

Electrochemical Doping of Perovskite Nanostructures: How Hole Injection Can Be Tuned

Dissertation

der Mathematisch-Naturwissenschaftlichen Fakultät
der Eberhard Karls Universität Tübingen
zur Erlangung des Grades eines
Doktors der Naturwissenschaften
(Dr. rer. nat.)

vorgelegt von
Theresa Katja Hettiger
aus Würzburg

Tübingen
2026

Gedruckt mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät der
Eberhard Karls Universität Tübingen.

Tag der mündlichen Qualifikation: 03.07.2026

Dekan:

Prof. Dr. Thilo Stehle

1. Berichterstatter/-in:

Prof. Dr. Marcus Scheele

2. Berichterstatter/-in:

apl. Prof. Dr. Heiko Peisert

The work within this dissertation was conducted in the group of Prof. Marcus Scheele at the Institute of Physical and Theoretical Chemistry of the Eberhard Karls University of Tübingen between December 2021 and December 2025.
© Theresa Katja Hettiger, 2026

Abstract

Lead halide perovskite nanocrystals (NCs) are important for future optoelectronic devices since they have a high photoluminescence quantum yield, show defect tolerance, and color tunability by their composition. The optical characteristics can be used in light emitting diodes (LEDs). However, the NCs need to fit simultaneously electronic requirements for their application in LEDs: long term stability under electrical bias, charge carrier balance, and facilitated charge injection are a prerequisite for their implementation. All three factors can be influenced by the organic ligand shell surrounding the NCs. By e.g. tight binding of ligands, the stability of the NCs can be improved. Hole and electron transfer rates can be tuned by ligand exchange and insulating surface ligands can be removed from the surface for easy charge transfer. Post-synthetic NC modification can lead to enhanced LED performance with reduced onset potential of luminance and high external quantum efficiencies for extended time periods. Still, for building efficient devices the underlying processes need to be understood and the energy barrier between the device layers determined. Therefore, charge injection of only one carrier needs to be studied depending on the surface chemistry of the NCs. Spectroelectrochemistry (SEC) is a method that helps understanding the role of surface ligands on charge injection into NCs. The combination of electrochemistry with photoluminescence (PL) spectroscopy makes the determination of the absolute valence (VB) and conduction band (CB) position possible. In addition, the effect of charging on the optoelectronic properties can be followed up.

In this cumulative dissertation, hole injection into CsPbBr₃ NCs is studied by PL SEC. The influences of the chemical environment on hole injection are investigated. Thereby, the focus of this work lies on the modification of the ligand shell and the self-assembly into supercrystals. The fundamentals of the examined NCs and the method used for studying charge injection are introduced in chapter 2.

Chapter 3 uses PL SEC for investigating improved LED performance of didodecyldimethylammonium bromide (DDABr) covered NCs compared to as-synthesized NCs covered with oleic acid (OA)/oleylamine (OAm). Single carrier devices show an increase in hole current for DDABr NCs. In the PL SEC study, the VB of both ligands with different ligand densities is determined. Beforehand, ligand stripping is performed to create free surface sites for facilitated charge injection. Here, PL SEC shows that the VB position shifts to a lower potential for DDABr than OA/OAm NCs, while ligand stripping leads to an increased onset potential of VB doping for both ligand systems. The chapter highlights the improved charge carrier balance, resulting from promoted hole injection in LEDs for DDABr covered NCs caused by a VB shift of approx. 0.3 eV compared to OA/OAm covered NCs.

In chapter 4, inductive effects mediated by cinnamic acid (CA) derivatives on the electrochemical p-doping of CsPbBr₃ NCs are studied. Protocols for the ligand exchange in solution are established in order to determine the hole injection potential for each system by PL SEC. The PL SEC study is supported by the performance

of the CA-derivative covered NCs in LEDs and hole-only devices, which are in accordance with the reduced electrochemical hole injection potential for electron withdrawing compared to electron donating ligands determined by PL SEC. As this observation is in contrast to literature on PbS nanoparticles, the result is attributed to a kinetic effect. The comparison of the inductive effects introduced by the ligands highlight that the charge injection potential in LEDs is not only determined by the electronic structure, but can also be modified by a kinetic barrier introduced by the surface ligands.

In the final chapter of this thesis, electrochemical hole injection into supercrystals (SCs) is investigated. Here, the NCs are pretreated by ligand stripping and self-assembled into SCs. The spectroelectrochemical cell is placed on top of a confocal high-resolution microscope, which allows for spatial mapping of the SCs. The SCs show a high stability against the electrolyte solution and hole injection. The performance under electrical bias emphasizes the future application of SCs in LEDs.

In summary, the thesis shows that the hole injection potential can be tuned by 0.3 eV depending on the chemical environment of the CsPbBr₃ NCs. Either by introducing DDABr as surface ligand or with electron withdrawing ligands, the hole injection potential can be tuned for a better alignment of the VB of the NCs with the hole transport layer in the LED. In addition, the assembly of NCs shows an increased stability after charge injection. The insights gained in this thesis demonstrate how charge carrier balance, and the long term stability under electrical bias as the electronic requirements of CsPbBr₃ NCs can be tackled in future LED technology.

Deutsche Zusammenfassung

Bleihalogenid Perowskit Nanokristalle spielen eine wichtige Rolle für zukünftige optoelektronische Anwendungen, da sie eine hohe Photolumineszenzquantenausbeute, Defekttoleranz und spektrale Einstellbarkeit durch Änderung ihrer Zusammensetzung aufweisen. Diese optischen Eigenschaften können für Leuchtdioden (LEDs) genutzt werden. Allerdings müssen die Nanokristalle dafür gleichzeitig mehrere elektronische Eigenschaften erfüllen. Diese bestehen aus der Langzeitstabilität unter hohen angelegten Spannungen, gleichmäßig injizierten Ladungen und einfachem Ladungstransfer. Alle drei Faktoren können durch die organische Ligandenhülle, die die Nanokristalle umgibt, beeinflusst werden. Beispielsweise kann durch die feste Bindung eines Liganden die Stabilität erhöht werden. Zusätzlich kann die Elektron- oder Lochtransferrate durch Ligandenaustausch modifiziert werden, und durch das Entfernen von Oberflächenliganden kann die Ladungsinjektion vereinfacht werden. Diese post-synthetischen Modifikationen können zu einer verbesserten LED Leistung beitragen, indem die notwendige Spannung für die Luminanz reduziert und die externe Quantenausbeute für einen längeren Zeitraum erhöht wird. Dafür müssen die zugrundeliegenden Prozesse verstanden werden und die Energiebarriere zwischen den einzelnen Schichten bestimmt werden. Daher wird die Untersuchung der Ladungsinjektion von einzelnen Ladungen, abhängig von der Oberflächenchemie an Nanokristallen, notwendig. Spektroelektrochemie ist eine Methode, die zur Aufklärung der Rolle der Oberflächenchemie bei der Ladungsinjektion in Nanokristalle, beitragen kann. Die Kombination aus Elektrochemie mit Photolumineszenz-Spektroskopie macht die Bestimmung der absoluten Valenz- und Leitungsbandkantenenergien möglich. Zusätzlich kann der Effekt der Ladung auf die optoelektronischen Eigenschaften nachverfolgt werden.

In dieser kumulativen Dissertation wird der Einfluss der chemischen Umgebung auf die Lochinjektion in CsPbBr_3 Nanokristalle mittels Photolumineszenz-Spektroelektrochemie (PL SEC) untersucht. Dabei liegt der Fokus dieser Arbeit auf der Modifikation der Ligandenhülle und der geordneten Kristallisation von Nanokristallen in Superkristalle. Die Grundlagen zu Nanokristallen, im speziellen Bleihalogenid Perowskit Nanokristalle, sowie zur verwendeten Methode für die Untersuchung von Ladungsinjektionsprozessen werden in Kapitel 2 eingeführt.

In Kapitel 3 wird PL SEC verwendet, um die verbesserte LED Leistung von Nanokristallen mit Didodecyldimethylammonium Bromid (DDABr) als Oberflächenligand im Vergleich zu dem System nach der Synthese (Ölsäure/Oleylamin, OA/OAm) zu untersuchen. Unipolare Lochleitungsbauelemente zeigen einen höheren Lochstrom für DDABr Nanokristalle. In der PL SEC Studie werden die Valenzbandpositionen beider Liganden mit zwei unterschiedlichen Ligandendichten an der Oberfläche bestimmt. Dafür werden zuvor Liganden von der Oberfläche entfernt, um freie Oberflächenstellen zu erzeugen, die für eine vereinfachte Ladungsinjektion sorgen. In dieser Arbeit wird gezeigt, dass die Valenzbandposition für DDABr bei niedrigeren Potenzialen als für OA/OAm Nanokristalle liegt, während eine

reduzierte Ligandendichte zu einem erhöhten Potenzial führt. Das Kapitel stellt heraus, dass das verbesserte Gleichgewicht zwischen Löchern und Elektronen in DDABr Nanokristall LEDs durch die verbesserte Lochinjektion aufgrund einer um +0.3 eV Valenzbandverschiebung im Vergleich zu OA/OAm zustande kommt.

Im vierten Kapitel wird der Einfluss von induktiven Effekten transferiert durch Zimtsäurederivate auf die elektrochemische Lochinjektion untersucht. Anleitungen für den Ligandenaustausch in Lösung werden etabliert, damit das Potenzial für die Lochinjektion mittels PL SEC bestimmt werden kann. Die PL SEC Untersuchungen werden von der Leistung der ausgetauschten Nanokristalle in LEDs und unipolare Lochleitungsbauelementen unterstützt, welche im Einklang mit den Ergebnissen aus der PL SEC Studie sind. Für die elektrochemische Lochinjektion in Nanokristalle mit elektronenziehenden Liganden wird ein niedrigeres Potenzial benötigt als für elektronenschiebende Liganden. Da diese Beobachtung im Gegensatz zur Literatur an PbS Nanopartikeln ist, wird das Ergebnis einem kinetischen Effekt zugeschrieben. Der Vergleich der induktiven Effekte zeigt, dass die Ladungsinjektion in LEDs nicht nur durch die elektronische Struktur gegeben ist, sondern auch durch einen kinetischen Effekt, der durch Oberflächenliganden beeinflusst wird, modifiziert werden kann.

Im letzten Kapitel der Dissertation wird die elektrochemische Lochinjektion in Superkristallen untersucht. Dafür werden Liganden von der Oberfläche entfernt und durch Selbstorganisation die Nanokristalle in Superkristalle angeordnet. Die PL SEC Zelle wird auf einem konfokalen hochauflösenden optischen Mikroskop platziert, welches orts aufgelöste Spektroskopie ermöglicht. Die Superkristalle zeigen eine hohe Stabilität gegenüber der Elektrolytlösung und der Lochinjektion. Die Leistung unter dem angelegten Potenzial hebt die mögliche Anwendung von Superkristallen in LEDs hervor.

Zusammenfassend zeigt diese Arbeit, dass das Lochinjektionspotenzial um 0.3 eV durch die chemische Umgebung von CsPbBr₃ Nanokristallen variiert werden kann. Entweder durch DDABr als Oberflächenstabilisator oder durch elektronenziehende Liganden kann das Lochinjektionspotenzial reduziert werden, um eine bessere Abstimmung der Energieniveaus des Valenzbands zur Lochtransportschicht in der LED zu erreichen. Zusätzlich zeigt die Selbstorganisation einzelner Nanokristalle eine erhöhte Stabilität nach der Ladungsinjektion. Die in dieser Arbeit erreichten Ergebnissen verdeutlichen, wie zukünftig das Ladungsgleichgewicht und die Langzeitstabilität unter angelegten Spannungen als elektronische Voraussetzungen für CsPbBr₃ Nanokristalle in LEDs angegangen werden können.

Abbreviations

1S _e	first non-occupied electronic state close to CB
1S _h	first occupied electronic state close to VB
AO	atomic orbital
APD	avalanche photodiode
B3PYMPM	(4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine)
BS	beamsplitter
BSE	backscattered electrons
CAs	cinnamic acid derivatives
CAH	cinnamic acid
CACF ₃	4-(trifluoromethyl)cinnamic acid
CAOMe	4-methoxycinnamic acid
CAN(Me) ₂	4-(dimethylamino)cinnamic acid
CB	conduction band
CCD	charged coupled device
CE	counter electrode
CV	cyclic voltammetry/cyclic voltammogram
DDABr	didodecyldimethylammonium bromide
DFT	density functional theory
DOS	density of states
DOSY	Diffusion-ordered NMR spectroscopy
EL	electroluminescence
EQE	external quantum efficiency
ES	electrolyte solution
<i>et al.</i>	<i>et alii</i> (and others)
ETL	electron transport layer
EtOAc	ethyl acetate
Fc	ferrocene
Fc ⁺	ferrocenium
FTO	fluorine-doped tin oxide
fwhm	full width at half maximum
GSP	giant surface potential
HOMO	highest occupied molecular orbital
HTL	hole transport layer
ITO	indium tin oxide
LED	light emitting diode
LHP	lead halide perovskite
LiClO ₄	lithium perchlorate
LPF	longpass filter
LUMO	lowest unoccupied molecular orbital
MeOAc	methyl acetate
MO	molecular orbital
NA	numerical aperture
NC	nanocrystal
NHE	natural hydrogen electrode

NMR	nuclear magnetic resonance
NOESY	Nuclear Overhauser effect spectroscopy
OA	oleic acid (oleate)
OAm	oleyamine (oleylammonium)
OD	optical density filter
ODE	octadecene
OLED	organic light emitting diode
PBE	Perdew-Burke-Ernzerhof
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
PDOS	partial density of states
PES	photoelectron spectroscopy
PeLEDs	perovskite-based light emitting diodes
PL	photoluminescence
PLQY	photoluminescence quantum yield
PNC	perovskite nanocrystal
PRE	pseudo-reference electrode
PTAA	poly-[bis-(4-phenyl)-(2,4,6-trimethylphenyl)-amin]
QDs	quantum dots
QLEDs	quantum-dot light emitting diodes
qNMR	quantitative NMR spectroscopy
RE	reference electrode
ref.	reference
SC	supercrystal
SCLC	space charge-limited conduction
SCV	staircase voltammetry
SE	secondary electrons
SEC	spectroelectrochemistry
SEM	scanning electron microscopy
SI	supporting information
SOP	spontaneous orientation polarization
TBA ⁺	tetrabutylammonium
TBAHFP	tetrabutylammonium hexafluorophosphate
TBA _m Br	tetrabutylammonium bromide
TEM	transmission electron microscopy
TOA _m Br	tetraoctylammonium bromide
TEM	transmission electron microscopy
TPBi	2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TRPL	time-resolved photoluminescence
UHV	ultrahigh vacuum
UPS	ultraviolet photoelectron spectroscopy
VB	valence band
VESTA	visualization for electronic and structural analysis
vs.	versus
WE	working electrode
XPS	X-ray photoelectron spectroscopy

Contents

1	Introduction	1
1.1	Motivation	1
1.2	Objective of this Work	3
1.3	Outline of this Work	3
2	Fundamentals	7
2.1	Semiconducting Nanocrystals	7
2.1.1	Optoelectronic Properties on the Nanoscale	7
2.1.2	Synthesis of Monodisperse Nanocrystals	10
2.1.3	Surface Chemistry of Nanocrystals	12
2.2	Perovskite Nanocrystals	16
2.2.1	Structure of Perovskite Nanocrystals	16
2.2.2	Optoelectronic Properties	18
2.2.3	Classical Synthesis of CsPbBr ₃ NCs	19
2.2.4	Confinement in Lead Halide Perovskites	20
2.2.5	Surface Chemistry of CsPbBr ₃ NCs	21
2.2.6	Post-synthetic Modifications of Perovskite NCs	24
2.2.6.1	Ligand Exchange on Perovskite NCs	25
2.2.6.2	Self-assembly into Supercrystals	27
2.2.7	LEDs from Perovskite NCs	28
2.2.7.1	LED Operation and Fabrication	28
2.2.7.2	Efficiency of an LED	29
2.3	Spectroelectrochemistry - Probing Electrochemical Doping	32
2.3.1	Electrochemical Charging by Cyclic Voltammetry	32
2.3.2	Resolving the Electronic Structure of Nanocrystals	34
2.3.2.1	SEC on Nanocrystals	36
2.3.2.2	High-resolution Spectroelectrochemical Setup	38
2.3.3	SEC on Perovskite NCs: State of the art	39
3	Studying Binding Group and Ligand Stripping on Hole Injection into NCs	43
3.1	Abstract	44
3.2	Introduction	44
3.3	Results and Discussion	47
3.3.1	Ligand Exchange and Film Morphology	47
3.3.2	Electronic Properties	49
3.3.2.1	Spectro-Electrochemistry	49
3.3.2.2	Photoelectron Spectroscopy	51
3.3.2.3	Single-carrier Devices	52
3.3.3	DFT Calculations	53

3.3.4	PeLEDs	56
3.4	Conclusion	60
3.5	Experimental Section	60
3.6	Supporting Information	66
4	Impact of Inductive Effects Mediated by the Ligand Shell on Hole Injection into NCs	77
4.1	Abstract	78
4.2	Introduction	78
4.3	Results	80
4.4	Discussion	85
4.5	Conclusion	87
4.6	Supporting Information	88
5	Spatial Mapping of Electrochemical Hole-Injection into Perovskite SCs	111
5.1	Abstract	112
5.2	Introduction	112
5.3	Results and Discussion	113
5.4	Conclusion	121
5.5	Supporting Information	122
6	Summary and Outlook	139
7	Appendix	143
	List of Tables	145
	List of Figures	147
A	List of Scholarly Contributions	151
B	Declaration of Contribution	155
C	Acknowledgements	157
	Bibliography	159

1 Introduction

In 2023, the Nobel Prize in chemistry was awarded to Moungi Bawendi, Louis E. Brus and Aleksey Ekimov for their contributions to nanocrystal (NC) synthesis,¹ and their studies of the optoelectronic properties of nanomaterials.²⁻⁴ The high photoluminescence quantum yield (PLQY), solution processability, and band gap tunability by the size of NCs led to a new field of research.⁵⁻⁷ This Nobel Prize shed a light on the potential of semiconducting nanomaterials (1-100 nm) in future devices such as applications for technology (telecommunication, semiconductors),⁸⁻¹¹ medicine (nanobots, staining),¹²⁻¹⁶ and energy conversion (solar cells, light emitting diodes (LEDs)).¹⁷⁻²¹ Nowadays, NCs are already incorporated into commercially available televisions, as so-called QLEDs.²²

1.1 Motivation

QLED TVs are using CdSe quantum dots (QDs) as color converters.²² The blue backlight created by an LED is converted by the CdSe QDs to the wanted emission with a narrow line width. However, the full advantages of the NCs with the high PLQY, thin device structure, and solution processability can only be used when the NCs are utilized as light source.^{10,23} Therefore, NCs need to be electroluminescent for the implementation as light source. Due to an applied potential, holes are injected from the hole-transport layer (HTL) and electrons from the electron-transport layer (ETL) into the NC layer. The charges recombine radiatively, as depicted in the typical device structure in Figure 1.1a.

However, commercial availability of electroluminescent NCs has not been reached yet since NCs need to fulfill electronic and optical requirements for their implementation. The optical requirements can be achieved easily by the advantages of NCs being the wide color gamut and purity.²⁴⁻²⁶ For electronic properties, easy charge injection, charge carrier balance, and long-term stability under high applied potentials are needed.

One outstanding material in its optical properties are lead halide perovskite (LHP) NCs.²⁷ These NCs show PLQYs up to 100% and narrow emission line widths (15-20 nm), as observed in the electroluminescence spectrum in Figure 1.1b.^{28,29} Additionally, their easy fabrication and color tunability by halide exchange gives them the potential for large scale applications.^{30,31} Nevertheless, the bottleneck in their application is their electronic properties.³² After synthesis, these are usually determined by the organic ligands surrounding the inorganic NC.^{33,34} Figure 1.1c shows a scheme of a green luminescent perovskite NC, which is typically covered by large aliphatic ligands, namely oleate (OA) and oleylammonium (OAm). These ligands tend to be insulating and show dynamic ligand binding.^{35,36} Hence, researchers came up with strategies to exchange this ligand shell by other molecules.³⁷ The goal of increasing the stability with stronger binding of the ligands to the NC surface has been addressed, as well as facilitating charge injection with either small or electronically active molecules attached to the NC surface was investigated.³⁸⁻⁴²

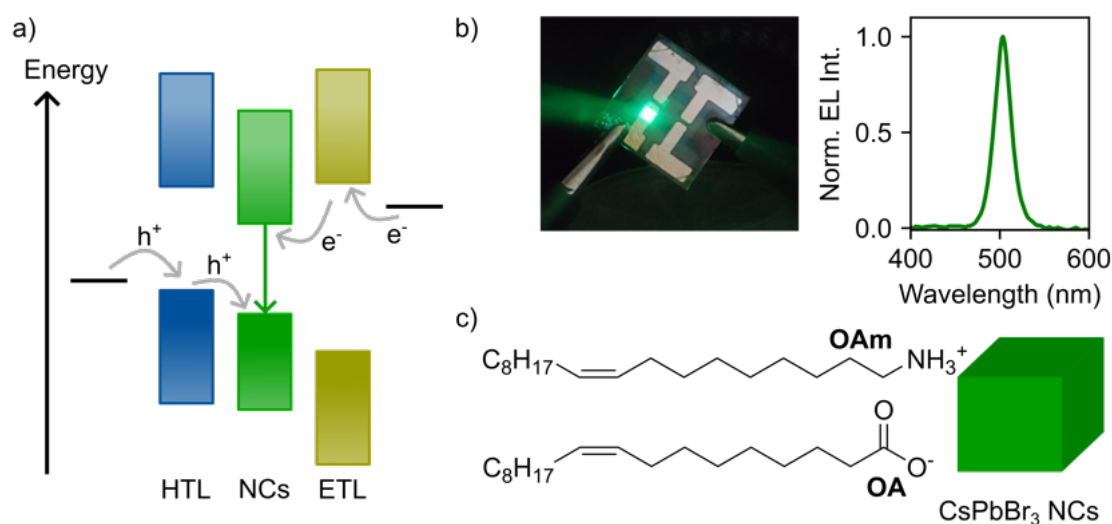


Figure 1.1: Introduction of CsPbBr₃ NCs in LEDs. a) Scheme of LED structure with hole and electron injection and resulting radiative recombination in the emissive layer (NCs) (own representation based on ref. [23]). b) Photograph of electroluminescent LED and corresponding electroluminescence spectrum. c) Scheme of CsPbBr₃ NC with oleylammonium (OAm) and oleate (OA) as surface ligands. Photograph in panel b) taken by Roshini Jayabalan.

Since the ligand shell affects charge injection into NCs, studying charge injection becomes necessary. This can be performed in LEDs, or in single carrier devices. Still, all layers, ETL and HTL, contribute to charge injection in the devices. Therefore, spectroelectrochemistry (SEC), a method which is combining photoluminescence (PL) spectroscopy and electrochemistry, can give information on either hole or

electron charging of NCs directly.^{43,44} The advantage of using SEC is the direct charge injection into the NC that can be determined by a simultaneous increase in current and a bleach in PL intensity.

This work is combining the surface modification of LHP NCs with their SEC investigation. During surface modification, altered binding groups are introduced and the electronic properties of the NCs are influenced. Therefore, the SEC studies show the dependence of the hole injection potential on the surface modifications.

1.2 Objective of this Work

The ligand shell is the key factor that must be addressed in order to bring LHP NCs into commercialization. The ligand shell can influence the stability, optical and electronic properties. It still lacks understanding how the electronic properties of LHP NCs can be influenced by organic ligands. Therefore, the objective of this thesis is investigating how hole injection can be tuned by the number of ligands, their binding group, and their electronic inductive effect. In the last part, hole injection into collectives of NCs, self-assembled supercrystals (SCs), which can be a step towards micro-LEDs, is investigated.

In short, this thesis tries to answer the question: „Which factors are influencing electrochemical hole injection into CsPbBr₃ NCs?“

1.3 Outline of this Work

The structure of this cumulative PhD thesis is graphically depicted in Figure 1.2 and described as follows:

Chapter 2 summarizes the fundamentals of NCs. Thereby, going into detail about the synthesis and optoelectronic properties arising from quantum-confinement. In the next part of chapter 2, LHP NCs and their outstanding optoelectronic properties are introduced, followed by the description of potential modifications. Furthermore, SEC as the main method for studying hole injection will be introduced.

Chapter 3 is showing how the binding group of ligands can influence hole injection into ligand exchanged and stripped perovskite LEDs. This chapter is based on the publication “Optimizing Carrier Balance in CsPbBr₃ Nanocrystal LEDs: The

Role of Alkyl Ligands and Polar Electron Transport Layers” published in *Advanced Optical Materials*.⁴⁵

Chapter 4 is demonstrating how electron withdrawing and electron donating ligands can impact electrochemical hole injection into CsPbBr₃ NCs during SEC and in LEDs. This chapter is based on the publication “Impact of Ligand-Mediated Inductive Effects on Electrochemical p-Doping of CsPbBr₃ Nanocrystals” published in *ACS Energy Letters*.⁴⁶

In chapter 5, SEC is performed on self-assembled CsPbBr₃ SCs for the first time. This chapter is based on the preprint “Spatial Mapping of Electrochemical Hole-Injection into Supercrystals of Perovskite Nanocrystals” published in *Nano Letters*.⁴⁷

Chapter 6 summarizes the thesis and gives an outlook to possible future modifications tackling the electronic requirements for large scale application of NCs in LEDs.

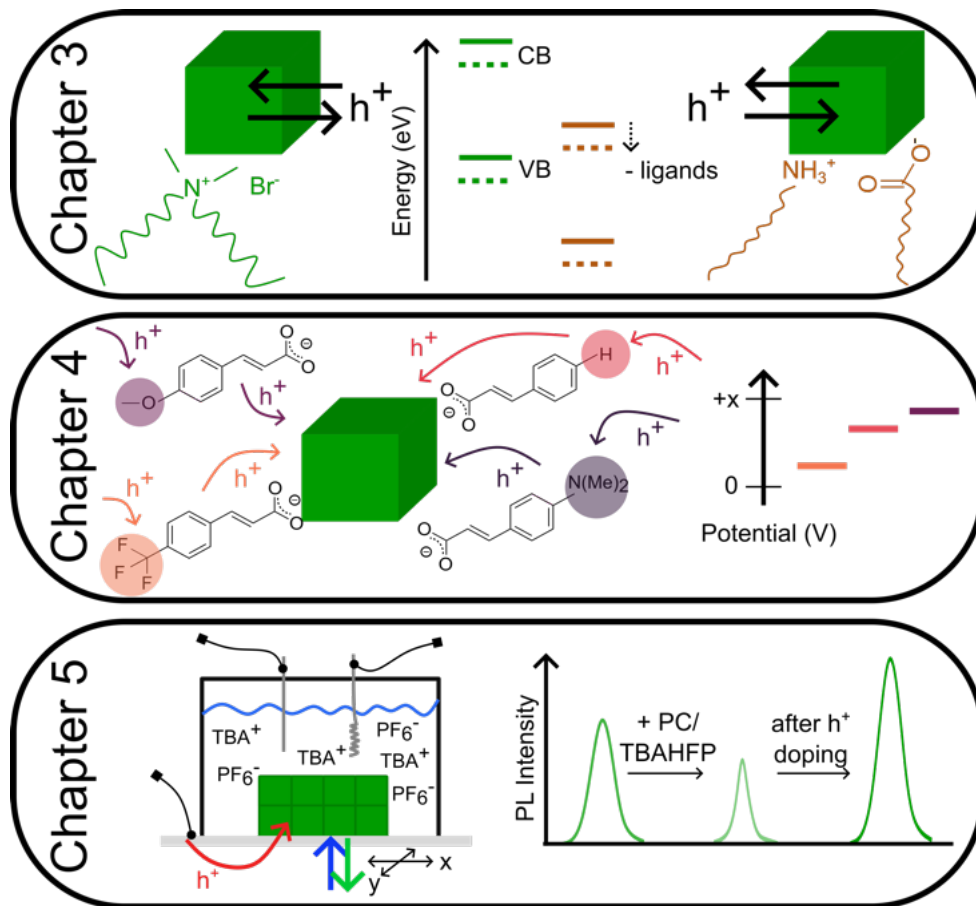


Figure 1.2: Graphical structure of this cumulative thesis. **Chapter 3:** Studying hole injection on ligand stripped DDABr and OA/OAm covered NCs. **Chapter 4:** Studying the influence of electronically-mediated inductive effects to NCs on hole injection. **Chapter 5:** Spatially-resolved optical spectroscopy, while electrochemical hole injection into self-assembled SCs.

2 Fundamentals

This chapter is introducing nanocrystals (NCs) as a new material class, then focusing on the outstanding properties of one specific kind of NCs, the LHP NCs. In the final part, SEC as a method for studying charge injection into NCs is described.

The whole chapter is highlighting the optoelectronic properties of nanomaterials, which make them interesting for the application as emissive layer in LEDs. The factors contributing to effective charge injection and possible modifications of NCs will be outlined in the following.

2.1 Semiconducting Nanocrystals

The interest in nanomaterials for the use in optoelectronic devices concerns semiconductors with a band gap in the visible range (1.8-3.1 eV, 390-700 nm).⁴⁸ In bulk semiconductors, the band gap depends on its composition. However, for nanomaterials, the band gap can also be altered by the size of the same materials' composition. This section describes how the size influences the band gap, outlines the synthesis of semiconducting quantum dots, and introduces the surface chemistry of NCs.

2.1.1 Optoelectronic Properties on the Nanoscale

Bulk semiconductors are defined by the band gap E_g , which describes the absence of electronic states between the energetically highest occupied (valence band (VB)) and the energetically lowest unoccupied band (conduction band (CB)). However, for semiconductors these two bands are still in close proximity (E_g : 25 meV (k_bT at room temperature) up to 3 eV), so that electrons can be raised in energy to the CB.⁴⁹ When an electron absorbs energy (e.g. light), it can be excited from the VB to the CB. This process leaves an absent electron in the VB, which is the positive charged counterpart, defined as hole h^+ .⁵⁰ Both charge carrier e^- and h^+ , the electron-hole pair, are called exciton.⁵¹ This exciton can recombine radiatively, going back to its energetic ground state.

The probability of electronic energies in the VB or CB is described by the density of states (DOS). In bulk semiconductors, many states are allowed and electrons can move freely within the VB. When the size of the semiconductor is decreased to a number of 100-10.000 atoms to the nanometer regime (1-100 nm), the electronic properties change depending on the size of the material.⁵² The energy levels near the band gap become discrete.⁵³ Hence, the energy levels are defined close to the VB/CB edge. When the size is further decreased, the band structure model is not suitable anymore for describing the electronic structure. Instead for molecules, the molecular orbital (MO) theory is used with discrete energy levels as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

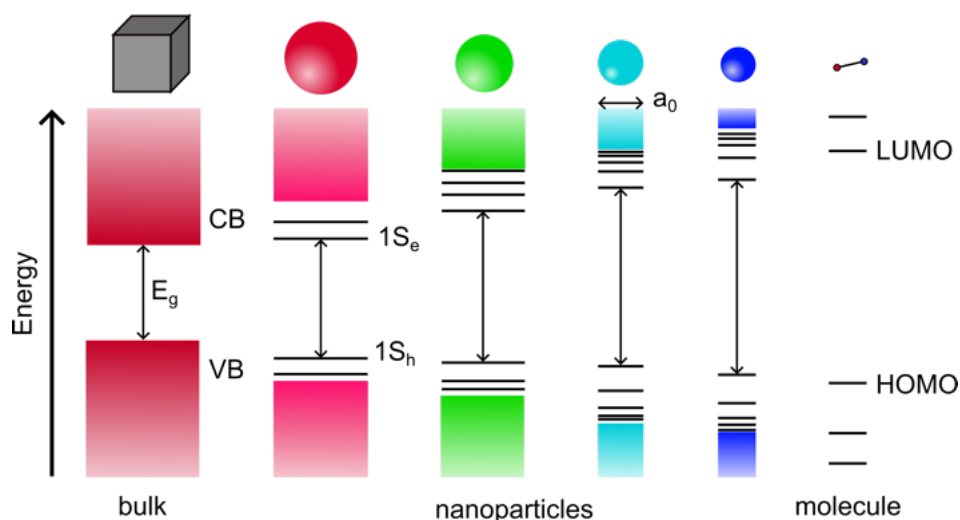


Figure 2.1: Scheme of electronic structures and energy levels of bulk semiconductors, different sizes of NCs, and a molecule with its HOMO and LUMO (own representation based on ref. [54]).

Nanomaterials can be described by both methods. As depicted in Figure 2.1, nanomaterials show close to the band edges discrete energy levels and going further to lower energies, the electrons can again have continuous energies and move freely in the VB. As the size decreases further, the number of defined states rises. The first defined states are called $1S_{h/e}$, the second ones $1P_{h/e}$, followed by $1D_{h/e}$.⁵⁵

Additionally, the size dependent increase in the band gap is illustrated. This is the so-called size quantization effect.⁵⁶ The size quantization effect can be described by the particle-in-a-box model.^{57,58} As the size of the box decreases, the distance of the energy levels rises and therefore, the band gap increases. The consequences of the discretization and size dependence are summarized in the Brus

equation in Equation 2.1.⁵⁸ The band gap of the quantum dot $E_{g,QD}$ is composed of the bulk band gap of the material $E_{g,bulk}$ and the size quantization effect depending on the NC radius r .² The third term describes the Coulomb interaction of the electron-hole pair and represents their attraction, which reduces the band gap depending on r .

$$E_{g,QD} = E_{g,bulk} + \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon r} + \text{smaller terms} \quad (2.1)$$

$\hbar$ is the reduced Planck constant, m_e^*/m_h^* the effective mass of electron/hole, e the elemental charge, ϵ the permittivity of the material, and smaller terms describes the polarization energy of the second charge.⁵⁹

As r increases, the band gap approaches $E_{g,bulk}$ and as r decreases, the second term becomes more pronounced, which is resulting in a larger band gap.

The exciton Bohr radius a_B serves as a criterion for the importance of size quantization.⁶⁰ It is a material specific value, describing the size of the exciton.

$$a_B = \frac{\hbar^2 \epsilon}{e^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad (2.2)$$

For CdSe, CsPbBr₃, and PbS, the exciton Bohr radius is 6, 7, and 20 nm, respectively.^{29,61,62}

Depending on how many dimensions are confined, the DOS is getting increasingly discrete. Nanomaterials are differentiated by the degree of discretization. Figure 2.2a shows the description of the materials depending on how many dimensions are confined.

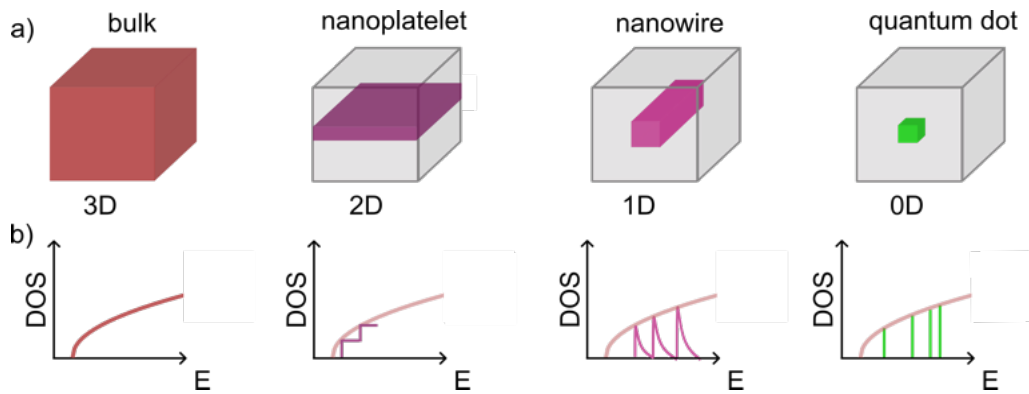


Figure 2.2: Definition of nanomaterials depending on the dimensions being below the exciton Bohr radius. a) Schematic depiction, and b) corresponding DOS and possible energy values (own representation based on ref. [63]).

If a material is confined in one dimension, the material is called 2D (e.g. nanoplatelets). When two dimensions are confined, then it is a 1D material (e.g. nanowires, nanorods), and finally material confined in all three dimensions are 0D materials, also referred to as quantum dots.^{63–65} In Figure 2.2b, the proportionality of DOS to the energy is shown. The mathematical descriptions of the plots are summarized in Table 2.1. The proportionality shows at first a continuous set of possible energies of electrons. When the dimensions are reduced, the energies get more discrete. Until for 0D material, the DOS is described with a δ -function of one specific value.⁴⁹

Table 2.1: Proportionality of DOS to energy levels of different nanomaterials.

dimensionality of nanomaterial	3D	2D	1D	0D
DOS	$\propto \sqrt{E}$	$\propto E$	$\propto 1/\sqrt{E}$	$\propto \delta(E)$

2.1.2 Synthesis of Monodisperse Nanocrystals

Since the band gap and the emitted light by the NCs depend on size, ideally a synthesis should yield a uniform size distribution of NCs. In general, for NC synthesis, two approaches exist: going from the bulk to the small (top-down, exfoliation^{66,67} and ball-milling^{68,69}) or building up NCs from its monomers (bottom-up, hot-injection synthesis^{70–72}). Since monodisperse NCs are desired, the goal of building up NCs by adjusting as many synthesis parameters as possible is one approach. Bawendi and co-workers performed the first monodisperse (< 5%) synthesis of inorganic CdSe NCs, which was awarded by the Nobel committee.¹ In the following, the theoretical approach to NC formation and the consequences for hot-injection synthesis are described.

In the 1950s, LaMer and Dinegar published a theoretical description of the formation of nuclei depending on the monomer concentration.⁷³ Their work is considered as the kinetic approach to the formation of NCs.⁷⁴ The LaMer model distinguishes three regimes depending on the monomer concentration and resulting saturation of the solution S :

- regime I: induction, which considers monomer formation from the precursors until the critical saturation S_{crit} is reached
- regime II: nucleation, when the concentration of the monomer reaches the supersaturation level S_{sup} , the nuclei are rapidly formed and are thermodynamically stable

- regime III: growth, where the formed nuclei in regime II take up more monomer until the monomer concentration is below $S_{\min}$

The three regimes with the monomer concentration dependent nuclei formation are summarized in the LaMer model in Figure 2.3a.

NC formation has different consequences resulting from the LaMer model. First, all of the three regimes need to be separated.^{75,76} Second, the nucleation of particles should be on a small time scale, since the already formed NCs are entering regime III and growing.⁷⁷ This would result in a broad size distribution.⁵⁴ The three regimes can be separated by the application of hot-injection syntheses.⁷⁷ The precursors are heated-up separately to a specific temperature until all monomers are formed. The second monomer solution is added quickly to the precursors, which is initiating burst nucleation and particle formation. After particles are formed, the solution is quenched rapidly by a temperature drop to stop further particle formation and growth.⁷⁸

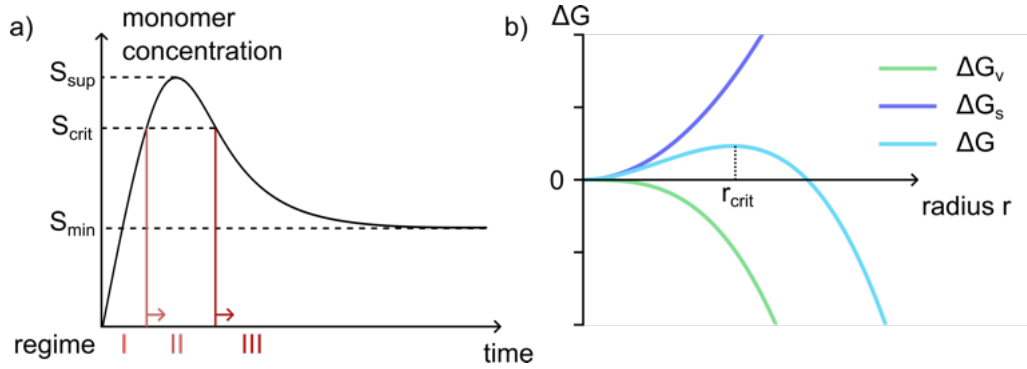


Figure 2.3: Theoretical approach to NC nucleation. a) LaMer model describing monomer concentration and nuclei formation divided into three regimes (own representation based on ref. [73]). b) Gibbs free energy of the formation of nuclei with determination of critical radius (own representation based on ref. [77]).

The formation of NCs or particles can be described by the classical nucleation theory.^{79,80} This theory describes particle formation as a thermodynamic process that follows minimizing the Gibbs free energy.⁸¹ During particle formation, the Gibbs free energy of the particle consists of the Gibbs free surface energy ΔG_s and the Gibbs free bulk energy ΔG_v as shown in Equation 2.3.

$$\Delta G = \Delta G_v + \Delta G_s = -\frac{4\pi}{3}r^3\rho\Delta\mu + 4\pi r^2\gamma \quad (2.3)$$

Here, ρ is the density of the particle, μ is the chemical potential, and γ is the surface tension.

The Gibbs free surface energy describes particle formation and increases the Gibbs free energy by the radius r^2 of the formed particle, while the Gibbs free bulk energy depends on the volume of the particle with a proportionality to r^3 . These two terms counteract. Particle formation and growth only happens when ΔG_v is larger than ΔG_s . Figure 2.3b shows the contributions to the Gibbs free energy of particle formation. The value determining the formation of new nuclei is the critical radius r_{crit} .⁸² When r is below r_{crit} , particles dissolve. When r is above r_{crit} , particles are formed and they grow.

However, r_{crit} can shift to larger sizes or smaller ones depending on different factors as stated in Equation 2.4.⁸²

$$r_{\text{crit}} = \frac{2\gamma}{\rho k_b T \ln S} \quad (2.4)$$

Here, k_b is the Boltzmann constant, T the temperature, and S the entropy.

As r_{crit} depends on the entropy of the system, r_{crit} is low when the nucleation of particles starts (in regime II) and rises as soon as more monomer is used during particle growth.

This has consequences for the monodispersity of NCs. After burst nucleation, r_{crit} is small and the reactivity of small particles is high, which leads to a fast growth of small particles compared to larger particles. This behavior is named size focusing.⁸³ As more monomers are used up, the entropy sinks and therefore, r_{crit} rises (see Equation 2.4). This leads to the dissolution of particles smaller than r_{crit} and monomers can be taken up by larger particles - growing further.⁸⁴ This process is called Ostwald ripening and results in a broad size distribution.⁸⁴

Therefore, yielding monodisperse NCs can be achieved by fast nucleation of particles followed by size focusing. At the same time, Ostwald ripening should be avoided by stopping the synthesis quickly to a temperature where monomers are not reactive anymore.^{78,85}

2.1.3 Surface Chemistry of Nanocrystals

NCs consist of an inorganic core, for example CdSe, PbS or InP. However, to gain colloidal stability, these NCs are covered by organic ligands. Since NCs have a high surface-to-volume ratio, the surface of the NCs plays an important role, when it comes to stability and optoelectronic properties.⁸⁶ Therefore, full surface passivation of NCs is necessary as it can improve the PLQY. In addition, the electric conductivity can be influenced by ligand alteration.

In the following, the concept of surface passivation will be explained using CdSe NCs as an example.⁸⁷ CdSe NCs have Cd and Se atoms on their surface. When Cd^{2+} is removed from the surface, Se^{2-} exhibits an occupied atomic orbital (AO) on the surface.⁸⁸ These dangling bonds can create electronic states in the band gap, as depicted in Figure 2.4a, which are called trap states.⁸⁹ Trap states lead to non-radiative decays, reduced PLQY, and can lead to red-shifted emission.^{90,91} Therefore, passivation of the NC by organic molecules gets necessary as the electronic states can be removed from the band gap.^{87,88}

Figure 2.4b shows an inorganic CdSe core with ligands being organic molecules with a polar headgroup and a nonpolar tail group.⁵³ Both have functionalities for the NC: the nonpolar tail ensures the colloidal stability and enhances the solubility in organic solvents, while the polar binding group passivates the undercoordinated surface atoms.⁵³

Typically, ligands have a long aliphatic carbon chain ($\text{C}_8\text{-C}_{18}$) to achieve stability in solvents such as hexane, toluene or dichlorobenzene. Additionally, the ligands reduce the reactivity of the NC surface.⁸⁷

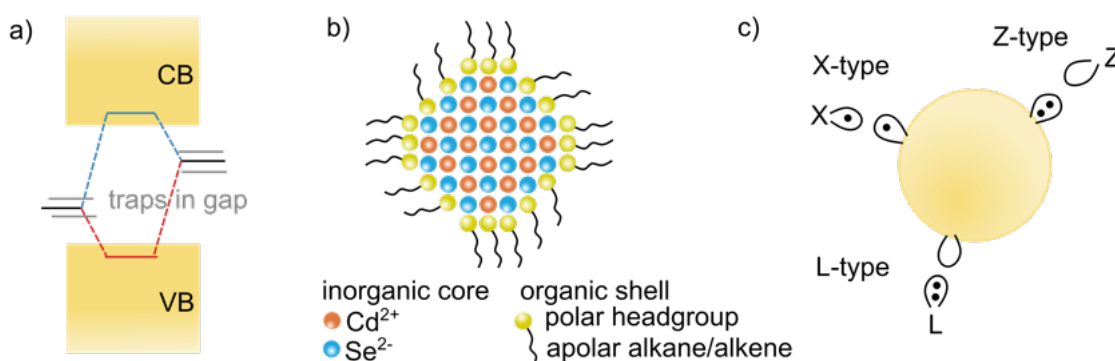


Figure 2.4: Surface chemistry of NCs. a) In-band gap trap formation of CdSe NCs (own representation based on ref. [92]), b) sketch of CdSe NC with surface ligands, and c) L, X, Z-type ligand binding motifs to NC surface (own representation based on ref. [88]).

The polar binding group passivates electronic traps introduced by dangling bonds. Depending on the electronic state, i.e. when they are filled with electrons, the passivating ligands are chosen. Here, M. L. H. Greens covalent bond classification can be applied to NCs.^{93,94} Figure 2.4c gives a description of the bond formation and the shared AO. If the AO of the dangling bond has two free electrons, a ligand with an unoccupied AO is needed for passivation (Z-type). When the atom is filled with one electron, then one electron in the ligand is needed (X-type) and the L-type is the Z-type *vice versa*. Typical examples for Z-type ligands are metal halides or metal carboxylates. For X-type ligands, halides, carboxylates and thi-

oles are used, and L-type ligand examples are primary amines or tertiary phosphines.⁹⁵

In the following, three examples of surface passivation are briefly described: achieving high PLQY by creating core-shell heterostructures, by ligand exchange, and improving electrical conductivity between NCs by ligand exchange.

The first CdSe NC synthesis reported a PLQY of 9.6%.¹ For the implementation into devices, researchers tried to increase the PLQY by employing different strategies. The first strategy is growing core-shell heterostructures. Here, a second semiconducting material is epitaxially grown on the surface of a CdSe NC core. Figure 2.5 shows the example by Peng *et al.* of a CdSe/CdS heterostructure. The group around Peng grew a 0.7 nm CdS shell surrounding a 3.9 nm CdSe core (as depicted in Figure 2.5a).⁹⁶ The electronic structure is described in Figure 2.5b. The electronic wave function of the hole is spatially confined to the CdSe core, while the electron can move freely in the CB of both materials. Due to the restriction of the hole to the core, the PLQY can increase, since the hole is not exposed to surface traps anymore. The increase in PLQY depending on the shell thickness of CdS covering the CdSe core can be followed up in Figure 2.5c.

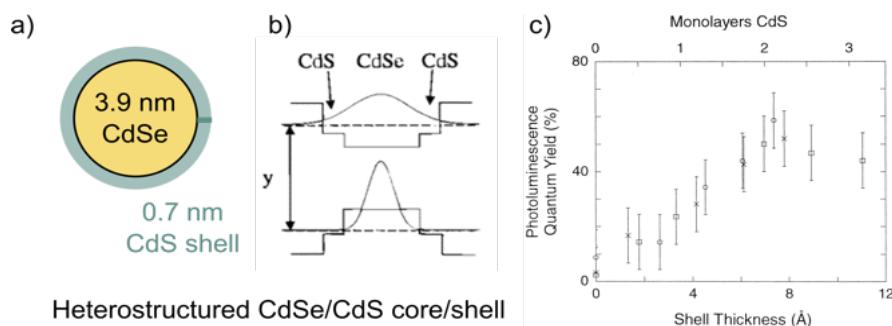


Figure 2.5: Enhancing PLQY of CdSe NCs by a CdSe/CdS heterostructure by Peng *et al.* a) Shelling of CdSe NCs with CdS, b) electronic structure of CdSe/CdS heterostructure, and c) increase of PLQY due to CdS shelling of CdSe NCs. Panel b) and c) reprinted (adapted) with permission from ref. [96]. Copyright © 1997 American Chemical Society.

Post-synthetic surface treatment can also improve the PLQY of NCs. Arjan J. Houtepens group demonstrated PLQY enhancement of CdTe NCs up to 90% by Z-type ligand treatment (with InCl_3).⁹⁷ They extended their study to CdSe, CdS, and InP NCs and could show that the ligand treatment gradually increases the PLQY.⁹⁷

The electronic properties of NCs can also be altered by exchanging the surface molecules.⁹⁸ In devices, thin films of NCs are fabricated either by spin-coating⁹⁸ or at

the liquid-liquid/air interface.⁹⁹ However, charge transport is one prerequisite for the implementation into devices. Therefore, it is important to ensure that the ligand shell is non-insulating, which means that electrons and holes can easily surpass the organic ligand shell and get transported to the connected electrodes. Hence, ligand exchange reactions to coupled organic-inorganic nanostructures were established to increase the electrical conductivity. Examples range from interconnecting PbS NCs with small difunctionalized diamines¹⁰⁰ and dithiols^{101–104}. Further functionalizing NCs by large π -conjugated molecules^{105,106} such as porphyrins¹⁰⁷ or aryleneethynylene¹⁰⁸ are other strategies.

