incorporated MAPbBr₃ was calculated and plotted against the stoichiometric coefficient. As explained in **Section 2.1.5**, changes in the band gap (and, therefore, in the PL spectra) of a solid solution as a function of composition can be described by a second-order polynomial function.^{67,117,121,232} At low halide substitution concentrations, as is the case in this work, the modification of the band gap is well described by a linear function.^{117,118} The mean change in the PL peak energy was fitted to a linear function $\Delta h \nu_{\rm PL peak}(\tilde{z}) = (h \nu_{\rm PL peak}(1) - h \nu_{\rm PL peak}(0))\tilde{z}$, where $h \nu_{\rm PL peak}(0)$ is the PL peak energy of MAPbBr₃ Lys- α and the parameter $h \nu_{\rm PL peak}(1)$ is the PL peak energy of MAPbCl₃ or MAPbI₃. **Figure 5.8a** and **b** show the relative mean change in the PL peak energy of MAPbCl_xBr_{3-x} and MAPbI_yBr_{3-y} samples, respectively, with fitted linear function displayed as grey lines. In both cases, the relative mean energetic position of the PL peak exhibits a linear relationship with x and y. From the obtained fits, given that $h \nu_{\rm PL peak}(0) = 2.30$ eV, the estimated PL peak positions of MAPbCl₃ and MAPbI₃ are 3.46 and 1.80 eV, respectively. These values are slightly higher than the experimentally measured values in the literature.^{236,237} This discrepancy likely stems from several factors: the model does not account for changes in exciton binding energies upon halide substitution,^{58,73,80} and it considers only the PL peak position shift without incorporating changes in the PL FWHM upon alloying. Importantly, the observed linear trend is a direct indication that Lys incorporation hinders post-synthetic halide exchange of both Cl⁻ and l⁻, as the magnitude of the energetic shift of the maximum PL intensity is directly proportional to the exchanged halide content. This finding aligns with the observations made using IC and XRD experimental techniques.



Figure 5.8: Halide-exchange related mean change in PL peak energy. Mean change in the PL peak energy of a) $MAPbCl_xBr_{3-x}$ and b) $MAPbI_yBr_{3-y}$ crystals relative to the PL peak energy of $MAPbBr_3$ at different Lys incorporation levels. Grey lines represent linear fits to the data, as discussed in the main text.

Overall, the findings in this chapter unanimously indicate that incorporated Lys hinders post-synthetic Cl⁻ and I⁻ diffusion into bulk MAPbBr₃ and shows the impact of molecular inclusions and A-site cation engineering on the physical properties of crystalline hosts. The hinderance of post-synthetic halide diffusion following a partial substitution of the initial Asite in a LHP with another material has been observed in the literature. For example, the mixed formamidinium FAPbBr_{1.8}I_{1.2} LHPs with partially substituted MA⁺ cations exhibited hindered photoinduced halide segregation.²⁸ In another example, Γ transport through MAPbI₃ crystals was reduced due to the strong increase in the diffusion activation energy by substituting native MA⁺ with low concentrations of guanidinium molecule.²⁹ Another similar study arrived at the conclusion that partially substituting MA⁺ cations by acetamidinium molecules in MAPbI₃ induced lattice distortions that created a steric effect effectively impeding ion migration pathways and increasing iodide diffusion activation energy.³⁰

The reduction in post-synthetic halide diffusion in Lys-incorporated MAPbBr₃ crystals can be attributed to the "bridging effect" of Lys. It has been suggested that Lys incorporation can occur via two main pathways: 1. the more likely mechanism, in which Lys's two NH_3^+ amino groups substitute two adjacent MA⁺ ions, either creating a Br⁻ vacancy or, more probably, bending around it; 2. The less likely mechanism, in which Lys's two NH_3^+ amino groups substitute two neighboring MA⁺ ions in a unit cell, while the ionized carboxyl COO⁻ group substitutes an X-site halide Br⁻; In both cases, Lys incorporation induces lattice contraction. The bridging effect of Lys can hinder subsequent halide diffusion within LHP crystals after the initial surface exchange by preventing Br⁻ vacancy formation, which is essential for intracrystalline halide diffusion and exchange efficiency. Additionally, Lys can act as a physical barrier to halide migration, increasing the activation energy required for halide diffusion within the LHP.