This section has been highlighting how the electronic structure can be influenced by the size of NCs and by the organic ligand shell. Both factors need to be considered, also for the material class of LHP NCs in the context of their optoelectronic properties and ligand passivation. Therefore, the following section is introducing LHPs with the discussion of organic ligands and their role in stability enhancement and influence on charge injection.

2.2 Perovskite Nanocrystals

This section gives a thorough background on the structure and composition of LHP NCs since they are the material investigated in this thesis. Their outstanding optoelectronic properties are described, and this section outlines some possible modifications for altering optoelectronic properties, resulting in improvements for the application as electroluminescent light source in LEDs.

2.2.1 Structure of Perovskite Nanocrystals

LHP NCs are defined by their crystal structure as they crystallize in an ABX_3 lattice. This crystal structure was found first in $CaTiO_3$ by Gustav Rose in 1839, and he named it after the mineralogist Lev Perovski.^{109,110} Using X-ray diffraction, the structure was determined by Tom Barth in 1925 as $[TiO_6]^{4-}$ octahedra with Ca^{+} ions in the octahedral gaps.¹¹¹ In the following year, Victor M. Goldschmidt gave a theoretical description of the crystal structure.¹¹² He established the Goldschmidt tolerance factor, which states if ions can crystallize in a perovskite structure depending on ionic radii r .¹¹² In Equation 2.5, the calculation of the tolerance factor t is given. If t is between 0.8 and 1.0, the ABX_3 structure can crystallize in a perovskite lattice.¹¹²

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.5)$$

With this formula on hand, mineralogists found other oxides, nitrides and fluorides ($BaTiO_3$, $ThTaN_3$, and $KMnF_3$) crystallizing in a perovskite structure.^{113,114} However, the discovery of LHPs took some decades. In 2009, the first use of LHPs (with $A = MA^{+}$ (methylammonium), $MAPbBr_3$ and $MAPbI_3$) as photosensitizer started the interest of researchers in using LHPs in solar cells.¹¹⁵ In the following five years, perovskite based solar cells achieved a power conversion efficiency over 10%.¹¹⁶ Due to the high mobility of electrons and holes in LHPs, the interest of researchers extended to implementing LHPs in LEDs.¹¹⁷ Therefore, the advantages of LHPs and NCs, as being the color tunability by size, needed to be combined.

In 2014, the first organic/inorganic LHP NCs were published ($MaPbBr_3$ NCs).¹¹⁸ These NCs showed PLQY of 17% and emission at 530 nm.¹¹⁸ In 2015, Protesescu *et al.* succeeded in synthesizing fully inorganic LHP NCs with PLQYs over 50%.²⁹ In Figure 2.6a, the crystal structure of $CsPbBr_3$ NCs is shown with $[PbBr_6]^{4-}$ octahedra and Cs^{+} in their voids, which are crystallizing as cubes with a size of 3-12 nm.²⁹ A characterization of $CsPbBr_3$ NCs by scanning electron microscopy (SEM), PL and absorbance spectroscopy after synthesis is depicted in Figure 2.6b and c. The NCs show a size of 7.4 ± 0.8 nm in the SEM image and in solution, they exhibit a PL

maximum at 503 nm with the first excitonic maximum at 495 nm in the absorbance spectrum.

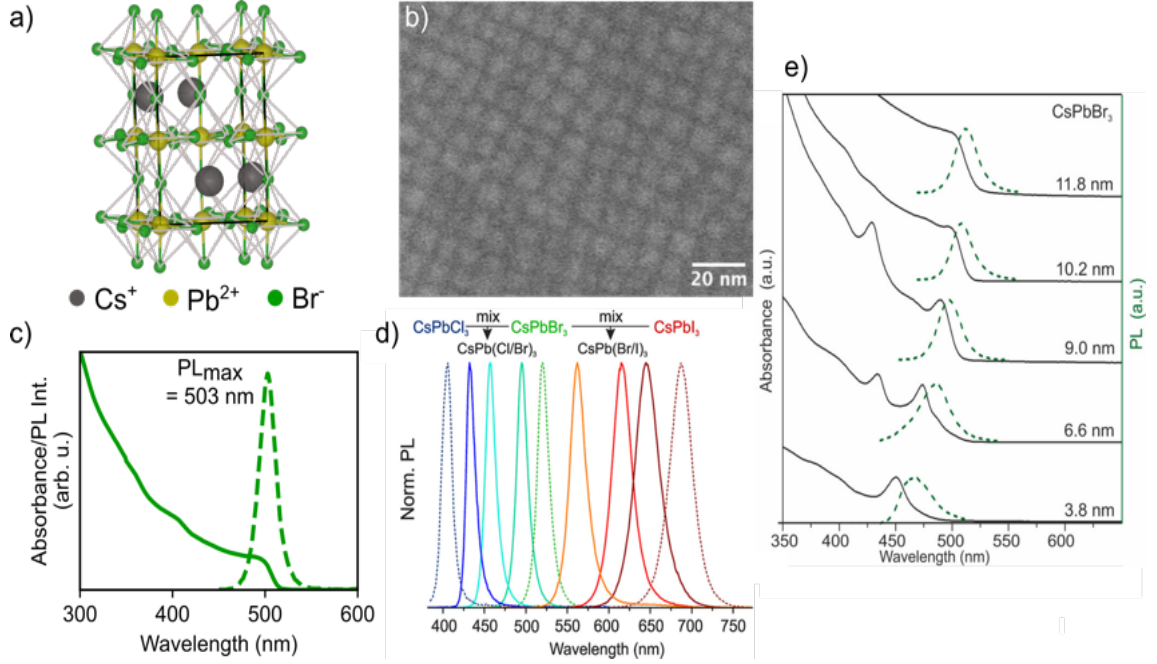


Figure 2.6: Characterization of CsPbBr₃ NCs. a) Depiction of the perovskite crystal structure (created with VESTA¹¹⁹), b) SEM image of a spin-coated NC film, c) PL (dashed line) and absorbance spectra (solid line) of CsPbBr₃ NCs in solution, d) color tunability of PL by anion exchange in CsPbX₃ NCs, and e) color tunability due to quantum confinement in CsPbBr₃ NCs. Panel c) reprinted (adapted) with permission from ref. [31]. Copyright © 2015 American Chemical Society. Panel d) reprinted (adapted) with permission from ref. [29]. Copyright © 2015 American Chemical Society.

By synthesizing mixed halide, pure chloride or iodide perovskite NCs, CsPb(Br/I)₃ (red, 530-700 nm) and CsPb(Br/Cl)₃ (blue, 420-480 nm), the whole visible spectrum can be covered.²⁹ Also, easy anion exchange reactions can be achieved by mixing the NCs in toluene with lead salts (PbI₂ or PbCl₂)³¹ or with halides mixed in OAm³⁰ (see Figure 2.6d). Additionally, the emission wavelength can be tuned by reducing the NC size below the exciton Bohr radius (Figure 2.6e, with a_B depending on the halide composition) as described in subsection 2.1.1 for NCs in general.²⁹

The outstanding properties of high PLQY and easy emission tunability were the foundation for a decade of further investigations on perovskite NCs. In the following, the optoelectronic properties and synthesis of this material, specifically for CsPbBr₃, are discussed in detail. In addition, possible modifications of the composition, as well as, the organic ligand shell as bottleneck for large scale

application and long-term stability will be outlined. In the end, NC ensembles (SCs) and the potential application in LEDs are highlighted.

2.2.2 Optoelectronic Properties

As mentioned before, the optoelectronic properties of LHP NCs are outstanding. While other semiconducting materials are in need of shelling of the inorganic core to gain higher PLQYs,^{96,120} LHP NCs show PLQYs of 50-90% directly after the first discovery in 2015.²⁹ One reason for this outstanding property is the electronic alignment of MOs in LHP NCs, resulting in the so-called defect tolerance.¹²¹ The defect tolerance describes the formation of no traps or shallow traps close to or in the VB maximum or CB minimum, when undercoordinated molecular orbitals are formed. LHP NCs are semiconductors made from Cs^+ , Pb^{2+} and Br^- atoms. In contrast to other semiconducting NCs, the VB is composed from the 3/4/5p orbitals of Br^- and 6s orbital of Pb^{2+} , forming antibonding character as depicted in Figure 2.7a.^{122,123} The CB is made from the 6p orbitals of Pb^{2+} .¹²²

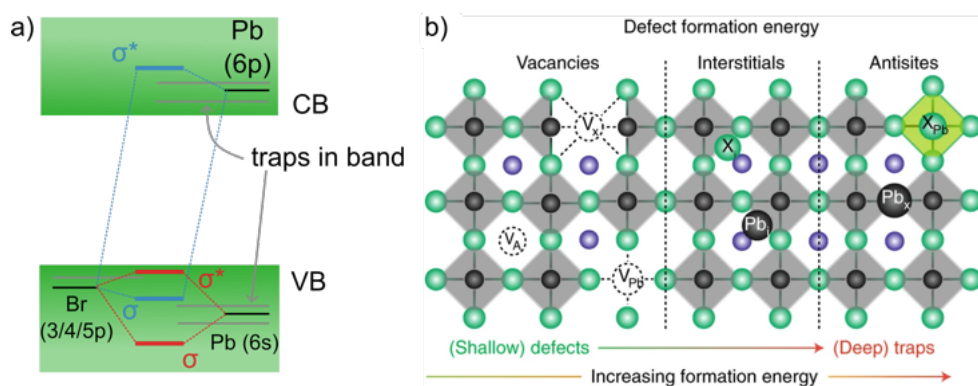


Figure 2.7: Effects contributing to the defect tolerance of perovskite NC. a) Energy band alignment in perovskite NC (own representation based on ref. [122]), and b) Formation of lattice defects. Panel b) reprinted (adapted) with permission from ref. [122]. Copyright © 2018 Springer Nature.

For other semiconductors, such as CdSe and ZnS, the VB maximum shows bonding character. Here, the formation of deep traps can occur, reducing the band gap.¹²² Typically, these traps are either passivated by (L, X, Z-type) organic ligands (as described in subsection 2.1.3, see Figure 2.4) or by shelling with another inorganic material (core-shell heterostructures: CdSe/CdS, CdSe/ZnS).^{96,120,124}

Another reason for the defect tolerance is the low formation energy of vacancies (V_{Br} and V_{Cs}), leading to shallow traps close to the band edges.¹²³ The formation of antisites and interstitials is energetically not favored since their formation requires higher energies.¹²³ The last factor contributing to the defect tolerance of LHP NCs

is the soft ionic lattice.¹²⁵ Charges can be screened over the whole NC by the soft ionic lattice.

2.2.3 Classical Synthesis of CsPbBr₃ NCs

The first synthesis of CsPbBr₃ NCs established in 2015 is based on an ionic metathesis reaction (reaction equation in Figure 2.8a).²⁹ It is a typical hot-injection synthesis following the LaMer model describing NC formation, as explained in subsection 2.1.2.²⁹ The precursors PbBr₂ and Cs₂CO₃ are dissolved by the addition of OA or OAm in a high-boiling solvent, namely octadecene (ODE).²⁹ The nucleation and growth of NCs starts when the Cs(oleate) precursor is added to the mixture of Pb(oleate), halides and OAm.²⁹ After 5 s, the reaction is stopped by an ice-bath.²⁹ The size of the NCs can be controlled by the hot-injection temperature rather than the reaction time.^{29,126,127} A typical lab setup and the influence of reaction temperature on the NC size are shown in Figure 2.8b and c.

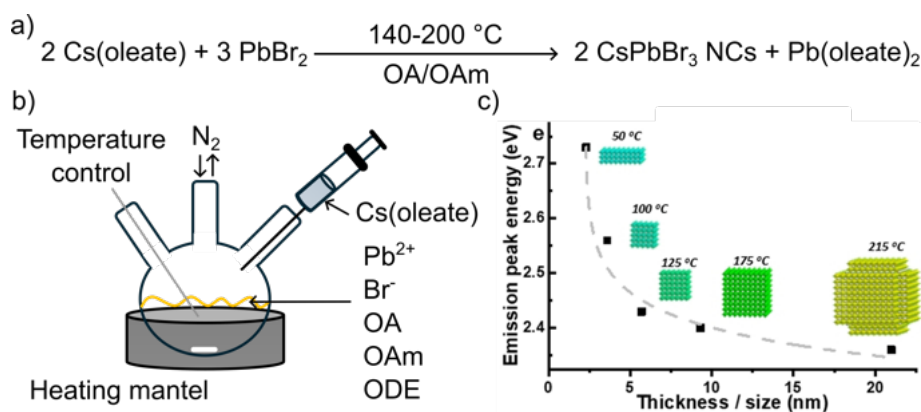


Figure 2.8: Hot-injection synthesis of CsPbBr₃ NCs. a) Reaction equation, b) scheme of setup in the lab with three neck-flask and hot-injection of Cs(oleate) precursor, and c) size tunability of LHP synthesis by reaction temperature. Panel c) reprinted (adapted) with permission from ref. [126]. Copyright © 2021 Angewandte Chemie International Edition published by Wiley-VCH GmbH.

Within some years, researchers found out that Br⁻ in excess in the synthesis and stoichiometric control are beneficial.¹²⁸ However, using PbBr₂ as lead and halide source would not fit the required parameters. Therefore, Yassitepe *et al.* synthesized CsPbBr₃ NCs with an ammonium bromide salt as halide source.¹²⁹ Additionally, this synthesis results in amine-free NCs since a quaternary ammonium halide is employed (see chapter 4).¹²⁹ A second method to gain stoichiometric control over the reaction is using benzoyl halides in the synthesis.¹²⁸

2.2.4 Confinement in Lead Halide Perovskites

Confined LHPs exist in different morphologies (Figure 2.9). The earlier described synthesis results in cubes of sizes from 3-12 nm depending on the synthesis temperature.²⁹ These nanocubes are shown as 0D material in the transmission microscopy (TEM) image in Figure 2.9a.

Another 0D material of perovskites are quantum dots (3-13 nm), which are showing a round shape.^{130,131} Their synthesis, introduced by Akkerman *et al.*, is conducted at room temperature, and with different ligands than conventional OA and OAm.¹³⁰ As ligand for PbBr_2 , the weakly binding and charge neutral tetraoctylphosphine oxide (TOPO) was used with Cs-diisooctylphosphinate as a second precursor.¹³⁰ Since Cs^+ is the only positive charge in the system, nucleation starts upon its addition followed by QD growth.¹³⁰ After the QD synthesis, the weakly binding ligands were exchanged by the zwitterionic tightly binding lecithin.¹³⁰ The size could be tuned by varying the dilution of the precursor with the addition of hexane.¹³⁰

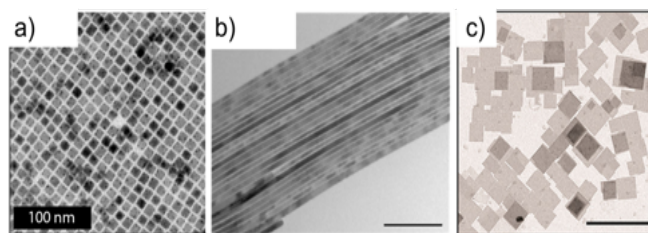


Figure 2.9: TEM images of variation of CsPbBr_3 nanostructures, still crystallizing in the perovskite lattice. a) Nanocubes, b) nanorods (scale bar: 100 nm), and c) nanoplatelets (scale bar: 1 μm). Panel a) reprinted (adapted) with permission from ref. [132]. Copyright © 2018 American Chemical Society. Panel b) reprinted (adapted) with permission from ref. [133]. Copyright © 2015 American Chemical Society. Panel c) reprinted (adapted) with permission from ref. [134]. Copyright © 2016 American Chemical Society.

A 1D material are nanorods (shorter) up to nanowires (starting at 100 nm up to μm long). Nanowires can be synthesized by reacting the conventional Protesescu *et al.* synthesis for an extended time at high temperature.^{133,135} After 40-60 minutes, long nanowires form out of the nanocubes.¹³³ An exemplary TEM image is shown in Figure 2.9b. Another synthesis of nanowires with different confinements can be conducted by tuning the ratio of short chain carboxylic acids to amines.¹³⁶ With the addition of the carboxylic acid, the width decreases.¹³⁶

The synthesis of LHP nanoplatelets is often a byproduct of the quantum-confined synthesis of NCs at low temperatures (see Figure 2.9c).^{127,137} When yielding only nanoplatelets, a synthesis at low temperature (70 °C) is described that starts with precursor transformation (PbBr_2 with OA and OAm and Cs(oleate)) upon addition

of the antisolvent acetone.^{138,139} For monolayer control, HBr is added to the precursor solution.¹³⁸ More HBr forms thinner platelets.¹³⁸

The ligand length can determine if the synthesis yields nanoplatelets or nanocubes.¹⁴⁰ During high temperature syntheses, the amine length can determine the shape, while the acid only determines the size of the NC.¹⁴¹ At low temperature, the influence of the acid/amine is not as pronounced, since the formation of cubes is reduced and platelets are formed.¹⁴¹ However, pure nanocubes can be also synthesized by using diamines instead of OAm in the synthesis.¹³²

2.2.5 Surface Chemistry of CsPbBr₃ NCs

The surface of LHP NCs plays a critical role in colloidal and long term stability. Therefore, the surface needs passivation by a layer of organic molecules, also referred to as ligands. First of all, the surface termination of the NC itself needs to be considered.

Two possibilities of surface termination exist. Bodnarchuk *et al.* describe in their theoretical publication the LHP NC by the core, (inner) shell, and the capping (outer) shell.¹⁴² The core is [CsPbBr₃], followed by the surface (PbBr₂ or CsBr), and the ligand shell {AX' or AX'₂}. This description gives two crystals structures: [CsPbBr₃](PbBr₂){AX'} and [CsPbBr₃](CsBr){AX'₂}. Depending on the ratio of Br/Pb either the (PbBr₂) or (CsBr) surface termination (inner shell) of the crystal is favored.¹⁴² However, CsBr is experimentally rarely observed, since it would require a 2.5 times higher ligand coverage and it would lead to restructuring of the [PbBr₆]⁴⁻ octahedra.¹⁴²

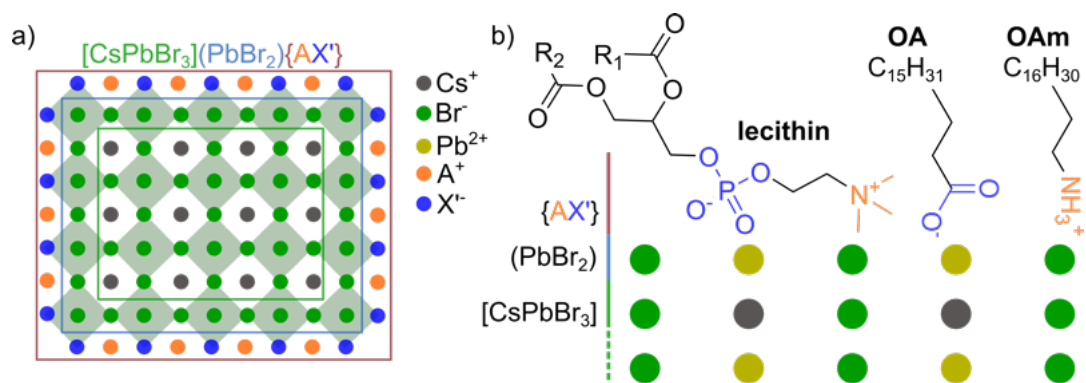


Figure 2.10: Surface chemistry of LHP NCs. a) Termination of crystal structure, and b) excerpt from the crystal structure of the surface with passivation by typical {AX'} molecules. Legend of panel a) also applies to panel b) (own representation based on ref. [142]).

The PbBr_2 termination is depicted in Figure 2.10a with $\{\text{AX}'\}$ possible binding sites displayed as blue and orange dots. In Figure 2.10b, the NC with the same surface is shown. In addition, some exemplary organic molecules replacing the $\{\text{AX}'\}$ surface are depicted. The zwitterionic lecithin molecule can passivate both surface sites with the phosphate binding to Pb^{2+} and trimethylammonium binding to Br^- . The combination of OA and OAm passivation as first introduced by Protesescu *et al.* is also shown.²⁹ In this example, OA binds to Pb^{2+} , while OAm passivates Br^- ions. A detailed description of OA and OAm passivation will follow in Figure 2.11b. This surface passivation can also be exchanged to gain colloidal stability or optoelectronic enhancements, which will be discussed in subsection 2.2.6.

When the surface passivation of LHPs is discussed, also the binding strength and the determination of the ligands need to be considered since LHPs are prone to decomposition compared to conventional II-VI semiconductors.¹²²

Since the surface of NCs is covered by organic molecules, the surface needs to be characterized by a method that probes the organics, instead of the typical characterization methods used for the inorganic core. ^1H NMR spectroscopy is used for probing the surface and the ligand shell of NCs.¹⁴³ NMR spectroscopy resolves the protons of the ligand sphere and can distinguish between the bound and free state of the ligand. When molecules are bound to the NC, the electron density of the proton shifts.¹⁴⁴ This can be observed by a chemical shift either upwards or downwards depending on the shift of the electron density. Additionally, the peaks are broadened due to restricted rotational mobility.¹⁴⁵ Sometimes, the traces of the protons close to the NC even disappear when the integral is not high enough.¹⁴⁶

Figure 2.11a shows the chemical structure with the specific characteristics of OA and OAm. The signal of the vinyl peaks of OA and OAm appears at approx. 5.6 ppm. This peak is broadened when it is in a bound state and a slight downfield shift can be observed.¹⁴⁷ In the case of Figure 2.11a, both species are present: the bound OA/OAm can be identified by peak broadening up to 5.8 ppm and the free OA/OAm can be observed as the indicated multiplicity at 5.6 ppm.

Given the qualitative NMR spectroscopy description, researchers are also interested in how good the surface passivation by molecular ligands is. This can be achieved by quantitative ^1H NMR spectroscopy with the addition of a specific amount of a molecular standard species. One requirement for this approach is that there are no excess ligands in solution. During quantitative NMR spectroscopy, NCs are decomposed and the ligands are released from the surface. This makes the integration of the proton signals possible, which can be then compared to the one of

the quantitative standard. By Equation 2.6, the molar amount of the ligand n_L can be calculated.

$$n_L = n_{St} \cdot \frac{I_L}{N_L} \cdot \frac{P_{St}}{P_L} \quad (2.6)$$

n_{St} is the molar amount of the standard, I_L is the integral of the vinyl protons of the ligand, N_L is the number of protons contributing to the integrated signal of the ligand, and $P_{St/L}$ is the purity of the standard or ligand, respectively.

When the implemented amount of NCs for ligand quantification is known, the quantity of surface ligands per NC can be calculated. This makes monitoring washing or quantitative ligand exchange procedures possible.

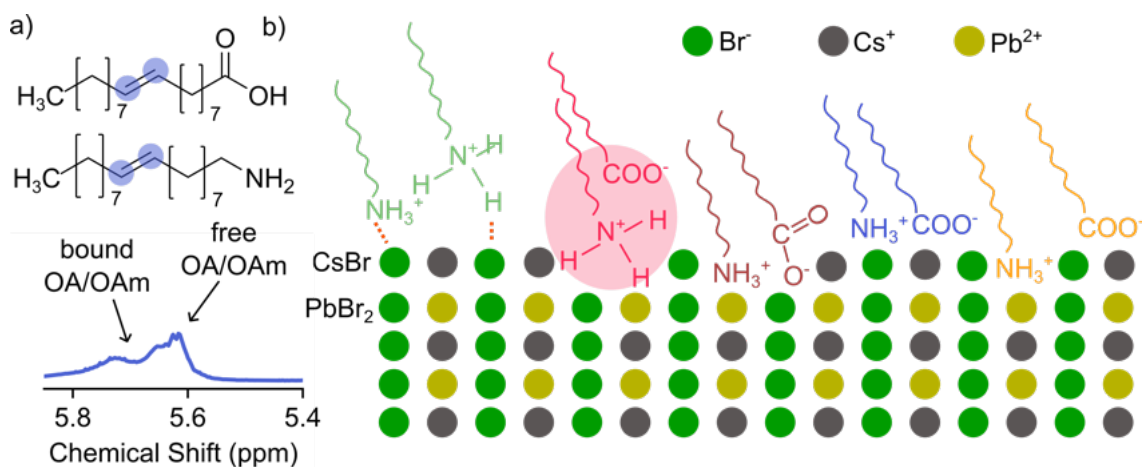


Figure 2.11: Probing surface chemistry of LHPs. a) NMR spectroscopy of vinyl protons of OA/OAm (indicated in chemical structure by blue dots) in toluene- d_8 , and b) different binding motifs of OA/OAm introduced by different publications indicated by the color codes (own representation based on ref. [40]).

Additionally, NOESY (Nuclear Overhauser effect spectroscopy) and DOSY (Diffusion-Ordered NMR spectroscopy) can be recorded to gain insights into the surface chemistry of NCs.¹⁴⁸ 2D NOESY spectra show rotational tumbling rates of protons in a molecule. When the tumbling rate is high, it gives a positive NOE peak. If the tumbling rate is reduced, because the molecule is bound to a NC, the signal gets negative.^{149,150} De Roo *et al.* found oleylammonium-bromide (OAm-Br) binding to the NC surface.³⁵ Using DOSY, they determined the diffusion coefficient of the OAm-Br species. The comparison of the diffusion coefficient to the one of the free molecule revealed a reduced diffusion, which is attributed to the bound state. Additionally, the Stokes-Einstein equation can be applied, which gives a correlation to the NC size.¹⁴⁸ This procedure revealed for LHP NCs a high diffusion coefficient for the size of the measured NCs, concluding a fast exchange between free and bound OAm-Br species.³⁵ This fast exchange is referred to as dynamic ligand binding.

In literature many more models of the binding of OA and OAm and the resulting surface passivation exist.⁴⁰ These are briefly described in the following and schematically depicted in different colors in Figure 2.11b. De Roo *et al.* explain their NMR spectroscopy results by a favored electrostatic binding of the OAm-Br species to the surface (depicted in green) than the formation of the covalent character of Pb(oleate) species on the surface.³⁵ In addition, they explain the deprotonation of HBr by the stronger acidity than the one of OA. Hence, the binding of OA is not favored.³⁵ The second picture of ligand binding suggests OAm replacing Cs^+ ions and forming hydrogen bonds with Br^- ions on the surface (depicted in red).¹⁵¹ The functionality of OA is attributed to charge neutralization.¹⁵¹ Ten Brinck *et al.* propose the occupation of halide vacancies by oleate molecules, instead (shown in brown chemical structures).¹⁵² The fourth study (shown in blue) outlines the binding of OA to Cs^+ and OAm to Br^- ions,¹⁵³ while the last study suggests OAm in Cs^+ vacancies and oleate passivating surface Cs^+ (depicted in yellow).¹⁵⁴

All these different results exist on the surface passivation by only OA and OAm, probably due to the dynamic binding of the surface molecules. However, it is important to highlight that these ligands are still used often in colloidal synthesis and then, afterwards exchanged to gain increased stability or enhanced optoelectronic properties.

2.2.6 Post-synthetic Modifications of Perovskite NCs

One strategy to alter the surface passivation is by post-synthetic ligand exchange, which is facilitated due to the dynamic ligand binding of OA/OAm. Here, NCs are synthesized with OA/OAm on the surface, and afterwards the ligands are exchanged without altering the crystal structure. Due to dynamic ligand binding, access to the crystal structure is given, which is favoring anion exchange reactions and ligand exchange in solution.³⁵ However, drawbacks of working with the NCs exist caused by the dynamic ligand binding. The stability of the NCs is reduced since ligands desorb and the NCs are prone to surface reactions. Therefore, researchers come up with different strategies to passivate the NC core post-synthetically with the aim of increasing the stability and enhancing the optoelectronic properties.

Here, the exchange of the organic ligand shell will be highlighted (as performed in chapter 3 and chapter 4), and the self-assembly of NCs into SCs is outlined (chapter 5).

2.2.6.1 Ligand Exchange on Perovskite NCs

Ligand exchange reactions are used to alter the surface of NCs. This can result in enhancements of the stability against polar solvents,^{41,155} long-term stability, the PLQY,^{28,156} and electronic conductivity.^{157,158} In the following, some ligands are demonstrated that improve the performance of NCs.

First, the stability of the NCs, especially concerning their stability against polar solvents, will be addressed. Due to dynamic binding to the surface, the reduction of the diffusion coefficient had to be addressed. The group of Maksym Kovalenko put many efforts into this research question.^{41,155,159} They used different kinds of zwitterionic ligands, such as natural lecithin, sulfobetaines, and γ -aminoacids.^{41,155} All these molecules are binding with both of their charges to the surface. Thereby, the diffusion coefficient could be reduced and the concept of tight binding was established.⁴¹ With lecithin as surface ligand, which can be easily bought and is used in many nutrients, the colloidal stability could be increased, and high concentrated solutions were prepared.¹⁵⁵ However, lecithin turned out to not be a perfect fit for the A-site moieties. Therefore, the quaternary ammonium was replaced by a smaller sized primary ammonium (phosphoethanolamine, see Figure 2.12a(i)), which is fitting better to the crystal structure of CsPbBr₃ NCs and further enhancing the binding strength.¹⁵⁹ In a more recent publication by the workgroup from the ETH Zürich, guanidinium-bromide is described as a surface ligand, which binds dynamically, but also allows for several purification steps with the addition of polar solvents.¹⁶⁰

The first results on enhanced optoelectronic properties of NCs could be achieved by using didodecylammonium bromide as a surface molecule (Figure 2.12a(ii)).^{157,161} With its shorter carbon chain length (C₁₂), the carrier mobility in LEDs could be improved, which resulted in an up to 30-fold increase in the external quantum efficiency (EQE).¹⁵⁷ In addition, the PLQY of the NCs itself could be improved and the surface-treated NCs showed a longer stability.¹⁵⁶ In combination with a partial removal of ligands from the NC surface, the EQE could be further improved up to 15%.¹⁶²

Another ligand leading to a PLQY up to 100% is thiocyanate (SCN⁻).²⁸ Excess Pb on the surface introduces shallow trap states. By SCN⁻ treatment, the surface Pb could be removed and the PLQY increased.²⁸ The third described ligand is used for studying energy transfer from this kind of NCs. The NC is used as triplet donor, while naphthalene (depicted as molecule (iii) in Figure 2.12a) acts as triplet acceptor.^{163,164} 1-Aminopyrene (molecule (iv) in Figure 2.12a) was used for

studying charge transfer, when the NC is photoexcited during transient absorption spectroscopy.¹⁵⁸ The molecule on the surface acts as hole acceptor and leads to darkening of the NCs' PL.¹⁵⁸ The interest of implementing chiral properties to NCs has risen in the past couple years. Therefore, (S)-(-)- α -methylbenzylamine (v) and (R)-(+)- α -methylbenzylamine (vi) were incorporated into layered 2D perovskites.¹⁶⁵ These layered materials show circular dichroism and circularly polarized PL, which opens up new ways for spin-selective optoelectronic devices.^{165,166,162}

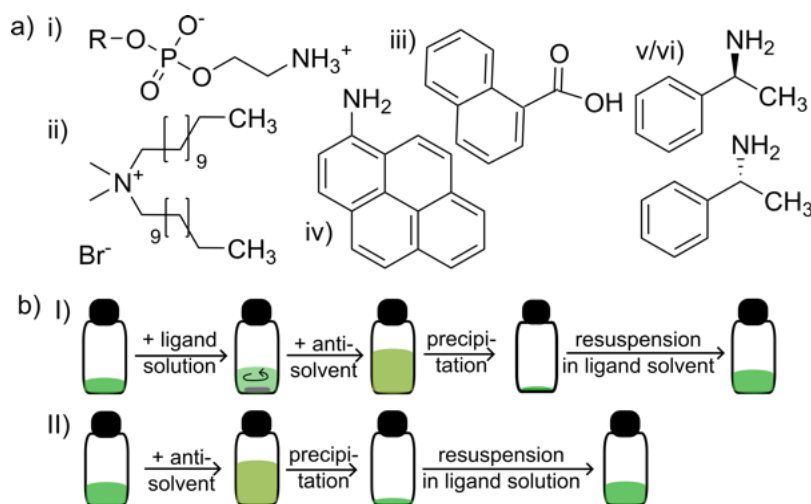


Figure 2.12: Tuning the optoelectronic properties of LHP NCs by ligand exchange. a) Possible surface ligands for tuning optoelectronic properties of NCs, and b) methods of post-synthetic ligand exchange on OA/OAm NCs.

All these described phenomena can be tuned by ligand exchange. Hence, ligand chemistry bares the potential of tuning the stability, the PLQY, the electronic and optical properties. The method of post-synthetic ligand exchange is rather simple. In general, two strategies are employed: one is a solution ligand exchange (I),¹⁶⁷ the other one is removing the ligand shell and then adding new ligands to the precipitated NCs (II).^{107,168} The scenarios are schematically depicted in Figure 2.12b. In the upper panel (I), new ligands are added into solution and the solution is stirred. Afterwards, OA/OAm, the ligands after synthesis, are removed from solution by precipitation with hexane as antisolvent. In the second method, the NCs are first precipitated by a polar antisolvent, followed by resuspension in the new ligand solution. The first concept is better applicable when the ligand is more polar and dissolved in a polar solvent, while the second method is better suited for a nonpolar/nonpolar ligand exchange. By the first strategy, a nonpolar new ligand would be also removed from the surface during precipitation, since it is soluble in hexane.

The two described methods are simple to conduct. However, these NCs are prone

to decomposition caused by the limited stability in polar solvents and the dynamic ligand binding, which complicates ligand exchange reactions.

2.2.6.2 Self-assembly into Supercrystals

Self-assembly of NCs into ordered arrangements bares the potential of enhanced electronic properties.¹⁶⁹ Due to structural order and close proximity of NCs to each other, electronic coupling arises. Therefore, the application of so-called superlattices or SCs is of interest for the implementation in photodetectors and in LEDs.

Superlattices are already known for several years. CdSe and PbSe superstructures were crystallized in the late 90s and early 2000s.^{170–173} By crosslinking the NCs in their superstructures with organic molecules, improved charge transport could be achieved.¹⁷⁴ Self-assembly with crosslinking of NCs is also of interest for LHP NCs, since electronic transport is one prerequisite for their application. In addition to enhanced charge transport, the optoelectronic properties can be tuned. Here, a red-shift of the emission can be observed due to so-called "mini-band" formation, which is an overlap of the electronic structures of NCs.^{175–178}

SCs can be self-assembled by slow evaporation, gravitational sedimentation or solvent destabilization.^{179,180} In this thesis, slow evaporation is used for SC formation from LHP NCs. Figure 2.13a shows the formation of SCs. Therefore, the NCs are drop-cast on a tilted substrate (glass for optical spectroscopy, polyimide for X-ray scattering, and fluorine-doped tin oxide (FTO) for SEC). In the evaporation chamber, a supersaturated solvent atmosphere is created by a solvent reservoir. After several days of solvent evaporation, SCs are formed with a size of 10-20 μm , which can be observed by light microscopy (see Figure 2.13b). However, NCs in the SC can only be resolved by electron microscopy.

X-ray scattering techniques revealed that the SC formation is a size selective self-assembly.¹⁸¹ Due to this size refinement, the SC shows structural coherence.^{181,182} The structural coherence can be observed as collective phenomena. For example, superfluorescence of self-assembled NCs is possible at low temperatures.¹⁸³ The PL of an uncoupled film is shown as green line in Figure 2.13c.¹⁸³ When the NCs are assembled into a SC, the PL splits up into a red-shifted collective signal and an uncoupled NC signal (as black solid line in Figure 2.13c).¹⁸³ The uncoupled PL can be compared to the one emitted by the NC thin-film. The coupled emission can be fitted by Lorentzian fit, while the uncoupled emission can be fitted by a Gaussian fit.¹⁸³

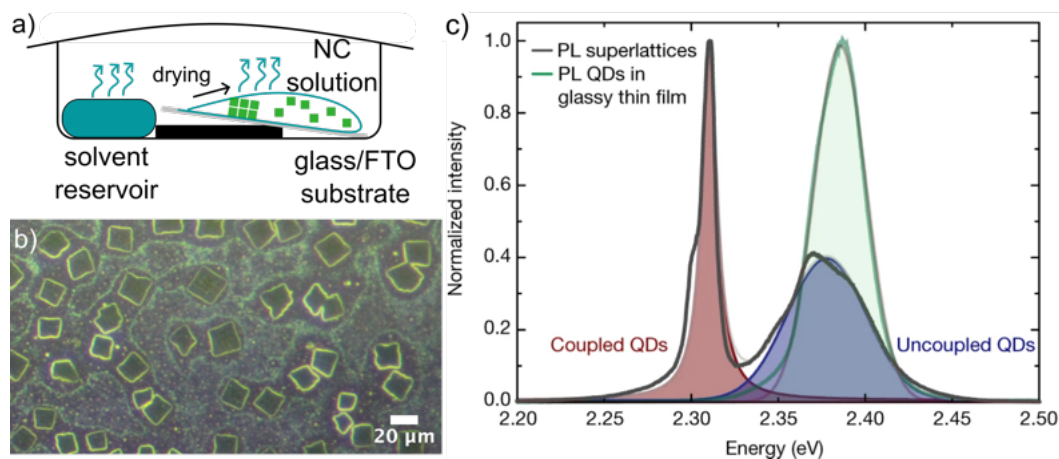


Figure 2.13: Introduction of self-assembled SCs. a) Schematic depiction of self-assembly process, b) dark-field microscopy image, and c) PL spectrum of single NCs and self-assembled NCs in a SC showing superfluorescence. Panel c) reprinted (adapted) with permission from ref. [183]. Copyright © 2018 Springer Nature.

2.2.7 LEDs from Perovskite NCs

Since the motivation of this work is a potential application of perovskite NCs in future LED devices, the performance of the altered NCs in LEDs is of interest. Therefore, this chapter briefly describes LED operation, fabrication and typical characterization methods that lead to the most common figure of merit for LEDs, the EQE.

2.2.7.1 LED Operation and Fabrication

As already shown in Figure 1.1a, several layers of materials are incorporated into an LED. The working principle of QLEDs is comparable to the one of organic LEDs (OLEDs). Here, the emission is generated by a semiconducting material with a band gap in the optical range.¹⁸⁴ The emissive layer is sandwiched between wide band gap semiconducting ETL and HTL as shown in Figure 2.14a.^{185,186} ETL and HTL are connected to electrodes. By the application of an electrical bias, electrons and holes are injected into the LED.⁴⁸ Electrons are conducted by the ETL, and holes by the HTL. When the electrical bias, the applied potential V , is high enough, the electrons and holes can be injected into the emissive layer, the NCs.¹⁸⁵ In this layer, the injected electron-hole pair can recombine radiatively.¹⁸⁷ This process is called electroluminescence (EL).¹⁸⁶

Before starting the fabrication, ETL and HTL have to be chosen. The absolute positions of the VB and CB of the NCs are used as a criterion for selecting the HTL and ETL material. Both of the energy levels should be close to each other, since

hole and electron injection into the emissive layer should be with a reduced energy barrier.¹⁸⁸ Typically, the band edge positions are determined by X-ray photoelectron spectroscopy (XPS) or ultraviolet photoelectron spectroscopy (UPS).¹⁸⁹ Afterwards, the material is chosen accordingly. Figure 2.14a shows an LED structure that is used in chapter 4. Therefore, the band edge positions were either determined by SEC PL, XPS/UPS or can be followed up in the literature.^{45,190,191} Note here, the VB is depicted as lower edge of the box, and the band gap is filled by the color.

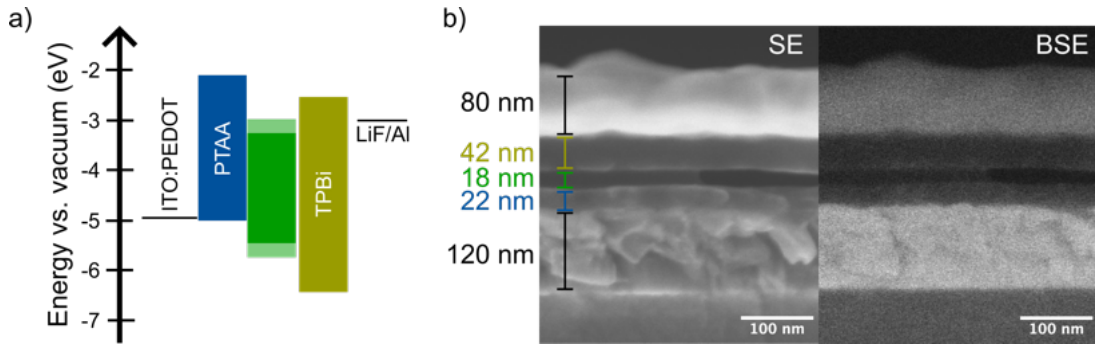


Figure 2.14: Structure of an LED. a) Typical flat-band energy diagram of an LED with PTAA as HTL, TPBi as ETL and NC as green emissive layer,⁴⁶ and b) SEM cross-section of a typical LED with stated thicknesses of the layers (on the left: secondary electron image (SE), on the right: back scattered electron image (BSE)).

The fabrication starts with a conductive electrode on the bottom, where indium tin oxide (ITO) is used. The next layer is the HTL. In the case of Figure 2.14a, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) and poly-3,4-ethylenedioxythiophen (PEDOT) are used, which are both organic molecules (chemical structures are given in chapter 7).^{192,193} The emissive layer is depicted in green, exemplifying the NCs. HTL and the emissive layer are spin-coated on-top of the ITO substrate. As ETL material, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) is evaporated on the NC.¹⁹² The second electrode consists of 0.5 nm LiF and Aluminium, which are both also evaporated in ultrahigh vacuum.

Figure 2.14b shows an SEM image of a cross-section cut through an LED. Here, starting from the glass on the bottom, the thicknesses of each material can be determined. The layer thicknesses are stated in the figure. Mono- or bilayers of NCs are used as emissive layer.¹⁹⁴

2.2.7.2 Efficiency of an LED

The efficiency of an LED is measured by its EQE η_{EQE} . The definition of η_{EQE} is given in Equation 2.7.¹⁹⁵ The efficiency is determined by a contribution from the LED architecture and the optical properties of the emissive material. η_{QY} is the

quantum yield of the emissive layer. Here, the quantity of radiatively decaying and emitted photons is taken into account. The charge carrier balance γ is stating how many electrons/holes are injected into the emissive layer, and contributing to η_{QY} . It can be reduced by electrons or holes surpassing the emissive layer and getting further transported to HTL or ETL, respectively. Therefore, the LED design with the energy levels is considered by γ .¹⁹⁶

$$\eta_{EQE} = \gamma \cdot \eta_{QY} \cdot \eta_{out} \quad (2.7)$$

The outcoupling factor η_{out} is also device dependent. It describes how many photons leave the device and contribute to EL.¹⁹⁷ Reabsorbed and quenched photons are not included.

The EQE is determined by measuring the current j and the luminance L depending on the applied voltage. As a general description, it accounts for the number of emitted photons by the number of injected electron-hole pairs.¹⁹⁵ Equation 2.8 shows the calculation of the EQE from the experiment. The measuring device parameters are summarized in the constant factor C .

$$\eta_{EQE} = \frac{n_{\text{emitted photons}}}{n_{\text{injected electron-hole pairs}}} = C \cdot \frac{L}{j} \quad (2.8)$$

A typical LED characterization looks as depicted in Figure 2.15a. First, at a specific voltage, the current increases at ~ 2.4 V, while the luminance rises at ~ 2.6 V. The determined EQE in this example states that the performance of the LED is high at low currents. Therefore, charges can be injected directly and no trap filling is given before the luminance rises. However, at high current densities >1 mA/cm², the EQE drops fast and hints the decomposition of the NCs in the LED.

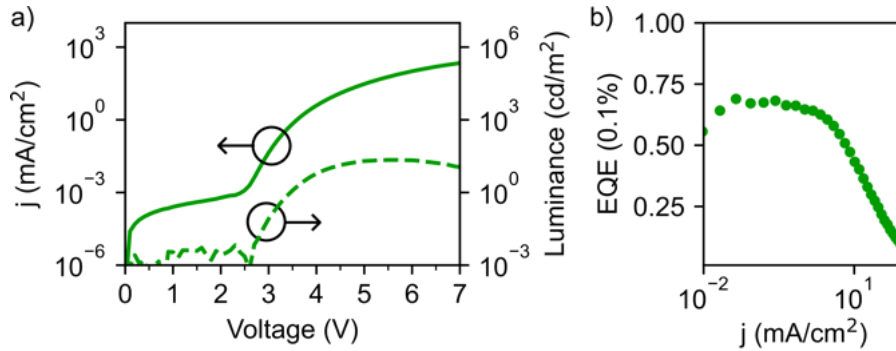


Figure 2.15: Characterization of LED performance. a) jVL plot of NC LED with current density j (solid line) and luminance (dashed line), and b) determined EQE by jVL plot.

This section has introduced the material investigated in this cumulative thesis. It has been presented in how many different ways LHP NCs can be altered to gain stability, enhance charge injection and to change, in general, their optoelectronic properties. All these factors can be investigated by SEC, which bares the potential of deducing the gained insights to the application in LEDs.

2.3 Spectroelectrochemistry - Probing Electrochemical Doping

In this section, SEC is introduced as a combination of electrochemical charging with optical spectroscopy. Therefore, electrochemical charging by cyclic voltammetry (CV) is described in more detail with a focus on the influencing processes of diffusion and heterogeneous charge transfer. In the end, SEC for probing charge injection into NCs is highlighted and the state-of-the-art of SEC on LHP NCs is briefly summarized.

2.3.1 Electrochemical Charging by Cyclic Voltammetry

Charge injection into molecules can be studied by electrochemical methods. Quantitative and qualitative analyses can be conducted, the HOMO/LUMO energies can be determined and reaction mechanisms can be clarified. Here, CV will be explained since it is the electrochemical method used in chapter 3 and chapter 4.

A three-electrode setup used for studying oxidation and reduction processes is depicted in Figure 2.16a. It includes a working electrode (WE, glassy carbon, Pt, ITO or FTO), a reference electrode (RE, Ag wire, AgCl or calomel electrode), and a counter electrode (CE, graphite or Pt).¹⁹⁸ During the experiment, the potential is applied by the potentiostat between the WE and RE, and the current is recorded between CE and WE. All three electrodes are placed into an electrolyte solution, that consists of a solvent (mostly organic for NCs) and a salt (tetrabutylammonium hexafluorophosphate, TBAHFP (chemical structure see chapter 7), LiClO_4) to ensure conductivity.¹⁹⁹ Since there exists a potential drop between the surface of the WE and the CE, the RE is employed and additionally, iR compensation is conducted by the potentiostat to correct for the ohmic drop by the electrolyte solution.²⁰⁰

When performing the experiment, the potential can be either scanned in oxidative or reductive direction, by increasing or reducing the potential, respectively. With the application of CV as electrochemical method, the potential is scanned up or down toward a certain maximum or minimum potential, hereafter referred to as the switching potential E_λ . Afterwards, the potential scan direction is reversed (see Figure 2.16b). This procedure makes the reversibility of charge injection accessible. In Figure 2.16c, a reversible one-electron process of the redox couple ferrocene/ferrocenium (Fc/Fc^+) is shown with the corresponding recorded CV in Figure 2.16d. The potential is raised, which corresponds to an oxidative scan.²⁰¹ First, capacitive current is recorded which is attributed to the formation of the electrochemical double layer by the electrolyte. At 0.13 V, the current starts increasing, which means that an electron-transfer to the electrode is recorded. This is the

heterogeneous charge transfer with the transfer rate k^0 . The charge transfer reaches a maximum when all molecules close to the WE are in their oxidized form (Fc^+). Figure 2.16d shows schematically the Fc/Fc^+ molecules in front of the WE and the dependence of the Fc concentration c_{Fc} on the distance from the WE x . When more molecules are in the oxidized form, the diffusion layer expands. At this point, the non-oxidized molecules have to diffuse to the surface of the WE. The diffusion leads to a decrease in current.²⁰² After reversing the potential scan direction, the oxidized species (Fc^+) is reduced back to the non-charged form of the molecule (Fc). Note here, as long as positive current is recorded, one speaks of oxidative current. When the current is negative, it is reductive current. Thus, after reversing the scan direction, the oxidation is still occurring and dominating the recorded current.

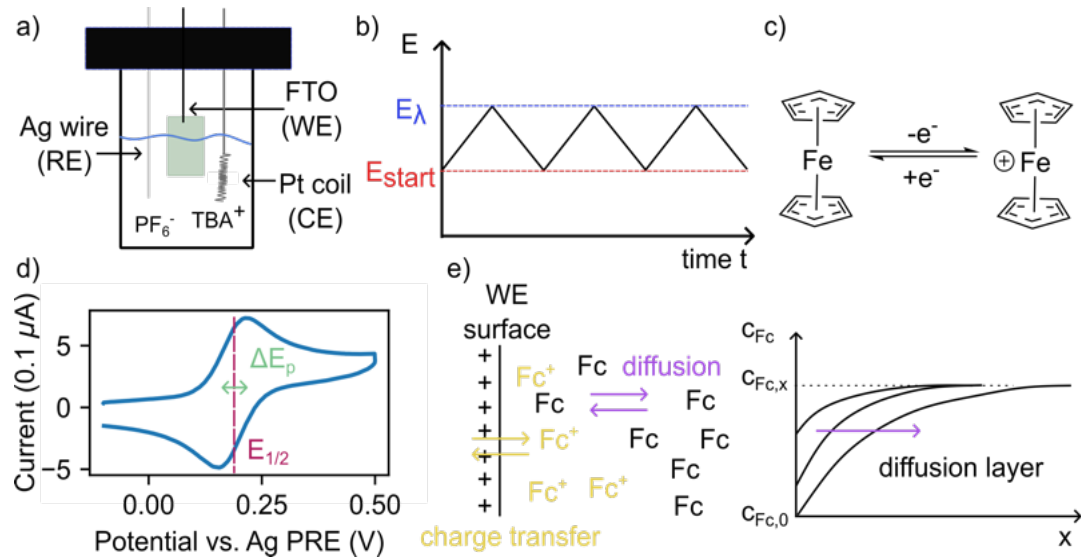


Figure 2.16: Basics on CV. a) Electrochemical setup, b) time-dependent potential scan, c) redox reaction of Fc/Fc^+ , d) CV of reversible one-electron transfer of Fc/Fc^+ , and e) schematic depiction of electrochemical doping on the WE surface ($x=0$) with the concentration gradient of Fc c_{Fc} on the WE surface.

As qualitative and quantitative parameters, the half-wave potential $E_{1/2}$ and the peak separation ΔE_p can be extracted from the CV. First, $E_{1/2}$ is a characteristic value for each material. Second, ΔE_p gives information about the reversibility of the electron transfer. Here, the charge transfer (k^0) and the diffusion are determining ΔE_p .²⁰² Is k^0 ($k^0 > 10^{-1} \text{ cm/s}$) large, then the diffusion is the rate-determining step. Therefore, the oxidation and reduction peak are close together (like exemplified for the redox couple Fc/Fc^+) and the mechanism is electrochemically reversible. As soon as k^0 ($10^{-1} > k^0 > 10^{-5} \text{ cm/s}$) decreases, the heterogeneous charge transfer gets more important and the peaks separate. The electrochemical reaction is called quasi-reversible. Is k^0 ($k^0 < 10^{-5} \text{ cm/s}$) the rate-determining step, then ΔE_p gets

large and the reaction is electrochemically irreversible. One reason could be that the second peak is not existing due to a following chemical reaction of the oxidized form or the peaks are very far apart from each other.

The interpretation of CVs includes information on reaction mechanisms. However, the determined potentials are recorded in a specific geometry of the electrochemical cell and the electrolyte solution employed. This makes the comparison of absolute values measured by many researchers difficult. Therefore, the convention is measuring the redox couple Fc/Fc^+ , determining its half-wave potential and then transferring all potentials to the scale of Fc/Fc^+ (vs. Fc/Fc^+).²⁰³

2.3.2 Resolving the Electronic Structure of Nanocrystals

Before introducing how the electronic structure of NCs can be resolved and how this can be achieved by combining optical spectroscopy with a electrochemical method, the main differences between NCs and molecules such as Fc/Fc^+ are discussed.

As discussed in subsection 2.1.3 and subsection 2.2.5, NCs consist of the inorganic core and the organic ligands, giving the NC its colloidal stability. One prerequisite for performing electrochemistry is that these ligands are not insulating. Thus, charges can surpass the organic ligand shell and go into the NC core. These ligands should not be electrochemically active in the electrochemical window, which means that they are not reduced or oxidized before charges can be injected into the NC. Additionally, NCs are not monodisperse, showing a small inhomogeneity in their size. This can either result in different quantities of electron-transfer to the NC (e.g. one or two e^- per NC) and probably different potentials for charge injection are necessary as the band gap is affected by the size. Defects on the surface play also an important role for charge injection. Electronic traps can be filled or electrons can be extracted from the surface of the NCs. Electrochemistry can be used to determine traps, but also traps make direct charge injection into the NCs VB or CB difficult. The differentiation between trap filling and electrochemical doping of the NCs cannot be achieved by performing electrochemistry solely since only the current is recorded. The increase in current can be either due to trap filling or the doping of NCs.

All these mentioned factors are making the interpretation of CVs of NCs challenging. Therefore, the combination of optical spectroscopy and electrochemistry is a tool to facilitate the interpretation of potential dependent electrochemical doping of NCs. Due to PL and absorbance spectroscopy, the electronic structure, which is characteristic for NCs, is made visible before and as charges are injected into the

electronic structure. Figure 2.17 is demonstrating the effect of hole or electron charging in a schematic representation of the electron transfer from (oxidative scan) or to (reductive scan) the band edges and the resulting consequences in PL intensity and the recorded current.

Note, here the band gap of the NCs is shown on the energy scale vs. vacuum. However, the energy scale is flipped for electrochemical methods. Therefore, going into the direction of the VB, which means a decrease in energy vs. vacuum corresponds to an increase in the absolute potential of the system against the Fc/Fc^+ redox couple or in general the applied potential in the electrochemical cell (vs. Ag pseudo-RE).²⁰⁴

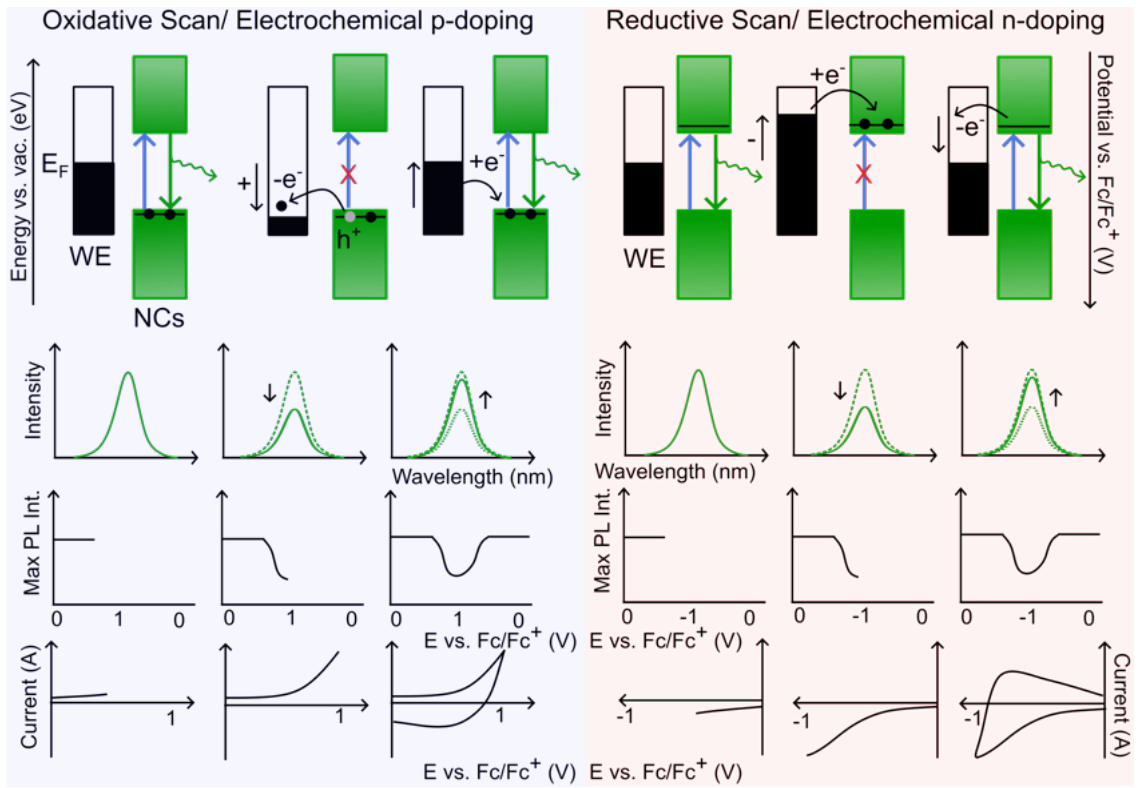


Figure 2.17: Explanation of PL SEC in oxidative (on the left, blue background) and reductive scan direction (on the right, red background). a) Depletion/population of VB/CB with electrons of NCs due to E_F tuning of WE, b) recorded PL spectra during the application of a potential, c) maximum PL intensity trace, and d) recorded CV during the oxidative/reductive scan.

When the Fermi level E_F of the WE is decreased (see Figure 2.17, transparent blue box) by the applied potential, E_F is approaching the VB. Due to continuous excitation of the NCs, the PL is recorded with constant intensity (1st depiction). As soon as, E_F is at the energetic position of the VB, electrons can be extracted from the VB.²⁰⁵ This process leads to an increase in current, as described for CV in

general, but simultaneously a decay in PL intensity is recorded (center panel). When the scan direction is reversed, electrons can be injected again to the VB and the PL should recover to the intensity from the beginning with the CV showing reductive current (3^{rd} scenario).

The same effect of PL intensity decay occurs in reductive scan direction by filling up the CB with electrons (Figure 2.17, transparent red box).²⁰⁵ Here, the difference is the recorded negative current in the forward scan and the positive current in the reversed scan.

For SEC in absorbance, a reversible bleach of the absorption maxima can be recorded with the advantage that the bleach can be directly attributed to the band edge positions.^{43,206,207} PL measurements are sensitive to non-radiative trap-states, but can also help identifying them.^{208–210}

2.3.2.1 SEC on Nanocrystals

In the following, the differentiation of band edge bleaches and trap filling will be explained based on current literature on different kinds of NC SEC and additional features will be mentioned, that influence the charge injection potential during SEC. The determination of VB and CB band position can be achieved by either absorbance or PL spectroscopy. However, all electronic states in one band can only be resolved by spectroscopy in absorbance. Here, excitonic transitions can be assigned, as for example $1S_{h/e}$, $1P_{h/e}$ transitions, and the start of the potential dependent absorbance bleach can be determined.^{43,206,207} If NCs are not strongly absorbing, the absorbance signal can be enhanced by performing potential modulated absorbance spectroscopy (EMAS).^{211–213} Due to absorbance SEC, heterostructures and their charge transfer depending on the surface ligands can be resolved.^{214,215} PL spectroscopy makes in-gap states accessible.^{208–210} Figure 2.18a shows the combined results of SEC in absorbance and PL in reductive scan direction on bare CdTe NCs by van der Stam *et al.*²¹⁶ The absorbance shows a bleach at -1.1 V, while the PL increases upon the application of a reductive potential. The schematic representation of the trap passivation by electrochemical charging is depicted in Figure 2.18b. The electron trap in front of the energetic position of the CB can be filled with electrons by the applied potential. This opens up the radiative pathway for excitons. Thus, the PL rises. The publication shows how this trap can be passivated by Z-type ligands ($CdCl_2$), removing the trap from the surface. With the passivation, the PL rises again and the onset of the PL bleach caused by electron injection can be correlated to the absorption bleach at -1.1 V and the CB edge, in Figure 2.18c.

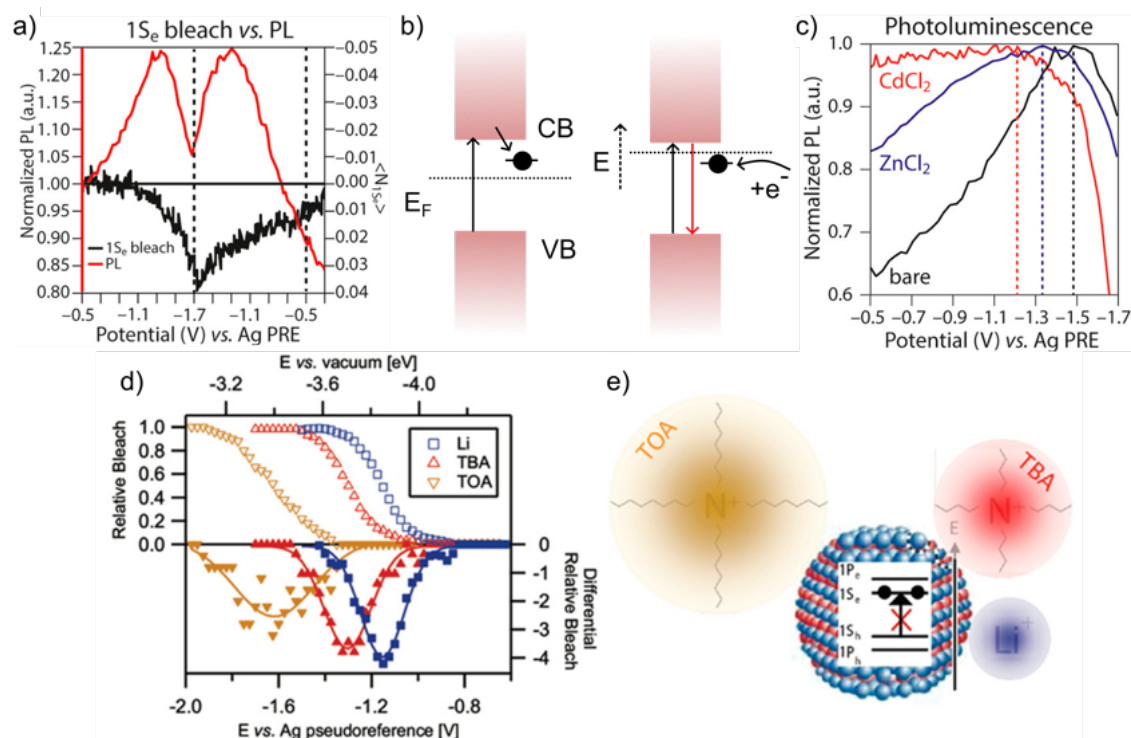


Figure 2.18: SEC on NCs. a) SEC in PL and absorbance ($1S_e$ bleach) on bare CdTe NCs, b) schematic band representation with trap in the band gap of NCs, c) SEC PL after X-type ($ZnCl_2$) and Z-type ($CdCl_2$) ligand passivation on bare CdTe NCs with determination of CB position highlighted by a dashed line, d) SEC in absorbance of CdSe NCs with in different electrolyte solutions, and e) summary of increased $1S_e$ level with increasing counterion size. Panel b) and c) reprinted (adapted) with permission from ref. [216]. Copyright © 2018 American Chemical Society. Panel d) and e) reprinted (adapted) with permission from ref. [217]. Copyright © 2013 American Chemical Society.

In addition, the electrochemical environment can also play an important role during charge injection.²¹⁷ Due to different counterion sizes, the onset of the absorbance bleach can be tuned (see Figure 2.18d).²¹⁷ Hence, charge injection is facilitated for counterions that can be easily brought into close proximity of the NC.²¹⁷ Figure 2.18e shows that a higher potential needs to be applied to observe a bleach of the $1S_e$ level, when large cations TOA^+ and TBA^+ are used compared to Li^+ .²¹⁷ This result has also consequences for ligand chemistry on NCs, when determining the onset potential of VB depopulation and CB population with electrons.

As highlighted in this section, the band edge positions can be determined by this kind of spectroscopy. The energy alignments are of importance for the incorporation into devices (both solar cells and LEDs) as the energetic alignment contributes directly to the efficiency of the devices (as described for LEDs in subsection 2.2.7). Typically, these values can only be obtained by ultra-high vacuum methods, like XPS and UPS.

However, SEC PL is a method resembling a dynamic system and charges are injected coming from the conductive substrate in the device. Therefore, SEC PL bares even in high-resolution the potential of learning about the band edge positions and the charging behavior of the NCs depending on the surface chemistry.

2.3.2.2 High-resolution Spectroelectrochemical Setup

For SEC, the WE has to be a transparent conductive material (ITO or FTO). This conductive substrate is built into a SEC cell, which can be placed either into an absorbance beampath, where the light is transmitted, or it can be placed on top of a confocal laser scanning microscope to measure PL. The SEC cell used in the experiments throughout this work was built by Jonas Hiller in 2021 and is depicted in Figure 2.19a.²¹⁸ The FTO WE is exchangeable since NC films are prepared for their electrochemical investigation. The upper and lower part of the SEC cell therefore require tight sealing by an O-ring. The setup uses an Ag wire as pseudo RE and a Pt coil as CE. The cell bares a microscope cavity on the bottom and can even be used with an oil immersion objective to achieve high resolution.

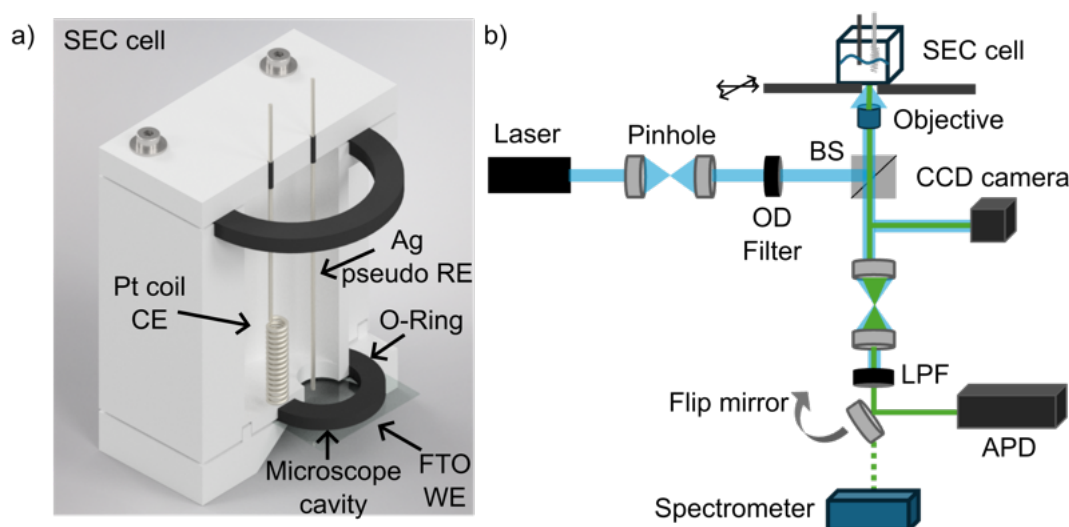


Figure 2.19: Spectroelectrochemical setup at the University of Tübingen. a) SEC cell constructed by Jonas Hiller²¹⁸, and b) high-resolution optical setup for investigating NCs in PL (BS = beamsplitter, OD = optical density, LPF = longpass filter). Panel a) created by Jonas Hiller.

In Figure 2.19b, the confocal optical setup is schematically depicted. The samples are excited by a 405 nm laser, which is focused by a pinhole and the objective onto the substrate. The emitted light passes again a pinhole and can be either directed to a CCD camera for imaging, an APD for high-resolution imaging and time-resolved PL spectroscopy, or to the spectrometer.

The optical resolution limit of the setup is determined by the Rayleigh criterion.²¹⁹ In Equation 2.9, the Rayleigh criterion is applied to determine the horizontal resolution r_{xy} for the used spectroscopic setup. It can be calculated with the numerical aperture of the used objective ($\text{NA} = n \sin \theta$, where n is the refractive index, and θ is the half-angle that exits the lens) and the excitation wavelength λ .

$$r_{xy} = \frac{1.22\lambda}{2n \sin \theta} = \frac{0.61\lambda}{\text{NA}} = \frac{0.61 \cdot 405 \text{ nm}}{0.6} = 411 \text{ nm} \quad (2.9)$$

In Equation 2.10, the vertical resolution r_z is given.

$$r_z = \frac{\lambda n}{(\text{NA})^2} = 1.8 \mu\text{m} \quad (2.10)$$

Additionally, the sample can be moved on a piezo stage, which is giving spatial information on the sample. Due to spatial resolution, larger structures can be imaged depending on the overall optical resolution. The optical resolution in the following experiments is limited by the objective used in the experiments. Here, a long-range objective was employed since the needed working distance was large due to a thick FTO substrate ($d=1.1 \text{ mm}$). A higher optical resolution can be achieved when a glass coverslip ($d=0.15 \text{ mm}$) and a high NA (e.g. $\text{NA}=1.25$) oil immersion objective are used ($r_{xy}=198 \text{ nm}$).

2.3.3 SEC on Perovskite NCs: State of the art

In this cumulative thesis, SEC is performed on LHP NCs. Before describing the results achieved in this thesis, the current state of the art is summarized in this subsection and the main challenges in performing SEC PL on LHP NCs will be introduced.

The first report on SEC on LHPs from 2018 is given by Samu *et al.*²²⁰ SEC in absorbance of CsPbBr_3 and MAPbI_3 thin-films was performed in DCM/TBAHFP.²²⁰ The results are shown in Figure 2.20a and b. The absorbance increases in oxidative scan direction at 0.6 V , while during reduction the absorbance decreases at -1.2 V .²²⁰ In combination with XPS after SEC, the group concluded that electrochemical degradation processes occur in oxidative and reductive direction.²²⁰ In oxidative scan direction, they find fluorination on surface Cs^+ , while in reductive direction Pb^0 can be found.²²⁰ However, the conclusion says that electrochemical n-doping was successful and they established a "safe-zone" for performing electrochemistry on CsPbBr_3 (-1.0 - 0.6 V vs. Ag/AgCl).²²⁰ In the "safe-zone", no decomposition reaction due to electrochemical charging should be occurring.

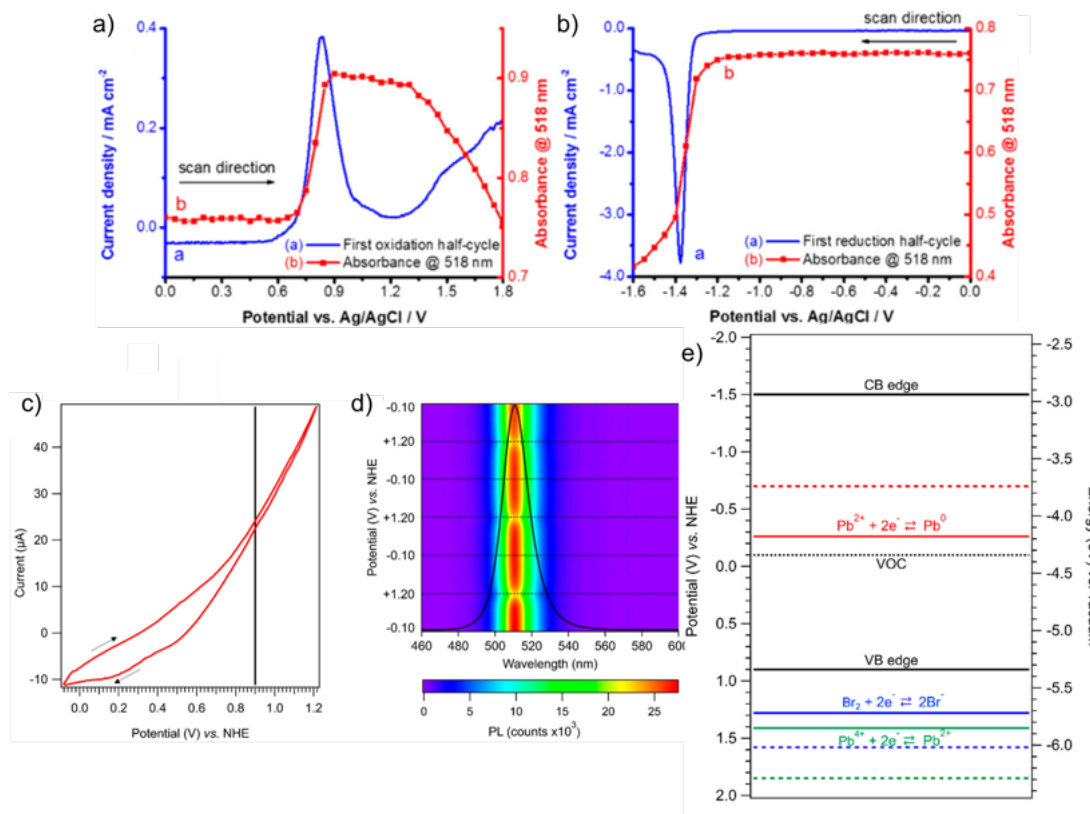


Figure 2.20: State-of-the-art SEC on CsPbBr₃. Upper panels: SEC in absorbance of CsPbBr₃ thin-film by Samu *et al.*, recorded current and first excitonic maximum depending on applied potential a) oxidative scan, and b) reductive scan. Lower panels: SEC PL of CsPbBr₃ NCs by Mulder *et al.* c) CV, d) PL depending on applied potential, and e) determined potentials on the energy scale vs. vacuum and potential scale vs. NHE. Panel a) and b) reprinted (adapted) with permission from ref. [220] Copyright © 2018 American Chemical Society. Panel c), d) and e) reprinted (adapted) with permission from ref. [221] Copyright © 2021 American Chemical Society.

Since LHP NCs are known as being defect-tolerant and the PLQY is even in a defective state high, the prospect of performing PL SEC seemed promising. Mulder *et al.* successfully injected reversibly holes into CsPbBr₃ NCs by SEC in absorbance and PL.²²¹ They could observe a coinciding band edge bleach of the PL and the absorbance, while the current in the CV increased (see Figure 2.20c and d). They also tried electrochemical n-doping. However, this process could not be achieved because Pb²⁺ reduction occurred before the CB could be populated with electrons. Supported with DFT calculations, the in-gap state was confirmed due to this reduction. It is important to point out that this group also found out that the oxidative scan direction is limited by bromide oxidation. The limitations with their

electrochemical potentials are summarized in Figure 2.20e.

Being still interested to know if electrons can be injected into the NCs' CB, the same group took a closer look into the electrochemical stability of the NCs in different solvents.²²² Here, the use of polar solvents was found to be beneficial compared to non-polar solvents.²²² The result is unexpected since the NCs are prone to complete decomposition when exposed to polar solvents.²²² Although there is the risk of complete decomposition, polar solvents shift the equilibrium of the binding strength of the ligands to a bound state, giving the surface a higher stability and reduced ionic mobility.²²² Therefore, propylene carbonate (PC) and TBAHFP are recommended as electrolyte solution.²²²

All three publications highlight the difficulties in performing electrochemical hole or electron injection into LHPs.²²⁰⁻²²² The insulating layer due to shelling by organic ligands, the decomposition reactions limiting the electrochemical window, and the overall long-term stability of the NCs in the electrolyte solution are mentioned in the publications. Still, SEC is a powerful tool for studying charge injection. Therefore, continuing SEC on NCs is promising since SEC data can be correlated to the performance in devices such as LEDs. With the implementation of the SEC cell on top of a high-resolution confocal microscope, additional information can be gained concerning the spatial resolution and highly sensitive spectral information on a small sample size can be achieved.

The current reports lack the consideration of the ligand shell influencing charge injection into LHP NCs, either due to the binding group or due to an electronically changed environment. Within the following work, the considerations by the already published publication are implemented and extended to a thorough analysis of effects introduced by organic ligands on the surface of LHP NCs. Additionally, the effect of electronic coupling of NCs in ordered superstructures during electrochemical hole injection is investigated by using the advantages of spatially resolved mapping.

3 Optimizing Carrier Balance in CsPbBr₃ Nanocrystal LEDs: The Role of Alkyl Ligands and Polar Electron Transport Layers

Roshini Jayabalan¹, Girish K. Hanumantharaju¹, Theresa Hettiger², Arup Sarkar³, Fengshuo Zu⁴, Aladin Ullrich¹, Anna Abfalterer⁵, Alexander S. Urban⁵, Norbert Koch⁴, Denis Andrienko³, Marcus Scheele², and Wolfgang Brütting^{1,*}

1. Institute of Physics, University of Augsburg, 86135 Augsburg, Germany.
2. Institute for Physical und Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany.
3. Max Planck Institute for Polymer Research, 55128 Mainz, Germany.
4. Institute of Physics and IRIS Adlershof, Helmholtz-Zentrum Berlin for Materials und Energy GmbH, 12489 Berlin, Germany.
5. Nanospectroscopy Group, Nano-Institute Munich, Ludwig-Maximilians-Universität München, 80539 München, Germany.

* Corresponding author

Within this chapter, PL SEC was conducted on two different surface ligand systems, namely OA/OAm and DDABr, with two ligand densities surrounding the NCs after one and two washing steps. The comparison of the recorded PL SEC data reveals that hole injection into DDABr covered NCs is facilitated compared to OA/OAm independent of the ligand density on the NCs.

The results of this chapter are published in ref. [45].

Reprinted (adapted) with permission from Adv. Optical Mater. 13, no. 28 (2025). Copyright © 2025 Wiley-VCH GmbH. The publication is licensed under Creative Commons-BY 4.0 License.

3.1 Abstract

The study of lead halide perovskite nanocrystal based light-emitting diodes (LEDs) has advanced significantly, with notable improvements in stability and optical properties. However, optimizing charge carrier injection and transport remains a challenge. Efficient electroluminescence requires a balanced transport of both holes and electrons within the emitting material. Here, cubic CsPbBr₃ nanocrystals passivated with oleylamine and oleic acid are investigated, comparing them to ligand-exchanged nanocrystals with didodecyldimethylammonium bromide (DDABr). Nuclear magnetic resonance spectroscopy and transmission electron microscopy confirm successful ligand exchange, revealing reduced ligand coverage in DDABr-treated nanocrystals. Photoelectron spectroscopy, spectroelectrochemistry, and single-carrier devices indicate improved hole injection in DDABr-capped nanocrystals. Density functional theory calculations further reveal the influence of ligand type and coverage on energy levels, with oleic acid introducing localized states in native nanocrystals. Additionally, incorporation of a polar electron transport layer enhances LED performance by over an order of magnitude in DDABr-capped nanocrystals, driven by improved charge balance arising from the spontaneous orientation polarization of the electron transport layer. These findings highlight the critical role of ligand selection, passivation degree, and charge transport control by the adjacent organic transport layers in optimizing LED efficiency.

3.2 Introduction

Lead halide perovskite nanocrystals (LHP-NCs) have gained significant attention in the field of optoelectronics due to their extraordinary optical and electronic properties, which make them highly promising candidates for light-emitting applications, particularly in perovskite-based light-emitting diodes (PeLEDs).²⁹ The typical composition of these materials is denoted by the formula ABX₃, where A is an organic or inorganic monovalent cation (e.g., methylammonium (MA⁺), formamidinium (FA⁺), or cesium (Cs⁺)), B is a divalent metal cation (typically lead, Pb²⁺), and X is a halide anion (Cl⁻, Br⁻, or I⁻). By varying the halide composition, the emission wavelength of LHP-NCs can be precisely tuned across the entire visible spectrum. This flexibility makes them attractive for full-color displays with narrow emission linewidths (full-width at half-maximum, (FWHM) of less than 20 nm), providing high color purity while exhibiting high photoluminescence quantum yield (PLQY) close to unity.²⁹

One of the key advantages of LHP-NCs is their solution-based colloidal synthesis,

which allows for low-cost, scalable manufacturing methods like spin-coating or inkjet printing.^{223–225} This positions them as an alternative to other materials like organic emitters²²⁶ and quantum dots (QDs)²²⁷, which often require more complex or expensive deposition and synthesis techniques. Another attractive property of LHP-NCs is their defect tolerance.²²⁸ Their ability to maintain high PLQYs despite the presence of crystal defects reduces the need for extensive defect engineering, which is often required in other semiconductors like II-VI quantum dots or III-V materials.^{227,229} These properties make LHP-NCs highly attractive for next-generation displays, lighting, and lasers, as well as other optoelectronic applications. However, despite their outstanding properties, there are still several challenges that must be addressed to fully realize their application potential.^{40,230}

A significant bottleneck in leveraging LHP-NCs for device applications lies in their imbalanced charge transport characteristics. Efficient charge injection in LHP-NC-based devices is often hindered by the insulating nature of the long alkyl chain ligands typically oleylamine (OAm) and oleic acid (OA) used during synthesis (Figure 3.1a,b). These ligands not only act as capping agents and aid precursor dissolution for colloidal NC formation,¹²⁶ but their structural features such as the bent conformation of oleic acid due to the cis-double bond at the 9th carbon reduce van der Waals interactions among hydrocarbon chains, enhancing NC dispersibility and influencing their morphology and size.^{37,40,231}

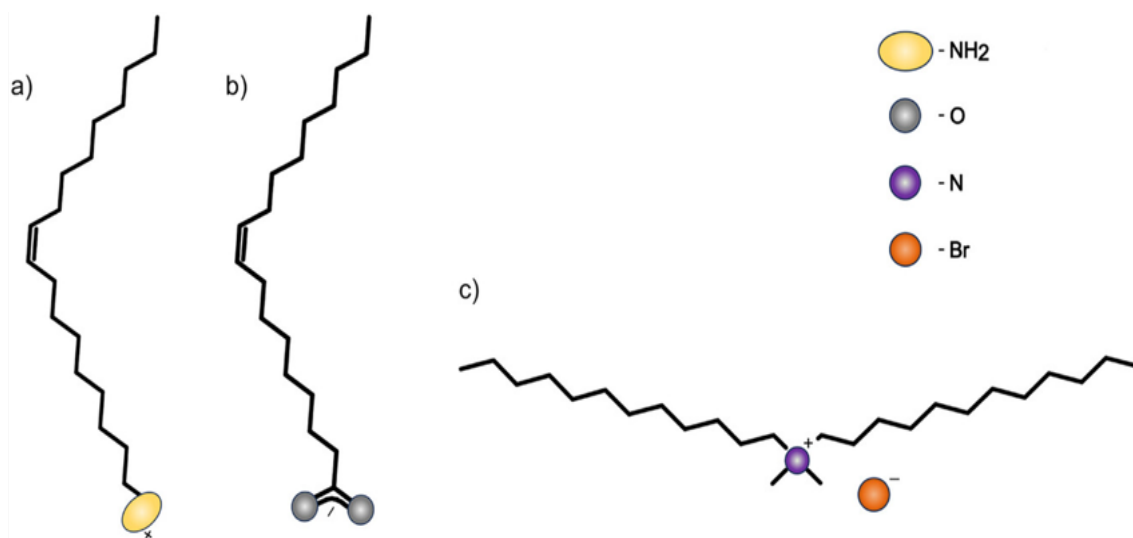


Figure 3.1: Schematic of a) oleylamine, b) oleic acid, and c) didodecyldimethylammonium bromide (DDABr).

While these long-chain ligands ensure colloidal stability and support high PLQY, they simultaneously impede charge transport in PeLEDs. Additionally, the inherent imbalance between electron and hole transport can further reduce PeLED efficiency,

likely due to enhanced Auger recombination losses.²³² One promising strategy to address these limitations involves ligand exchange, which directly tunes the optoelectronic properties of the NCs.⁴⁰ This typically entails replacing insulating ligands with shorter or more conductive alternatives,²³¹ or introducing multidentate and zwitterionic ligands to strengthen surface binding.⁴¹ Although parameters like alkyl chain length and ligand coverage have been systematically investigated for their effects on PeLED performance,^{162,233} the specific role of the ligand's anchoring group remains comparatively underexplored.

Didodecyldimethylammonium bromide (DDABr) (Figure 3.1c) has emerged as one of the most promising candidates for ligand exchange in LHP-NCs for LED applications.²³⁴ DDABr is a quaternary ammonium salt with a bromide anion (Br^-) and a large organic cation (DDA^+) that offers multiple advantages in surface passivation and device performance. For example, the Br^- anion can fill halide vacancies in the perovskite structure, reducing surface defects that would otherwise lead to non-radiative recombination and lower PLQY, while the double alkyl chains of DDA^+ cations provide steric protection to the perovskite NCs,^{40,235} preventing them from aggregating and maintaining colloidal stability. The length of the carbon chain is reduced in comparison to OA/OAm, implying a potentially closer packing of NCs with improved charge transport. In addition to this, several reports suggest an improved operational stability and higher efficiency in PeLEDs while employing DDABr ligands onto their NCs.^{157,234,236–239}

In this work, we address the importance of the anchoring group in these alkyl ligands attaching to the NC surface and its effect on carrier injection and transport in PeLEDs. Specifically, we investigate changes in film morphology, electronic properties and carrier transport following ligand exchange on “native”, i.e., CsPbBr_3 NCs originally capped with OA and OAm, and comparing them to DDABr-exchanged NCs. Quantification on the ligand coverage, the NC packing and electrical accessibility of the NCs is supported by transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) spectroscopy and spectroelectrochemistry. The origin for the enhanced performance in PeLEDs with DDABr capped NCs is revealed by photoelectron spectroscopy and single carrier devices in combination with density functional theory (DFT) studies providing insights into the ligands' influence on the electronic properties of the NCs. In addition to ligand influence, the impact of spontaneous orientation polarization (SOP), particularly when using electron transport layers (ETLs) with a significant permanent dipole moment, further improves charge carrier balance in PeLEDs.

3.3 Results and Discussion

3.3.1 Ligand Exchange and Film Morphology

The as-received native colloidal NC suspensions incorporate X-type OA and L-type OAm ligands (Figure 3.1a,b) as passivating molecules.²⁴⁰ As mentioned earlier, although long alkyl ligands are essential for colloidal stability, they are not favorable for charge injection. Despite various proposed mechanisms on the binding of OA and OAm ligands, it is established that they bind only weakly and are highly dynamic.⁴⁰ As a result, these ligands can easily detach from the surface, compromising colloidal stability. In contrast, DDABr (Figure 3.1c), with its shorter alkyl chains, significantly improves colloidal stability by simultaneously exchanging anionic and cationic sites on the NC surface.^{40,235} A detailed description on ligand exchange and film fabrication processes is provided in the Experimental section.

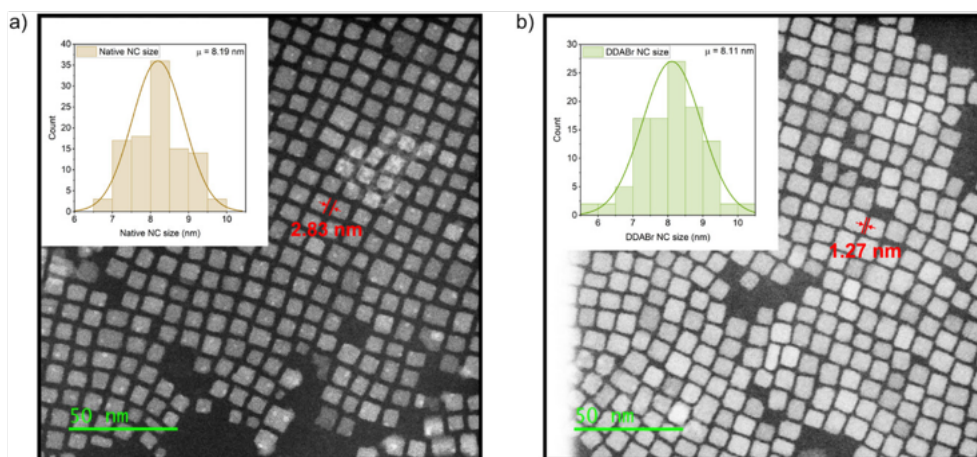


Figure 3.2: TEM image of a) OA/OAm covered NCs and b) DDABr covered NCs with size distribution as inset.

Transmission electron microscopy images of both the native and ligand-exchanged NCs are presented in Figure 3.2a,b. Although some etching of the NCs during ligand exchange was expected,^{235,241} these images show that the size distribution of the ligand-exchanged NCs remains largely unchanged compared to the native system, with an average NC size of approximately 8 nm in both cases. However, the inter-particle distance in the ligand-exchanged system is more than halved relative to the native NCs, from about 2.8 to 1.3 nm. This reduction in inter-particle distance could be attributed to two factors. First, the ligand exchange process includes intermittent washing steps which remove a significant portion of the surface ligands, resulting in partial coverage by DDABr only (see Experimental section for further information). Second, the two aliphatic tails of the DDABr ligands may adopt a

conformation in which they lie nearly parallel to the NC surface, further reducing inter-particle spacing. This reduced spacing enhances electronic coupling between NCs, which is advantageous for charge transport, however, in the next section, we shall discuss that this improvement mostly affects the positive carriers, i.e., holes only.

To confirm the exchange of the organic ligand shell, ^1H NMR spectroscopy was performed. Figure 3.3 shows a comparison of the spectra of native NCs covered with OA/OAm, DDABr-covered NCs and DDABr alone in toluene- d_8 . The spectra display the disappearance of the alkene protons of OA/OAm at approximately 5.5 ppm (marked by $\times$) for DDABr NCs. In addition, a signal at 4 ppm arises in the exchanged sample, which can be assigned to the protons at the methyl groups of DDABr (marked by *).^{35,235} This signal shows a peak broadening and a downfield shift which is consistent with a DDABr species bound to NCs. Both of these determined signals indicate a successful ligand exchange from OA/OAm to DDABr. Further investigations by quantitative-NMR (qNMR) spectroscopy (see Figure 3.11, Supporting Information) on the ligand coverage indicate about 226 ligands/NC for DDABr NCs after two washing steps.

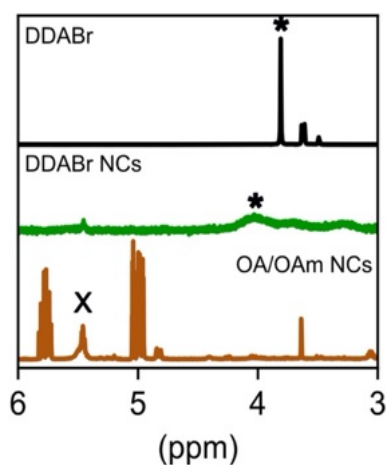


Figure 3.3: ^1H NMR spectra (in toluene- d_8) of DDABr as reference (black), ligand exchanged DDABr-covered NCs (green) and native OA/OAm NCs (brown).

Additionally, PLQY and time resolved photoluminescence (TRPL) measurements were performed on the native and ligand exchanged samples in solution as well as thin films (see Supporting Information, Table 3.1, Table 3.2, Table 3.3 and Figure 3.12). Since the ligand exchange strategy was inspired from the approach of Dai *et al.*,¹⁶² particular care was taken to avoid damaging or etching the NC surfaces during processing. The consistently high solution-state PLQY values of about 88% for

both samples confirm that the ligand exchange preserves the structural and optical integrity of the nanocrystals. For thin-film samples we observe a decrease to about 55 % for the native NCs, while the value for DDABr-exchanged NCs is significantly lower, most likely due to the effect of ambient exposure of these samples, as discussed in the Supporting Information. Analysis of the PL decay curves indicates longer exciton lifetime for DDABr-ligand exchanged NCs in solution (see Supporting Information, Table 3.2 and Figure 3.12). However, since PLQY remains basically unchanged, both the non-radiative and radiative rates decrease to some extent. For thin films we find shorter PL lifetimes than in solution, with the values for DDABr ligands again being probably affected by ambient exposure.

3.3.2 Electronic Properties

3.3.2.1 Spectro-Electrochemistry

One way to investigate the absolute band edge positions of NCs is by spectro-electrochemistry (SEC).^{220,221,242} The basic idea is that by electrochemical charge injection into the NCs, their PL intensity decreases, which can be monitored simultaneously by optical spectroscopy. In this work, the valence band (VB) position of OA/OAm and DDABr capped NCs has been studied by SEC in the oxidative regime. Additionally, the effect of varying ligand coverage on the NC surface has been investigated, since ligand stripping was reported to improve the performance of NC LEDs.¹⁶²

An exemplary measurement of DDABr capped NCs after one washing step is shown in Figure 3.4a–d. SEC-PL measurements are conducted with a potential scan of 2 mV/s in a propylene carbonate/tetrabutylammonium hexafluorophosphate solution (PC/TBAHFP) against a Ag pseudo-reference electrode (Ag PRE). Before applying a potential to the samples, photobleaching of the sample due to laser power is determined, with detailed information in the Supporting Information (Figure 3.13). Cyclic voltammetry in the oxidative direction (Figure 3.4a) displays a current increase starting at 0.75 V, indicating the oxidation of NCs, i.e., electron transfer from the NC to the working electrode, followed by a potential sweep reversing at 1.2 V. The PL spectra is recorded under applied bias in steps of 2 mV, and is depicted as a heat map in Figure 3.4b. From the PL intensity over the applied bias (Figure 3.4c), a PL decay at the oxidation potential is observed. Thereafter, a partial recovery of PL is observed as the potential returns to the initial value. Spectral slices at the oxidation onset and the switching potential reveal a slight red shift of the oxidized NCs (Figure 3.4d). These measurements were also performed on twice washed DDABr capped NCs and

the native, i.e., OA/OAm capped NCs, also for single and doubly washed samples (Figure 3.15, Figure 3.16, and Figure 3.17).

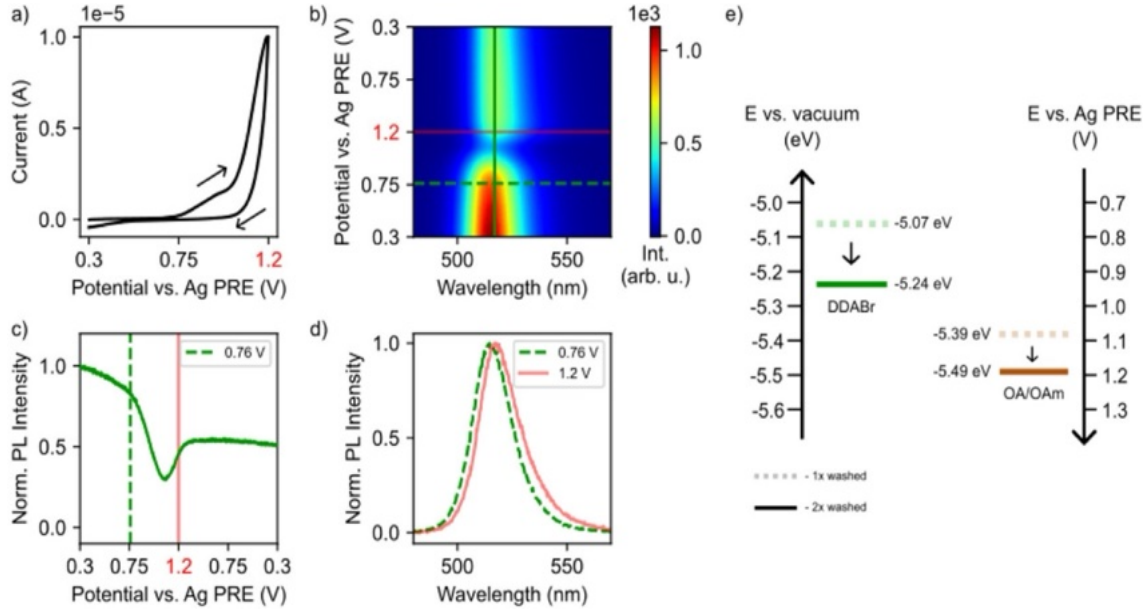


Figure 3.4: Exemplary spectro-electrochemistry measurement on DDABr-capped CsPbBr₃ NCs (after one washing step). a) Cyclic voltammetry scan measured at a scan speed of 2 mV/s in PC/TBAHFP (0.1 M) with arrows indicating the scan direction. b) Potential-dependent PL spectra with marked onset potentials of the oxidation (green dashed line) and the switching potential (red solid line). c) Normalized potential-dependent PL intensity at the emission peak extracted from b). d) Spectra slices at the oxidation potential and switching potential extracted from b). e) Graphical summary of the results for native and DDABr capped NCs after one and two washing steps.

Finally, Figure 3.4e summarizes the oxidation potentials determined for the four samples referenced to a ferrocene/ferrocenium redox couple (Figure 3.14, Supporting Information) and to the vacuum scale. The obtained values are in good agreement for the VB edge position in the range of -5.07 eV to -5.5 eV vs. vacuum, in comparison with previous work by Mulder *et al.*²²¹ Overall, two trends can be deduced from this data. First, washing leads to a decrease in the VB onset potential by approximately 0.17 eV for DDABr-exchanged NCs and 0.1 eV for native NCs. Second, DDABr shifts the VB edge by approximately 0.3 eV toward the vacuum level compared to OA/OAm at similar ligand densities. It is to be noted that the DDABr once-washed samples (with their VB energy at -5.07 eV relative to the vacuum level) have been used further on throughout the remainder of this work.

3.3.2.2 Photoelectron Spectroscopy

To gain deeper insight into the energy levels of CsPbBr₃ NCs before and after ligand exchange, photoelectron spectroscopy (PES) was conducted on thin films used in PeLEDs. NC films were deposited on ITO/PEDOT:PSS substrates coated with PTAA (Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]), which serves as the hole transport layer (HTL) in PeLEDs. Ultraviolet photoelectron spectroscopy (UPS) was used to determine the energy level alignment at the PTAA/NC interface. As shown in Figure 3.5a (upper panel), the VB onset appears at 0.28 eV for PTAA, 0.65 eV for native NCs and 0.38 eV for DDABr-capped NCs. The secondary electron cutoff, i.e., the work function (Figure 3.5a, lower panel) indicates a slight vacuum level shift for native NCs. The corresponding energy level alignment depicted in Figure 3.5b and reveals a significantly reduced hole injection barrier of only about 0.1 eV from PTAA into the NCs for DDABr ligands, while the barrier is almost 0.4 eV for native NCs.

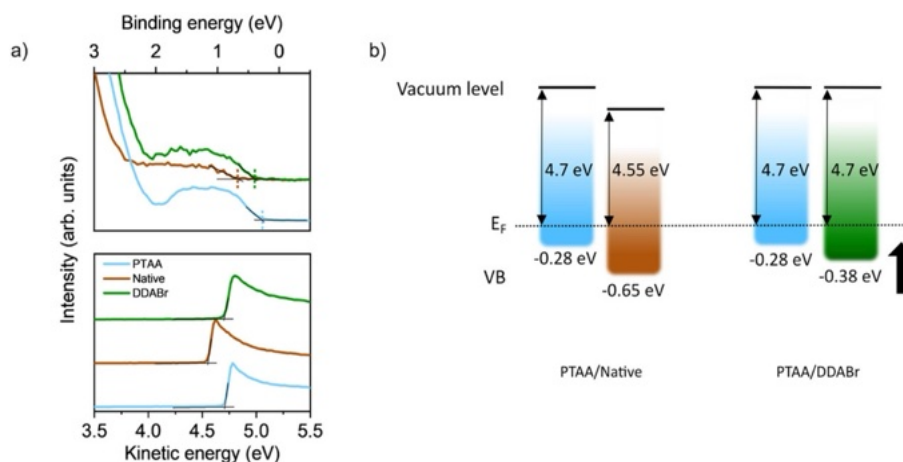


Figure 3.5: UPS data on native (brown) and DDABr capped NCs (green) spincoated on PTAA-covered ITO/PEDOT:PSS substrates (blue). a) Valence band (top) and secondary electron cut-off (bottom) spectra. b) Schematic representation of energy level alignment obtained from UPS data.

X-ray photoelectron spectroscopy (XPS) further confirmed the chemical composition of both NC systems. Survey spectra (Figure 3.18, Supporting Information) show an increased photoelectron signal from perovskite core levels (Cs 3d, Pb 4f, Br 3d) relative to C 1s in DDABr NCs, indicating successful ligand exchange. Quantitative XPS analysis (Figure 3.19 and Table 3.4, Supporting Information) reveals a Br/Pb ratio increase from 1.85 (native NCs) to 2.57 (DDABr NCs), suggesting halide vacancies in native NCs, which are subsequently filled by Br⁻ ions during ligand exchange. These vacancies introduce n-type defect states,²⁴³ which likely contribute to the observed energy-level shifts.