Although this study focuses on MAPbBr₃, the underlying mechanism by which Lys incorporation reduces post-synthetic halide exchange is likely applicable to other LHP systems as well. This approach may help supress undesired halide diffusion at perovskite interfaces and address the issue of photoinduced halide segregation in LHPs, which reduces the open-circuit voltage in mixed-halide perovskite solar cells.²²²

Chapter 6

Conclusions and Outlook

The goal of this work was to study the interaction between lead LHPs and organic molecules, with a focus on their potential applications as alternatives or improvements to multi-perovskite devices as well as in other optoelectronic and photocatalytic devices. To this end, this study explored two approaches: 1. donor-acceptor CsPbBr₃ QD-molecule hybrid systems, where molecules were attached to QD surfaces to tune the optical properties of the system, and 2. bio-inspired bulk MAPbBr₃-Lys composites, in which Lys molecules were incorporated inside the crystals to modify the structural properties of these hybrid organicinorganic perovskites (HOIPs).

Main findings of this work include:

Efficient energy transfer from CsPbBr₃ QDs to closely-bound ATTO610 dyes proceeds via Dexter exchange mechanism.

Luminescent ATTO610 dyes, which contain dimethyl iminium binding group with high binding affinity to LHPs' ionic surfaces, were attached to weakly confined CsPbBr₃ QDs, forming a hybrid donor-acceptor system. The strong binding affinity of ATTO610 dyes to QD surfaces minimized the donor-acceptor distance, crucial for their efficient interactions. Steady-state and time-resolved PL spectroscopy revealed that, ET from CsPbBr₃ QDs to ATTO610 dyes does not occur via Förster resonance energy transfer (FRET) due to negligible donor emission-acceptor absorption spectral overlap - necessary for efficient FRET. Instead, ET proceeds via the Dexter exchange mechanism, where binding of the dyes to the QD surface facilitates spatial wavefunction overlap between isoenergetic donor-acceptor states an important prerequisite for this mechanism. Excitations in the newly formed donor-acceptor hybrid states can relax to energetically lower acceptor states via rapid vibrational relaxation and internal conversion. The dye's binding group, as part of its conjugated system, likely additionally contributes to the ET efficiency.

At an ATTO610-per-QD ratio of 10, ET results into a 300-fold enhancement of ATTO610 PL, with an ET-related PL quantum yield of up to 11%. Furthermore, the dual emission of the QD-ATTO610 system, combined with transmitted blue excitation light, was leveraged to

create a solution-based white-light emitter, where green and red emissions originate from the QD-dye hybrid system.

Dyes with dimethyl iminium binding group exhibit strong excited-state interactions with CsPbBr₃ QDs.

Various QD-dye systems, featuring dyes with dimethyl iminium binding group, each with distinct chemical formulas and optical properties, were prepared. Steady-state PL spectroscopy showed significant quenching of QD PL at low dye-per-QD ratios, indicating efficient excited-state interactions between them.

Ferrocene-functionalized ligands efficiently dissociate excitons in CsPbBr₃ QDs via hole capture.

Multi-functional ligands for QDs were synthesized at ambient conditions via the Menshutkin reaction, combining three key aspects: high binding affinity, colloidal stability, and a ferrocene functional molecule (hole scavenger) capable of interacting with QDs. High ligand loading ensured long-term colloidal stability, while integrating the functional group into the ligand structure minimized the donor-acceptor distance, enhancing interaction efficiency.

QDs exclusively capped with multi-functional ligands were synthesized. Steady-state PL spectroscopy experiments showed that ferrocene molecules engage in efficient excited-state interactions with QD only when part of the multi-functional ligands, emphasizing the importance of donor-acceptor distance for efficient interaction. Time-resolved PL and transient absorption spectroscopy revealed that ferrocene efficiently dissociates excitons on QDs by capturing holes, with an efficiency of 99.9%. Furthermore, it was found that structural reorganization of ferrocene upon positive charge acquisition alters its molecular orbital structure, creating a strong driving force for electrons on the QDs to localize on the positively charged ferrocene, thereby influencing charge separation efficiency.

Lysine incorporation into MAPbBr₃ crystals hinders post-synthetic Cl⁻ and I⁻ exchange.