3.3.2.3 Single-carrier Devices

A persistent challenge in PeLEDs that have native NCs as emitter system is the imbalance in carrier transport, particularly, poor hole transport.²⁴⁴ In this regard, single-carrier devices were fabricated to assess the hole and electron transport in both the native and ligand-exchanged NC systems. Figure 3.6 illustrates the hole-only (hollow circles) and electron-only (filled circles) devices for the native and ligand exchanged systems. The analysis uses simple power-law dependencies of current density (j) on the applied voltage (V), which are characteristic for different transport regimes.²⁴⁵

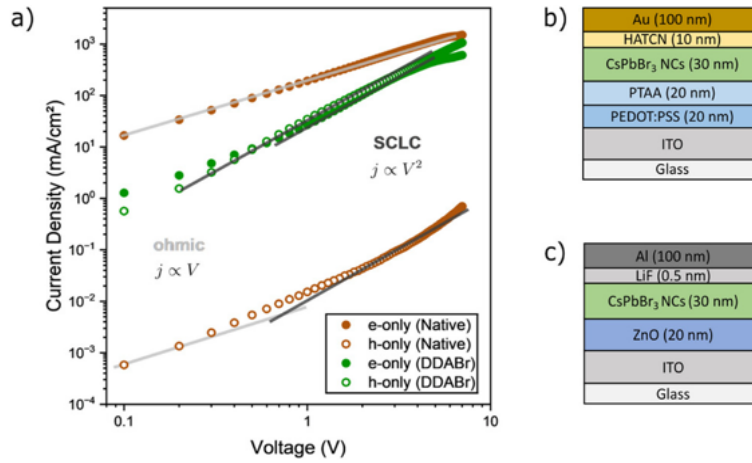


Figure 3.6: a) Current density vs. voltage characteristics of single-carrier hole-only (hollow circles) and electron-only (filled circles) devices with native and DDABr-capped NCs. Device stack of b) hole-only and c) electron only devices.

A first examination of the native system (brown color) reveals a high electron current with an ohmic dependence on voltage, indicating low resistance in electron conduction through the native system. In contrast, the hole current is extremely low, about four orders of magnitude lower than the electron current, and follows an almost quadratic dependence on voltage, which is typical for space charge-limited conduction (SCLC) according to the relation, $j_{\text{SCLC}} = (9/8) \epsilon \epsilon_0 \mu \times (V^2/d^3)$. With a NC layer thickness of $d = 30$ nm and a dielectric constant of $\epsilon = 7$,²⁴⁶ the hole mobility μ was determined to be approximately $6.5 \times 10^{-10} \text{ cm}^2/\text{Vs}$. Note that due to the absence of SCLC, electron mobility could not be reliably estimated for the native NC system. However, DDABr-capped NCs exhibit a more balanced carrier transport (green color), with a significantly improved hole current compared to the native system. Based on the observed SCLC behavior, the hole and electron mobilities are estimated at approximately $2.1 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and $1.5 \times 10^{-6} \text{ cm}^2/\text{Vs}$, respectively. Notably, the hole mobility increases by more than three orders of magnitude after

ligand exchange, providing strong evidence of enhanced hole injection and transport in DDABr-exchanged NCs.

3.3.3 DFT Calculations

Density functional theory calculations were carried out using the CP2K software package²⁴⁷ (version 9.1) to understand the electronic structure of native NCs and the effect of the various ligands on the frontier molecular orbitals, i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which corresponds to VB and conduction band (CB), respectively. First, a neutral cubic model of CsPbBr₃ containing 189 atoms (Cs₅₄Pb₂₇Br₁₀₈) possessing a dimension of 1.7 nm was chosen with the Cs-Br terminated surface or facet to begin the calculation on a bare NC¹⁴² – see Figure 3.7. Numerous experimental and theoretical reports support the fact that the Cs-Br terminated surface is the commonly exposed surface rather than the Pb-Br facet.^{107,142,152,248,249} Furthermore, the anion/lead ratio (Br/Pb) was fixed at 4.0 for this composition of the NC, which is the upper bound and somewhat overestimated compared to the commonly encountered ratio of 2.7-3.3.¹⁴² At this geometry and composition, the bare NC exhibited a bandgap of 2.69 eV (also denoted as HOMO-LUMO gap in the following), which is a little larger than the experimental value of 2.3 eV. This discrepancy can be attributed to the size chosen for the bare perovskite NC, (which was minimized to reduce computational cost), as well as the use of the PBE functional in DFT calculations, which inherently involves a trade-off, balancing the accuracy of the HOMO-LUMO gap estimation. This has also been encountered in previous reports on electronic structure determination of cubic NCs.^{107,142,152,248} As expected, the VB (or HOMO) states are dominated by the halide (Br) 4p-orbitals and the CB (or LUMO) states consist of virtual or anti-bonding p-orbitals from both Pb and Br atoms (see Figure 3.7, bottom row, partial density of states (PDOS)).

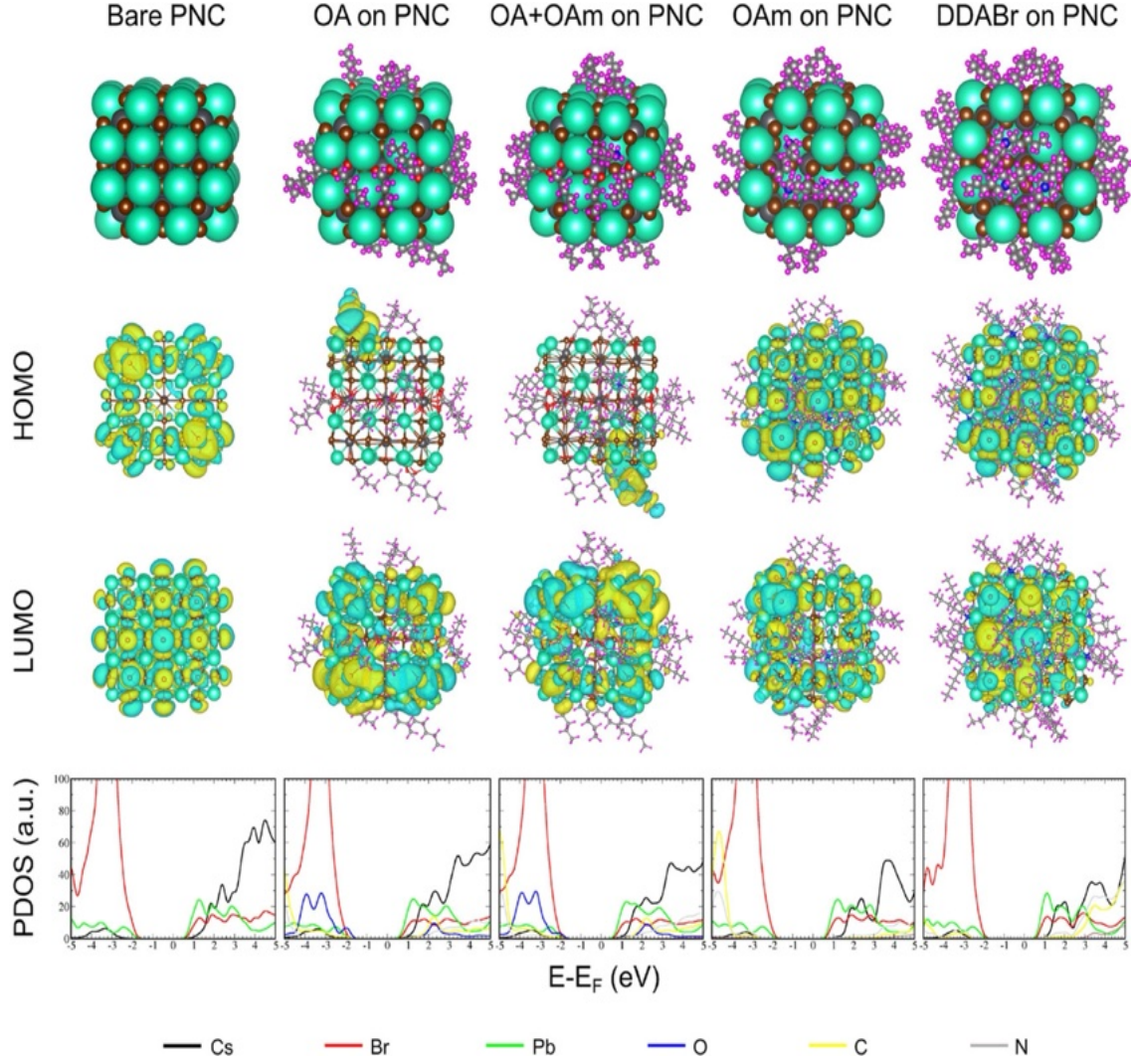


Figure 3.7: Schematic representation of the bare perovskite NC (PNC) along with the various ligands attached to the surface. Top row from left to right represent the space-filling model of the bare NC, a NC with 18 hexanoates (mimicking OA), a NC with 18 OA and one hexylammonium (mimicking OAm), a NC with 18 OAm and, finally, a NC with 18 dihexylammonium (mimicking DDABr). Second and third rows from left to right represents the PBE-D3 computed HOMO and LUMO, respectively, of the corresponding species shown at the top. (Color code: Cs- light green; Pb- dark grey; Br- brown; O- red, N- blue; H-light pink and C- light grey.) Bottom row from left to right represents the PDOS calculated from the frontier molecular orbitals with the contributions of the different atoms labeled in different colors as given below the graph.

In the next step, the ligands under study, namely, OA, OAm and DDABr were successively attached at the NC surface in all six directions ($\pm x$, $\pm y$ and $\pm z$) to understand their effect on the frontier molecular orbitals and the density of states. To reduce the computational cost and allow for efficient attachment of the

ligands onto the NC surface, the large chain lengths were reduced to six-numbered carbon-containing ligands for all the cases.¹⁰⁷ Hexanoate ligands were added to the Cs–Br facet of the NC successively by removing bromide anions one by one from each side of the NC. In every case, the charge neutrality of the entire system was maintained. In the case of oleate ligands, irrespective of their density around the NC, ligand-centered HOMO or localized states were observed, which are also seen as trap states in the valence region of the partial density of states (Figure 3.7, OA on PNC). Depicted as blue curves on the PDOS plot, these trap states are dominated by the carboxylic oxygen-centered p- and/or π -orbitals. These trap states are present even when a combination of OA and OAm ligands are attached to the Cs–Br surfaces of the NC (Figure 3.7, OA + OAm on PNC). However, when the ligands that are attached to the surface are either OAm only or DDABr ligands, no ligand-centered trap states were observed in the PDOS of the valence region and the HOMO is delocalized over the entire NC (Figure 3.7, OAm on PNC / DDABr on PNC).

Furthermore, DFT calculations have also been performed at moderate and excess concentrations of ligands. The obtained absolute energies of the frontier molecular orbitals are plotted in Figure 3.8. It can be seen that oleates or, particularly, the carboxylate oxygen create hole trap states in between the usual Br and Pb-centered HOMOs and LUMOs. On the contrary, this trap (or ligand-centric HOMO) is absent in the case of OAm or DDABr ligands. Notably, the energy gap increases when these ligands are attached to the NC. Very importantly, in the case of the DDABr, the HOMO is lifted in energy compared to the OA/OAm bound NCs, in agreement with the SEC and UPS measurements. In order to investigate the origin of trap states, the nature of the binding mode of oleate ligands to the NC surface was examined. A similar kind of study²⁵⁰ has already been performed on CdSe QDs, where oleate binding on different facets of CdSe QDs could result in the occurrence of trap states.^{250,251} By contrast, NCs are cubic and therefore have equivalent facets on all sides. The only difference that could arise is to which atom the oleate binds, i.e., Pb^{2+} or Cs^+ , which depends on the termination of the surface and defects. To generate models for binding the anionic ligands such as oleate to the NC surface, anion vacancies were created by removing bromide anions from the surface. Here, two different scenarios were considered that can both represent the oleate passivated surface but, concurrently, show two completely different binding modes. In Figure S10 (Supporting Information), the two different modes of binding of oleate ligands are shown. In one case, two carboxylate groups are directly coordinated to Cs^+ ions (Figure S10a,b, Supporting Information), whereas in the other case, all the carboxylate oxygen(s) are directly coordinated to a Pb^{2+} ion (Figure 3.20c,d

Supporting Information). It is to be noted here that both possibilities generate a charge-neutral cluster model in order to accommodate the oleate group. Interestingly, these two scenarios produce quite different natures of HOMOs. In one case, the HOMO is ligand or oleate centric, whereas, in the other case, the HOMO consists of the usual bromide-based molecular orbitals. The former possibility is more likely to occur experimentally as it is already known that the Cs-Br surface termination is more probable as the NC size increases. Since commercial NCs have been used in this work, it is difficult to comment on the amount of ligands on the surface and the exact composition of the NCs. However, it is clear that the presence of OA impedes carrier injection into the NC as well as inter-particle transport, in particular, for holes.

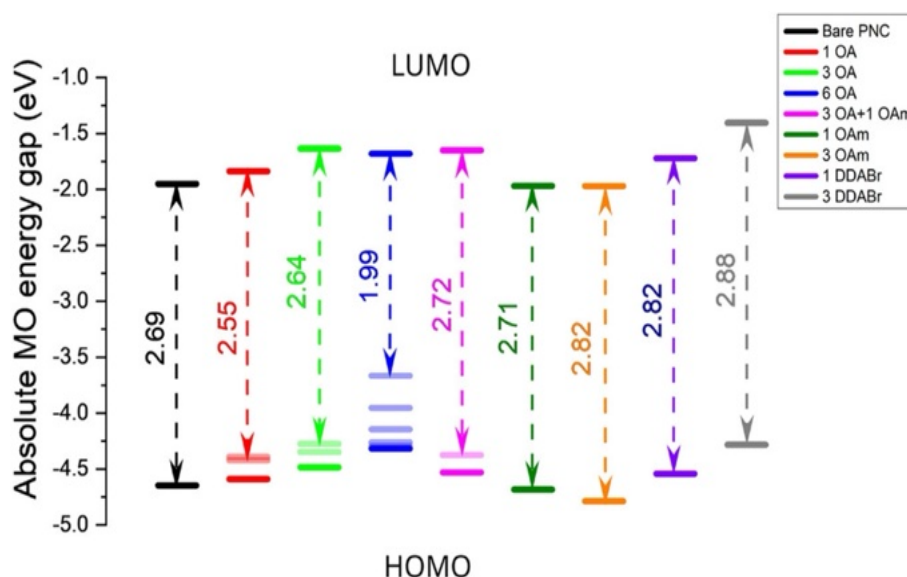


Figure 3.8: PBE-D3 computed frontier molecular orbital energies of perovskite NCs bonded with the various quantities of ligands per facet. The transparent levels represent the ligand-centric hole trap states. OA - Oleate (hexanoate); OAm - oleylammonium (hexylammonium); DDABr - di-hexylammonium ligands.

3.3.4 PeLEDs

A major challenge in achieving efficient LEDs based on native CsPbBr₃ NCs is their inefficient hole injection, resulting in imbalanced carrier transport, and subsequently excited-state quenching by Auger-like recombination. This leads to low efficiency and pronounced efficiency roll-off at higher currents, as demonstrated in our previous study on LiTFSI-doped NCs.²⁴⁴ Based on our findings so far, ligand exchange with DDABr is expected to mitigate this issue by reducing the hole injection barrier and achieving balanced carrier mobility. However, successful LED fabrication also

requires appropriate (organic) transport layers as highlighted by some recent studies on PeLEDs.^{252,253} As a first step, PTAA was chosen as the HTL due to its superior hole mobility compared to PVK [Poly(9-vinylcarbazole)]. Additionally, the role of the ETL must be considered, as it not only facilitates electron transport and injection into the NCs but also functions as an optical spacer, enhancing light outcoupling, similar to its role in organic LEDs.¹⁹⁶

Commonly used materials in PeLEDs include B3PyMPM (4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine) and TPBi [2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)], to name two prototypical materials. While these materials exhibit different energy levels and electron mobilities, their most significant difference is often overlooked in the context of PeLEDs. TPBi, owing to its notable permanent dipole moment, tends to exhibit SOP upon evaporation, which in turn induces a non-vanishing electric field across the organic film, also known as giant surface potential (GSP).^{254,255} The direction of this field hampers electron flow through the ETL at low applied voltages, while simultaneously promoting hole injection and accumulation at the HTL/emitter interface even before the device reaches its turn-on voltage.

Figure 3.9a illustrates the current (density)-voltage-luminance (jVL) characteristics of native NC PeLEDs employing B3PyMPM, a non-polar ETL exhibiting almost no GSP, and TPBi as polar ETL. Details on the LED fabrication process can be found in the Experimental section. The native PeLED with the non-polar ETL (yellow) exhibits a lower turn-on voltage (V_{on}) at about 1.7 V, however, the luminance onset is at a higher voltage of about 2.2 V. This is an indication of imbalanced carrier injection, i.e., the current is dominated by one carrier type, while luminance sets in later when the second carrier type is injected. Correspondingly, the external quantum efficiency (EQE) shown in Figure 3.9b is rather low (in the $10^{-1}\%$ range) and exhibits a strong dependence on the current density itself with a maximum in the range of 10^{-1} - 10^{-2} mA/cm². Such carrier density dependent behavior is typical for a competition of different processes, like trap-assisted recombination, bimolecular recombination and Auger quenching.²³²

In the case of native PeLED employing the polar ETL (brown), an obvious shift in the current onset (V_{on}) to about 2.4 V is seen; however, the luminance onset is only slightly higher at 2.7 V. The higher V_{on} arises from the GSP of the polar ETL, which has to be overcome before electrons can flow through the ETL. The GSP value of TPBi on native NCs is about 112 mV/nm (see Figure 3.21, Supporting Information), which is two times higher than the reported values in organic devices.²⁵⁵ Importantly, the native TPBi PeLED reaches a significantly higher EQE of almost 1%, specifically at very low current density of 10^{-3} mA/cm². This is again a direct consequence of

the GSP in the TPBi ETL, which leads to hole accumulation in the HTL prior to reaching the turn-on voltage (Figure 3.9c), similar to OLEDs, where this process is well established.²⁵⁴ This means that carrier balance is improved by this sub-turn-on hole accumulation, but with increasing current this advantage disappears and the EQE of the native TPBi device also drops significantly. Finally, both devices (native B3PyMPM and TPBi) reach the same maximum luminance of about 200 cd/m² at 7 V.

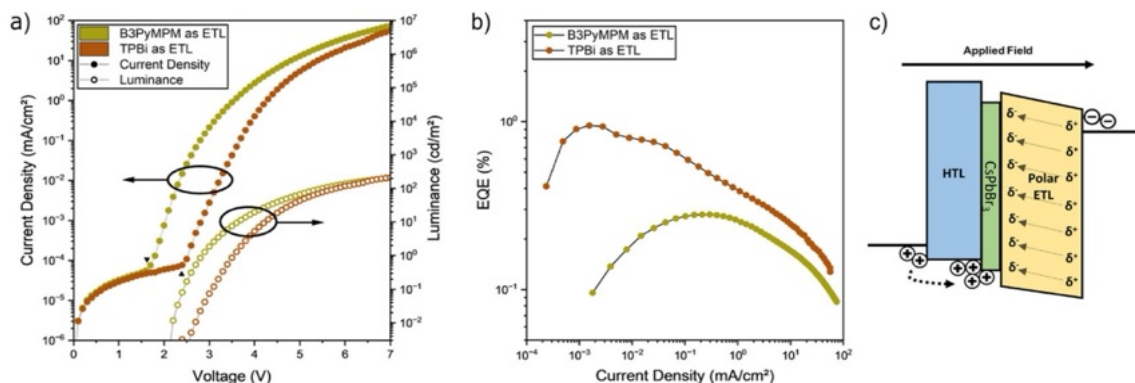


Figure 3.9: a) jVL and b) EQE vs. current density plots of native PeLEDs comparing the performance of TPBi (polar) and B3PyMPM (non-polar) as ETLs. c) Schematic representation of hole accumulation before V_{on} due to SOP in the polar ETL.

In order to improve charge injection, the native NCs were washed with ethyl acetate once and LEDs utilizing TPBi have been fabricated (Figure 3.22, Supporting Information). These LEDs exhibited a higher current density in comparison to unwashed NCs with slightly improved luminance of about 400 cd/m² at 7 V. However, they demonstrated a similar trend with EQE against current density with a peak EQE at the beginning of about 2.3%, followed by a roll-off at higher current densities. Despite the improved EQE achieved with TPBi as the ETL, the native NC PeLEDs continue to face challenges, including a relatively large hole injection barrier between the PTAA HTL and the native NCs (as evidenced by the SEC and UPS data presented before). Additionally, hole trap formation as a result of the binding of OA ligands to the NC surface remains an issue (as indicated by the DFT calculations).

To address these concerns, we proceeded to fabricate PeLEDs using NCs with DDABr-ligand exchange and the polar TPBi ETL. Figure 3.10a presents the jVL characteristics of native and DDABr-ligand exchanged NC PeLEDs in comparison. DDABr NC LEDs demonstrate similar V_{on} as the native NC LEDs at around 2.3 V (with a GSP value of TPBi at 126.8 mV/nm, see Figure 3.21, Supporting Information) and luminance onset at about 2.6 V. However, they reach higher luminance, with

peak brightness close to 1000 cd/m^2 at 7 V, at a reduced current density. This directly translates to an improved EQE (Figure 3.10b) of up to 4%. Most importantly, this high EQE is preserved over a broad range of current densities, which is a clear indication to a balanced carrier injection and recombination in the case of DDABr-capped NC PeLEDs. Note that the achieved EQEs are in good agreement with the results published by Dai *et al.*¹⁶² on a similar PeLED stack.

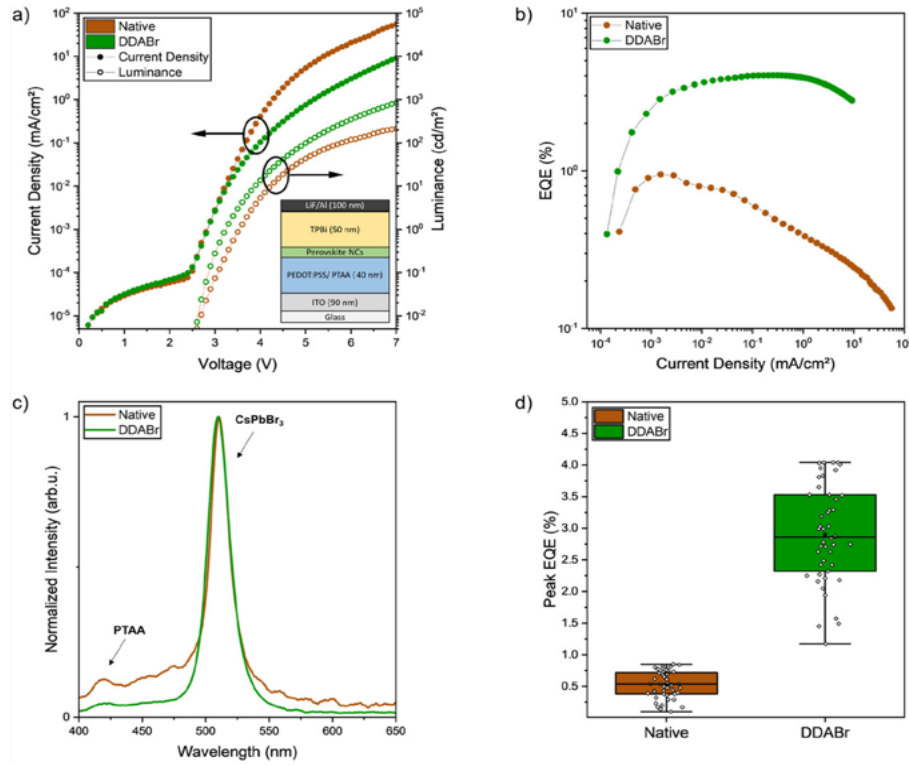


Figure 3.10: a) JVL curves (with device stack represented as inset image), b) EQE vs. current density, c) EL spectra, and d) reproducibility statistics of native and DDABr PeLEDs.

Both native and DDABr ligand-exchanged devices exhibit electroluminescence (EL) with a peak emission at 513 nm and a full-width at half-maximum of approximately 17 nm (Figure 3.10c). However, the native NCs show an additional weak emission centered around 425 nm, which is attributed to some parasitic emission from the PTAA layer. This suggests that in the case of native NCs, the large excess electron current is partially injected into the HTL and recombines with holes in that region, a phenomenon that is significantly reduced in the DDABr-capped NC devices, where the recombination is more localized within the NC layer, as desired.

Figure 3.10d presents the reproducibility statistics of the ligand exchange process, where the peak EQE of ten samples, with each sample having four pixels, yielded

an average (peak) EQE of 3% for DDABr and about 0.49% for native NC PeLEDs. Importantly, the devices with DDABr ligands reach their peak EQE at application-relevant current densities of 1 mA/cm^2 , while the LEDs with native NCs have their peak at very low currents (10^{-3} mA/cm^2).

Furthermore, we note that a two fold increase in operational lifetime of the device is obtained in ligand exchanged PeLEDs (see Supporting Information, Figure 3.24) highlighting the critical role in choosing the right ligand to improve carrier balance in PeLEDs, through the combined effect of better energy level alignment for hole injection and a reduction of hole traps on the NC surface along with the incorporation of a polar ETL, which collectively enhances the performance of PeLEDs.

3.4 Conclusion

The present work highlights the impact of alkyl ligands, specifically OA, OAm and DDABr, on carrier transport and the optoelectronic performance of CsPbBr₃ NC based PeLEDs. Though obtaining high PLQY in native NCs can be realized through complete passivation of the surface with OA/OAm ligands, this approach is counter-productive with respect to electrical accessibility. Apart from the insulating nature of these alkyl ligands, it is evident from SEC and UPS that the functional groups attached to the surface influence the band-edge position, thereby regulating the charge injection properties. From single-carrier data, it is furthermore clear that charge transport properties are also dictated by these ligands, notably in the case of native ligands, where hole transport is impeded with respect to electrons. Our DFT calculations indicate that OA is not an ideal passivating ligand for PeLED applications, due to the presence of hole traps resulting from the carboxylate group binding to Cs⁺. We also demonstrated that the ligand exchange process using DDABr is reproducible, yielding minimal yet sufficient coverage for LED applications. This ligand exchange improves hole transport and enhances valence band alignment with the HOMO of the hole transport layer favorably. Together with the use of a polar ETL, DDABr NC LEDs yield a more stable EQE over a broad range of current densities. These findings highlight the role of ligands and a polar ETL in modulating the properties of CsPbBr₃ based NCs for efficient LED applications.

3.5 Experimental Section

Sample Preparation - Materials

ITO (indium tin oxide) substrates with dimensions $2 \text{ cm} \times 2 \text{ cm}$ were purchased from

Kintec (Hong Kong) with a layer thickness of 90 nm on a 23 nm SiO₂ buffer sitting on a 0.7 mm thick glass substrate. PEDOT:PSS in a low-conductive formulation CH8000 was purchased from Heraeus Germany GmbH & Co. KG. CsPbBr₃ solution (10 mg/mL in toluene, product ID 900746), DDABr (98% purity, product ID 359025) and ZnO nanoparticle ink (2.5 wt. %, viscosity 2.1 cP, product ID 808253) were purchased from Merck Germany KGaA. PTAA (MW = 56 kDa, PDI = 2.87) was purchased from Ossila B.V. TPBi (98%, product ID LT-E302H) was purchased from Lumtec, Taiwan.

Sample Preparation - Ligand Exchange

- Equal volumes (X) of 10 mg/mL CsPbBr₃ NC solution and ethyl acetate solution were mixed and centrifuged at 12 RCF for 10 minutes and the supernatant was discarded.
- X volume of toluene was added to the precipitate and redispersed with X volume of ethyl acetate, centrifuged at 12 RCF for 10 minutes and the supernatant was discarded.
- X volume of DDABr solution (10 mg/mL in toluene) was added along with X volume of ethyl acetate, centrifuged at 12 RCF and the supernatant was discarded.
- X volume of toluene was added to the precipitate and redispersed with X volume of ethyl acetate, centrifuged at 12 RCF for 10 minutes and the supernatant was discarded.
- Finally X/2 volume of toluene was added to re-disperse the precipitate.

Sample Preparation - Device Fabrication

All samples were initially cleaned with industrial grade detergent (alconox), DI water, acetone (technical), isopropyl alcohol (technical) and isopropanol (UV grade). The samples were then treated under UV ozone for 15 minutes, immediately followed by spincoating PEDOT:PSS at 4000 rpm for 30 s and annealed at 135 °C for 15 minutes. The samples were transferred from the cleanroom to a nitrogen filled glove box for further preparation. PTAA solution (5 mg/mL in dichlorobenzene) was spincoated at 3000 rpm for 45 s and annealed at 145 °C for 15 minutes. The NC solution was spincoated by a two step process (500 rpm for 30 s and 2000 rpm for 5 s). Samples were then transferred to a vacuum deposition chamber with a pressure less than 10⁻⁶ mbar, without exposing to air. The samples fabricated until this step were the same for LEDs, hole-only devices and PES measurements.

LEDs: TPBi (50 nm) was evaporated at about 0.1 nm/s, followed by LiF and aluminium at 0.03 nm/s and 0.1 nm/s, respectively.

Hole-only devices: HATCN (10 nm) was evaporated at 0.03 nm/s followed by gold at 0.1 nm/s.

PES: The samples were prepared as mentioned before on an unpatterned ITO substrate. All procedures up until the nanocrystal deposition remain the same.

Electron-Only Devices: ITO substrates were cleaned and transferred to the glove box. ZnO was dropcasted onto the substrate through a PTFE filter (0.45 μm), spincoated at 3000 rpm for 30 s and annealed at 170 °C for 15 minutes. This was followed by spincoating NC solution at 500 rpm for 30 s and 2000 rpm for 5 s and evaporating LiF and aluminium at 0.03 nm/s and 0.1 nm/s, respectively.

LED Measurements

jVL curves are recorded with a Keithley 2612B source meter unit (SMU) at a sweep-rate of 0.1 V/s. A photodiode of known diameter at known distance is used for luminance detection. The electroluminescence spectrum was measured with the Phelos system from Fluxim AG (Switzerland). Combined with a Lambertian approximation and a pixel area of 4.8 mm², the EQE was determined.

PLQY and TRPL Measurements

All PL and TRPL measurements were performed under ambient conditions. PLQY values were determined using the direct excitation method for sample solutions and thin films, with corresponding PL measurements conducted on a Horiba Fluoromax-Plus photospectrometer using a quanta- Φ integrating sphere attachment. For solution measurements, the samples resided inside 3 mL quartz cuvettes (Hellma QS111-10-40). The absorbance of the sample solutions was adjusted to ~ 0.1 at the excitation wavelength of 465 nm. The thin films were prepared by drop-casting dilute sample solutions onto the polymethylmethacrylate (PMMA)-coated side of a PMMA-coated fused silica substrate (1 mg/ml in toluene, spincoated at 3000 rpm for 30 s and annealed at 150 °C). As a reference sample, toluene (GPR Rectapur, VWR Chemicals) inside a 3 mL quartz cuvette (Hellma QS111-10-40) was used for solution measurements, and a PMMA-coated fused silica substrate in the case of thin film measurements. The excitation light was from a Xenon lamp, with the excitation wavelength set to 465 nm. The excitation and emission monochromators were configured with a bandpass ratio of 10:1 to maximize the excitation peak signal of the reference sample while keeping it within the linear range of the photomultiplier tube detector. Both monochromators used gratings with 1200 grooves/mm; however, the excitation monochromator's grating was blazed at 330 nm, whereas the emission

monochromator used a grating blazed at 500 nm. PL measurements were performed with the sample residing inside the integrating sphere, in 1 nm steps. The PL spectra were dark-count corrected and corrected for light intensity fluctuations of the excitation source. Additionally, the sensitivity of the emission path was calibrated for and considered, and both monochromators were wavelength-calibrated. Using the Quantum Yield determination tool of Horiba's Fluorescence software, the sample's PLQY values were determined using the formula

$$PLQY = \frac{PL_B - PL_A}{E_A - E_B} \quad (3.1)$$

where E_A and E_B are the integrated areas under the excitation peak for the reference and sample measurement, respectively, and PL_A and PL_B are the integrated areas under the photoluminescence peak for the reference and sample measurement, respectively. For solution measurements, the integration interval was from 455 to 472 nm for the excitation peak and from 472 to 575 nm for the photoluminescence peak. For thin film measurements, the integration interval was from 455 to 475 nm for the excitation peak and from 475 to 580 nm for the photoluminescence peak.

For PL decay measurements on a home-built PL microscope setup, the samples were exsopercited at a center wavelength of 465 nm with a 4.88 MHz repetition rate by the SuperK Fianium FIU-15 supercontinuum white light fiber laser coupled to a SuperK SELECT (both from NKT Photonics), a multi-channel tunable filter based on Acousto-Optic Tunable Filter technology. The excitation light was cleaned using both a bandpass filter (465 ± 15 nm) and a shortpass filter (790 nm cut-off wavelength). A diffusor lens expanded the excitation beam at the sample position. Excitation light was directed toward the sample by a 495 nm cut-on longpass dichroic mirror and focused onto the sample using an objective (CFI-TU-Plan-Apo-Epi 100x, Nikon). Emitted PL got collected through the same objective, transmitted through the longpass dichroic mirror, further filtered by a longpass filter (496 nm cut-on wavelength), and focused onto the fiber of a fiber-coupled MPD avalanche photodiode (Micro Photon Device). The PL signal was processed by a TCSPC card (PicoQuant, TimeHarp 260). The excitation power was $5.3 \mu\text{W}$ at the sample position for solution measurements and $5.2 \mu\text{W}$ for thin film measurements. The stop condition was 10 000 counts for all measurements. Additional neutral density filters were placed in the emission path to keep the photon detection rate below 2% of the laser repetition rate to avoid pulse pile-up.

UPS Measurements

UPS was conducted using a monochromatized helium discharge lamp with a photon

energy at 21.22 eV (HIS 13 FOCUS GmbH) and a hemispherical SPECS Phoibos 100 analyzer in an ultrahigh vacuum (UHV) system (base pressure of 1×10^{-9} mbar). The monochromator eliminates the visible light and further reduces the UV flux by a factor of 100 as compared to that of the standard helium lamp. The overall energy resolution was set at 110 meV for the UPS measurements.

NMR Measurements

The ^1H NMR and qNMR were performed using the Bruker Avance IIITMHD 400 MHz NMR spectrometer. For qNMR, 64 scans were accumulated with an acquisition time of 4 s and spectral width of 20.03 ppm along with a relaxation delay of 40 s.

SEC PL Measurements

SEC PL measurements were conducted in a specific home-built electrochemistry cell. As working electrode, a transparent fluorine-doped tin oxide glass substrate (20 ohm/sq, 1.1 mm thickness, Dyenamo) was used. On top of that, the NCs were drop-cast in a nitrogen-filled glovebox. The cell assembly was conducted at air. As reference electrode, an Ag wire was used and as counter electrode a Pt coil. The 0.1 M electrolyte solution was prepared in the glovebox out of five times recrystallized tetrabutylammonium hexafluorophosphate (TBAHFP, 98% AlfaAesar), ferrocene (98%, Acros Organics) and propylene carbonate (PC, 99.5%, Thermo Scientific). For electrochemistry, the electrodes were connected to a BAS50 potentiostat (Bioanalytical Systems Inc.). For SEC, the electrochemical cell was placed on top of a confocal laser setup. The NCs were exsupercited by a 405 nm laser (PicoQuant LDH series). The laser passed optical density filter and was focused by an air objective (Olympus LMPlan FLN, 50x, 0.5 NA) on to the sample. After excitation, the laser intensity was filtered out by a 485 nm long pass filter. Spectra were recorded by an Acton SP300i spectrometer. For all measurements, the open circuit potential was determined and iR compensation was applied by the potentiostat. Measurements started at approx. the open circuit potential and the integration time of the spectrometer was set to 1 s.

Simulation

All the DFT calculations have been carried out using the CP2K (version 9.1) software package.²⁴⁷ A combination of gaussian basis sets with plane waves as auxiliary basis sets known as the gaussian plane waves (GPW) method was chosen to solve the equations efficiently during all the electronic structure calculations. Double-zeta-valence-polarized (DZVP-MOLOPT-SR-GTH) basis sets²⁵⁶ along with Goedecker-Teter-Hutter²⁵⁷ pseudopotentials for all the elements were used in combi-

nation with Perdew–Burke–Ernzerhof (PBE)²⁵⁸ generalized gradient approximation (GGA) functional. Grimme’s DFT-D3²⁵⁹ correction protocol was also performed to account for the van der Waals interactions. Periodic boundary conditions were invoked during geometry optimization and single-point calculations, and a large cubic box size of $75 \text{ \AA} \times 75 \text{ \AA} \times 75 \text{ \AA}$ dimensions where the CsPbBr₃ nanocluster was placed inside to avoid spurious interactions between the periodic images. All the structures were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimizer, with the maximum force criteria set to 1×10^{-4} Hartree/Bohr ($\sim 5 \text{ meV/\AA}$). The grid cutoff for the gaussian plane waves was chosen to be 350 Ry during all the geometry optimisation and single-point calculations, and it was increased to 450 Ry during density-of-states (DOS) calculations.^{107,248} The electronic temperature was set to 300K and Fermi-Dirac distribution was employed during DOS calculations. All the self-consistent field (SCF) iterations were converged with a 10^{-6} a.u. cutoff. For modeling the perovskites and visualization of the molecular orbitals, Atomistic Simulation Environment GUI (ASE GUI) and VESTA¹¹⁹ programs were used.

3.6 Supporting Information

S1. Quantitative NMR

The concentration of DDABr NCs in toluene before qNMR was determined. Following the procedure as in Dai *et al.*,¹⁶² with the difference of using ethylene carbonate standard (14 mM in DMSO-d₆), A specific amount of NCs was dissolved in 0.5 ml of the ethylene carbonate/DMSO-d₆ solution and thereby decomposed. The amount of ligands was determined as 6000 ligands/NC for excess DDABr, 443 ligands/NC for once washed NCs and 226 for twice washed NCs, resulting in a ligand density of appx. 1 ligand/nm² and 0.6 ligand/nm² for once and twice washed NCs, respectively.

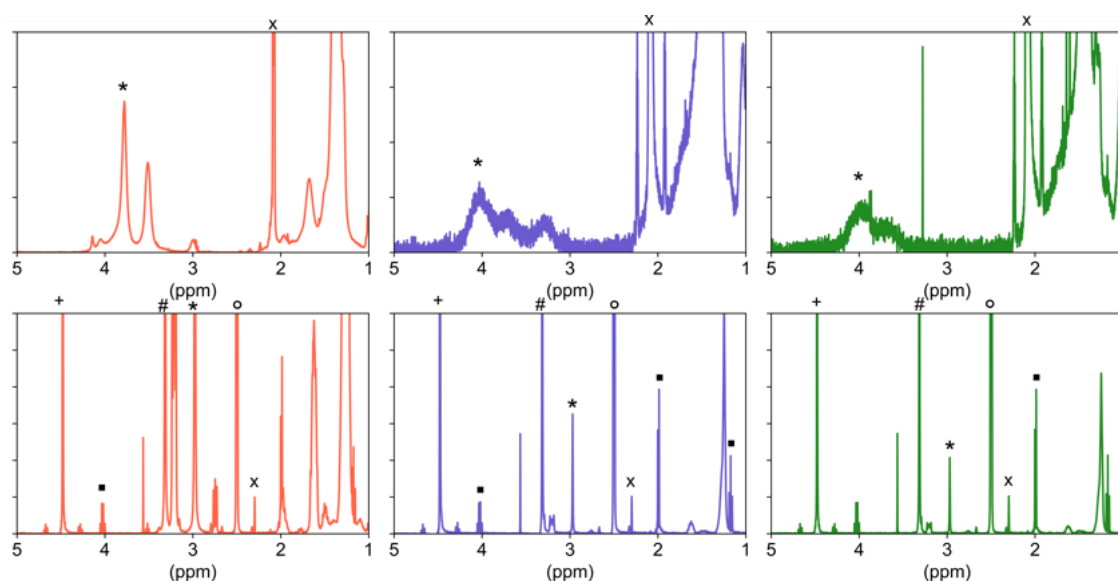


Figure 3.11: ¹H NMR spectra of top row: bound DDABr to NCs in toluene-d₈, bottom row: quantitative NMR with ethylene glycol (+) as standard in DMSO-d₆. In red: NCs with excess DDABr (methyl groups), in blue: NCs covered with DDABr after one washing step, in green: NCs covered with DDABr after two washing steps. Additional markers show impurities: DMSO (o, 2.5 ppm), H₂O (#, 3.33 ppm), EtOAc (., 1.99, 4.03, 1.17 ppm), toluene (x, 2.3 ppm).

S2. Photoluminescence quantum yield (PLQY) and time-resolved photoluminescence (TRPL)

- PLQY

PLQY measurements were performed using a quanta-Φ integrating sphere attachment to a Horiba Fluoromax-Plus photospectrometer under ambient conditions. The measurements were performed on solutions at an absorbance value of 0.1 using a 465 nm excitation source. It should be noted that thin-film

measurements were performed on drop-cast samples, as the spin-coated films showed absorbance values that were too low.

As shown in Table 3.1, we find comparably high values for solutions with either native or DDABr-ligand exchanged NCs, indicating that air exposure does not affect the results. However, for the thin-film samples we find a more than expected reduction of PLQY in NCs with DDABr ligands, which we ascribe to the effect of ambient exposure and the low ligand coverage of these NCs. Remarkably, the native nanocrystal films are obviously less affected by air exposure, because they are covered densely by oleic acid and oleylamine ligands, protecting them much better from ambient effects.

Table 3.1: PLQY values of solution and thin film native and DDABr samples.

Sample	PLQY (solution)	PLQY (thin-film)
Native	88%	55%
DDABr	88%	25%

- TRPL

TRPL measurements were performed on a home-built PL microscope setup. For each PL decay curve, time 0 was adjusted to align with the time bin exhibiting the maximum PL intensity. All PL decays were normalized to their respective maximum intensity values. The PL lifetime τ_{total} of each sample was extracted as the time corresponding to a normalized PL intensity of $1/e$ (~ 0.368) from the decay curve. For the solutions, a single TRPL measurement was performed per sample, with τ_{total} values reported in Table 3.2. For thin film samples, three measurements were taken at different spots on the film. The PL lifetime values presented in Table 3.3 represent the average ($\overline{\tau_{total}}$) over these three measurements, as well as the associated standard deviations σ , which were calculated based on the following equation,

$$\sigma = \sqrt{\frac{\sum (\tau_{total,i} - \overline{\tau_{total}})^2}{n - 1}} \quad (3.2)$$

where, n represents the number of spots measured on the sample ($n = 3$).

The TRPL curves of solutions and representative TRPL decay curves of thin films are shown in Figure 3.12. Using the previously determined PLQY values for each sample, the radiative (κ_{rad}) and non-radiative recombination rate ($\kappa_{non-rad}$) were calculated using the following formulae, akin to previously

calculated by Shamsi *et al.*²⁶⁰

$$\kappa_{total} = \kappa_{rad} + \kappa_{non-rad} = \frac{1}{\tau_{total}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{non-rad}} \quad (3.3)$$

$$PLQY = \frac{\kappa_{rad}}{\kappa_{total}} = \frac{\tau_{total}}{\tau_{rad}} \quad (3.4)$$

The τ_{total} values from Table 3.2 and $\overline{\tau_{total}}$ from Table 3.3 were used for calculations for solution and film measurements, respectively. Again, for solutions, we obtain a clear trend with DDABr-exchanged NCs having longer exciton lifetime than native NCs, while the thinfilm measurements on DDABr are most likely affected by ambient air exposure, resulting in a strong reduction of the lifetime in this case.

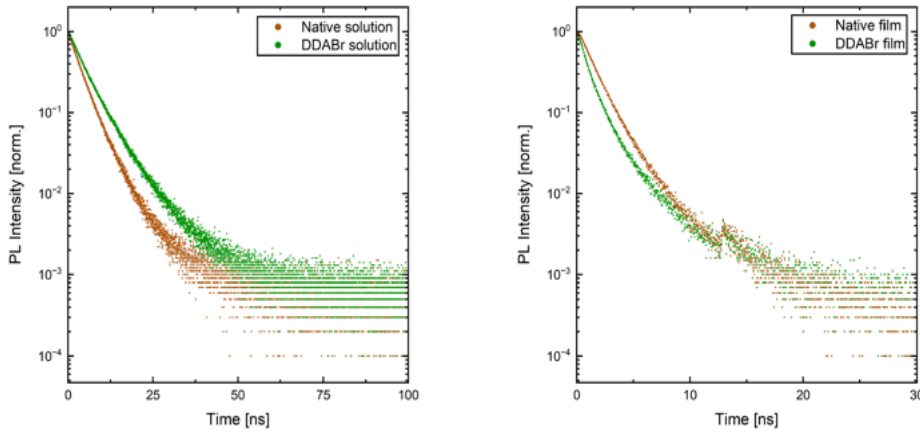


Figure 3.12: Decay curves of native and DDABr solution (left) and thin-film (right) samples.

Table 3.2: Lifetime and rates computed from decay curves and PLQY data of solution samples.

Solution	τ_{total} (ns)	κ_{rad} (ns ⁻¹)	$\kappa_{non-rad}$ (ns ⁻¹)
Native	3.6	0.24	0.034
DDABr	4.8	0.18	0.025

Table 3.3: Lifetime and rates computed from decay curves and PLQY data of thin-film samples

Film	$\overline{\tau_{total}}$ (ns)	σ (ns)	κ_{rad} (ns ⁻¹)	$\kappa_{non-rad}$ (ns ⁻¹)
Native	1.6	0.025	0.34	0.27
DDABr	0.93	0.14	0.29	0.81

S3. Spectroelectrochemistry

- Photobleach of NCs in SEC cell with electrolyte solution

In this section, the PL of NCs within the electrolyte solution at the open circuit potential is shown to determine the degree of photobleaching. DDABr capped NCs exhibit mostly linear and weaker photobleaching in comparison to native NCs.

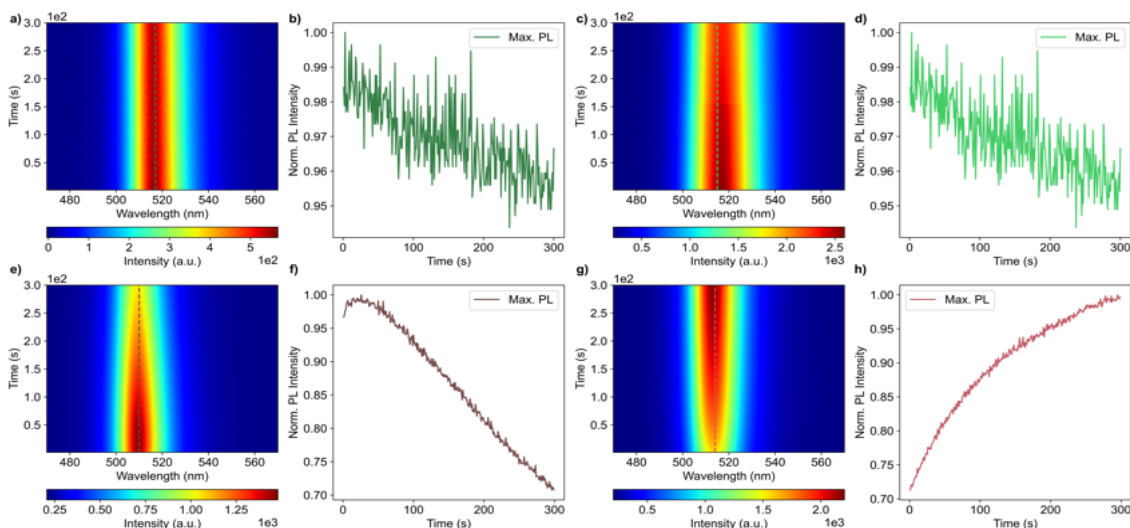


Figure 3.13: PL intensity maps (on the left, a,c,e, and g) and extracted maximum PL intensity (on the right, b,d,f, and h) of DDABr and OA/OAM covered NCs with PC/TBAHFP on top for 300 s. a) and b) DDABr covered NCs after one washing step, c) and d) DDABr covered NCs after two washing steps, e) and f) OA/OAM covered NCs after one washing step, and g) and h) OA/OAM covered NCs after two washing steps.

- Referencing of Ag PRE by ferrocene/ferrocenium redox couple

This section shows the CV of ferrocene in the same electrochemical cell which is used to transfer the values obtained vs. Ag PRE onto the Fc/Fc^+ redox couple scale and the scale vs. vacuum in Figure 3.4e in the main manuscript.

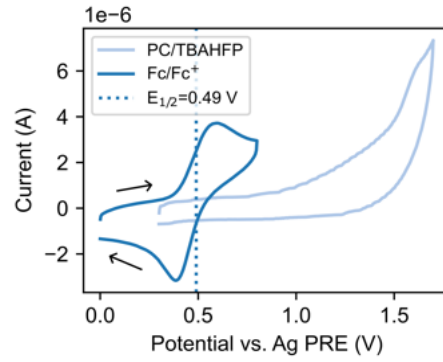


Figure 3.14: Reference measurement of electrolyte solution and ferrocene/ferrocenium couple in 0.1 M PC/TBAHFP at a scan speed of 50 mV/s with half-wave potential of $E_{1/2} = 0.49$ V vs. Ag PRE.

- SEC measurements of other samples in this study

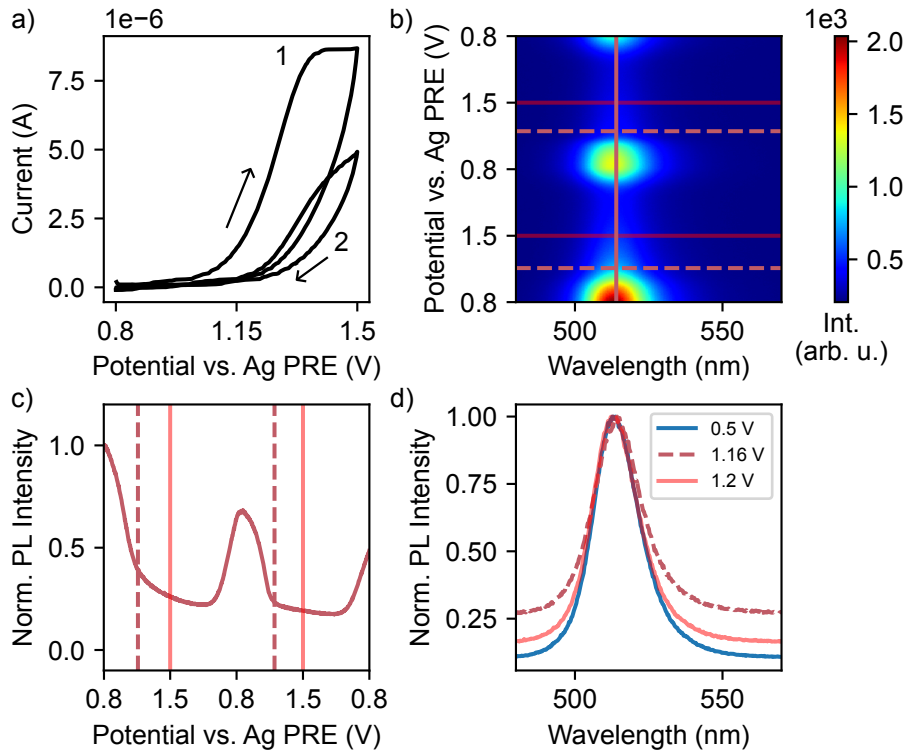


Figure 3.15: SEC PL on once washed OA/OAm covered NCs in 0.1 M PC/TBAHFP with a scan speed of 2 mV/s. a) CV of NCs, b) Emission spectra shown as intensity map correlated to every potential, c) extraction of normalized PL maximum at 512 nm of the NCs, and d) single spectra extracted at the specified lines from (b).

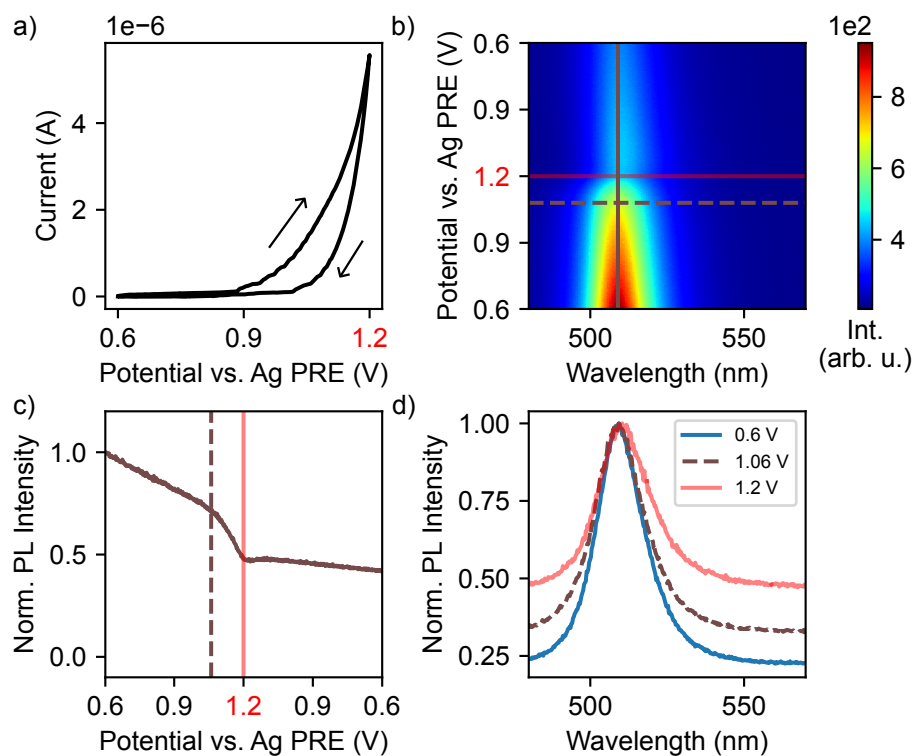


Figure 3.16: SEC PL on twice washed OA/OAm covered NCs in 0.1 M PC/TBAHFP with a scan speed of 2 mV/s. a) CV of NCs, b) Emission spectra shown as intensity map correlated to every potential, c) extraction of normalized PL maximum at 512 nm of the NCs, and d) single spectra extracted at the specified lines from (b).

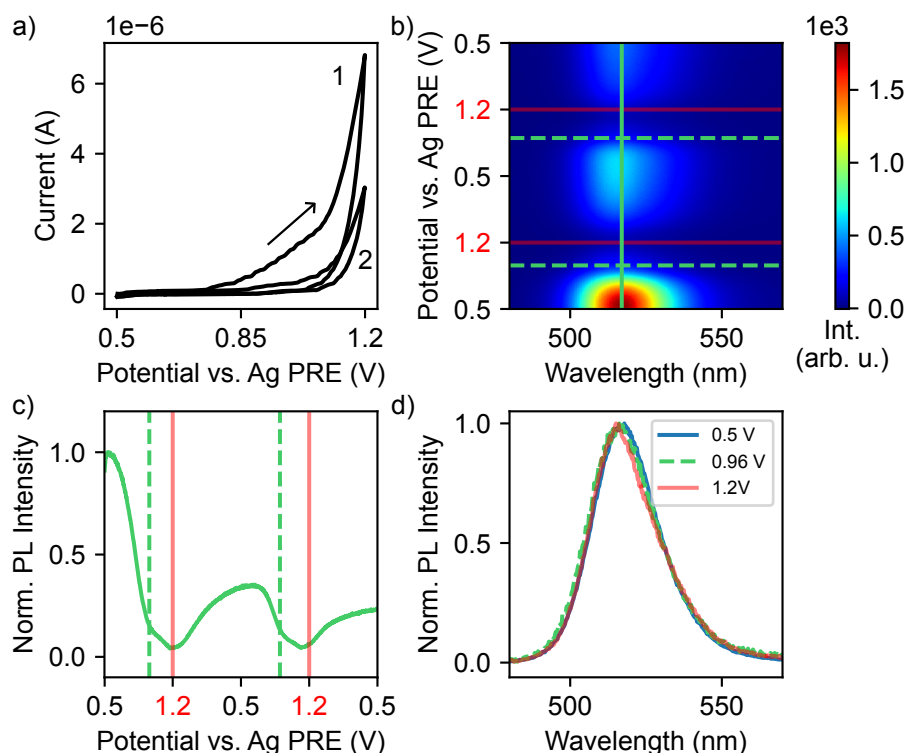


Figure 3.17: SEC PL on twice washed DDABr covered NCs in 0.1 M PC/TBAHFP with a scan speed of 2 mV/s. a) CV of NCs, b) Emission spectra shown as intensity map correlated to every potential c) ,extraction of normalized PL maximum at 516 nm of the NCs, and d) single spectra extracted at the specified lines from (b).

S4. X-ray photoelectron spectroscopy (XPS)

XPS measurements was performed on the same samples used for UPS measurements. XPS was performed at a JEOL JPS-9030 UHV system (base pressure of 1×10^{-9} mbar) using a monochromatized Al $K\alpha$ (1486.6 eV) radiation. All spectra were acquired at room temperature and normal emission. The overall energy resolution was set at 900 meV for these measurements.

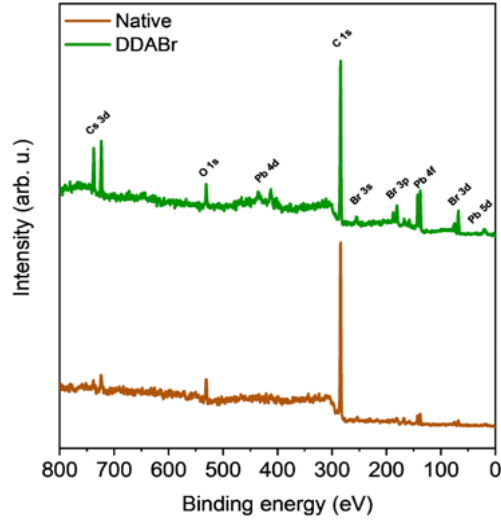


Figure 3.18: XPS survey spectra of native and DDABr NCs.

The elemental composition was determined by fitting the characteristic spectral peaks with Gaussian functions and quantifying the integrated peak areas.

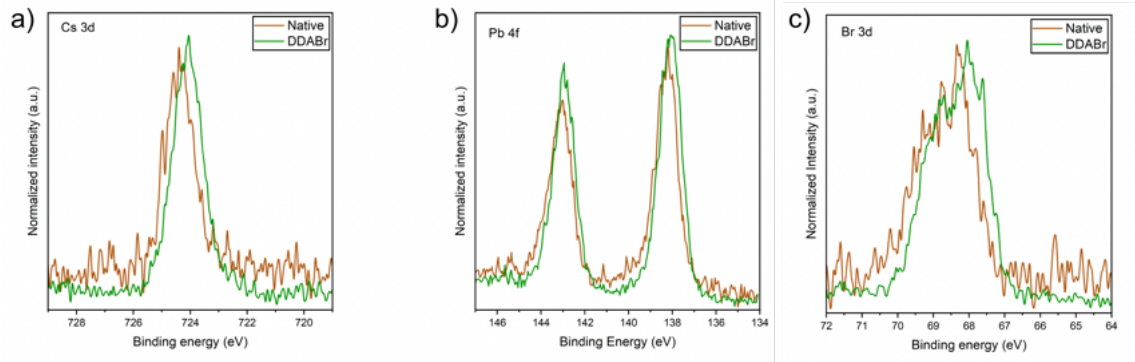


Figure 3.19: XPS core levels of the individual elements in native and DDABr NCs.

Table 3.4: Relative atomic ratios calculated by integrating XPS core level spectra for native and DDABr NCs.

	Pb 4f 7/2	Br 3d 5/2	Cs 3d 5/2	Br/Pb
Native	27.1%	50.2%	22.7%	1.85
DDABr	21.7%	55.8%	22.5%	2.57

S5. Additional DFT calculations

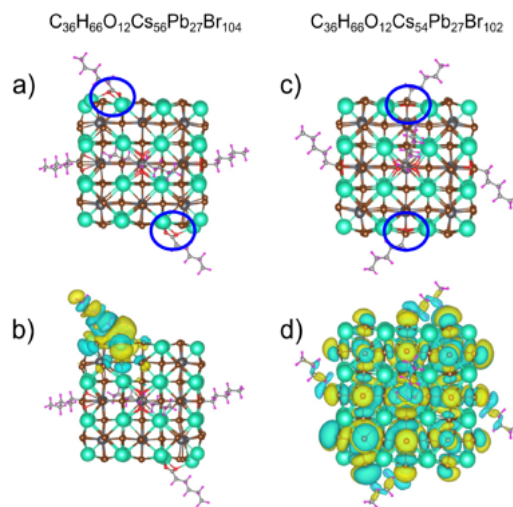


Figure 3.20: Two different binding modes of the carboxylate oxygen atoms in the hexanoate (mimicking the oleate ligand) group which are attached to the PNC surface (encircled). a and b are the cases where two of the carboxylate oxygens are bonded to the Cs^{+} ions. c and d represents the other less likely binding modes where all the carboxylate oxygens are directly bonded to the Pb^{2+} sites.

S6. Kelvin probe measurements

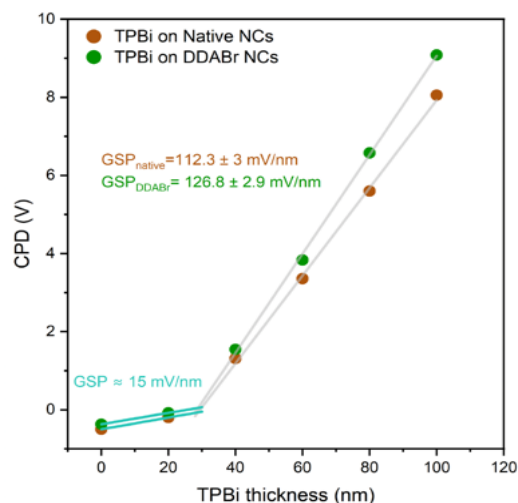


Figure 3.21: Contact potential difference (CPD) measured from Kelvin probe vs. thickness of TPBi evaporated on native (brown circles) and DDABr (green circles). GSP is extracted from the slope of the resulting linear fit on plotted data.

S7. Washed vs. unwashed native LEDs

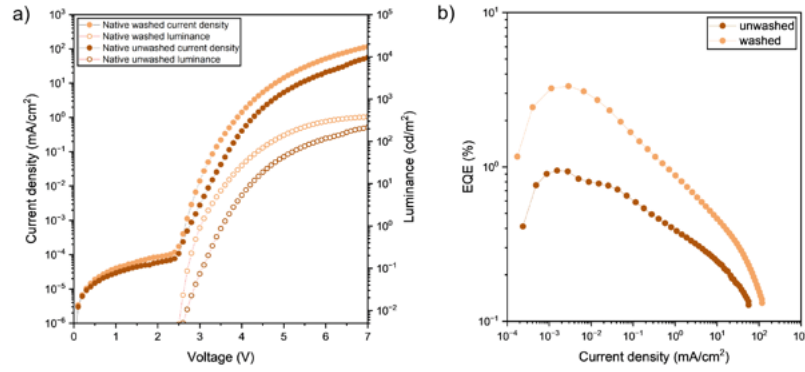


Figure 3.22: J-V-L and EQE plots of washed vs. unwashed native NC LEDs.

S8. Exciplex emission of bilayer device

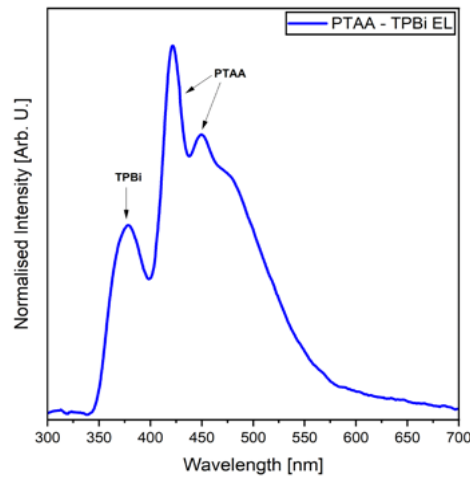


Figure 3.23: EL spectrum of PTAA/TPBi bilayer device (same device stack as PeLED without the PNC layer). The peaks in the EL spectrum correspond well with the PL spectra of the respective organic transport layers,^{261,262} followed by an exciplex shoulder at longer wavelengths.

S9. Device operational lifetime

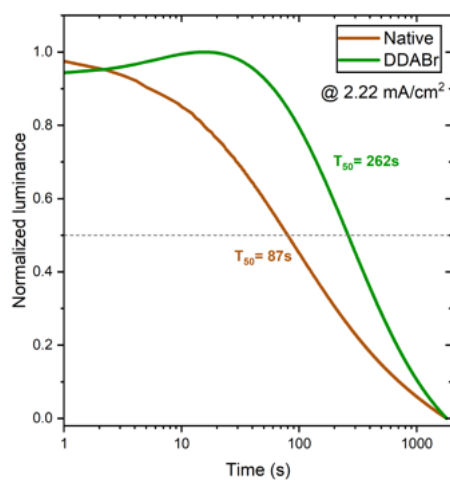


Figure 3.24: Device operational lifetime of native and DDABr NC PeLEDs.

4 Impact of Ligand-Mediated Inductive Effects on Electrochemical p-Doping of CsPbBr₃ Nanocrystals

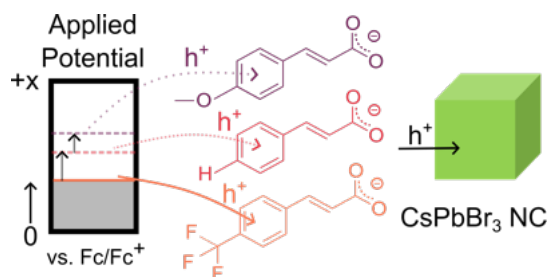
Theresa Hettiger¹, Roshini Jayabalan², Arup Sarkar³, Jonas L. Hiller¹, Max Nusshör¹, Denis Andrienko³, Wolfgang Brütting², and Marcus Scheele^{1,*}

1. Institute for Physical und Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany.
2. Institute of Physics, University of Augsburg, 86135 Augsburg, Germany.
3. Max Planck Institute for Polymer Research, 55128 Mainz, Germany.

* Corresponding author

In this chapter, inductive effects introduced by cinnamic acid derivatives as surface ligands on the electronic structure of CsPbBr₃ NCs are investigated by PL SEC. LEDs and hole-only devices built from the exchanged NCs show increased current due to facilitated charge injection.

The results presented here are published in ref. [46].



Reprinted (adapted) with permission from *ACS Energy Letters*, 2026, 11, 1, 567–572. Copyright © 2026 American Chemical Society. The publication is licensed under Creative Commons-BY 4.0 License.

4.1 Abstract

Lead halide perovskite nanocrystals (NCs) are promising materials for light-emitting diodes (LEDs) due to their wavelength tunability, narrow emission line width, and high photoluminescence quantum yield. Oftentimes, these devices suffer from charge carrier imbalance and reduced charge injection because as-synthesized NCs are covered by long aliphatic ligands. Here, we report ligand exchange to small electron-withdrawing or -donating cinnamate ligands. We probe the influences of the ligands' inductive effect on hole injection by photoluminescence spectroelectrochemistry (PL SEC). We find that hole injection into NCs covered by electron-withdrawing ligands is facilitated, and hole-only devices exhibit higher currents compared to electron donating ligands. Our work highlights the potential of PL SEC as a powerful tool to rationalize the performance of lead halide perovskite NCs in LEDs.

4.2 Introduction

Lead halide perovskites have attracted the attention of many researchers due to a small exciton binding energy, emission wavelength tunability, and a trap-free band gap.^{122,263} All these properties make them interesting for the application in LEDs or solar cells.^{264–269} For both devices, efficient and balanced charge injection/extraction is essential. This requires that the absolute energy level of the perovskite layer is well-aligned with those of the hole and electron transport layers, enabling efficient energy transfer and ensuring that charge carriers can be injected/extracted effectively.²⁷⁰ Both problems can be addressed by small organic molecules.²⁷¹ For instance, in solar cells, electrode surfaces are modified by organic molecules to improve charge extraction.^{272–275}

When considering LEDs, perovskite NCs are used because of their high photoluminescence quantum yield, easy tunability through halide exchange, and narrow emission profile.^{29–31,122,156} These NCs are covered by an organic ligand shell that provides the possibility of tuning charge injection and their optoelectronic properties.^{107,276,277} In solution, the same ligand shell is crucial for the colloidal stability of the NCs.⁴⁰ In comparison to other NCs, the organic ligand shell of CsPbX₃ (X = Cl, Br, I) NCs is described by a dynamic ligand binding model.^{35,278} Here, de Roo et al. have reported, following the synthesis according to Protesescu et al., that oleylamine (OAm) binds to the surface, while oleic acid (OA) binds only when OAm is present in excess.³⁵ Chen et al. have presented another model with OA binding to Cs⁺ on the surface.²⁷⁹ Given the low stability and the inconsistent picture of the surface ligands, researchers try to modify these NCs to increase their stability either by

introducing zwitterionic ligands like lecithin or using didodecyldimethylammonium bromide (DDABr) and other amine containing ligands.^{41,168,235} Both of these systems still lack one characteristic that is essential for building devices: Due to the presence of aliphatic ligand chains, injecting holes or electrons into NCs covered by these ligands becomes more challenging. This can only be achieved by ligand stripping or using π -conjugated ligands.^{45,107,157,162}

In this context, cinnamic acid (CA) derivatives provide an opportunity to study the influence of electron withdrawing and electron donating groups on the charge injection into perovskite NCs, similar to work performed on PbS NCs.¹⁶⁷ Via substitution at the phenyl ring, these functional groups can exert large inductive effects on the NC via a short π -conjugated system. An additional advantage of these molecules is their cost-effectiveness and widespread availability.

Testing charge injection by probing the absolute energy levels can be done by performing ultrahigh vacuum methods like X-ray and UV photoelectron spectroscopy (XPS, UPS).²⁸⁰ This probes the energy levels of the NC directly. Using this method, Kroupa et al. determined that the valence band (VB) of PbS NCs with electron withdrawing ligands on their surface shifts to higher energies, resulting in a hindered hole injection, while hole injection into NCs covered by electron donating ligands is facilitated.¹⁶⁷ Lu et al. probed charge transfer on cinnamate and 3,5-difluorocinnamate-covered CsPbBr₃ NCs indirectly by determining their photoredox activity. Their results showed easier electron extraction due to the attached π -conjugated system.²⁸¹ However, precise values in how strongly electron extraction can differ between these attached ligands to the NCs are still missing.

Another way of probing charge injection is spectroelectrochemistry (SEC). Here, an electrochemical method, e.g., cyclic voltammetry (CV), is combined with a spectroscopic technique, like PL or absorbance measurements.^{220,242,282} By this method, the NCs with their organic ligand shell are drop-cast or spin-coated on a transparent working electrode, which allows for simultaneous charge injection and optical measurements. This makes the measurements sensitive to influences by the surface ligands on charge injection. Mulder et al. were already able to electrochemically p-dope CsPbBr₃ NCs at 0.9 V vs. NHE.²²¹ Using this method to probe perovskite NCs is challenging, since they are prone to decomposition. Additionally, the electrochemical window is limited by Pb²⁺ reduction and oxidation and Br⁻ oxidation.^{221,222} Still, staying within a moderate electrochemical window and looking at the emission simultaneously make SEC a powerful method to study charge injection.

In this work, we demonstrate a successful ligand exchange of oleate-covered CsPbBr₃ NCs to 4-trifluoromethylcinnamate (CACF₃) as an electron withdrawing ligand, and cinnamate (CAH), methoxycinnamate (CAOMe), 4-dimethylaminocinnamate

(CAN(Me)₂) as electron donating ligands. We study these modified NCs using SEC PL on a confocal optical setup and determine the necessary potential for hole injection, depending on the functionality of the ligand. Our results show that charge injection can be tuned by 0.31 eV. The facilitated hole injection behavior of CACF₃-covered NCs is supported by their performance in LEDs and in hole-only devices.

4.3 Results

We synthesize oleate-covered CsPbBr₃ NCs following the method of Yassitepe *et al.*¹²⁹ By using tetraoctylammonium bromide, the ligand sphere of the NCs consists exclusively of carboxylates, which we find beneficial for ligand exchange. These NCs are cubic with an average size of 8.9 nm and show absorption at 505 nm and a PL peak at 510 nm. We exchange the oleate ligands with cinnamic acid derivatives using precipitation and resuspension method. Additionally, we remove OA from the surface of the NCs by precipitating the particles with hexane as antisolvent. Figure 4.1 shows a scheme of the ligand exchange process with the different CAs, each distinguishable by their color code, along with an exemplary characterization of the NCs after exchanging the ligand with CACF₃ as the surface molecule. We find a peak PL at 509 nm, and an average size of 8.7 nm, which is within its standard deviation before the ligand exchange.

We provide full exchange protocols and characterization of the exchanged NCs in the Supporting Information in section 4.6, as well as in Figure 4.5, Figure 4.6 and Figure 4.7. To monitor the success of ligand exchange, we employ ¹H NMR spectroscopy in SI - Figure 4.8, and SI - Figure 4.9.

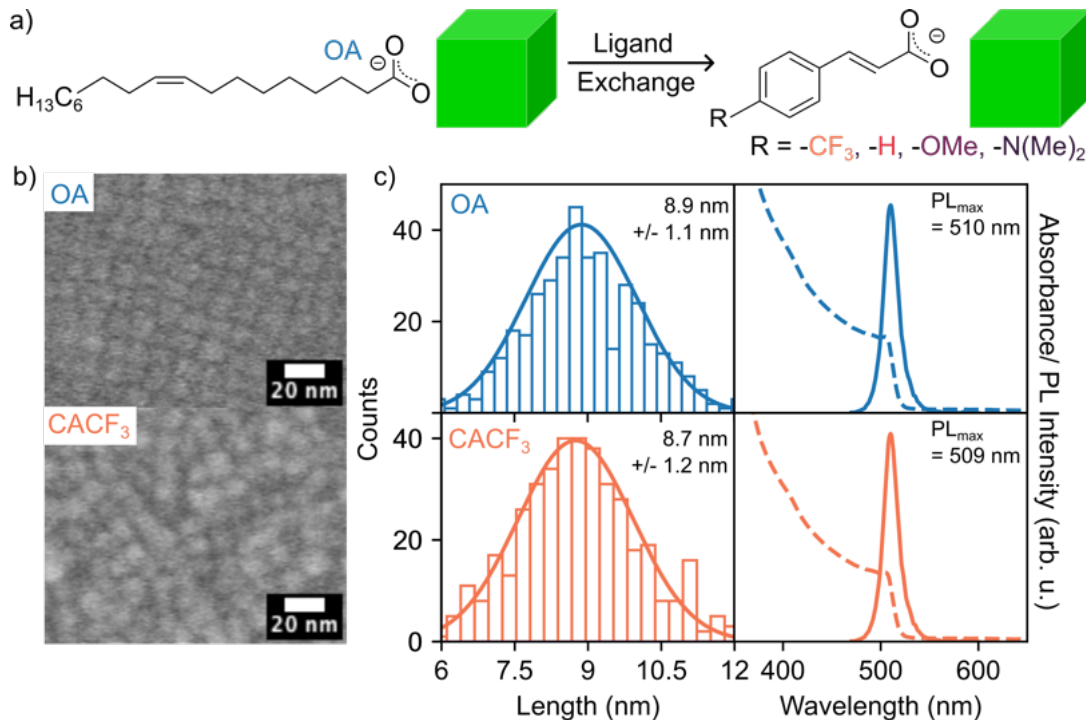


Figure 4.1: a) Scheme of surface ligand exchange of OA-covered CsPbBr₃ NCs to R-CA-covered NCs with R = CF₃, H, OMe, and N(Me)₂. b) SEM images of OA-covered NCs (top) and CACF₃-covered NCs (bottom). c) Extracted sizes fitted to normal distribution (on the left), PL (solid lines), and absorbance spectra (dashed lines) of OA-covered NCs (top) and CACF₃-covered NCs (bottom) on the right.

We investigated charge injection into R-CA-covered NCs with SEC PL according to the simplified schematic in Figure 4.2a. Briefly, we excite the NCs at 405 nm (blue arrow) and monitor the variation in PL intensity (green arrow) under varying electrochemical potential. While applicable to oxidation and reduction alike, we limit ourselves here to the oxidative direction and the effect of electrochemical p-doping. To this end, we lower the potential of the working electrode (WE, E_F) starting from the open circuit potential (E_{OC}) toward the valence band (VB) of the NC (right-hand side, Figure 4.2a). As E_F approaches the VB, electrons are extracted from the NC, leading to vacancies in the VB, that is, p-doping. This reduces the rate of absorption (red cross, right-hand side; Figure 4.2a) and, consequently, the PL intensity. The success of p-doping and the required electrochemical potential can therefore be inferred from the potential-dependent PL scans.

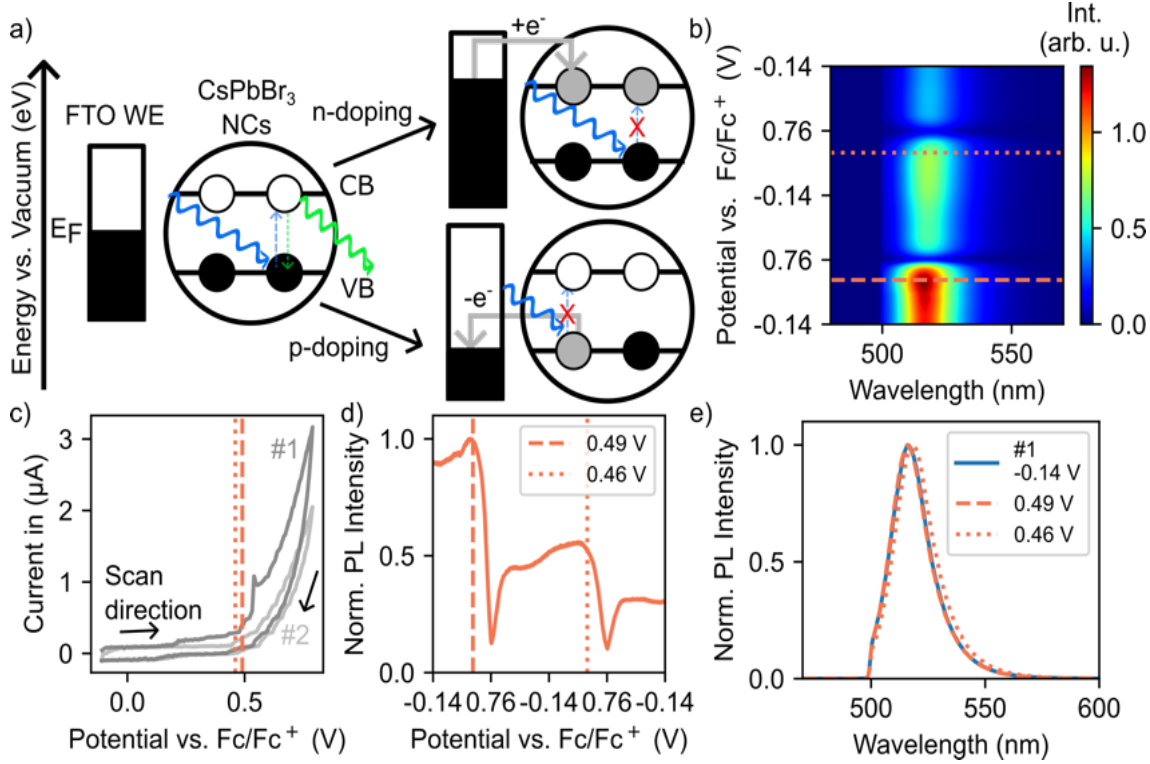


Figure 4.2: a) Schematic illustration of electrochemical p- and n-doping of the electronic structure of the NC with its conduction (CB) and valence band (VB) and the resulting dark state of the NC. b) PL spectra of CACF₃-covered NCs with a scan speed of 2 mV/s with a marked switching potential at 0.76 V and marked onset potential of VB (dashed, orange). c) Two consecutive CV scans in the oxidative direction during SEC PL with marked onset potential determined by PL intensity decay from d). d) Maximum PL intensity trace of CACF₃ NC emission extracted from panel b (solid, orange). e) Extracted single spectra at the beginning of the measurement (blue, -0.14 V) and onset potentials of charge injection (dashed, orange).

We note that all R-CA-covered NC samples exhibit some degree of photobleaching caused by the exposure to the electrolyte solution (CH₃CN/TBAHFP) and/or laser radiation without applying any potential as detailed in the SI - Figure 4.11. This is expected due to the poor tolerance of lead halide perovskites to polar solvents. By convention, we reference all SEC data against the half-wave potential of the ferrocene/ferrocenium redox couple (Fc/Fc⁺) in the same electrochemical cell and electrolyte solution (SI - Figure 4.12, spectroelectrochemistry cell in SI - Figure 4.13).

We display the results of an exemplifying SEC PL spectral series for CACF₃-covered NCs in Figure 4.2b with a 2 mV/s sweep rate and 1 s spectral integration time. The recorded cyclic voltammogram during this measurement is depicted in Figure 4.2c. A spectral slice of the series in Figure 4.2b taken at the PL maximum reveals abrupt

darkening at 0.49 V (Figure 4.2d), which we attribute to the beginning of the hole injection. To prevent oxidative decomposition, we switch the scan direction at 0.76 V toward the open circuit potential at -0.14 V, after which we initiate the next scan cycle. The mostly identical shape compared to the first cycle, including a comparable potential for hole injection (0.46 V), indicates a large degree of reversibility of this action. This is supported by the spectral shape of the three PL measurements taken at the open circuit potential and the onset potentials of charge injection, which are overlaid in Figure 4.2e to showcase their almost identical shape and spectral position.

We continue with an analogous SEC PL analysis of CAH- and CAOMe-covered NCs in Figure 4.3. Both samples exhibit qualitatively similar behavior to the previously discussed scan for CACF₃-covered NCs in Figure 4.2d, however at significantly more oxidative potentials (0.72-0.77 V). Figure 4.3c provides a summary of the statistical average ($n = 6$ to 11) of all three hole injection potentials with 0.49 V for CACF₃-covered NCs, 0.7 V for CAH- and 0.8 V for CAOMe-coverage. For device purposes, we note that these values correspond approximately to -5.39 eV, -5.63 eV, and -5.7 eV on the electronic energy scale vs vacuum for CACF₃-, CAH- and CAOMe-coverage, respectively, taking the Fc/Fc⁺ half-wave potential at -4.9 eV vs. vacuum as a widely accepted reference point.²⁰⁴

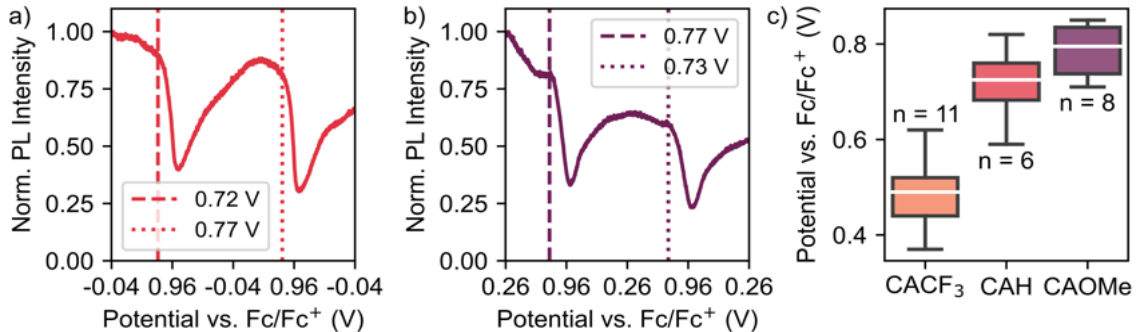


Figure 4.3: Normalized PL intensity trace as a function of the applied potential for a) CAH-covered NC. b) CAOMe-covered NCs. c) Summary of onset potentials for hole injection of different CA-R-covered NCs with number of measurements n and medians of hole injection onset potentials (in white) at 0.49 V (CACF₃), 0.73 V (CAH), and 0.8 V (CAOMe) vs. Fc/Fc⁺.

We did not succeed with reversible hole injection into CANMe₂-covered NCs (see SEC PL data in the SI – Figure 4.17a). Our CV data of pure CANMe₂ suggests that the ligand itself decomposes irreversibly before holes are injected into the NCs (see SI – Figure 4.17b).

We investigate the performance in LEDs in Figure 4.4 of the three R-CA-covered NC

systems that exhibit a reversible hole injection. Since exceptionally high colloidal stability is crucial for device fabrication, we had to modify the NC ligand exchange procedure according to Protesescu *et al.*²⁹ Briefly, we first precipitated the as-synthesized NCs and exposed them to a mixture of OAm (which increases colloidal stability) and one of the three R-CA derivatives. For each CA, the ratio of ligands was kept the same, with the goal of addressing differences in the LED behavior relative to the introduced CAs. In addition, NCs after two precipitation/washing steps without adding new ligands (washed) are investigated as a reference.

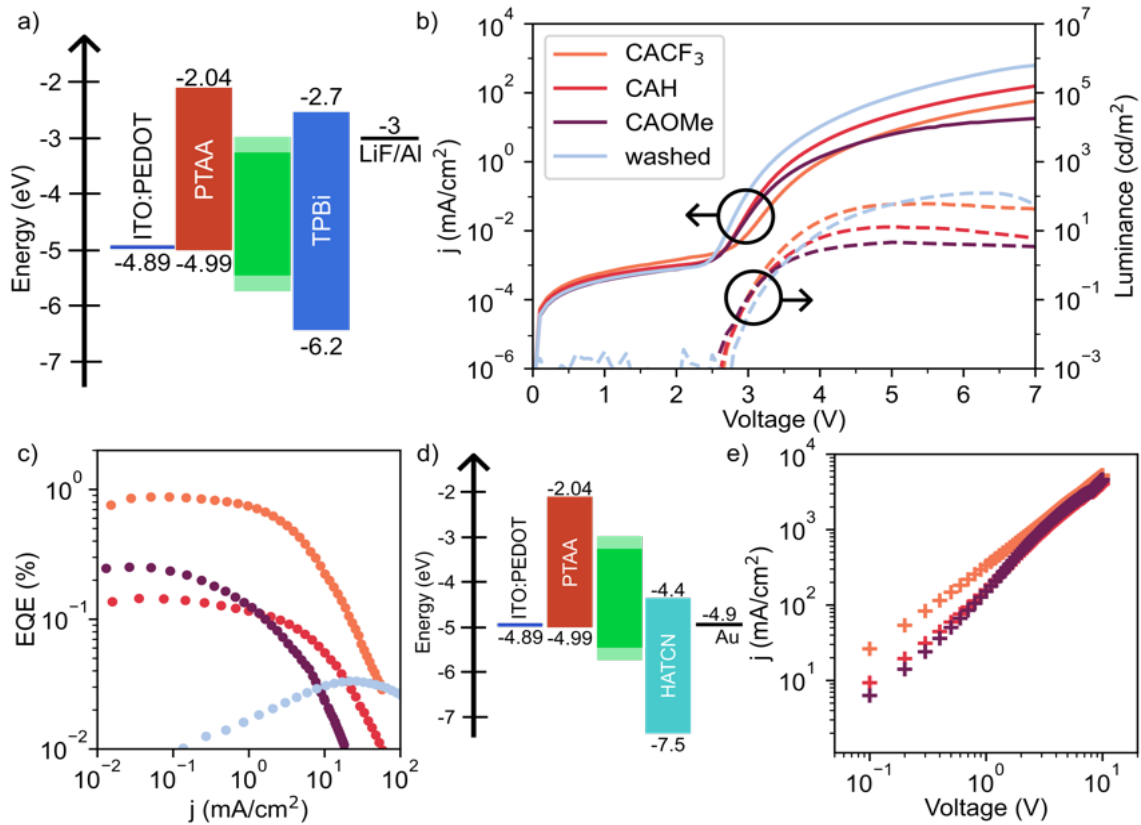


Figure 4.4: Characterization of CA-R/OAm and ligand-stripped NC (washed, light blue) LEDs. a) Flat-band energy diagram of LED with CsPbBr₃ NCs as emissive layer (green). b) Current density (j , solid lines) and luminance (dashed lines) vs voltage. c) EQE vs. j . d) Flat-band energy diagram of hole-only device. e) j vs. voltage from single carrier devices (holes).

Figure 4.4 shows the energy level diagram of the built devices. Energy levels for the transport layers were sourced from previously published reports.^{45,190,191} In the case of the cinnamate-covered NCs, we extracted the valence band position from the hole-injection potential measured by SEC PL (-5.37 to -5.71 eV), while we obtained the conduction band position by adding the optical band gap determined from PL measurements. Figure 4.4b presents the current density–voltage–luminance (j -V-L)

characteristics of the fabricated LEDs including the ligand stripped (washed, light blue) LEDs.

In the case of ligand stripping, we observe V_{on} at ~ 2.4 V and a luminance onset at ~ 2.8 V with a maximum luminance of ~ 120 cd/m². While the facilitated charge injection compared to as-synthesized NCs (SI - Figure 4.25) may appear substantial, the EQE-j characteristics (Figure 4.4c) reveal a steady increase in EQE with rising current density, with a peak value of 0.033% at ~ 20 mA/cm², characteristic of trap-filling behavior, followed by a sharp roll-off. This is consistent with the more exposed NC surface after ligand removal. Moreover, the electroluminescence (EL) spectrum of these ligand-stripped devices (SI - Figure 4.26) displays a broad parasitic emission at ~ 420 nm, attributed to the PTAA hole transport layer (HTL),⁴⁵ indicating electron leakage through the emissive layer and subsequent recombination in the HTL.

In contrast, devices passivated with cinnamate ligands display lower current densities compared with the ligand-stripped NCs, but with comparable V_{on} (~ 2.4 V) and a slightly earlier luminance onset (~ 2.6 V). Among the cinnamates, CAOMe (purple) yields the lowest current density and reduced luminance output, indicating impeded carrier injection. We detected the highest luminance for CACF₃-covered NCs (orange), which can also be observed in their EQE-j characteristics (Figure 4.4c): CACF₃ exhibits more stable EQE values at low current densities ($\sim 0.8\%$) compared to CAH and CAOMe, suggesting improved carrier balance enabled by enhanced hole injection. EL spectra (SI - Figure 4.26) at 0.1 and 1 mA further confirm the trend that CACF₃ devices show stable emission exclusively from the NCs, whereas CAH and CAOMe devices exhibit additional parasitic emission from HTL. Despite these improvements, all cinnamate-based devices exhibit notable EQE roll-off at higher current densities, underscoring the limited stability of these NCs.

Additionally, we prepared hole-only devices (flat-band energy diagram²⁸³ in Figure 4.4d) to study single carrier injection that might indicate some correlation to the SEC PL measurements on hole injection directly into the NCs. Figure 4.4e shows the highest current for CACF₃ covered NCs followed by that for CAH and CAOMe. This result indicates that holes are more easily transferred to the NCs covered by CACF₃ than the electron donating ligands on the NC surface present in LEDs.

4.4 Discussion

We investigated the influence of π -conjugated cinnamate ligands with varying electron-donating and electron-withdrawing substituents on charge injection into CsPbBr₃ NCs. A general trend emerges: NCs functionalized with electron-withdrawing ligands exhibit hole injection at applied potentials lower than those of their electron-donating

counterparts (Figure 4.3c). This view is supported by the hole-only devices in Figure 4.4e where the electron-withdrawing ligand CACF₃ invokes the largest current densities. We note that these results are counterintuitive considering previous XPS studies on PbS NCs.¹⁶⁷ In those systems, the attachment of electron-withdrawing cinnamates shifted the absolute band edge positions toward higher potentials, thereby making hole injection more difficult. This discrepancy motivated us to compute the electronic structure near the band gap of CsPbBr₃ NCs covered with the three cinnamates applied here using PBE-D3 DFT functional (see Computational details in the section 4.6. As expected, the highest molecular orbital (HOMO) energies of the pure R-CA molecules follow the order -CF₃ < -H < -OMe, highlighting that CACF₃ has the highest ionization potential (SI - Figure 4.27). When these molecules are attached to the NC surface, the valence band edge positions of the NCs follow the same qualitative trend; that is, the potential for hole injection into CACF₃-covered NCs is the highest (SI - Figure 4.27). We varied the binding sites and the number of molecules attached to the NC surface to find that the differences in hole injection potential decrease and converge toward the value calculated for bare NCs upon using fewer ligands (SI - Figure 4.28). These computational results indicate that R-CA binding should have a significant effect on the hole injection potential of CsPbBr₃ NCs, and the effect is qualitatively comparable to the aforementioned studies with PbS NCs.¹⁶⁷ However, they are in contradiction to our SEC PL and LED results, suggesting that a kinetic, rather than thermodynamic, factor is important for hole injection into CsPbBr₃ NCs.

A likely source for kinetic hindrance of charge carrier injection into the as-synthesized perovskite NCs are the long-chain aliphatic ligands OA and OAm, which are electrically insulating. Both, LED (SI - Figure 4.25) and SEC PL measurements confirm negligible charge transfer for this system, and cyclic voltammograms display only capacitive currents (SI - Figure 4.29). Ligand stripping removes these insulating chains, exposing under-coordinated surface sites that facilitate direct charge injection into the NCs with notable effects on the LED performance (Figure 4.4b,c) and PL quenching in SEC experiments (SI - Figure 4.29). A disadvantage is the large number of traps formed by this action, for which we find evidence in the EQE determination (Figure 4.4c) that requires large current densities to become significant, presumably because traps need to be filled first.

A good compromise between the two extremes of a dense, insulating ligand sphere vs no ligands at all are the cinnamate ligands employed in this study. Their π -systems provide an efficient electronic bridge between the NC and the electrode. We hypothesize that in the most electron-withdrawing ligand CACF₃, electron density is shifted from the NC core toward the ligand, leading to stabilization of the VB electrons

through delocalization into the ligand π -system. In such a scenario, the VB of the NC and the HOMO of the ligand form a coupled electronic manifold. Hole injection into this shared state during SEC PL would therefore simultaneously deplete electron density from both NC and ligand, leading to a greatly reduced kinetic hindrance of hole injection. For the electron-rich cinnamates, the delocalization of the electron density from the NCs into the π -system is expected to be weaker.

Because SEC PL probes the coupled NC-ligand system as a whole, the trends observed in electrochemical measurements directly translate to LED operation: electron-withdrawing ligands facilitate hole injection and preserve emission intensity under high current densities, whereas electron-donating ligands exhibit reduced stability and higher injection barriers. This strong correlation between SEC PL and device data underscores the utility of SEC PL as a predictive tool for evaluating the interfacial charge-transfer properties in NC-ligand systems.

4.5 Conclusion

In this work, we have demonstrated successful ligand exchange strategies for cinnamic acid derivatives on CsPbBr₃ NCs. In addition, we have investigated charge injection into these NCs by SEC PL, focusing on hole injection. By using this method, we could derive an unexpected trend: hole injection into NCs with electron-withdrawing ligands attached is facilitated compared to electron-donating ligands. These findings are supported by the performance of the NCs in LEDs and hole-only devices. We address this behavior to different degrees of kinetic hindrance of charge carrier injection into the NCs through their ligand shell.

These findings emphasize the advantages of attaching directly π -conjugated ligands to NCs since they can influence the electronic properties and guarantee charge injection even at low bias. It also highlights the comparison of SEC PL and the performance in LEDs.

4.6 Supporting Information

S1. Materials and methods.

Materials. Pb(acetate) x 3H₂O (99.9%, trace metal basis, Adrich Chemistry), Cs(acetate) (99.998%, trace metals basis, Thermo Scientific), 1-octadecene (ODE, 90%, technical grade, Sigma Aldrich), oleic acid (OA, 90%, technical grade, Sigma Aldrich), tetraoctylammonium bromide (TOAmBr, 98%, Sigma Aldrich), toluene (99.85%, Acros Organics), hexane (97%, Acros Organics), methyl acetate (MeOAc, 99+%, Acros Organics), chlorobenzene (CB, 99.8%, analytical reagent grade, Fisher Scientific), dichloromethane (DCM, 99.9%, Acros Organics), acetonitrile (99.9%, Acros Organics), tetrabutylammonium hexafluorophosphate (TBAHFP, 98%, AlfaAesar), ferrocene (98%, Acros Organics), toluene-d₈ (99.5%, Deutero), THF-d₈ (99.5%, Eurisotop), DCM-d₂ (99.6%, Deutero), trans-cinnamic acid (CA, Fluorochem), trans-4-trifluoromethylcinnamic acid (CACF₃, Fluorochem), trans-4-methoxycinnamic acid (CAOMe, 98%, Thermo Scientific), trans-4-dimethyl(amino)cinnamic acid (CAN(Me)₂, 99%, Sigma Aldrich), lead bromide (PbBr₂, 99%, Acros Organics), caesium carbonate (CsCO₃, 99.92%, trace-metal basis, Acros Organics).

Synthesis of OAm-free CsPbBr₃ NCs according to Yassitepe *et al.*¹²⁹ For the synthesis, notes by Lu *et al.* were included.²⁸¹ 162 mg (0.47 mmol) Pb(acetate) x 3H₂O and 47 mg (0.25 mmol) Cs(acetate) were added in 25 ml ODE and 2 ml (6.3 mmol) OA into a three-neck flask. The solution was heated to 100 °C and degassed for half an hour. In a vial, 250 mg (0.46 mmol) TOAmBr were dissolved in 20 ml anhydrous toluene. This solution was preheated to 75 °C. Before the injection of TOAmBr, the atmosphere in the flask was changed to nitrogen and cooled down to 75 °C. TOAmBr was injected fast, and the reaction was quenched by an ice-bath. In the next step, excess toluene was removed by applying vacuum to the reacted solution. The received solution was centrifuged at 7000 rpm for 10 mins. The precipitate was redissolved in toluene and centrifuged again at 7000 rpm for 10 mins with MeOAc as anti-solvent. In the last step, agglomerates were removed at 2500 rpm in toluene and using a syringe filter. The resulting NCs are dissolved in toluene with a concentration of 0.5-1.5 μM.

Ligand Exchange and its Parameters (OAm-free synthesis). Ligand exchange was performed with a 1 μM stock solution in a nitrogen filled glovebox. The CAs were dissolved to a 2.5 mM solution in the corresponding solvent. CA and NCs were added in a ratio of approx. 1:3000-4000 (depending on the NCs

size). After stirring for half an hour, the NCs were precipitated at 4000 rpm for 10 mins by adding hexane as antisolvent. The precipitated NCs were resuspended in the CA solution. This procedure was repeated one more time. In the last step, CA was added again to achieve full surface passivation. The exchanged NCs were characterized by SEM, absorbance and PL measurements.

Solvents CAs.

CAH chlorobenzene

CACF₃ methyl acetate

CAN(Me)₂ dichloromethane

CAOMe chlorobenzene

Synthesis of OA/OAm NCs and ligand exchange to CA-R/OAm for LED devices. OA/OAm NCs were synthesized according Protesescu *et al.*²⁹ A flask with 162 mg (0.5 mmol) CsCO₃, 0.5 ml (1.6 mmol) OA and 8 ml ODE was heated to 100 °C in vacuum and degassed for 1.5 h. Afterwards, the atmosphere was changed to N₂ and briefly heated up to 150 °C to enable Cs(oleate) formation. A second three neck flask with 422 mg (1.15 mmol) PbBr₂ and 30 ml ODE was degassed at 100 °C for 1.5 h. After degassing, 3 ml (9.45 mmol) OA and 3 ml (9.12 mmol) OAm were added to the PbBr₂ flask and again degassed for 1 h at 100 °C. For synthesis, the atmosphere was changed to N₂ and the solution was heated up to 165 °C. At this temperature, 2.4 ml Cs(oleate) were rapidly injected and after 5 s, the reaction was quenched by an ice-bath. The resulting solution was precipitated once by 8000 rpm for 20 mins. The precipitate was redissolved in toluene and centrifuged at 2500 rpm for 10 min to remove agglomerates. The supernatant was filtered in the last step. The ligand exchange was performed with a 34.2 μl of NCs stock solution (7.6 μM), which was precipitated twice with MeOAc as anti-solvent for ligand removal. Afterwards, the NCs were redispersed in 500 μl of a 2.5 mM ligand solution consisting of CA/OAm in chlorobenzene.