MAPbBr₃ crystals with incorporated Lys molecules, which replace two adjacent MA⁺ ions with their two amine groups to form a "molecular bridge" in the LHPs unit cell, were investigated. Ion chromatography revealed that higher Lys incorporation reduces halide exchange in MAPbBr₃ crystals immersed in methylammonium halide (Cl⁻ or I⁻) solutions. X-ray diffraction analysis confirmed this effect for MAPbCl_xBr_{3-x} samples, where increased Lys content led to reduced halide diffusion-induced structural changes, indicating a lower Cl⁻ exchange rate. For MAPbI_yBr_{3-y}, structural changes were dependent on both exchanged I⁻ content and Lys incorporation, making it difficult to identify the impact of Lys on halide diffusion. PL spectroscopy further confirmed these findings, demonstrating that higher Lys incorporation correlates with a reduced PL shift related to Cl⁻ and I⁻ exchange, indicating an overall slower exchange process. Although this study focused on MAPbBr₃, the underlying mechanism is likely applicable to other perovskite systems as well. The work on CsPbBr₃ QDs and dimethyl iminium-based dyes provides a blueprint for designing efficient LHP QD-molecule hybrid systems by providing a fundamental understanding of their interaction mechanisms and the different parameters influencing them. It underscores the importance of selecting molecules with binding groups suited to LHP surfaces to minimize the donor-acceptor distance and enable highly efficient interaction between them. The facile multi-functional ligand engineering approach, combined with a clear understanding of the interaction mechanisms between LHP QDs and organic molecules, provides a foundation for designing LHP QD-molecular hybrids that are both efficient and colloidally stable over the long-term. Future research could focus on optimizing the design of multi-functional ligands through binding group, tail group and functional group engineering, allowing for the development of QD-molecular systems tailored for specific applications, such as white-light emitters, photocatalytic systems, and sensitizers. These systems have the potential to be applied in various optoelectronic and photocatalytic devices.

The work on bio-inspired MAPbBr₃-Lys composite crystals highlights the role of molecular inclusions in suppressing post-synthetic halide exchange. It contributes to existing literature on A-site engineering in LHPs, which has been shown to hinder halide migration inside the HOIPs, while also introducing a novel Lys "molecular bridge" that further mitigates the halide diffusion. Future research could explore the targeted design of such molecular bridges in bulk LHPs, aiming not only to suppress post-synthetic halide diffusion but also to prevent photo-induced halide segregation.
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Appendix

Chemicals

Lead(II) bromide (PbBr₂, 99.999%), cesium carbonate (Cs₂CO₃, 99.9%), trioctylphosphine oxide (TOPO, 99%), hexane (\geq 99%), acetonitrile (\geq 99.9%) heptane (\geq 99%) octane (min. 99%), chloroform (CHCl₃, \geq 99.5%), diisooctylphosphinic acid (DOPA, 90%), toluene (\geq 99.5%), 1-bromododecane (97%), ferrocene (98%), (dimethylaminomethyl)ferrocene (\geq 95%), oleylamine (OLA, technical grade 70%), oleic acid (OA, technical grade 90%), zinc iodide (ZnI₂, 99%), IR895 (97%) were purchased from Merck. Zinc chloride (ZnCl₂, 99.95%) was purchased from Alfa Aesar. ATTO610 carboxy (Atto) was purchased from ATTO-TEC. Pyronin Y (PY) and Crystal Violet (CV) were both purchased from Carl Roth. All chemicals were used without any further purification.

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List of Abbreviations

А	acceptor
APD	avalanche photodiode
BBO	barium borate
CB	conduction band
CCD	charge-coupled device
CT	charge transfer
CV	crystal violet
D	donor
DDAB	didodecyldimethylammonium bromide
DFT	density functional theory
DOPA	diisooctylphosphinic acid
e-h	electron-hole
EDS	energy-dispersive X-ray spectroscopy
ET	energy transfer
FA	formamidinium
FeDDAB	ferrocenylmethyl dodecyldimethylammonium bromide
FRET	Förster resonance energy transfer
FWHM	full width at half maximum
HR-PXRD	high resolution powder X-ray diffraction
HOIP	hybrid organic-inorganic perovskite
IC	ion chromatography
IRF	instrument response function
jDOS	joint density of state
LED	light-emitting diode
LHP	lead halide perovskite
LP	long pass
Lys	lysine
MA	methylammonium
NC	nanocrystal
OD	optical density
OA	oleic acid
OLA	oleylamine

PD	photodiode
PL	photoluminescence
PLE	photoluminescence excitation
PLQY	photoluminescence quantum yield
PY	pyronin y
QD	quantum dot
SE	secondary electron
SEM	scanning electron microscope
SHG	second harmonic generation
TAS	transient absorption spectroscopy
ТА	transient absoprtion
TCSPC	time-correlated single photon counting
TEM	transmission electron microscopy
TOPO	trioctylphosphine oxide
TRPL	time-resolved photoluminescence
VB	valence band
XRD	X-ray diffraction

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