¹H NMR spectroscopy. ¹H NMR spectroscopy was performed on a 400 MHz BrukerAvance400 III HD spectrometer. The deuterated solvents were used as purchased and the solvent peaks were calibrated according to Fulmer *et al.*²⁸⁴

SEM. For SEM imaging a HITACHI SU8030 was used.

Absorbance and PL spectroscopy in solution. Optical measurements were conducted by a UV/VIS spectrometer (Agilent Technologies, Cary 5000) and

a fluorescence spectrometer (PerkinElmer FL8500). Spectra were acquired under ambient conditions in the corresponding solvents at room temperature in a cuvette of 1 cm pathlength.

Design of SEC cell and Preparation of Measurements. Measurements were performed in a home-built SEC cell from polytetrafluoroethylene. As working electrode, a FTO glass was used on the bottom. The reference electrode is an Ag wire and as counter electrode was a Pt coil used.

Solvents were used as received. The electrolyte TBAHFP was five times recrystallized from EtOH/H₂O and dried for 5 days with vacuum at 120 °C. As electrolyte solution a combination of 0.1 M TBAHFP in acetonitrile was prepared in a glovebox.

The FTO was cleaned by ultrasound for 15 mins in acetone, extran solution and distilled water.

The NCs were drop-cast in a nitrogen-filled glovebox, but cell assembly was conducted at air. Before performing electrochemistry on the film, the open circuit potential was determined by the potentiostat and *iR* compensation is applied to each measurement. All cyclic voltammetry cycles were scanned at a speed of 2 mV/s.

Optical Setup. A confocal optical laser setup with a 405 nm laser (PicoQuant LDH series) focused by a long-range objective (Olympus LMPlan FLN, 50x, 0.5 NA) was used. Optical density filters were used to block excitation energy. After excitation, a 485 nm long pass filter was used for cutting off the laser profile. Spectra were collected by an Acton SP300i spectrometer. The integration time of the spectrometer was set to 1 s.

Time-resolved PL measurements were conducted with time-correlated single photon counting electronics (HydraHarp 400, PicoQuant GmbH) and a single photon avalanche diode (PDM series, Micro Photon Devices) at the same confocal laser setup. The data was acquired with 405 nm excitation wavelength, 10 MHz laser repetition rate, and 4 ps TCSPC bin width, recorded at low excitation densities to rule out photon pile-up effects.

LED fabrication.

Materials. Patterned ITO (indium tin oxide) substrates with dimensions 2 cm × 2 cm were purchased from Tsing glass with a layer thickness of 120 nm on a 25 nm SiO₂ buffer sitting on a 0.7 mm thick glass substrate. PEDOT:PSS (AI4083) was purchased from Heraeus Germany GmbH & Co. KG. PTAA (MW = 56 kDa, PDI = 2.87) was purchased from Ossila B.V. TPBi (98%, product ID LT-E302H) was purchased from Lumtec, Taiwan.

Fabrication. All substrates were initially cleaned with industrial grade detergent (alconox), DI water, acetone (technical), isopropyl alcohol (technical) and isopropanol (UV grade) under ultrasonication, stepwise at 5 minutes. The samples were then treated under UV ozone for 15 minutes, immediately followed by spincoating PEDOT:PSS at 3000 rpm for 30 s and annealed at 145 for 15 minutes. The samples were transferred from the cleanroom to a nitrogen filled glove box for further preparation. PTAA solution (5 mg/ml in dichlorobenzene) was spincoated at 3000 rpm for 45 s and annealed at 145 for 15 minutes. The NC solution was spincoated by a two step process (500 rpm for 30 s and 2000 rpm for 5 s). Samples were then transferred to a vacuum deposition chamber with a pressure less than 10^{-6} mbar, without exposing to air. The samples fabricated until this step were the same for LEDs and hole-only devices.

LEDs. TPBi (50 nm) was evaporated at about 1 Å/s, followed by LiF and aluminium at 0.3 Å/s and 1 Å/s, respectively.

Hole only devices. HATCN (10 nm) was evaporated at 0.3 Å/s followed by gold at 1 Å/s.

Characterization. $jV(L)$ curves of both LEDs and single carrier devices are recorded with a Keithley 2612B source meter unit (SMU) at a sweep-rate of 0.1 V/s. A photodiode of known diameter at known distance fitted with a candela filter is used for luminance detection. The EL spectra were measured with the Phelos system from Fluxim AG (Switzerland). Combined with a Lambertian approximation and a pixel area of 4.8 mm², the EQE was determined.

Computational details. The density functional theory (DFT) calculations on the perovskite nano-clusters (or PNCs) were carried out using the CP2K (version 9.1) program.²⁴⁷ The Perdew-Burke-Ernzerhof²⁵⁸ (PBE) functional was used during all the geometry optimization and single-point calculations. Grimme’s D3 dispersion²⁵⁹ correction was also accounted for the van der Waals interactions. A combination of gaussian basis set and plane waves (GPW) as the auxiliary basis function was employed during all the calculations. The double-zeta-valence-polarized²⁵⁶ (DZVP-MOLOPT-SR-GTH) basis set in combination with Goedecker-Teter-Hutter²⁵⁷ pseudopotentials were used for all the elements. Periodic boundary conditions were employed during the structural relaxation and single-point energy calculations. The PNC was placed inside a large unit cell with a dimension of 75 Å x 75 Å x 75 Å to avoid spurious interactions between the periodic images. All the structures were relaxed using the BFGS optimizer, with the maximum force criteria set to 1×10^{-4} Hartree/Bohr (~ 5 meV/Å). The grid cutoff for the gaussian was chosen to be 350 Ry during all the geometry optimization and single-point calculations,

and it was increased to 450 Ry during density-of-states (DOS) calculations.^{107,248} The electronic temperature was set to 300 K and the Fermi-Dirac distribution was employed during the estimation of partial density of state (DOS). All the SCF iterations were converged within a cutoff of 10^{-6} a.u. energy. The visualization and the models of the perovskite were acquired using VESTA¹¹⁹ and Atomistic Simulation Environment GUI (ASE GUI) programs, respectively.

DFT calculations were carried out to investigate the trend in oxidation potential in the cinnamate passivated CsPbBr₃ nanoclusters (PNCs). The electronic structure was modelled using a cubic CsPbBr₃ perovskite nanocube possessing a dimension of 1.7 nm obtained from the bulk cubic unit cell having Cs-Br terminated surface at each direction (see Figure 4.27). Previous experimental and theoretical reports support that the Cs-X (X = halide) terminated is the commonly encountered surface for ligand binding.^{45,107,142,152,248,249,285} The anion-to-lead ratio (Br/Pb) was kept fixed at 4.0 for this composition (Cs₅₄Pb₂₇Br₁₀₈) of the PNC, which is to some extent overestimated compared to the commonly encountered ratio of 2.7-3.3.¹⁴² In the case of the bare PNC, the PBE-D3 computed HOMO-LUMO gap was estimated to be 2.69 eV which is a little higher compared to the experimental gap of 2.3 eV. The overestimation of the band gap (or HOMO-LUMO gap) can be attributed to the interplay between the choice of DFT functional and the finite-size effects of the perovskites.^{45,152} Additionally, a different binding mode where the carboxylate groups are directly attached to the Pb-site was also investigated (see Figure 4.28) to understand their effect on the frontier molecular orbital energy levels. The different binding modes can be identified by their generic formula Cs₅₆Pb₂₇Br₁₀₈(CA)₂ (Cs-coordinated) and Cs₅₄Pb₂₇Br₁₀₆(CA)₂ (Pb-coordinated). Additionally, optical absorption energies (vertical excitations) were also computed using time-dependent density functional perturbation theory (TD-DFPT) using PBE-D3 functional.

Furthermore, the electronic structure of the bare ligands was also computed in the gas phase using the Gaussian 16 (Rev. B.01) program.²⁸⁶ The hybrid B3LYP functional²⁸⁷ with Grimme's D3 dispersion correction²⁵⁹ and the 6-31+G(d,p)²⁸⁸ basis set was used for all the elements to optimize the geometry and single-point energy calculation of the three bare ligands. Subsequent frequency calculations were also performed to ensure the stationary point.

S2. Characterization of exchanged NCs.

- CAH Ligand Exchange.

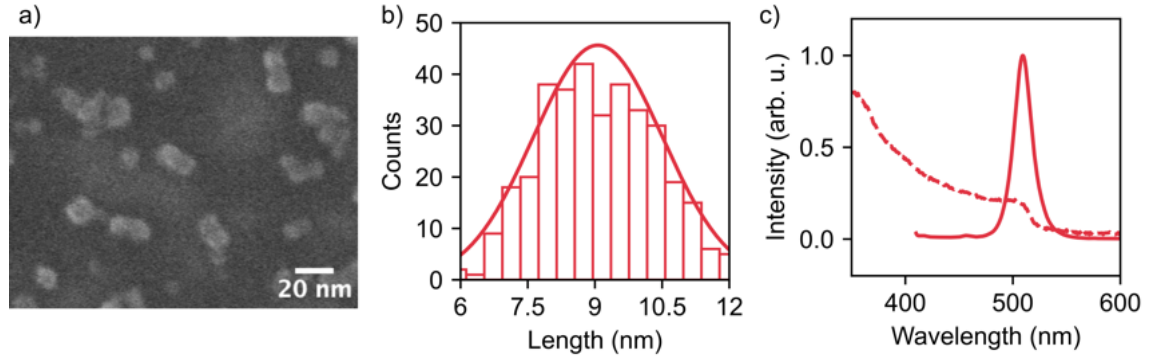


Figure 4.5: Characterization of CAH covered NCs a) SEM image, b) histogram with fitted normal distribution, and c) absorbance (dashed line) and PL spectra (solid line) in chlorobenzene.

- CAOMe Ligand Exchange.

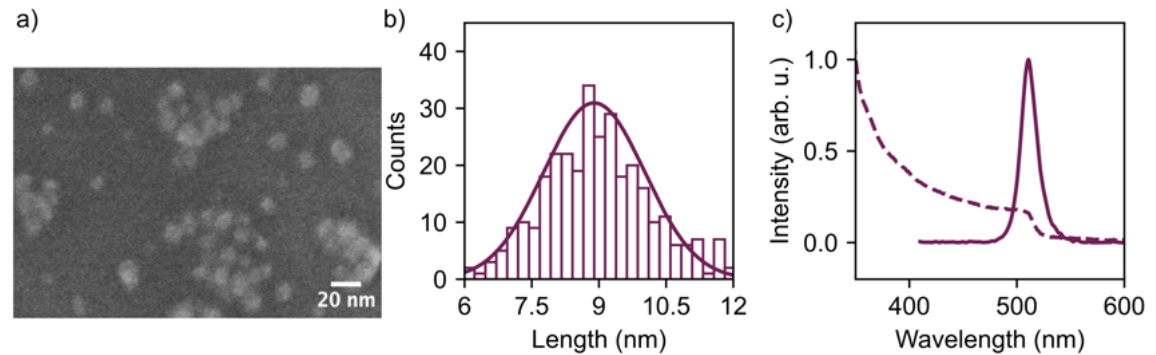


Figure 4.6: Characterization of CAOMe covered NCs a) SEM image, b) histogram with fitted normal distribution, and c) absorbance (dashed line) and PL spectra (solid line) in chlorobenzene.

- CAN(Me)₂ Ligand Exchange.

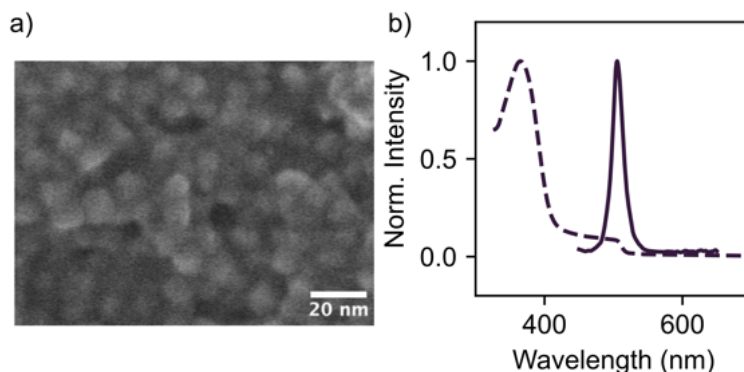


Figure 4.7: Characterization of CAN(Me)₂ covered NCs a) SEM image, b) histogram with fitted normal distribution, and c) absorbance (dashed line) and PL spectra (solid line) in chlorobenzene.

Table 4.1: Summary of extracted characterization for different CA covered NCs from Figure 4.5, Figure 4.6, and Figure 4.7.

Characteristics	CA NCs	CAOMe NCs	CAN(Me) ₂
Max. PL Intensity	509 nm	511 nm	501 nm
Full width half maximum (fwhm)	20 nm	17 nm	20 nm
NC size +/- standard deviation	9.4 +/- 1.7 nm	8.9 +/- 1.2nm	-

S3. ¹H NMR spectra of CAs and exchanged/bound CAs to NCs and full ¹H NMR spectrum of oleate bound NCs.

For each CA derivative, we display the spectra of the free as well as the NC-bound molecule. We observe peak broadening and highfield shifts for characteristic protons of each CA, indicating a bound state. By focusing on the vinyl protons of OA at 5.5 ppm, we verify the loss of OA for all CA-covered NCs in Figure 4.8e. In some cases, e.g. CAOMe-covered NCs, we observe a sharp signal in this spectral region, indicating some free, unbound OA. Full ¹H NMR spectra are provided in the SI – Figure 4.9 and Figure 4.10.

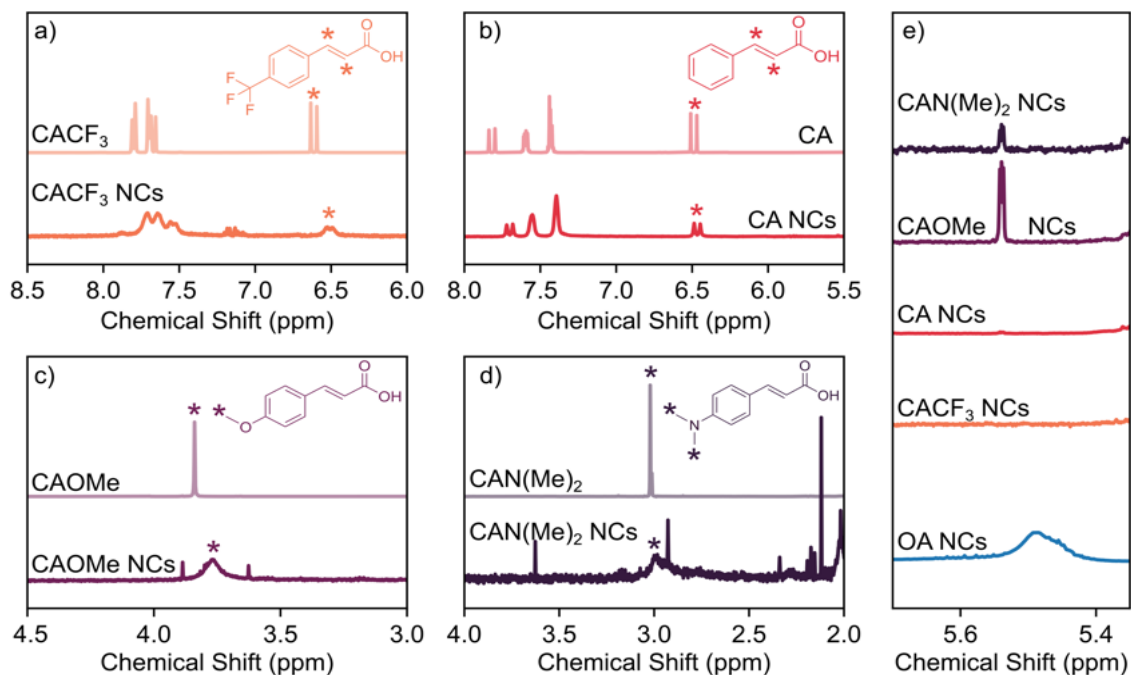


Figure 4.8: Zoomed-in ^1H NMR spectra of free CA (light, cinnamic acid) and exchanged NCs (dark, cinnamate) with characteristic peaks marked in the molecular structure and in both spectra a) CACF₃ in THF-d₈, b) CA in DCM-d₂, c) CAOMe in DCM-d₂, d) CAN(Me)₂ in DCM-d₂, and e) comparison of the signal of vinyl protons of oleic acid for each of the systems.

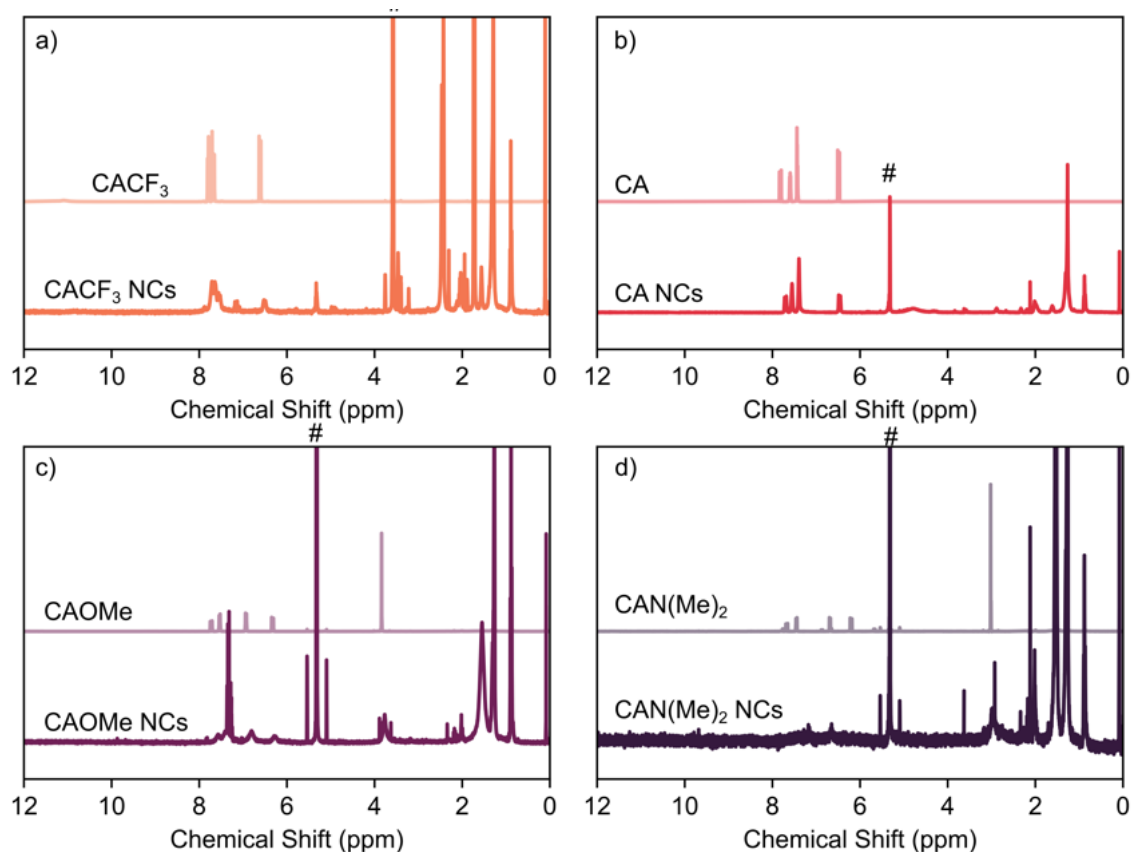


Figure 4.9: Full ^1H NMR spectrum of CAs (top) and cinnamates bound to NCs (bottom) for a) CACF₃ in THF-d₈, b) CA in DCM-d₂, c) CAOMe in DCM-d₂ and d) CAN(Me)₂ in DCM-d₂. Solvent signals marked by #, residues of water can be found at 1.52 ppm in DCM-d₂.

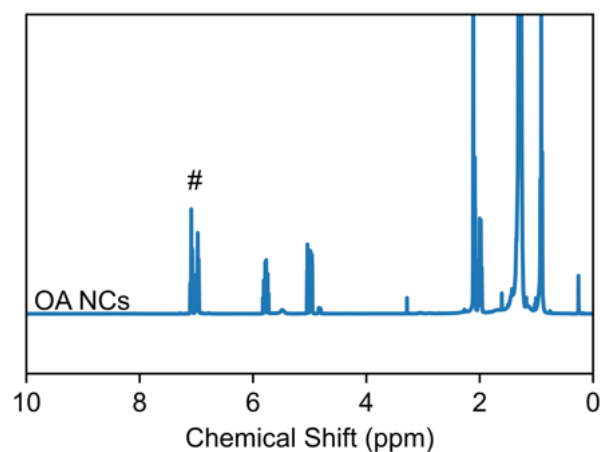


Figure 4.10: ^1H NMR spectrum of oleate bound NCs in toluene-d₈.

S4. Stability measurements of NCs in the electrochemistry cell with electrolyte solution on top for 300 s.

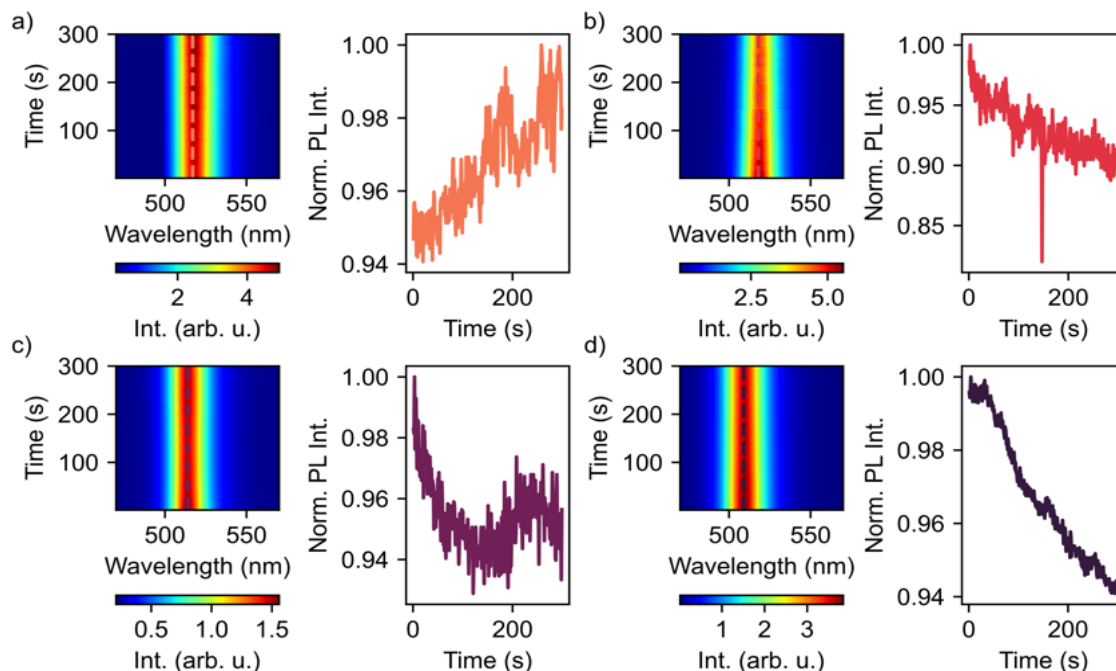


Figure 4.11: PL spectra (on the left) and maximum PL intensity trace (on the right) recorded before application of a potential with electrolyte solution on top of the NCs for a) CACF₃ covered NCs, b) CA covered NCs, c) CAOMe covered NCs, and d) CAN(Me)₂ covered NCs.

S5. Determination of half-wave potential $E_{1/2}$ of ferrocene/ferrocenium couple in CH₃CN/TBAHFP in the used electrochemistry cell.

Since measurements were far apart within a year, the most recent Fc/Fc⁺ reference measurement was used. Therefore, SEC PL data of CACF₃ covered NCs were referenced by 0.43 V vs. Ag PRE, while CAH and CAOMe covered NCs were referenced by 0.54 V vs. Ag PRE.

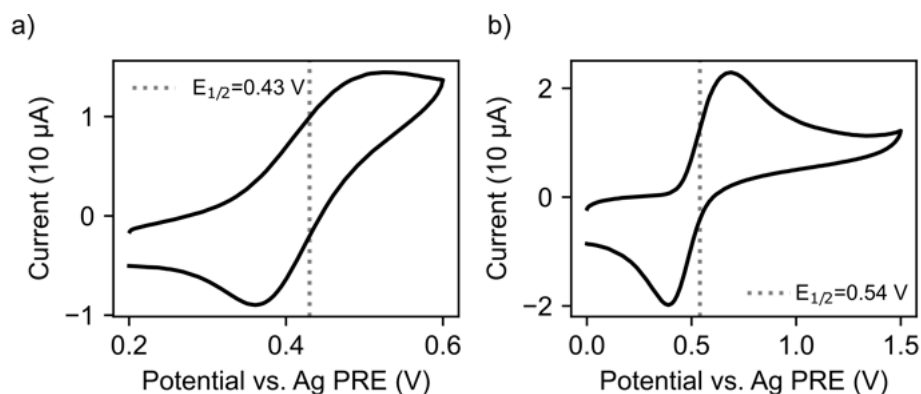


Figure 4.12: Cyclic voltammetry of ferrocene/ferrocenium couple in CH_3CN /TBAHFP against Ag pseudo-reference electrode (PRE). a) Measurement for referencing CACF_3 covered NC SEC PL data, and b) measurement for referencing CA and CAOMe covered NC SEC PL data.

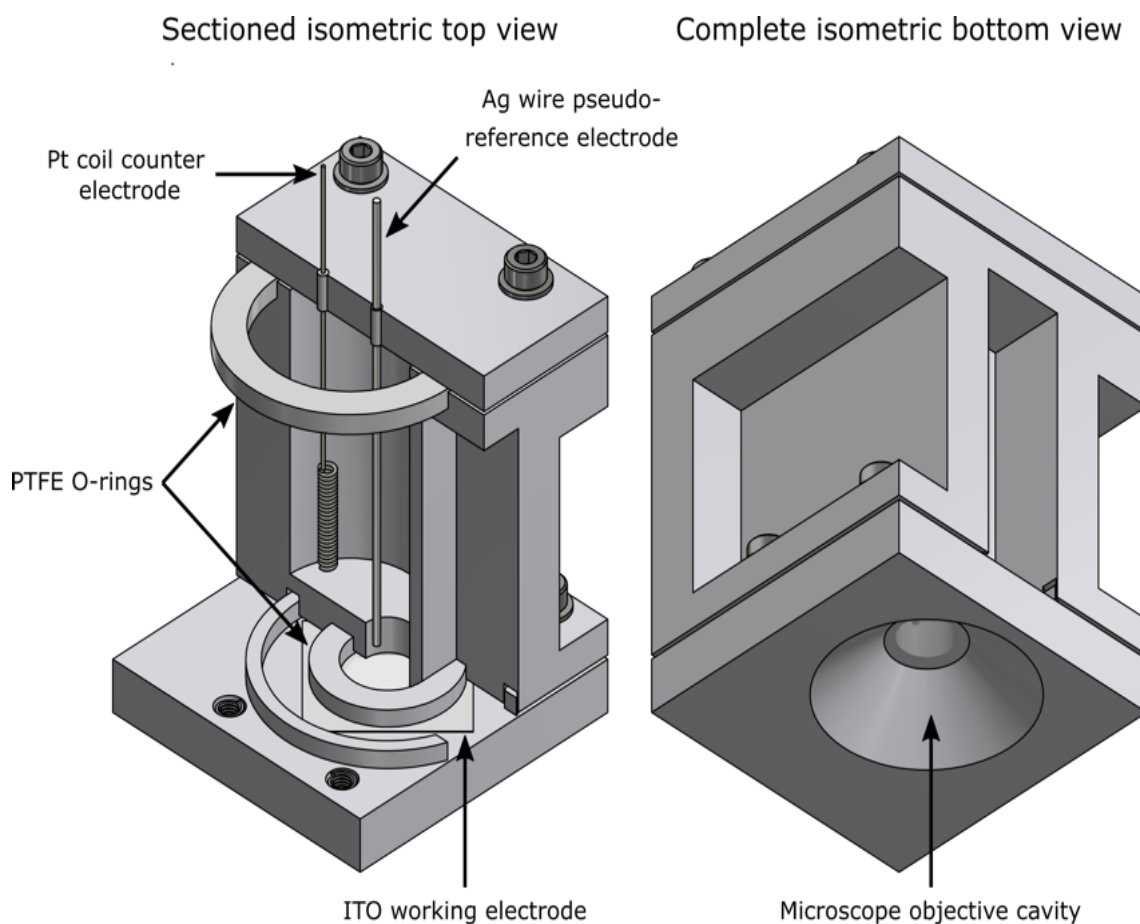


Figure 4.13: Schematic of the used spectroelectrochemistry cell.

S6. Reproducibility and statistics on SEC PL measurements of CA-R covered NCs.

In this subsection other examples of SEC PL on the exchanged samples are shown as a sign of reproducibility. The determined values of p-doping are included into the statistics in Figure 4.3c. All values included in this Figure are shown in Table 4.2.

- CACF₃ covered NCs.

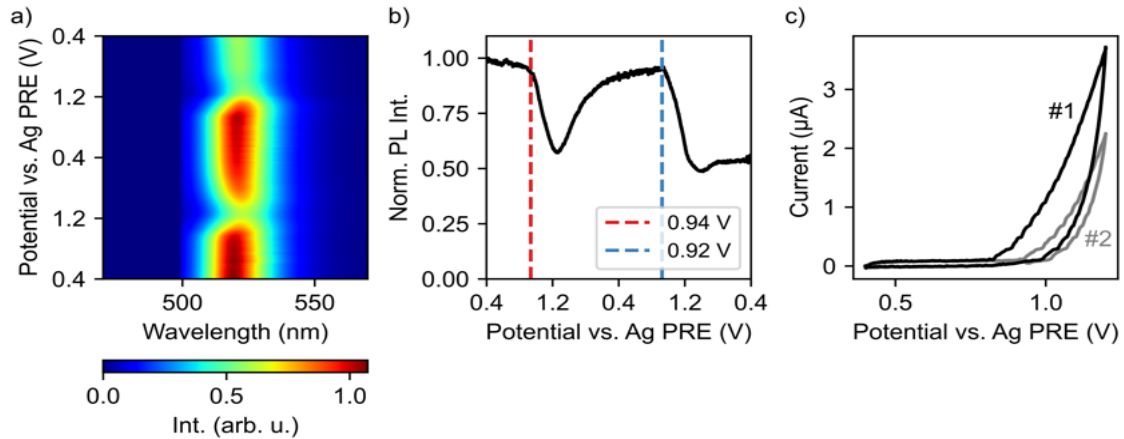


Figure 4.14: SEC PL on CACF₃ covered NCs. a) Heat-map of PL spectra assigned to potential sweep, b) maximum intensity trace with determined p-doping potentials at 0.94 for the first CV cycle, and 0.92 V for the second CV cycle, and c) corresponding CV with first and second CV scan indicated.

- CA

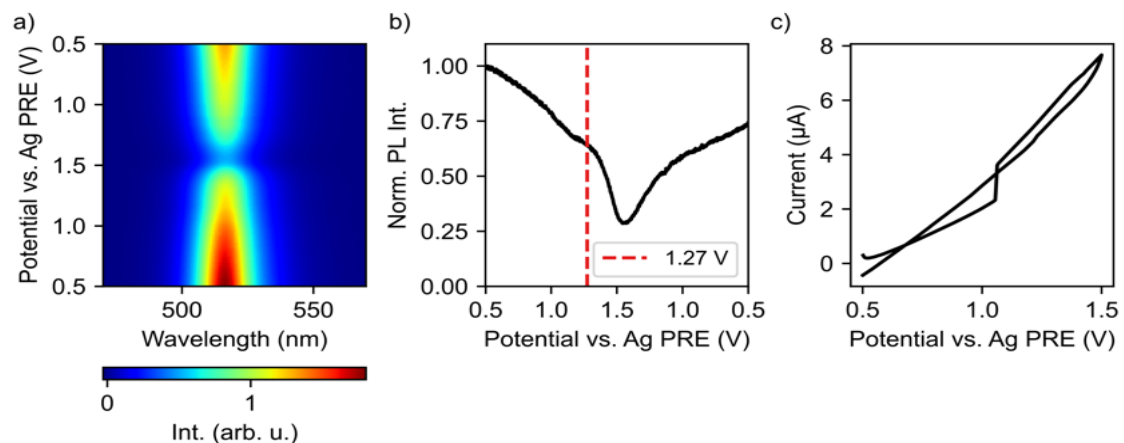


Figure 4.15: SEC PL on CA covered NCs. a) Heat-map of PL spectra assigned to potential sweep, b) maximum intensity trace with determined p-doping potentials at 1.27 V, and c) corresponding CV.

- CAOMe covered NCs.

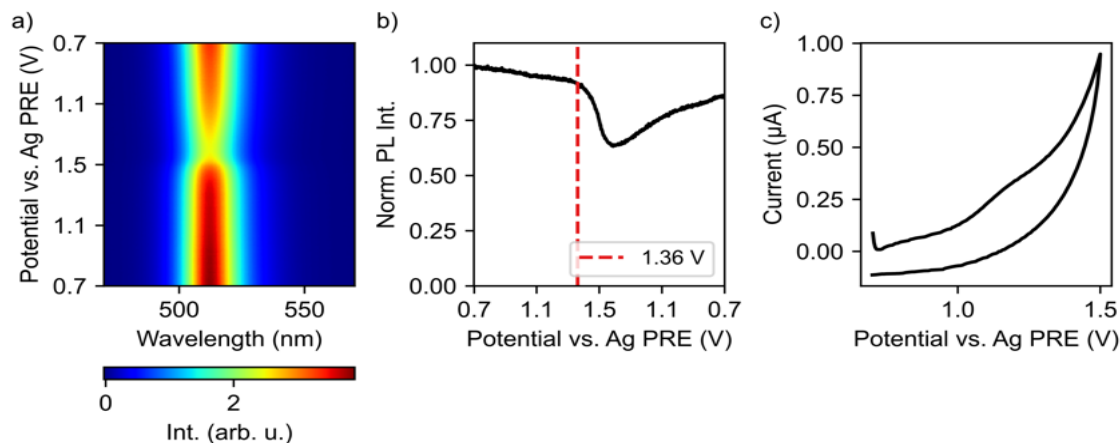


Figure 4.16: SEC PL on CAOMe covered NCs. a) Heat-map of PL spectra assigned to potential sweep, b) maximum intensity trace with determined p-doping potentials at 1.36 V, and c) corresponding CV.

- Statistics on p-doping of NCs.

Table 4.2: Summary of all potential values of p-doping for each of the cinnamic acid covered NCs and also referenced values.

CACF ₃ (11 values, referenced by E _{1/2} (Fc/Fc ⁺) = 0.43 V vs Ag PRE	CA (6 values, referenced by E _{1/2} (Fc/Fc ⁺) = 0.54 V vs Ag PRE	CAOMe (8 values, referenced by E _{1/2} (Fc/Fc ⁺) = 0.54 V vs Ag PRE
0.84 → 0.41	1.26 → 0.72	1.31 → 0.77
1.0 → 0.57	1.31 → 0.77	1.27 → 0.73
0.96 → 0.53	1.36 → 0.82	1.39 → 0.85
0.85 → 0.42	1.27 → 0.73	1.25 → 0.71
0.94 → 0.51	1.13 → 0.59	1.28 → 0.74
1.05 → 0.62	1.21 → 0.67	1.37 → 0.83
0.8 → 0.37		1.39 → 0.85
0.92 → 0.49		1.36 → 0.82
0.89 → 0.46		
0.94 → 0.51		
0.92 → 0.49		

S7. Evaluation of SEC PL on CAN(Me)₂ covered NCs.

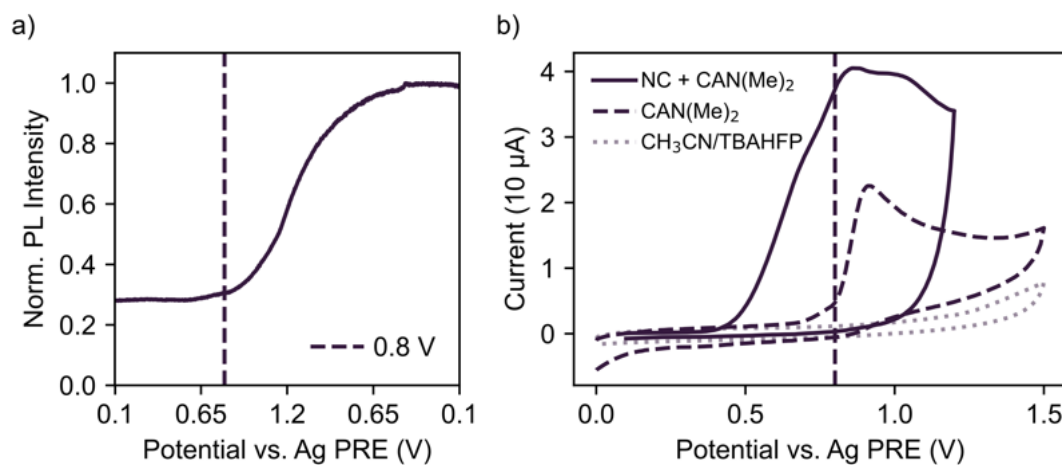


Figure 4.17: Determination of p-doping/oxidation of CAN(Me)₂ covered NCs. a) SEC PL on CAN(Me)₂ NCs with its maximum intensity trace, b) corresponding CV to SEC PL (solid line), CV of bare CAN(Me)₂ (dashed line), and CV of electrolyte solution (dotted line).

CAN(Me)₂ covered NCs show a different behavior than the other CA covered NCs. Instead of p-doping and a resulting bleach of the PL, the NCs show brightening starting at approx. 0.8 V vs. Ag PRE. Further investigations of the bare CA show that within the electrochemical window, the CA itself is oxidized. Due to the oxidation of the CA on the surface of the NC, the surface of the NC is altered, and this influences the PL intensity trace.

S8. Cyclic voltammetry of CAs in CH₃CN/TBAHFP.

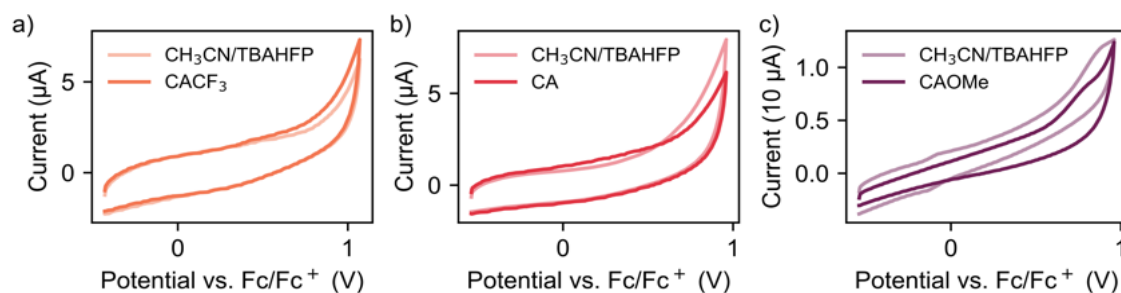


Figure 4.18: Cyclic voltammetry of a) CACF₃, b) CA, and c) CAOMe with background measurement of the electrolyte solution CH₃CN/TBAHFP.

S9. Characterization of CA-R/OAm NCs used in LEDs.

- Before ligand exchange.

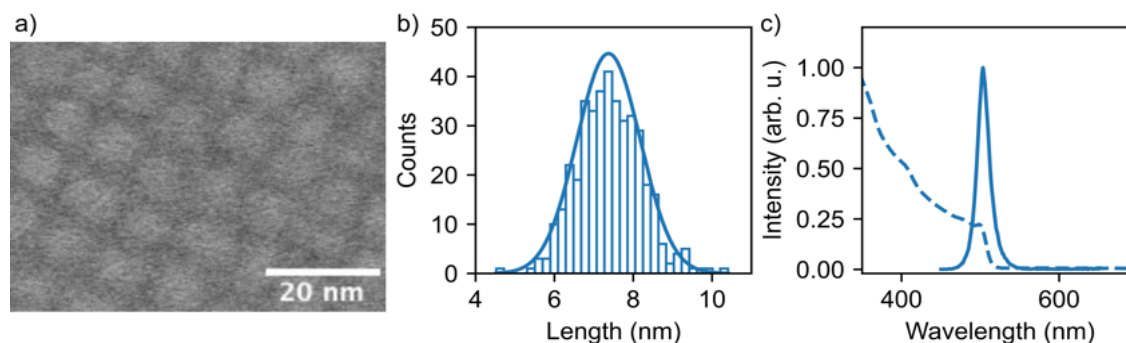


Figure 4.19: Characterization of OA/OAm covered NCs after synthesis. a) SEM image, b) size determination by SEM evaluation fitted to normal distribution (7.4 nm $\pm$ 0.8 nm), and c) PL (503 nm, fwhm: 17 nm) and absorbance spectra.

- After ligand exchange.

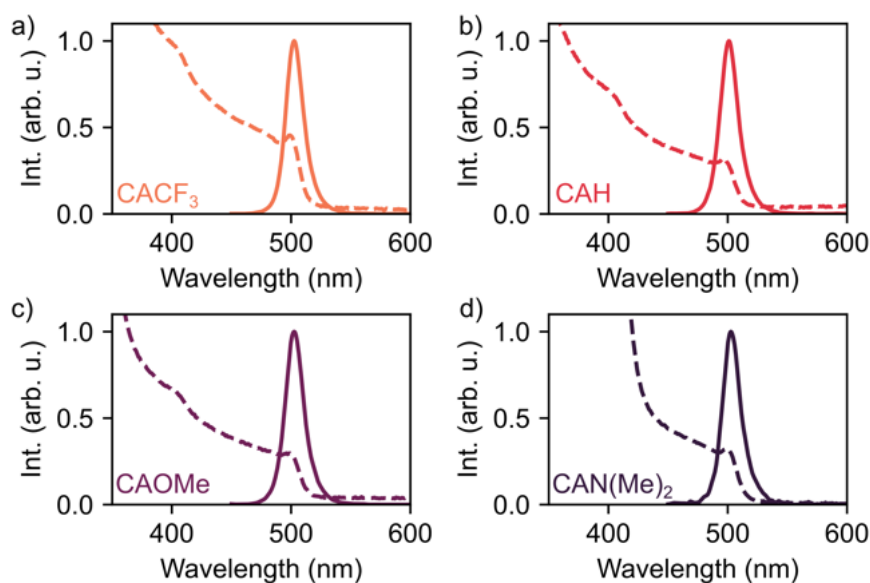


Figure 4.20: PL and absorbance spectra of CAR/OAm exchanged NCs in solution (chlorobenzene) before application in LED, a) CACF_3/OAm , b) CA/OAm , c) CAOMe/OAm , and d) $\text{CAN}(\text{Me})_2/\text{OAm}$ covered NCs.

Table 4.3: Extracted PL maximum and full width at half maximum of PL spectra in solution in Figure 4.20.

Characteristics	CACF ₃ /OAm NCs	CA/OAm NCs	CAOMe/OAm NCs	CAN(Me) ₂ /OAm NCs
PL max	503 nm	501 nm	503 nm	503 nm
fwhm (nm)	17	18	18	17

S10. Characterization of LEDs

- SEM cross-section

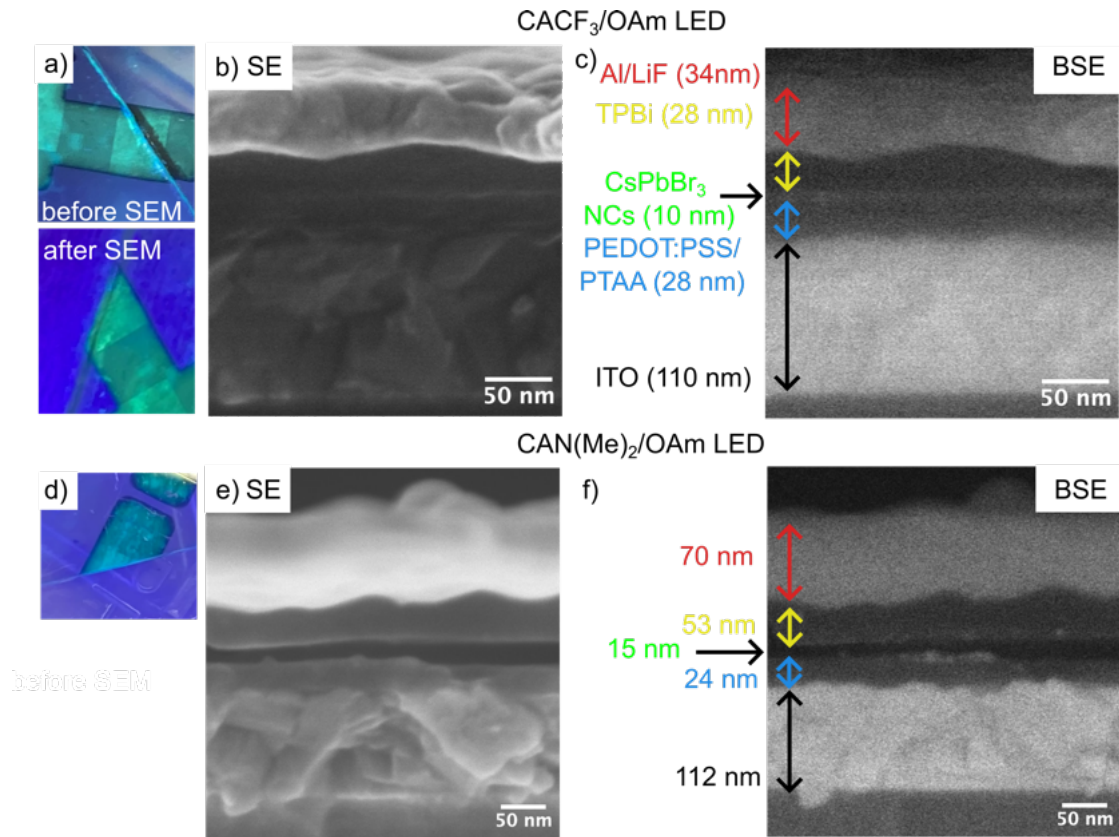


Figure 4.21: Characterization of CACF₃/OAm (top) and CAN(Me)₂/OAm (bottom) LEDs. a) Photo of UV-illuminated broken LED before and after SEM, b) secondary electron (SE) image of the cross-section, c) corresponding back-scattered electron (BSE) image with determination of layered materials and their thicknesses, d) Photo of UV-illuminated LED before SEM, e) SE image and f) BSE image of the same position with determination of layer thicknesses.

- Time-resolved PL

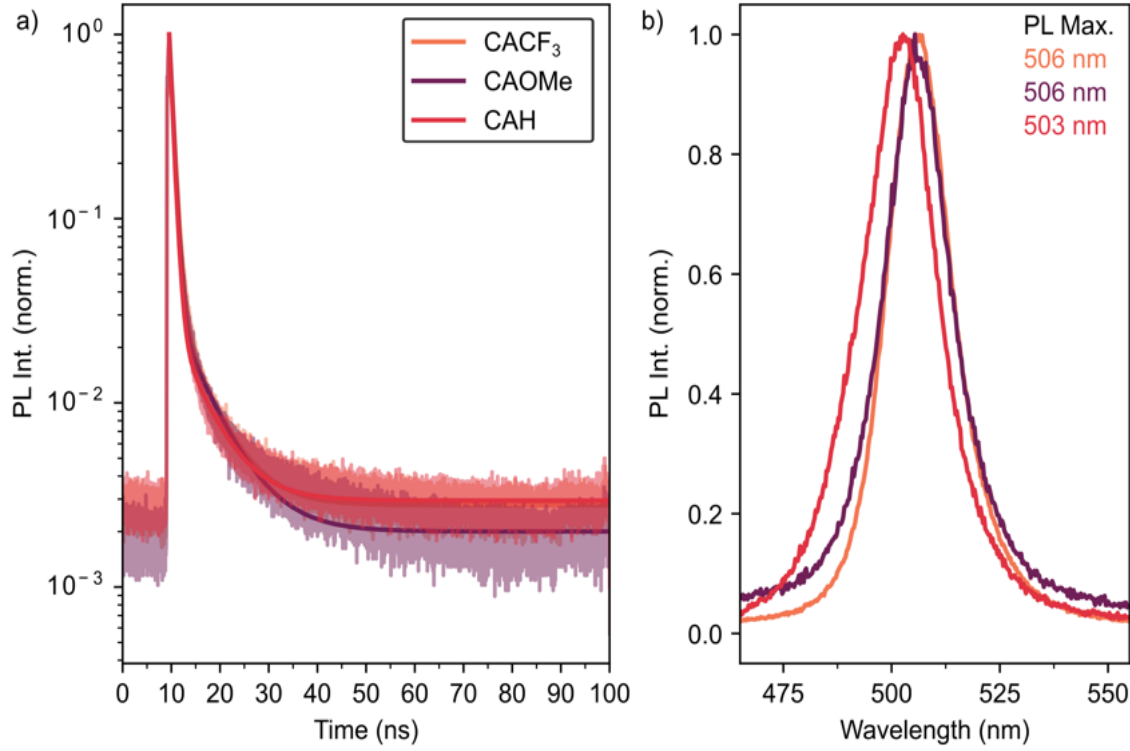


Figure 4.22: a) PL decays and their biexponential fits as solid lines, recorded by means of time-correlated single photon counting for different CA-R/OAm NC samples in LEDs. b) Steady-state PL spectra recorded from the samples.

Biexponential fit function:

$$I(t) = A_{rel,1} \exp\left(-\frac{t}{\tau_1}\right) + A_{rel,2} \exp\left(-\frac{t}{\tau_2}\right) \quad (4.1)$$

Table 4.4: Fitting parameters extracted from the biexponential fits of the PL decays in Figure 4.22).

Sample	$A_{rel,1}$	τ_1 (ns)	$A_{rel,2}$	τ_2 (ns)	$\tau_{Av,Amp}$ (ns)	$\tau_{Av,Int}$ (ns)
CACF ₃	0.9653	0.797	0.0347	6.01	0.9778	1.908
CAOMe	0.96814	0.716	0.03186	6.68	0.9061	2.12
CAH	0.97344	0.7031	0.02656	6	0.8439	1.703

S11. Performance of LEDs.

- Repetition of jVL measurements and determination of maximum EQE.

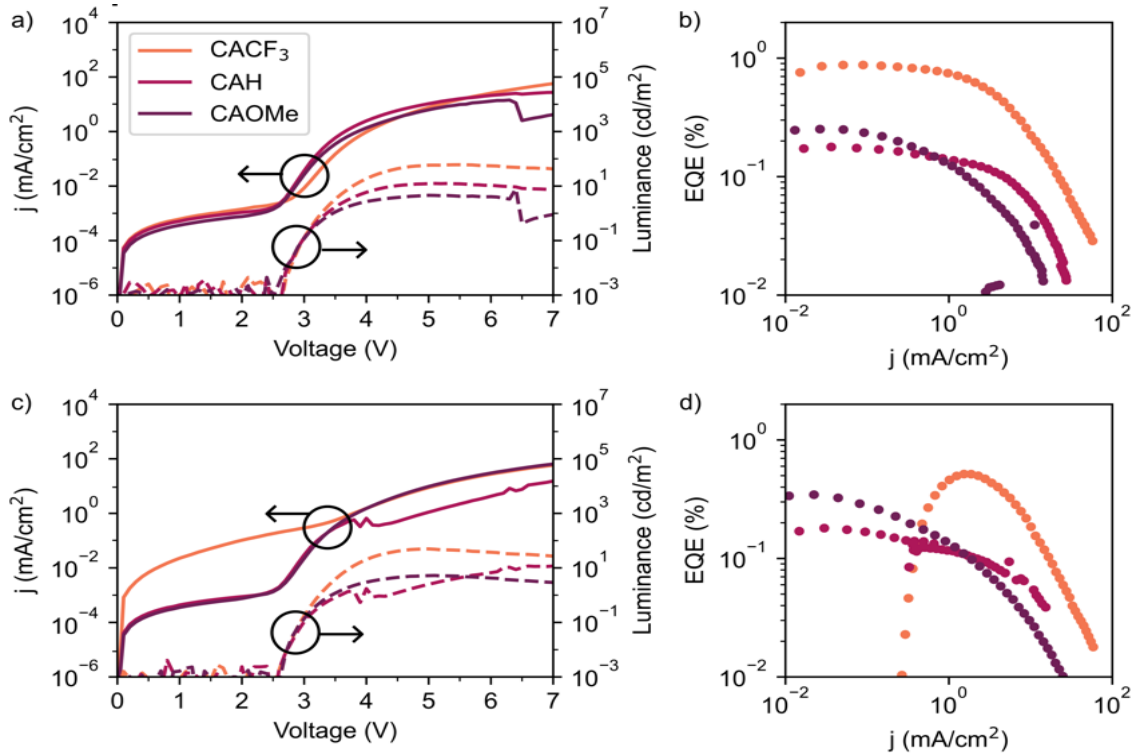


Figure 4.23: j-V-L and EQE of two different pixels for each of the CA-R LEDs. a) Pixel 1 j-V-L plot of CAH, CAOMe and CACF₃ NC b) corresponding EQE vs. j plot to Figure 4.23a, c) Pixel 2 j-V-L plot of the three CA-R/OAm covered NCs, d) extracted EQE vs. j plot from Figure 4.23c.

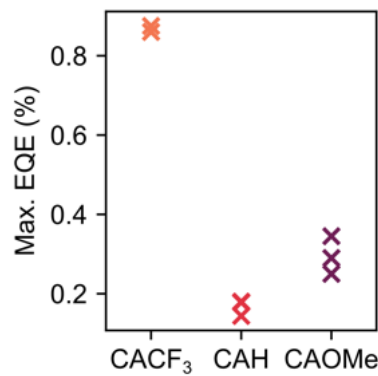


Figure 4.24: Determined maximum EQE values for three measurements (Figure 4.4 and Figure 4.23) of jVL of CACF₃/OAm (two measurements, without data from Figure Figure 4.23c), CAH/OAm and CAOMe/OAm LEDs.

- LEDs of as-synthesized NCs.

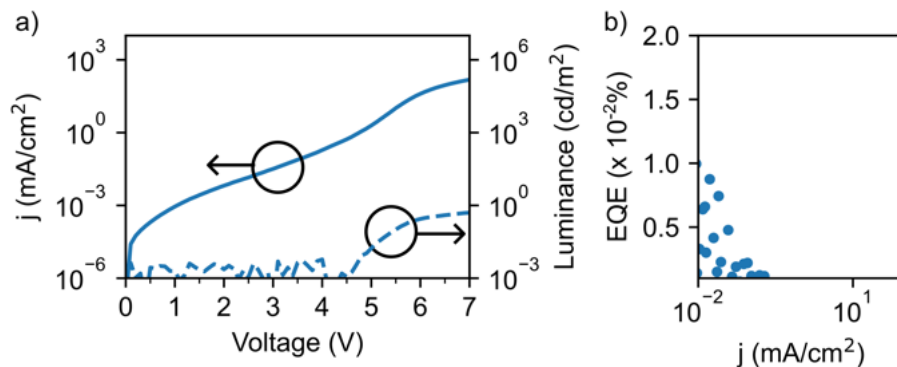


Figure 4.25: Characterization of as-synthesized OA/OAm NC LEDs. a) current density (j , solid line) and luminance (dashed line) vs. voltage, b) EQE vs. j .

- Electroluminescence (EL) of CA-R/OAm covered NCs.

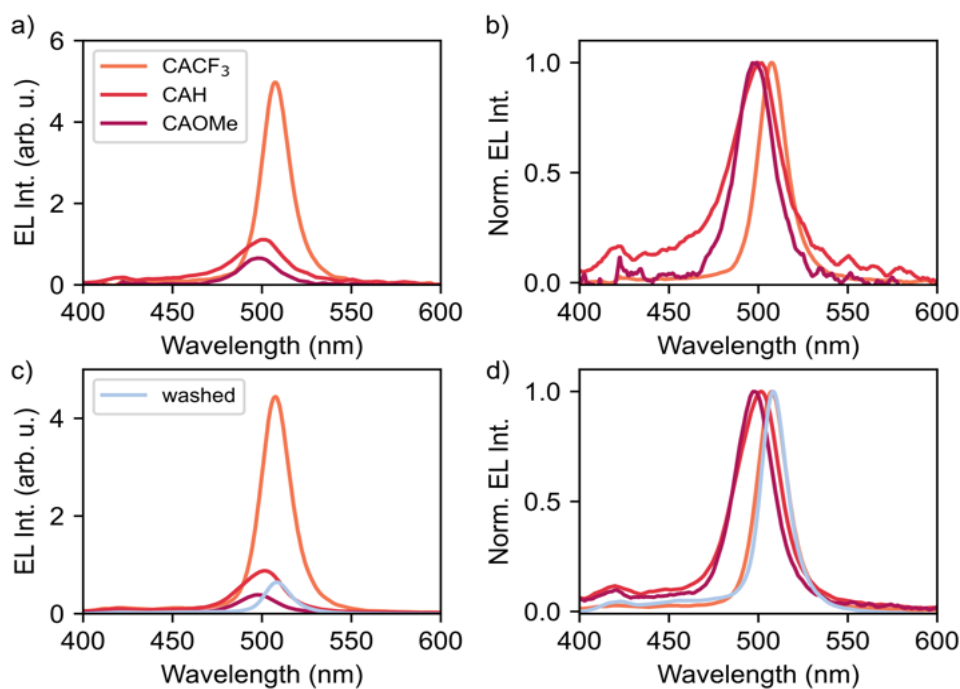


Figure 4.26: EL spectra of modified CA-R/OAm NCs operated at 0.1 mA (top) and 1 mA (bottom). a) EL spectra of CACF₃, CAH and CAOMe/OAm NCs, b) normalized EL spectra of Figure 4.26a, c) EL spectra at 1 mA of CA-R/OAm and washed NCs, and d) normalized EL from Figure 4.26c.

Table 4.5: Extracted EL maximum and full width at half maximum (fwhm) of electroluminescence in Figure 4.26, top 0.1 mA, bottom 1 mA.

Characteristics	CACF ₃ /OAm NCs	CA/OAm NCs	CAOMe/OAm NCs	Ligand Stripped
EL max	507 nm	500 nm	499 nm	-
fwhm (nm)	19	32	24	-
EL max	507 nm	501 nm	497 nm	508 nm
fwhm (nm)	19	30	26	17

S12. Theoretical calculations on CAs and CA-NC systems.

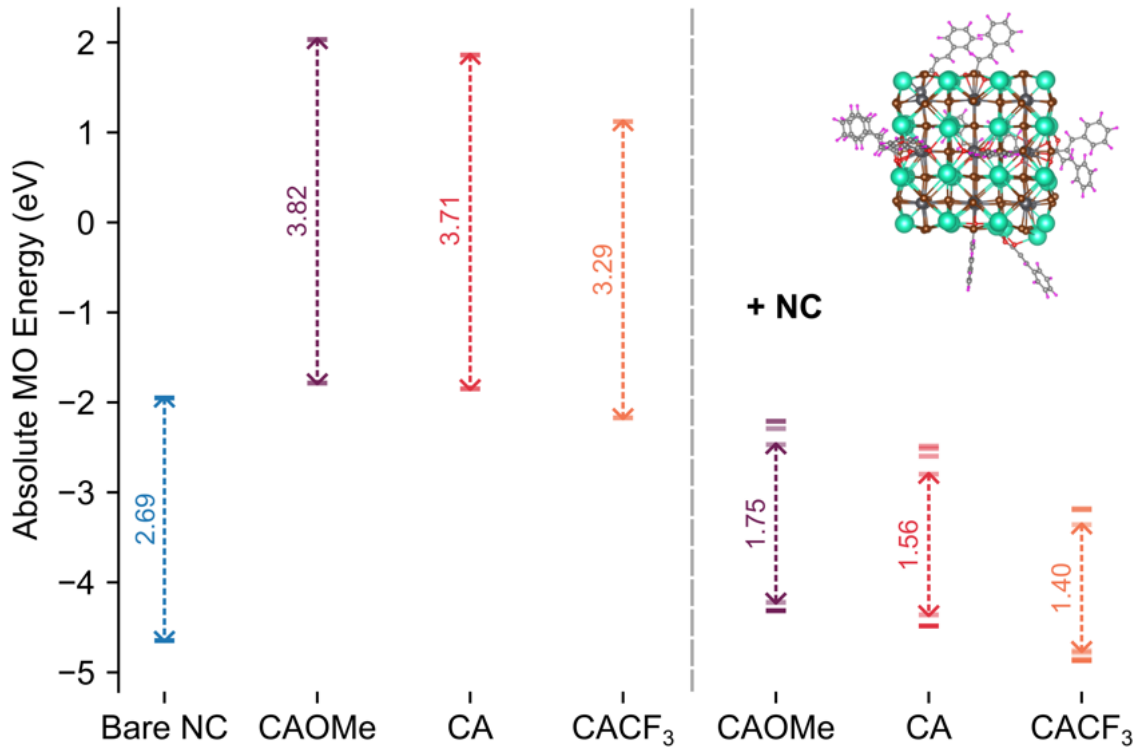


Figure 4.27: DFT-D3 computed molecular orbital energies (MO) of bare NCs, bare CAs, and 12 CAs attached to the NCs (two per side, Cs⁺ binding site) and their ligand-centric trap states (lightly colored).

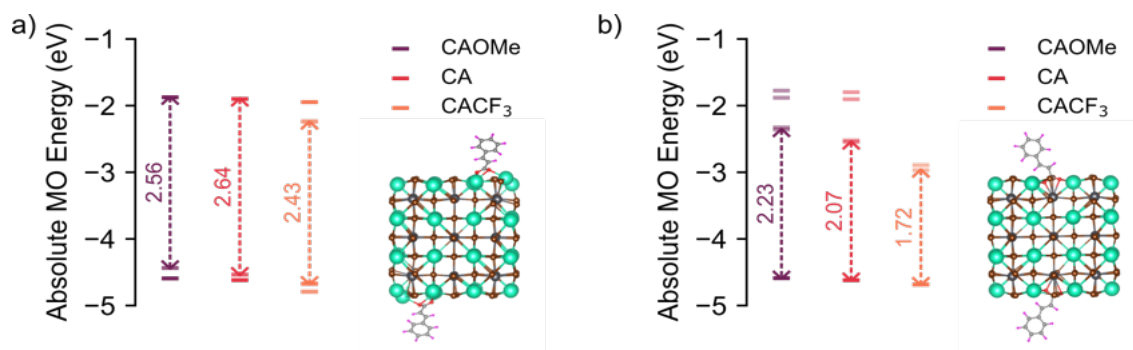


Figure 4.28: PBE-D3 computed molecular orbital energy levels of CA-R attached to NCs with ligand-centric trap states (lightly colored) of varied ligand binding site a) two ligands attached to Cs⁺ center, and b) two ligands directly attached to Pb²⁺ center).

Table 4.6: Absorption excitation energies obtained from Time-Dependent Density Functional Perturbation theory using PBE-D3 functional.

Species	TD-DFPT Excitation energy (eV) (Major Peaks)	Oscillator strength (a.u.)
CAH NCs	2.64	6.0E-04
	2.71	1.84E-04
CACF ₃ NCs	2.63	2.37E-02
	2.64	1.90E-02
	2.70	1.85E-04
CAOMe NCs	2.56	7.30E-04
	2.64	1.20E-04
	2.74	1.45E-03

S13. Evaluation of SEC PL on OA covered NCs.

Here, we are showing a comparison of SEC PL on OA/OAm NCs directly after synthesis (excess ligands) and with once washed OA covered NCs. Figure 4.29 shows typical photobleaching behavior of the NCs in the intensity profile and the CV does not show any rise in current at a specific applied potential. Instead, the current increases over the whole electrochemical window linearly. We attribute this rise in current as a charging up effect. The NCs are not charged (as can be observed in PL behavior), instead charge is injected into solution, but also the same way extracted in the reversed scan. Also, the wide electrochemical window can be highlighted in this measurement. Within this window Pb oxidation occurs, which would lead to direct decomposition of the NCs. In comparison, in Figure 4.30 charges are injected

into the NCs, the PL decays at 0.9 V vs Ag PRE and also in the current increases roughly at this potential.

These results show that charge injection into NCs can be only achieved by removing full surface coverage by long insulating ligands (OA/OAm).

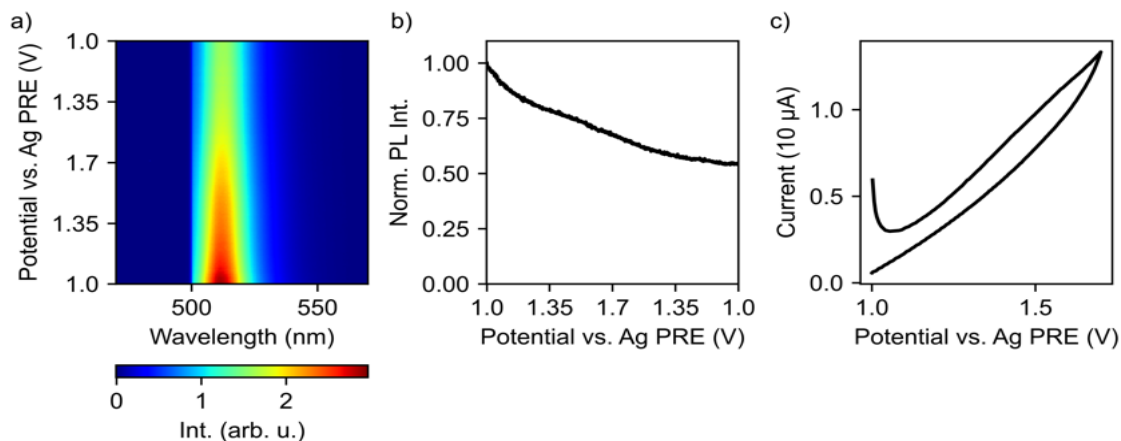


Figure 4.29: SEC PL on OA/OAm covered NCs in PC/TABHFP. a) Heat-map of PL spectra assigned to potential sweep, b) maximum intensity trace, and c) corresponding CV showing capacitive current at the beginning of the potential sweep.

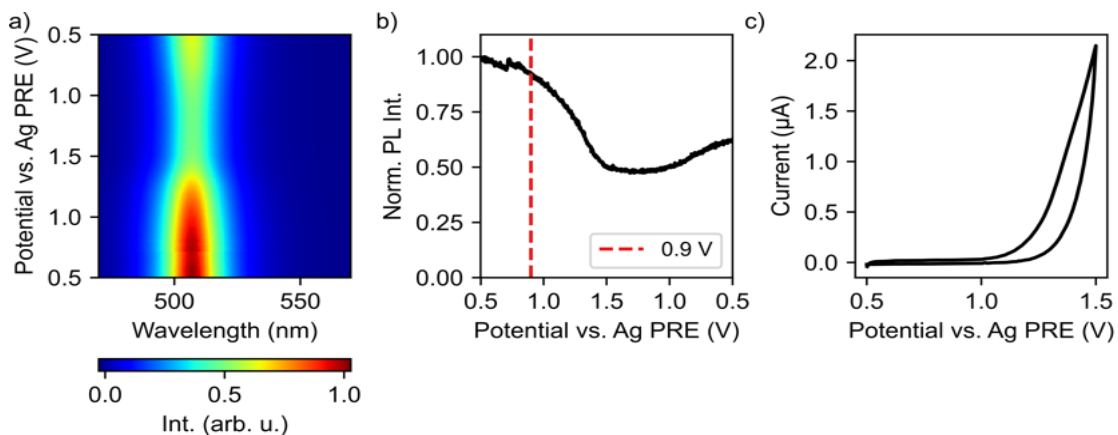


Figure 4.30: SEC PL on OA covered NCs (once precipitated with MeOAc!) in PC/TBAHFP. a) Heat-map of PL spectra assigned to potential sweep, b) maximum intensity trace with determined p-doping potentials at 0.9 V, and c) corresponding CV.

5 Spatial Mapping of Electrochemical Hole Injection into Supercrystals of Perovskite Nanocrystals

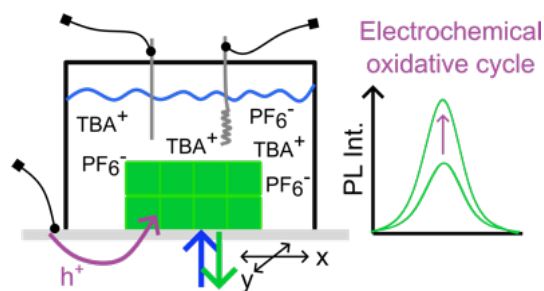
Theresa Hettiger¹, Jonas L. Hiller¹, Richard Hodak¹, Martin Eberle¹, Alfred J. Meixner¹, and Marcus Scheele^{1,*}

1. Institute for Physical und Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany.

* Corresponding author

The upcoming chapter covers PL SEC conducted on self-assembled CsPbBr₃ SCs. In combination with spatially resolved optics, PL brightening following electrochemical hole injection is reported.

The results presented here are published in ref. [47].



Reprinted (adapted) with permission from Nano Letters, 2026, 26 (29): 9403–9409. Copyright © 2026 American Chemical Society. The publication is licensed under Creative Commons-BY 4.0 License.

5.1 Abstract

Lead halide perovskite nanocrystals are of interest for the application as emissive layer in light emitting diodes (LEDs) due to their high photoluminescence quantum yield, their color tunability and their defect tolerance. For the application in LEDs, charges need to be easily transferred from the charge transport layers to the nanocrystal core without compromising their optoelectronic properties.

While charging of nanocrystals can be studied by spectroelectrochemistry (SEC) in general, in this work we combine SEC with diffraction-limited optical resolution. This allows studying hole injection into self-assembled supercrystals of CsPbBr₃ nanocrystals and determining the spatially dependent potential for this action. We find an overall brightening of the photoluminescence, which is gradually shifting from the edges to the supercrystal center, and a generally greater resistance toward electrochemical degradation in the supercrystals.

5.2 Introduction

Thin films of lead halide perovskite nanocrystals (NCs) are promising for the application in light emitting diodes (LEDs)^{289–291} since they show high photoluminescence (PL) quantum yield,^{28,292,293} narrow emission line width,²⁹ and a wide color gamut enabled by anion exchange.^{30,31} In addition to these properties, self-assembly of lead halide perovskite NCs into supercrystals (SCs)^{175,294} gives rise to collective coupling effects, such as superfluorescence,¹⁸³ minibands,^{175,295} and amplified spontaneous emission.²⁹⁶ The high PL intensities and narrow line widths resulting from these phenomena have sparked the idea to build micro-LEDs from single lead halide perovskite SCs.^{297,298} However, to realize such devices several obstacles that are specific to SCs need to be overcome. In particular, charge injection and transport through the SC are not trivial since typical SCs are much thicker ($> 1 \mu\text{m}$) than most active layers in NC-based LEDs ($< 100 \text{ nm}$). In addition, the poor long-term stability of lead halide perovskite NCs, especially under bias, remains a challenge.^{266,299,300}

We and others have recently shown that spectroelectrochemistry (SEC) is an ideal tool to address these questions.^{46,220,282,301} In particular, SEC is a powerful method to study band alignment in heterostructures,^{215,302} charge injection potentials,²¹⁷ and surface passivation/trap formation on the surface.^{216,303} Due to the high sensitivity of SEC, it is even possible to investigate single NCs and determine the number of transferred electrons.^{242,304,305}

However, SEC of individual lead halide perovskite SCs has not been reported, yet. Most likely, this is because of their dynamic surface chemistry³⁵ and halide mobility,²²¹

which leads to irreversible electrochemical oxidation and limits the time window for performing such measurements.^{221,306–308} Nonetheless, hole injection into thin films of CsPbBr₃ NCs has recently been demonstrated.^{45,46,221}

In this work, In this work, we successfully measure the PL under SEC control of individual CsPbBr₃ SCs with diffraction limited spatial resolution in the electrochemical window of hole injection. To this end, we alter the surface of the NCs to achieve facilitated charge injection and high stability in polar solvents. For SCs self-assembled from such modified NCs, we observe hole injection above 0.43 V vs. Fc/Fc⁺, followed by an increase in PL, starting from the edges toward the center of the SCs. Spectral mapping after SEC reveals an overall increase in PL intensity of the SCs, which highlights their robustness against degradation by electrochemical hole injection.

5.3 Results and Discussion

For the SEC experiments in this work, the NCs need to allow for relatively fast charging rates and high stability against polar solvents, such as propylene carbonate (PC),²²² which is typically not afforded by as-synthesized lead halide perovskite NCs in view of their insulating and labile oleic acid (OA)/oleylamine (OAm) ligand shell. In this work, we consider both factors in the pretreatment of the NCs. Therefore, we perform a ligand exchange in solution to a partial lecithin coverage. As a zwitterionic ligand, it is described to bind more tightly to the NC surface and shows higher stability against polar solvents during washing procedures.^{41,155} Afterwards, we precipitate the NCs with acetone as antisolvent to remove excess ligands. We monitor the effect of this pretreatment on the surface chemistry of the NCs by quantitative NMR spectroscopy. From SI – Figure 5.5, we can deduce a surface coverage of 561 OA/OAm and 50 lecithin molecules per NC. This deviation from the theoretical full-surface coverage of 953 ligands per NC, assuming 2.9 ligands/nm²,³⁵ facilitates charge injection through free surface sites. The sample preparation process is schematically depicted in Figure 5.1a.

Figure 5.1b displays the steady-state optical absorbance and PL spectra of the CsPbBr₃ NCs as obtained from synthesis and after successful ligand exchange in solution. Following the ligand exchange, a redshift of approx. 4 nm is observed. Specifically, the first excitonic transition (see inset) shifts from 499 nm to 504 nm, while the PL maximum shifts from 503 nm to 507 nm. This red-shift suggests a larger NC size after the exchange, which we corroborate by electron microscopy to find an increase of the average NC diameter from 7.4 ± 0.8 nm to 8.2 ± 0.9 nm (SI - Figure 5.6). The increase in size and PL maximum can be attributed to

Ostwald ripening during the ligand exchange by antisolvent precipitation.^{278,309–311} Additionally, the exchanged NCs exhibit more pronounced first and second excitonic transitions, along with a reduction in the PL full width at half maximum from 17.5 nm to 16.3 nm.

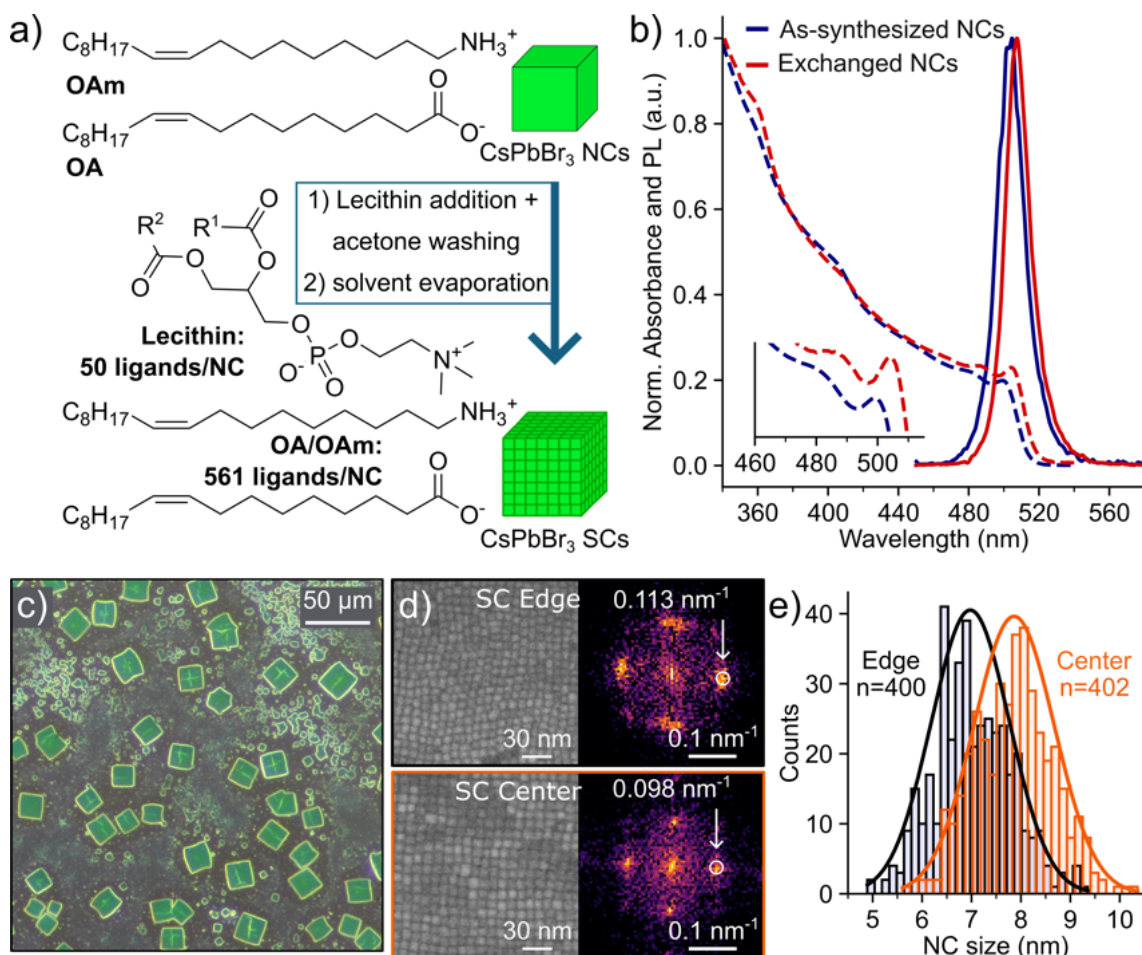


Figure 5.1: Characterization of CsPbBr₃ NCs and their self-assembled SCs. a) Scheme of the NC post-synthetic treatment. b) Absorbance (dashed lines) and PL spectra (solid lines) of as-synthesized NCs (blue) and NCs after partial ligand exchange (red). c) Dark field optical micrograph of SCs, self-assembled from the exchanged NCs by slow evaporation of the solvent on FTO substrates. d) High-resolution SEM characterization of a SC with comparison of NC sizes on the edges of the SC (black) to the center of the SC (orange). Size determination by FFT analysis of SEM image (in d)) and e) measuring edge lengths of n NCs and fitting to a normal distribution (right).

By slow evaporation of the solvent, square SCs form readily from the exchanged solutions on conductive and transparent fluorine-doped tin oxide (FTO) substrates, as shown in Figure 5.1c. These SCs range in size from approximately $5 \times 5 \mu\text{m}^2$ to $30 \times 30 \mu\text{m}^2$ (SI – Figure 5.7). Figure 5.1d shows high-resolution SEM images

acquired from the edge and the center of a representative SC and their respective fast Fourier transforms (FFTs). As evident from the SEM images and the azimuthal broadening of the first-order FFT signals, the order of the SC lattice is more pronounced in the center. From the reciprocal of the indicated distance to the zero-order frequencies, we determine an average NC center-to-center distance (NC + interdigitated ligand shell) of 8.8 nm and 10.2 nm at the SC edge and center, respectively. We compare these values with the manually measured edge lengths of the inorganic NC cores in the histogram in Figure 5.1e, yielding average edge lengths of approx. 7 nm and 8 nm at the SC edge and center, respectively. The difference accounts for the ligand shell with 1.8 nm at the edges and 2.2 nm in the SC center.

Figure 5.2a depicts a sketch of the cell used for SEC PL experiments. The cell creates a solvent-tight seal around the central part of a FTO working electrode (WE) in a volume containing an Ag wire pseudo-reference electrode (pRE) and a Pt coil counter electrode (CE). The cell, with all three electrodes connected to a potentiostat, can be placed on top of an inverted confocal laser-stage scanning microscope to track the response of the spatially-resolved PL to polarization changes of the working electrode. A detailed description of the cell and measurement setup is given in the Materials and Methods section of the SI. All potentials stated in this work are referenced to the half-wave potential of the ferrocene/ferrocenium redox-couple recorded in the SEC cell (SI – Figure 5.10, vs. Fc/Fc^+ , which will be omitted in the following).

Figure 5.2b displays maps of the PL intensity (top) and the peak wavelength (bottom) emitted by CsPbBr_3 SCs on the FTO working electrode. We find that the brightly emitting SCs are surrounded by a weaker emitting thin-film region of NCs. With 506 nm, the PL from this film exhibits roughly the same peak wavelength as the NCs in solution. In contrast, PL of the SCs is red-shifted and displays an increase in peak wavelength along a radial gradient from around 508 nm at the SC edges up to around 514 nm in the SC center. We attribute the overall red-shift of the NCs assembled in the SC to coupling/mini-band formation,¹⁷⁵ while the effect in red-shifted emission toward the SC center is presumably caused by the increase in NC size (see Figure 5.1e).

The corresponding maps of the same sample area after the addition of the electrolyte solution (ES), composed of tetrabutylammonium hexafluorophosphate (TBAHFP) in PC, recorded using identical acquisition parameters, are depicted in Figure 5.2c. We observe a drop in the overall PL intensity of around 50-60%, and no significant shift of the peak wavelength (SI - Figure 5.11).

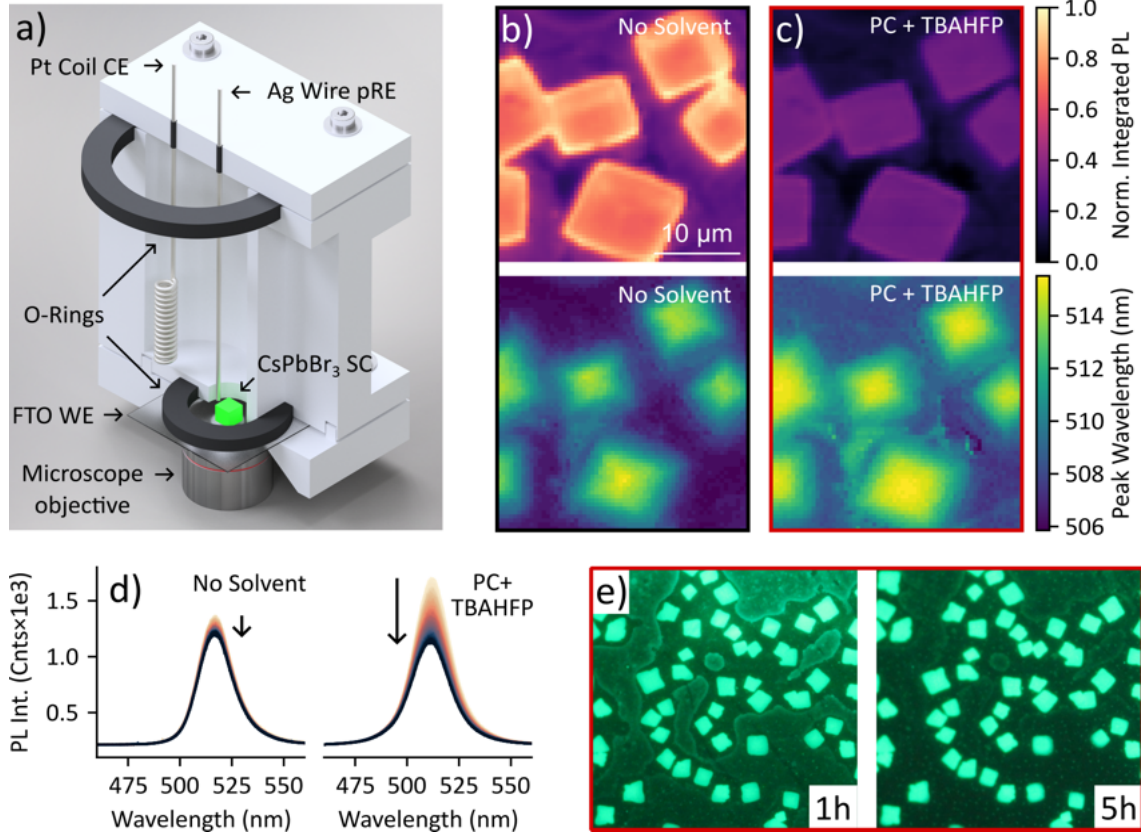


Figure 5.2: Stability of CsPbBr₃ SCs against the electrolyte solution. a) Sketch showing a sectioned view of the cell used for emission SEC experiments, where CE = counter electrode, pRE = pseudo-reference electrode, WE = working electrode. b), c) Corresponding maps of intensity (top) and peak wavelength (bottom) of a sample of CsPbBr₃ SCs on a FTO WE before and after the addition of ES to the cell, respectively. d) PL intensity bleaching of SCs under continued laser irradiation over 300 s both in the absence (left) and the presence (right) of ES. e) PL micrographs of a sample of CsPbBr₃ SCs on a FTO WE after exposure to the ES for 1 h (left) and 5 h (right) excited by a low-power UV LED.

For SEC experiments, the stability of the employed CsPbBr₃ SCs against both, degradation due to the polar ES and photobleaching due to the focused laser excitation, needs to be considered. We argue that we can rule out degradation of the NCs within the timeframe of the measurements (approx. 75 min for each combined intensity plus spectral map acquisition) as this would lead to a blueshifted emission due to NC shrinkage.^{312–314} Contrary to this, we observe a slight redshifting of the PL across the entire probed area on the order of 1 nm, which could be attributed to changes in the dielectric environment due to the presence of the ES. The evolution of the PL intensity recorded from SCs with and without the presence of the ES under 300 s of continuous focused laser excitation is depicted in Figure 5.2d. Although the exact rate of photobleaching varies between individual SCs even at a constant

excitation density, we generally observe more pronounced photobleaching in the presence of the ES, which we attribute to the polar environment promoting ligand detachment. Figure 5.2e displays photoluminescence micrographs recorded from the same area of CsPbBr₃ SCs on a FTO WE after 1 and 5 hours of continuous exposure to the ES. The SCs retain their morphology and exhibit bright emission even after 5 hours.

We conclude that, while focused laser excitation induces photobleaching, SCs assembled from NCs with partial lecithin ligand exchange are sufficiently stable in the chosen ES to enable spectroelectrochemical experiments.

In the next step, we perform SEC on the self-assembled SCs under 405 nm laser excitation. Therefore, we record an intensity map of a specific region, and we choose 15 equally distributed positions across the SC indicated by numbers. In Figure 5.3a, the positions and the scan direction are displayed. Before the application of a potential, we record single spectra at each position as a reference PL₀. The spectra are displayed in Figure 5.3b and show a redshift of 3 nm of the PL peak wavelength to the center comparable to the data in Figure 5.2c. As electrochemical method, we choose staircase voltammetry (SCV) since each potential step can be kept for a longer period of time (210 s). This time period allows us to record PL spectra at each spatial position, after which we increase the potential by 0.05 V. The procedure of recording single PL spectra is then repeated. To focus on electrochemical hole injection, we perform a forward and a reverse scan within the limits of 0.33-0.78 V, since electrochemical hole injection is expected at roughly 0.5 V from previous reports.^{46,221} Furthermore, we anticipate irreversible bromide oxidation in solution to start at 0.78 V which can lead to complete dissolution of the SCs (SI - Figure 5.12+ Figure 5.13). The SCV in Figure 5.3c shows the recorded current during the last 53 s, which is omitting the capacitive current. We observe an exclusively positive current, i.e. an oxidative current, in both scan directions. However, the magnitude is larger in the forward scan than in the reverse scan. The oxidative current onset is observed at 0.43 V.

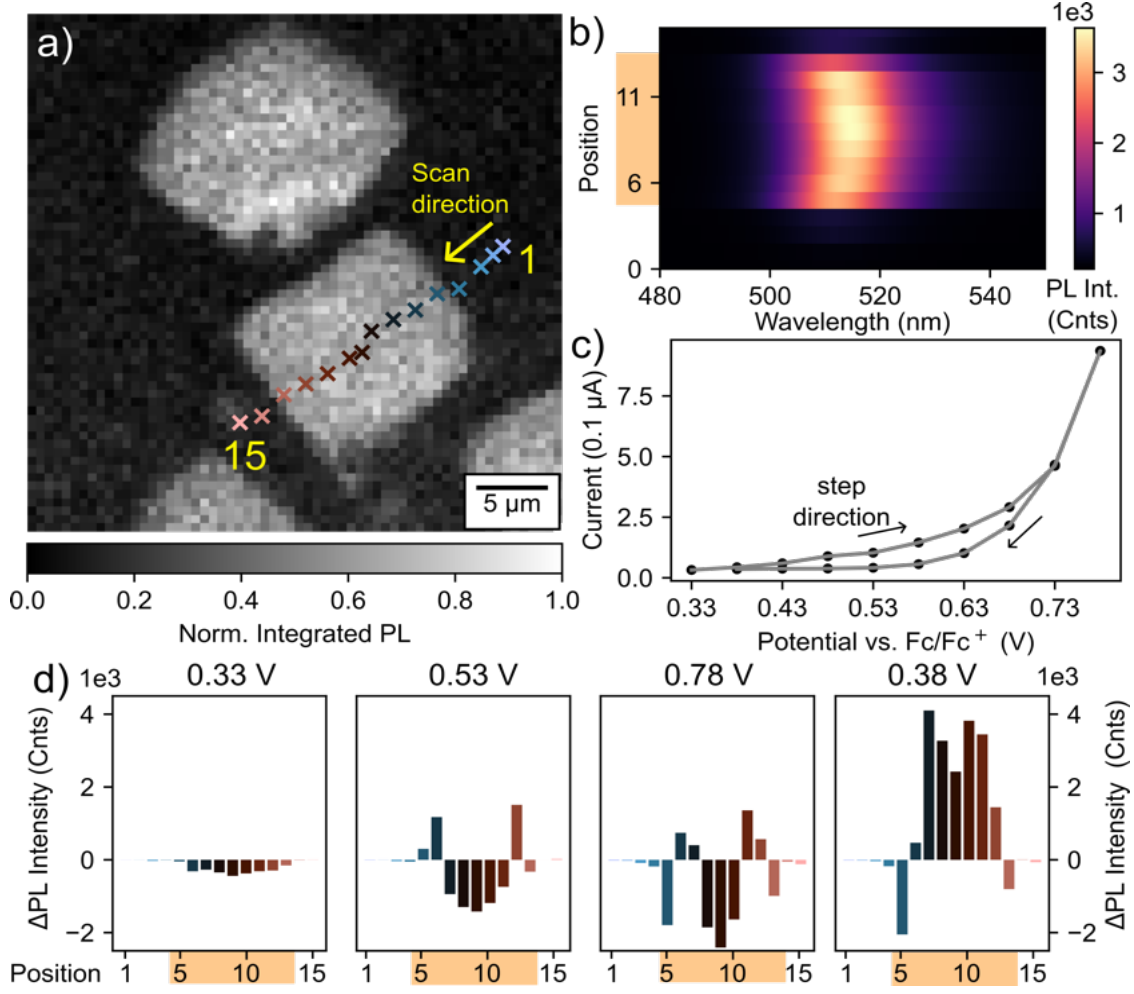


Figure 5.3: SEC PL on CsPbBr₃ SC. a) Spatially resolved normalized integrated intensity map of SCs on FTO with indicated scan direction and positions, where single spectra during SEC were acquired. b) PL spectra PL₀ before SEC recorded at the specific positions. c) Recorded current during staircase voltammetry in the oxidative scan direction with arrows indicating the forward and backward scan. d) Change in PL maximum intensity ($\Delta\text{PL} = \text{PL}_E - \text{PL}_0$) at each marked position from 1 (on the left) to 15 (on the right) during the application of a potential at $E = 0.33$, 0.53 and 0.78 V in the forward scan and 0.38 V in the reversed scan direction. All spectral numbers corresponding to positions in the SC are shaded in red.

Fundamentally, one would expect a decay in PL intensity as holes are injected into the VB, which is why we monitor any change in PL intensity (ΔPL) with respect to the PL intensity without applied potential (PL_0) in Figure 5.3d. The ΔPL of the first applied potential (0.33 V), in the middle of the oxidative scan (0.53 V), the maximum applied potential (0.73 V), and the final recorded spectra (0.38 V) are shown. Full spectra for each potential are shown in SI – Figure 5.14 as intensity maps. We find a PL bleach at every position for the first potential step at 0.33 V. Further increasing the potential (0.53 V) leads to an unexpected positive ΔPL on

the edges of the SC (positions 5, 6 and 12), while ΔPL is still negative in the center. At the maximum applied potential (0.78 V), the negative ΔPL persists at the center positions (8, 9, and 10), while the positions going further to the edges (6, 7 and 11, 12) exhibit positive ΔPL . At the very edges (position 5 and 13) a bleach reappears. The last panel in Figure 5.3d summarizes the ΔPL during the reversed scan at 0.38 V, revealing a significant brightening of the PL for most positions in the SC except for the very edges. In another visualization of the same data, we track the position-dependence of the potential required to invoke a positive ΔPL in the SC for the first time (SI – Figure 5.15). From this presentation, we deduce a shift of the onset potential of PL brightening by 0.1 V by stepping from position 5 to position 6 alone, that is, by scanning toward the center. We observe the same behavior for the opposite edge of the SC (Figure 5.15b). PL brightening in the center only starts when the scan direction is reversed (SI – Figure 5.16).

To verify our results, we perform similar measurements on another SC sample (Figure 5.18 + Figure 5.19) but in a less oxidative potential window from 0.03 - 0.63 V. Qualitatively, we obtain the same results however this time only the edges brighten significantly while the center of the SC recovers to approx. the starting PL intensity when the scan direction is reversed (SI – Figure 5.16). This is consistent with the previous observation that PL brightening in the SC center requires larger (over-)potentials than on the edges. In line with this, we determine the potential at which the initial bleach on the forward scan begins between 0.18 V (outer edges) and 0.43 V (center) in Figure 5.20.

To determine if holes could be electrochemically injected by the applied potential, we perform SEC in absorbance with a thin-film of the same surface-treated NCs and the same experimental SCV parameters. We find exclusively negative differential absorbance, with the greatest effect at 0.53 V (SI – Figure 5.24c). Since absorbance SEC is mostly unaffected by non-radiative trap states,^{208,210} we explain these observation with electrochemical hole injection starting between 0.38-0.43 V in the SCV (Figure 5.3c) and in the ΔPL plots (Figure 5.3d), which is in accordance with recent reports.^{45,46,221}

For further validation, we record spectral maps before (Figure 5.4a) and after one SCV cycle with successful hole injection (SC1 in Figure 5.4b). Consistent with the results in Figure 5.3d, we observe an overall increase in PL intensity of the SCs after SEC. This applies likewise to SCs, which were not exposed to long laser irradiation during a spectral linescan, but were only excited during the recording of the spectral maps (SC2 in Figure 5.4b).

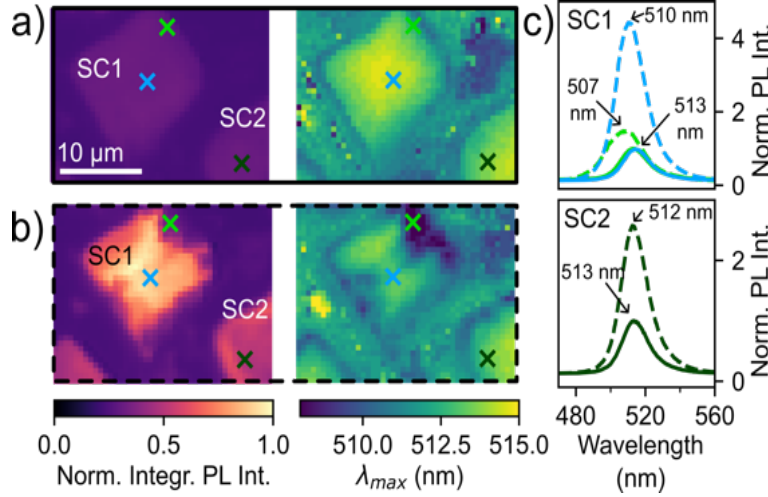


Figure 5.4: Spectral mapping of SC sample before and after SCV. a) Spectral map before SCV with normalized integrated intensity plot (on the left) and extracted PL maximum (λ_{max} , on the right). b) Spectral map after SCV. c) Extracted single spectra from spectral maps before SCV (solid line) and after SCV (dashed line) normalized to the maximum intensity before SCV with marked maximum PL intensities. The positions of the spectra in the spectral maps are highlighted in panel a) and b).

In Figure 5.4c, we extract four individual spectra for SC1 before (solid line) and after SCV (dashed line) from positions at the edge (green) and the center (blue). For SC2, where SCV was conducted without simultaneous excitation, the corresponding spectra before (solid) and after (dashed) are shown for a single position. The peak PL wavelength (λ_{max}) stays mostly constant in the center of the SCs. At the edges and along the line scanned by the laser, we observe occasional blueshifting of λ_{max} . The single spectra show 2.6-fold PL intensity increase for SC2, while SC1 exhibits a 1.5-fold PL brightening on the edge (green) and 4.4-fold PL intensity increase at the center position (bright blue). We also observed PL brightening for another sample of SCs after conducting the same SEC experiments (SI – Figure 5.26). The recorded spectral maps show that the SCs are resistant to degradation by electrochemical charge injection, and the charge injection is not limited by irreversible bromide oxidation (SI – Figure 5.13). Preliminary fluorescence lifetime measurements (Figure 5.27) after oxidative electrochemical cycling reveal that bright SCs exhibit longer average lifetimes (11 ns) than relatively dim SCs (2.9 ns). This indicates that electrochemically induced brightening may be linked to a depletion of (fast) non-radiative recombination.

To demonstrate the statistical relevance of our findings, we track the PL intensity changes during electrochemical cycling (0.33-0.73 V) of a larger sample area containing 22 SCs (Figure 5.27). We find PL brightening for over 90% of these SCs with a mean increase to $(126 \pm 22)\%$ of the initial PL intensity.

In general, PL brightening is not anticipated since electrochemical hole injection would typically result in PL bleaching. We suggest that one possible explanation for the unexpected PL enhancement (during hole injection) is oxidative defect passivation, similar to the previously described “photo-brightening” of lead halide perovskites.^{315,316} Briefly, it is reasonable to assume that exposure to the polar ES and/or the oxidative potential facilitates the formation of Br^- vacancies on the NC surface. Such vacancies have been shown to facilitate the reduction of Pb^{2+} to Pb^0 , which introduces trap states and a reduced PL.^{317,318} The following “brightening” due to trap state passivation is reported to occur by the formation of PbO on the surface³¹⁸ or due to electrochemical removal of electron-rich hole traps.³¹⁹ While these effects have been reported previously for bulk lead halide perovskites,³¹⁸ they were found to be weak, at a level of a few percent, in NC films.³¹⁹ The hypothesis of surface defect passivation is supported by the reduced PL intensity after the addition of ES (Figure 5.11), and the recovery of PL intensity of the overall SC sample after electrochemical oxidation (Figure 5.4c).

5.4 Conclusion

In conclusion, we have performed spatially resolved PL SEC on perovskite SCs self-assembled from CsPbBr_3 NCs. Our results highlight their stability towards the presence of polar electrolyte solution and electrochemical hole injection. Under mild oxidative cycling, the PL intensity is not only preserved throughout the SC but even enhanced, which we attribute to electrochemical filling of hole traps. Our work shows that SCs are robust to electrochemical degradation, an advantage that can help achieving long-term stability of SCs in LEDs under electrical bias. We note a recent work on CsPbBr_3 NC superlattice LEDs with greatly enhanced operational lifetime that supports our conclusion.²⁹⁸

5.5 Supporting Information

S1. Material and methods

Materials. caesium carbonate (Cs_2CO_3 , 99.92% trace-metal basis, Acros Organics), 1-octadecene (ODE, 90%, technical grade, Sigma Aldrich), oleyl amine (90%, technical grade, Sigma Aldrich), oleic acid (OA, 90%, technical grade, Sigma Aldrich), lead(II) bromide (PbBr_2 , 99%, Acros Organics), L- α lecithin (min. 97% phospholipids, Thermo Scientific), FTO (1.1 mm thickness, $20\ \Omega/\text{sq.}$, Dyenamo), propylene carbonate (PC, 99.5%, Thermo Scientific), acetone (99.8%, Acros Organics), toluene (99.85%, Acros Organics), DMSO- d_6 (99.9 atom %, Sigma Aldrich), ethylene carbonate (99.92%, TraceCERT®, Sigma Aldrich), toluene- d_8 (99.5%, Deutero), tetrabutylammonium hexafluorophosphate (TBAHFP, 98%, AlfaAesar), ferrocene (Fc, 98%, Acros Organics), tetrabutylammonium bromide (TBAmBr, 99%, Sigma Aldrich).

CsPbBr₃ Nanocrystal Synthesis according to Protesescu *et al.*²⁹ 163 mg (0.5 mmol) of Cs_2CO_3 , 0.5 ml (1.6 mmol) of OA and 8 ml of ODE were loaded into a three-neck flask and dried at 100 °C for one hour. Afterwards, the solution was heated up to 150 °C for 10 minutes in N_2 atmosphere to form Cs(oleate). In a second flask, 422 mg (1.15 mmol) PbBr_2 were added to 30 ml ODE and degassed at 100 °C for one hour. 3 ml (9.45 mmol) of OA and 3 ml (9.12 mmol) of OAm are added under N_2 . Again, the flask was heated up to 100 °C and degassed for half an hour. Afterwards, the temperature was elevated to 165 °C and 2.4 ml of Cs(oleate) were injected rapidly. The solution was cooled down to room temperature after 5 s by an ice-bath. The crude solution was centrifuged at 8000 rpm for 20 minutes and the precipitate was resuspended in toluene. Agglomerates were removed by slow centrifugation at 2500 rpm for 10 minutes. The supernatant passed a syringe filter and was characterized by fluorescence and absorbance spectroscopy in solution at a PerkinElmer FL8500 spectrometer and Agilent Technologies Cary 5000 UV/Vis spectrometer, respectively. The size of the NCs was determined by scanning electron microscopy. SEM images were recorded at a Hitachi SU8030.

NC Preprocessing. The partial ligand exchange (ideal: 141 lecithin/NC) was performed in solution by adding lecithin in toluene (0.75 mM, 434 μl) to the NC stock solution (7.6 μM , 300 μl) and stirring for 30 minutes. Afterwards, the solution was precipitated by adding twice the volume of acetone as anti-solvent. The partially ligand exchanged NCs were resuspended in toluene again.

Self-assembly into SCs. Before-self-assembly, the FTO substrates were cleaned by ultrasonication for 15 mins in each acetone, Extran® (Merck Millipore), and distilled water. For crystallization, the substrates were placed in a petri dish as crystallization chamber in a nitrogen filled glovebox. 150 μ l of a 0.25-0.4 μ M solution of NCs in toluene were drop-cast on the tilted FTO substrate (angle 10-20°). Additionally, a solvent reservoir filled with toluene was kept in the crystallization chamber to create an oversaturated solvent atmosphere. The solvent was left to slowly evaporate for 3 to 5 days. The SCs were identified at a light microscope.

Quantitative NMR sample preparation. A specific amount of NCs (300 μ l) of a 3 μ M solution was used for quantitative NMR spectroscopy. Here, the solution was dried and dissolved in 0.5 ml of a 15 mM ethylene carbonate DMSO- d_6 solution. 64 scans of protons were recorded with a relaxation time of 40 s. The spectra were recorded at a 400 MHz BrukerAvance400 III HD.

SEC PL setup. The spectroelectrochemical cell is home-built. It consists of an Ag wire as pseudo-reference electrode, a Pt coil as counter electrode, and a transparent FTO is used as working electrode. The cell was filled with 5 ml of a 0.1 M solution of PC/TBAHFP. TBAHFP was recrystallized five times from EtOH/H₂O and dried for five days under vacuum at 105 °C, beforehand. The cell containing the self-assembled NCs on FTO and filled with the ES was placed on top of an inverted confocal microscope. Then, the electrodes were connected to a CHI Instruments potentiostat (CHI760E), the open circuit potential was measured, and iR compensation was applied.

High-resolution optical characterization. Spectral mapping was performed using a home-built inverted confocal laser piezostage-scanning microscope. A 405 nm laser diode (LDH P-C-405, Picoquant GmbH), operated in continuous wave mode, was used as the excitation source. Focussing of the excitation light and collecting scattered and emitted light was achieved using an infinity corrected, long working distance 50x/0.6 numerical aperture air objective (Nikon). A 458 nm long-pass filter (RazorEdge LP Edge Filter 458 RU, Semrock) was inserted in the detection path to remove the excitation wavelength. Photoluminescence spectra were recorded by a DU4A01-BVF camera (Andor/Oxford Instruments) cooled to -60 °C attached to an SR-303i-B spectrometer (Andor/Oxford Instruments) using a 300 grooves/mm grating. Scanning of the piezo stage and interfacing with the spectrometer for spectral mapping was achieved by the HydraLabX1 controller (HydraSpex UG).

S2. Qualitative and quantitative ^1H NMR spectroscopy.

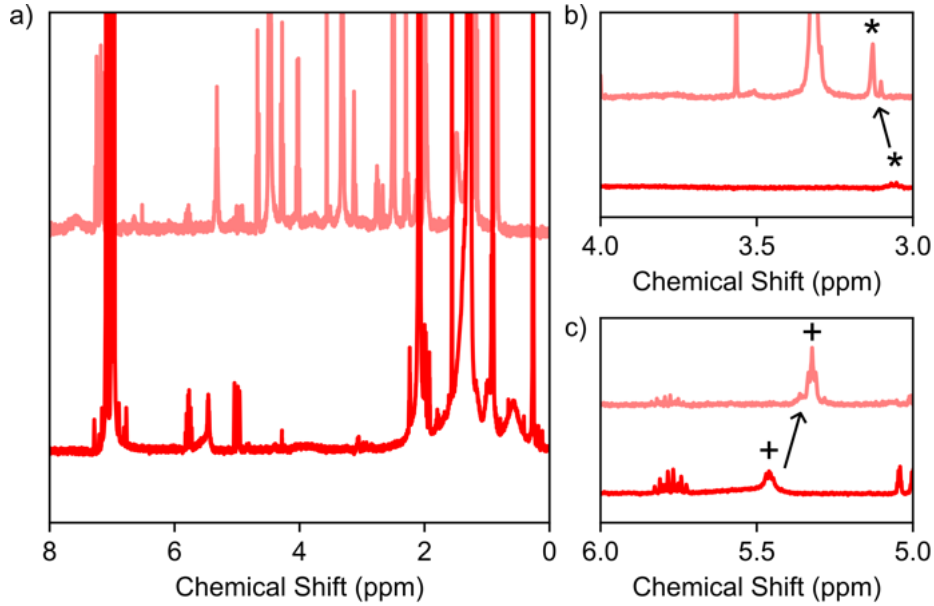


Figure 5.5: ^1H NMR of exchanged NCs, top (light-red): quantitative NMR with ethylene carbonate as standard (4.5 ppm) in DMSO- d_6 (2.5 ppm), bottom (dark-red): NC NMR in toluene- d_8 . a) full spectra, b) zoom-in between 4 and 3 ppm, highlighting methylgroups of the phosphocholin group (*), and c) zoom-in at vinyl protons of OA/OAm (+).

Calculation of ligands/NC from quantitative NMR spectroscopy.

$$n(\text{ethylene Carbonate}) = 2.25 \times 10^{-5} \text{ mol}$$

$$n(\text{max. NCs in qNMR, used for ligand exchange}) = 1.14 \times 10^{-9} \text{ mol}$$

$$\text{purity (lecithin)} = 97 \%$$

$$\text{purity (OA/OAm)} = 90 \%$$

$$\text{purity (ethylene carbonate)} = 99.92 \%$$

Table 5.1: Determined ligands per NC by the integrals from quantitative NMR spectroscopy.

	Integral	n(ligands)	ligands/NC
Vinylpeak (2 Hs, OA/OAm)	0.0511	$6.4 \times 10^{-7} \text{ mol}$	561
Methylgroups (9 Hs, lecithin)	0.0224	$5.7 \times 10^{-8} \text{ mol}$	50

S3. SEM characterization of NCs before and after ligand exchange (without crystallization).

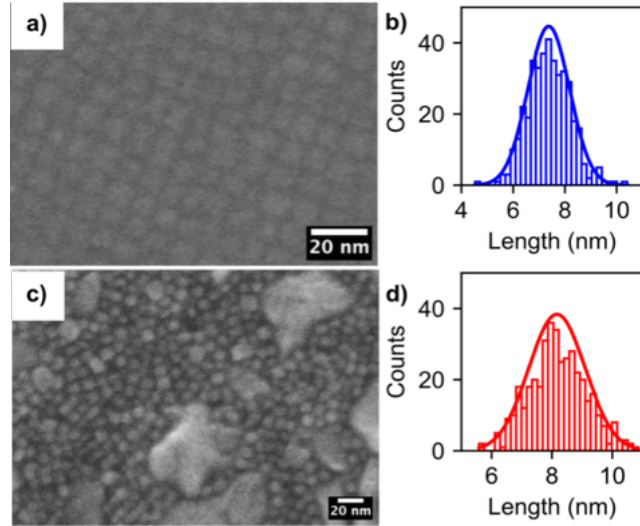


Figure 5.6: SEM characterization of NCs before (top) and after (bottom) ligand exchange. a) NCs spin-coated on a silicon substrate and determined average size of 7.4 ± 0.8 nm by fitting to normal distribution from SEM image, b) NCs spin-coated on FTO substrate and determined average size of 8.2 ± 0.9 nm by fitting to normal distribution.

S4. SC characterization.

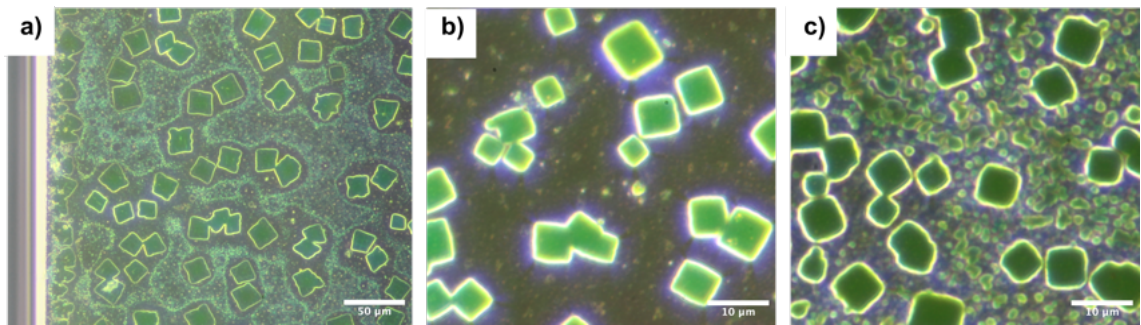


Figure 5.7: Light microscopy in the dark-field mode on three different samples with SCs.

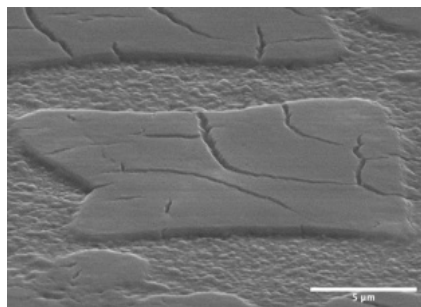


Figure 5.8: SEM of tilted SCs on FTO showing thickness of approx. $0.5\ \mu\text{m}$ for the SC and distribution of NCs over the whole sample.

S5. SEC PL cell and referencing by the Fc/Fc^+ redox couple.

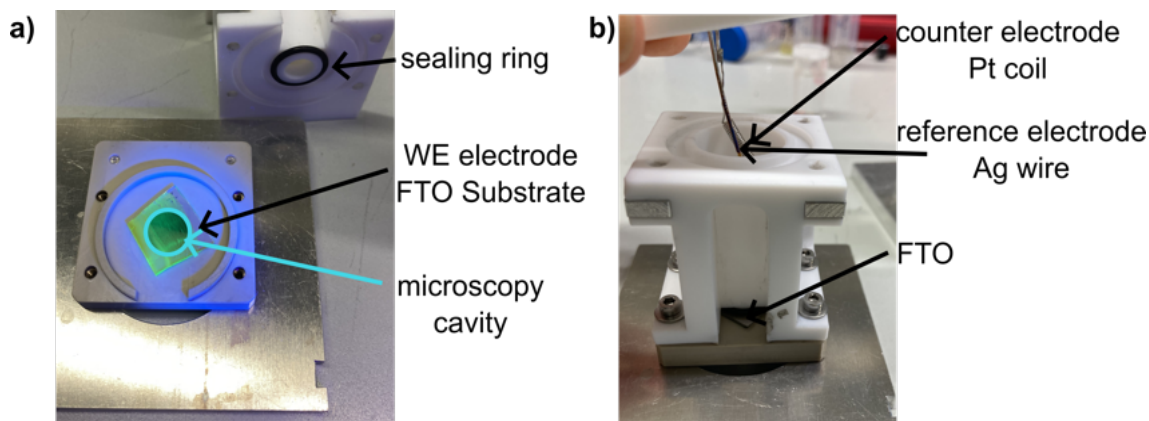


Figure 5.9: Photos of the SEC PL cell. a) bottom layer with exemplary SCs on a FTO substrate and b) assembled SEC cell for measurements.).

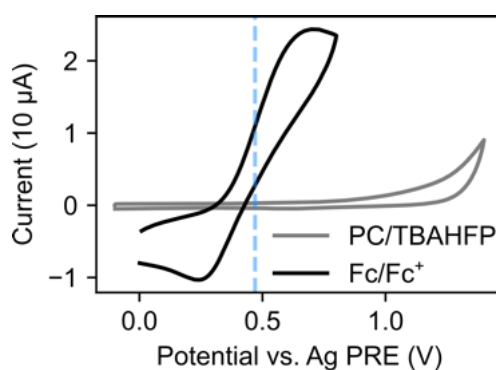


Figure 5.10: Cyclic voltammetry (CV) with a scan speed of $50\ \text{mV/s}$ of electrolyte solution (PC/TBAHFP, gray) and Fc/Fc^+ redox couple (black) with determination of the half-wave potential (dashed blue line) at $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.47\ \text{V vs. Ag PRE}$.

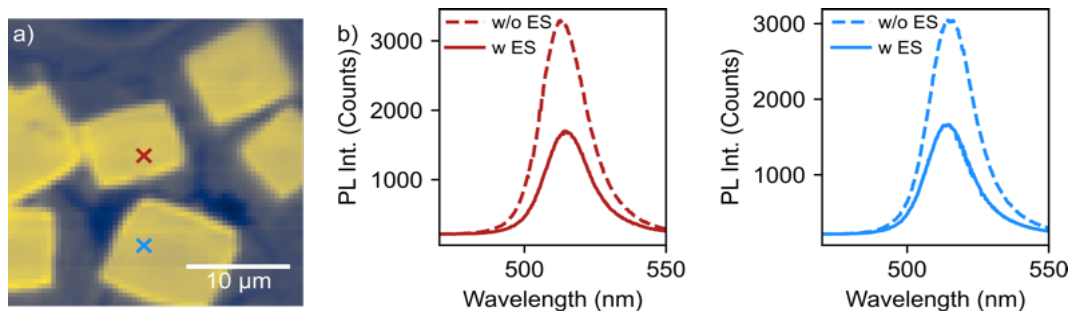
S6. PL spectra extracted from spectral map in Figure 5.2b+c.

Figure 5.11: Comparison of PL spectra at two positions without and with added electrolyte solution. a) integrated intensity map for positioning of extracted spectra, b) comparison of PL spectra of position 1 with electrolyte solution (ES, solid line) and without ES (dashed line), and c) PL spectra comparison of second position.

The PL decays by 49 and 47 % for position 1 and 2, respectively.

S7. SEC PL including bromide oxidation from solution.

In the following experiments, the SCV window was extended up to 0.98 V. In this electrochemical window, the oxidation of free bromide occurs. This oxidation leads to a complete dissolution of the SC, resulting in a rapid decay of the PL. The irreversible PL decay starts at 0.78 V as shown in Figure 5.12b. For further confirmation of the bromide oxidation, CV of tetrabutylammonium bromide (TBAmBr) in solution (Figure 5.13) was conducted (in the SEC PL cell). This CV shows the coinciding bromide oxidation at 0.78 V. For the conducted experiments in Figure 5.3, the consequence is that bromide oxidation is also occurring, but the potential and time window is sufficiently limited, so that the SCs are not decomposing within the measurement.

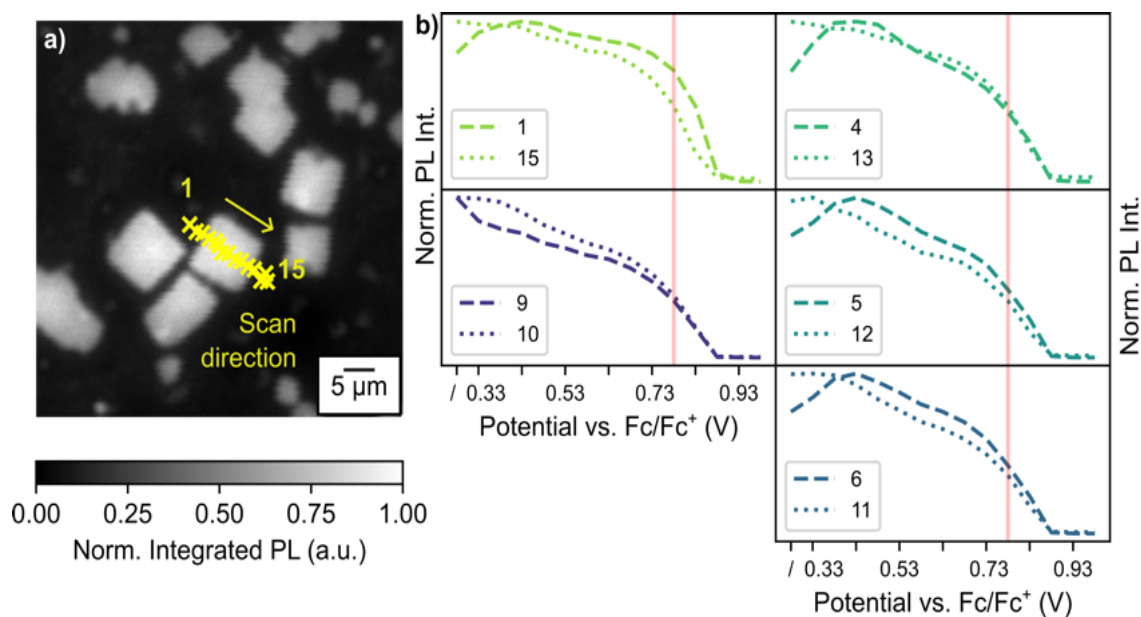


Figure 5.12: SEC PL on SC from 0.33-0.98 V. a) Intensity map of SC with chosen positions for probing PL intensity during the application of a potential. b) PL intensity trace for all positions with bromide oxidation resulting in complete dissolution of SCs.

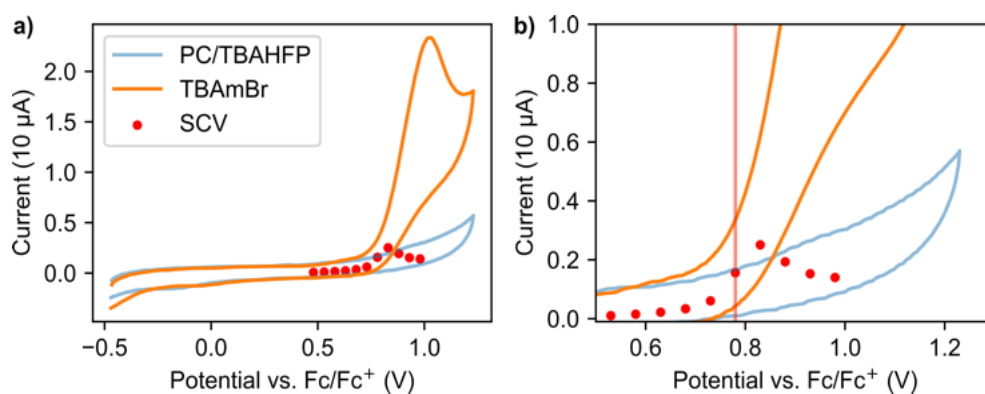


Figure 5.13: Electrochemical data recorded during SCV of SC (red dots, corresponding to Figure S7), CV of electrolyte solution (bright blue), and CV of TBAmBr in PC/TBAHFP (orange). Scan speed of CVs was set to 50 mV/s. a) Full CV plot, and b) zoomed-in CV plot.

S8. Evaluation of SEC PL in Figure 5.3.

In Figure 5.14, all spectra recorded at each potential step are shown. The first spectrum without the applied potential is the same as in Figure 5.3b without normalization. These spectra were used for calculating the differential PL in Figure 5.3d.

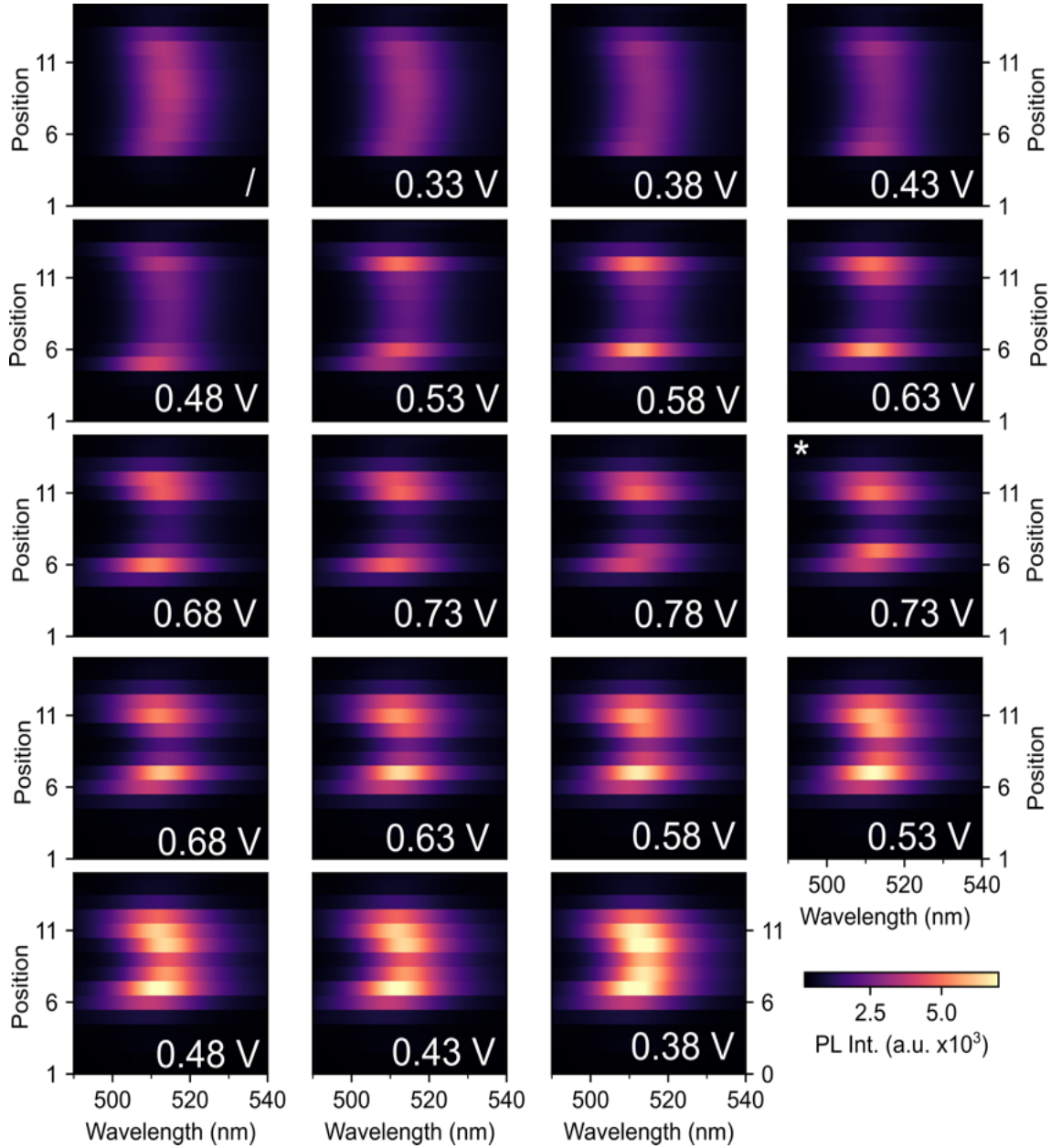


Figure 5.14: Single spectra recorded at each position and each potential (going from top left to bottom right). The asterisk highlights the first spectra recorded in the reversed scan direction.

More details can be gained when the PL intensity is plotted against the applied potential for specific positions. As apparent in Figure 5.7, the PL behavior changes

going from the edges to the center. Hence, we have chosen to investigate the PL intensity of both of the edges (light blue) going from position 5 and 6 into the center (dark blue) of the SC and from 13 to 11 as depicted in Figure 5.15. In Figure 5.15a, we observe that the increase in PL intensity starts with position 5 at lower potentials (0.38 V), while the PL increases drastically above 0.48 V for position 6. The shift in the onset potential of PL brightening can be also observed on the other edge going into the SC center in Figure 5.15b. The onset potential for position 13 and 12 is at 0.43 V, while for position 11, it is shifted to a higher potential (0.53 V).

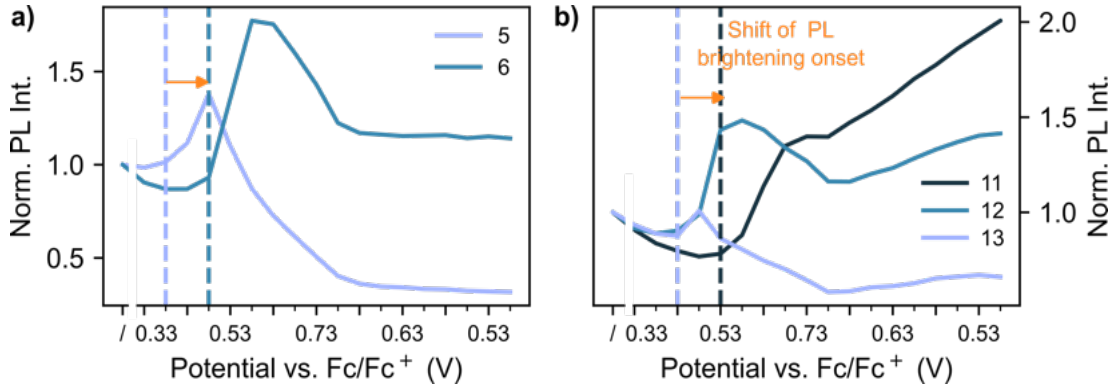


Figure 5.15: Plot of maximum PL intensity normalized to the maximum PL intensity without applied potential PL_0 with dashed lines indicating the onset potential of PL brightening a) for the right edge of the SC of positions 5 and 6, and b) for the left edge of the SC of positions 11, 12, and 13.

The center positions behave differently than the edge positions. Here, the PL increase can only be observed, when the maximum applied potential is surpassed and the scan direction is reversed.

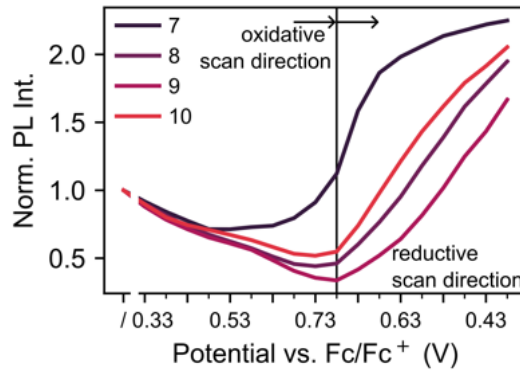


Figure 5.16: Plot of the peak PL intensity normalized to the peak PL intensity without applied potential PL_0 for the center positions of the SC 7, 8, 9, and 10 with the solid line at the maximum applied potential (0.78 V).

S8. Determination of hole injection potential depending on position in the SC.

In another measurement, we performed a SCV scan up to 0.63 V vs. Fc/Fc^+ , thereby avoiding the start of Br^- oxidation as it can be observed by the low current in the SCV in Figure 5.17c. The positions were again probed as in the main manuscript in Figure 5.4.

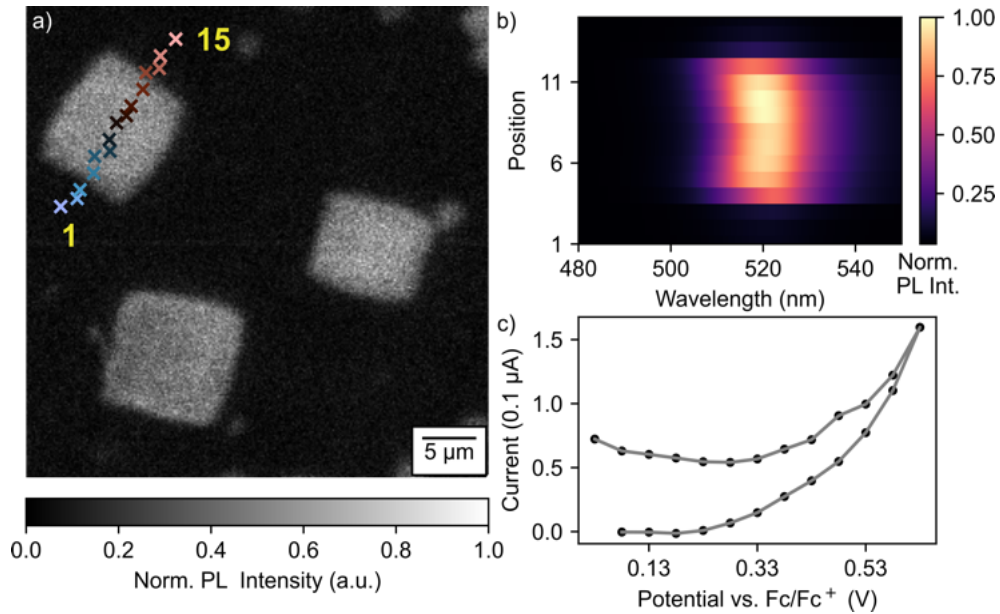


Figure 5.17: Spectral mapping of positions within a SC. a) PL intensity map of three SCs with the positions indicated on the probed SC, b) normalized PL spectra before SEC recording at specific positions, and c) SCV diagram.

In the next two figures, the PL intensity normalized to PL_0 is shown. The PL lines are split into upper and lower edge positions, going from the edge (light blue) to the SC center (dark blue). In the figures, the onset potential of PL decay is indicated as dashed line. At the next potential, the PL intensity decayed by $> 5\%$.

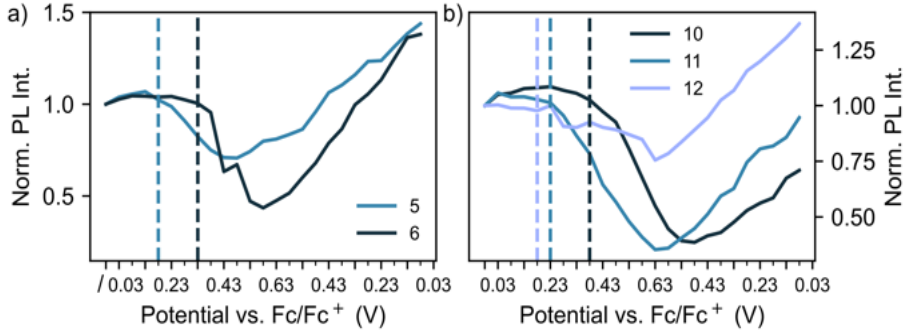


Figure 5.18: PL intensity trace with indicated onset potential of PL decay (dashed line) depending on the applied potential for a) position 5 and 6, and b) position 10, 11, and 12.

In Figure 5.19, we observe a PL decay in the SC center starting at 0.33-0.43 V. The PL starts increasing again, when the scan direction is reversed. For position 7 and 8, we observe a PL increase that reaches the initial PL intensity, and even for position 7 a PL enhancement. The PL intensity behavior of darkening at a specific potential and PL recovery in the reversed scan can be attributed to a reversible electrochemical hole injection.

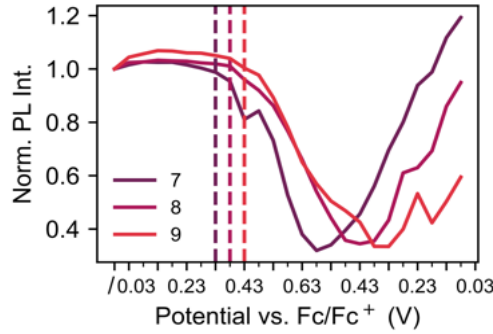


Figure 5.19: PL intensity trace with indicated onset potential of PL decay (dashed line) depending on the applied potential for the center positions of the SC.

The onset potentials of PL decays at different positions are summarized in Figure 5.20. The data is highlighting the shift of the onset potential to higher values in the SC center compared to the edges.

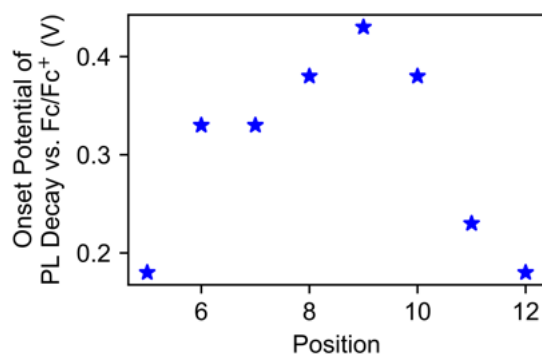


Figure 5.20: Summary of onset potentials of PL decay depending on applied potential for the positions in the SC.

S10. Absorbance SEC on NC thin-film.

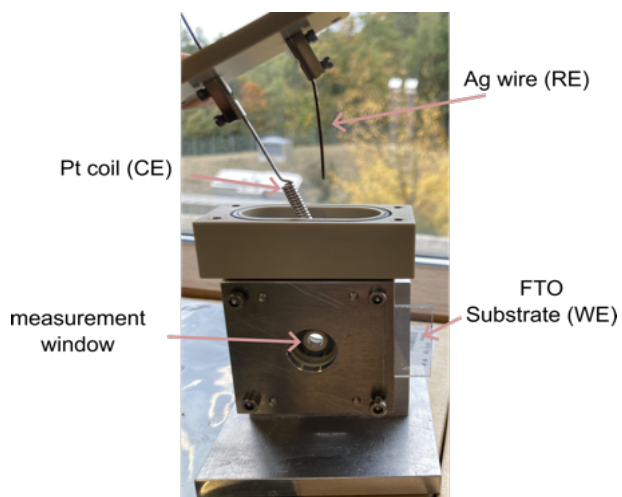


Figure 5.21: Photograph of the spectroelectrochemical cell for absorbance measurements.

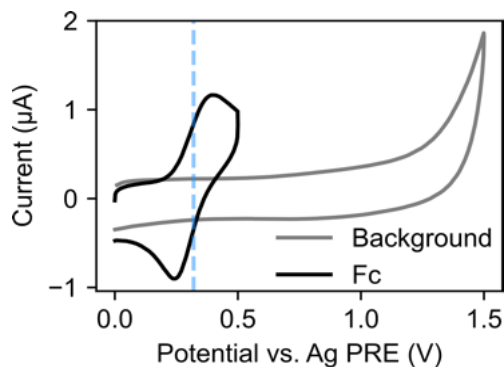


Figure 5.22: Reference measurement of Fc/Fc^+ redox couple in PC/TBAHFP in the SEC absorbance cell as depicted in Figure S12 with determined half-wave potential $E_{1/2} = 0.32 \text{ V vs. Ag PRE}$ (blue dashed line).

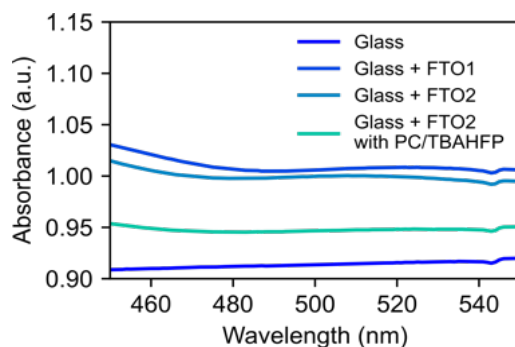


Figure 5.23: Absorbance of spectroelectrochemical cell used without any NCs drop-cast on the FTO WE.

SEC in absorbance was recorded on a NC thin-film since there is no optical resolution for these measurements to find specific SCs. We did apply the same SCV recording parameters as in Figure 5.3. Additionally, absorbance spectra of only added electrolyte solution and solvent were recorded in the same time window as the SCV spectra were recorded (1h 10 minutes, first spectrum dark, last recorded spectrum bright green).

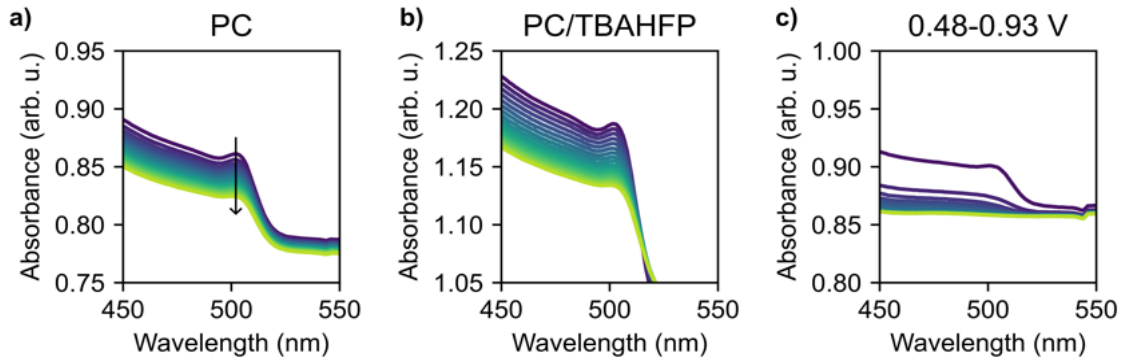


Figure 5.24: Absorbance spectra of a NC film over 1h 10 minutes. a) Only with added solvent propylene carbonate, b) with electrolyte solution (PC/TBAHFP), and c) with SCV scan from 0.48 – 0.93 V in 50 mV increments, each potential applied for 210 s.

SEC in absorbance was also recorded at different applied potentials w/o, -0.12 V, 0.18 V, and 0.68 V (keeping one potential) for 10 spectra, and then stopping and letting the absorbance recover.

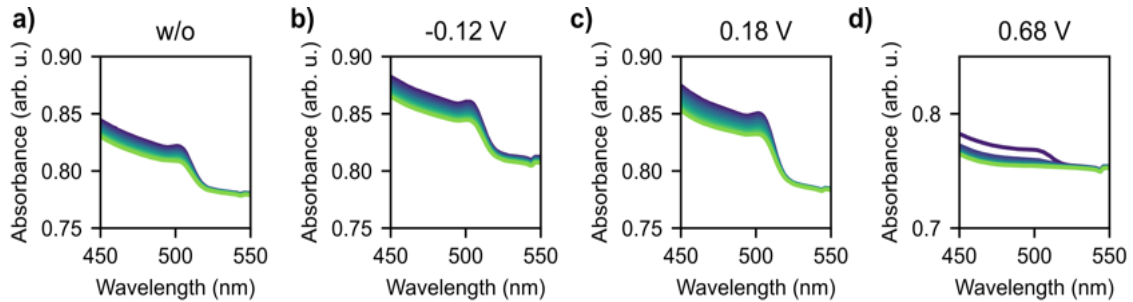


Figure 5.25: Potential-dependent absorbance of NC film a) without applied potential (with PC/TBAHFP), b) at -0.12 V, c) at 0.18 V, and d) at 0.68 V vs. Fc/Fc^+ .

The absorbance measurements conducted in PC, PC/TBAHFP and at the potentials of -0.12 and 0.18 V show a gradual decrease of the first excitonic transition. The gradual decrease in absorbance can be attributed to the instability of the NC thin-film in PC since the gradual decrease is recorded already for the NCs only covered by PC in Figure 5.24a. In Figure 5.24c and Figure 5.25d, an additional absorbance bleach can be detected in the second recorded spectrum. The absorbance bleach in Figure 5.24c can be assigned to the applied potential of 0.53 V. The constant applied potential of 0.68 V in Figure 5.25d is higher than 0.53 V and results in a decay of absorbance. In this plot, the first excitonic maximum of the first recorded spectrum is not as pronounced as in Figure 5.24c, which is already indicating that the absorbance bleach is already recorded in the first spectrum. Both SEC in absorbance

measurements show the absorbance bleach at a higher potential than 0.53 V, which is now considered as the hole injection potential.

S11. Spectral mapping of another SC example.

The same SEC PL parameters were applied to another sample of SCs on a FTO WE. Before and after SEC PL, spectral maps were recorded. The spectral maps (Figure 5.26a+b) show PL brightening of approx. 100% of integrated PL intensity of the SC after conducting SCV. Only a shift of 1 nm in maximum peak wavelength can be observed for extracted single spectra in the SC (Figure 5.26c).

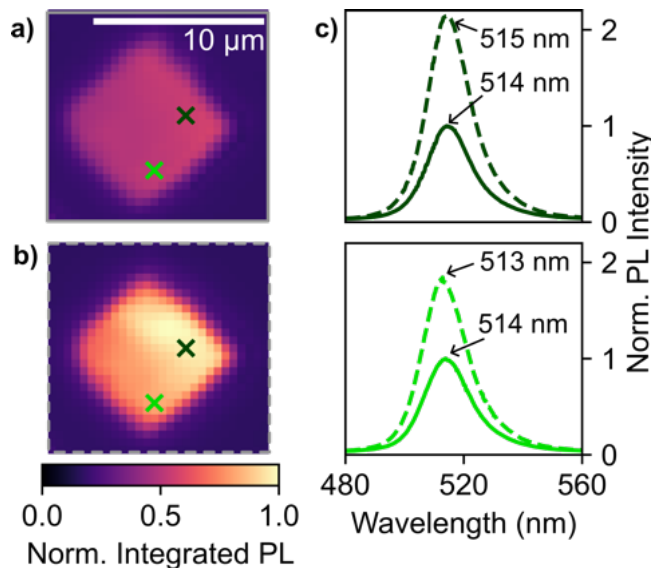


Figure 5.26: Spectral map before (top) and after (bottom) application of SCV in a potential range of 0.33-0.78 V vs. Fc/Fc^+ . a) Normalized integrated PL intensity of SCs before applied potential, with added electrolyte solution. b) Normalized integrated PL intensity after SCV. c) Extracted single spectra from recorded spectral maps before (solid line) and after SCV (dashed line) normalized to PL intensity before SCV.

S12. Time-resolved PL after electrochemical hole injection.

We performed time-resolved PL measurements on SC samples before and after SCV. For the measurement before SCV, we summed up the PL decays of the SCs shown in Figure 5.28. The histograms after SCV were recorded at specific positions in the SCs. Two positions show only moderate brightening (blue and red), while the third position shows strong brightening. After fitting the decays to a biexponential fit function, we can determine the lifetimes of the fast and slow component. Here, the lifetimes reveal a decrease from 1.7 to 0.7 ns in the short lifetime for the dim SCs,

while the long lifetime does not change significantly (7.7 to 6.9 ns). However, the strongly brightened position (red) shows an extended lifetime for the long component (7.7 to 15 ns), while the short component is comparable to the one of the SCs before SCV (1.7 to 1.6 ns).

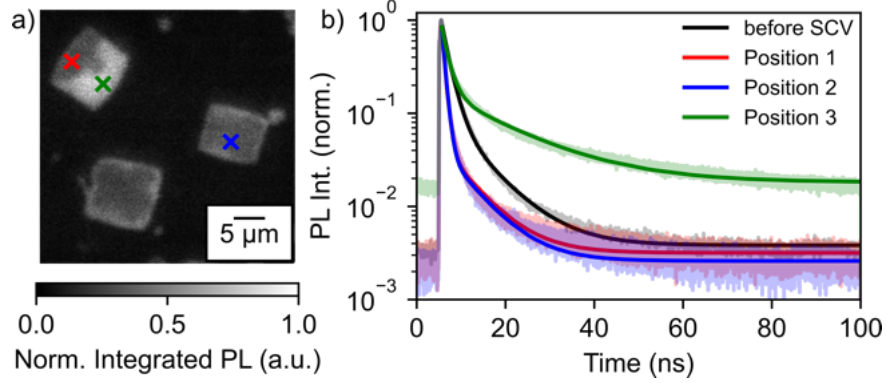


Figure 5.27: Time-resolved PL of SC at different positions on the SC sample. a) PL intensity map and b) PL decays and their biexponential fit, recorded by means of time-correlated single photon counting for the positions indicated in a) compared to PL decay before SCV in black.

Biexponential fit function:

$$I(t) = A_{rel,1} \exp\left(-\frac{t}{\tau_1}\right) + A_{rel,2} \exp\left(-\frac{t}{\tau_2}\right) \quad (5.1)$$

Table 5.2: Fitting parameters extracted from the biexponential fits of the PL decays in Figure 5.27).

Sample	$A_{rel,1}$	τ_1 (ns)	$A_{rel,2}$	τ_2 (ns)	$\tau_{Av,Amp}$ (ns)	$\tau_{Av,Int}$ (ns)
Before SCV black	0.8894	1.71	0.1106	7.7	2.37	3.87
1 - red	0.94628	0.7234	0.0537	6.91	1.056	2.9
2 - blue	0.9488	0.734	0.0512	6.89	1.05	2.8
3 - green	0.8223	1.56	0.177	15	4	11

S13. Statistics on PL enhancement after conducting a SCV scan.

In the following, two spectral maps with a larger sample area were recorded. A SCV scan in the potential range of 0.33-0.73 V was conducted, comparable to the SCV scan in the main manuscript. During that time, the sample was not exposed to laser

irradiation. Afterwards, the SCs show a higher PL intensity while the NC film starts degrading (lower edge of Figure 5.28b).

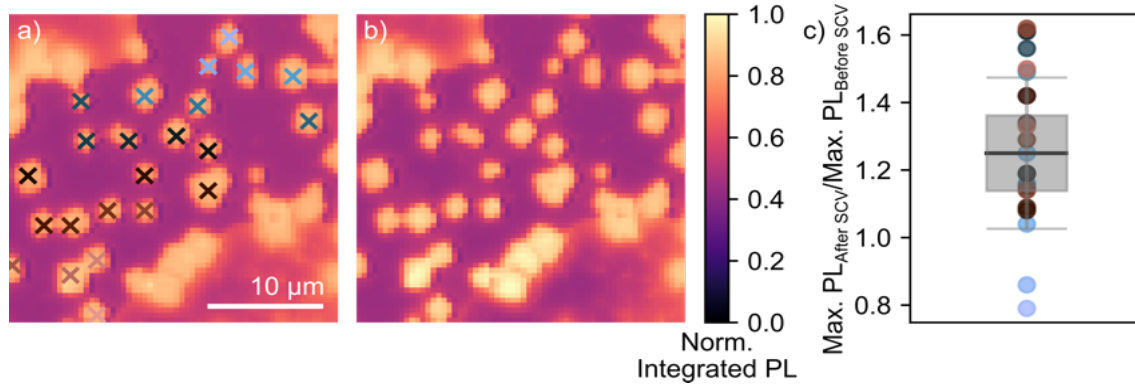


Figure 5.28: Spectral comparison of spectral maps before and after a SCV scan with many SCs. a) Integrated PL intensity map before SCV, b) integrated intensity map after SCV, and c) change in PL intensity after SCV scan of 22 SCs, indicated in panel a.

Summarizing, we find in the spectral map 22 evaluated SCs, where two do not show PL enhancement (9%). The intensity change is 1.26 ± 0.22 .

S14. Effect of edge brightening.

After conducting a SCV scan in the potential range of 0.03-0.63 V, the comparison of the PL intensity maps before and after SCV show PL brightening and edge brightening of all recorded SCs in the probed region. For SC2 and SC3, the non-probed SCs during SCV, we find PL 1.4 and 1.7-fold PL brightening, respectively.

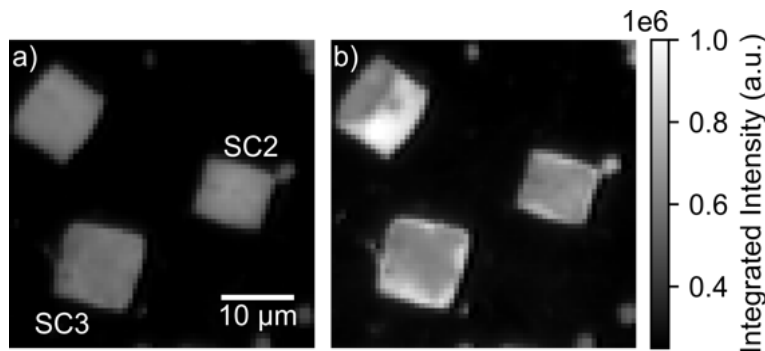


Figure 5.29: PL intensity map of SCs before (panel a) and after SCV scan (panel b) from 0.03 up to 0.63 V.

6 Summary and Outlook

LHP NCs as emissive layer play an important role in future LED technology. Therefore, studying charge injection processes by a precise method is of interest. SEC helps identifying optoelectronic changes during charging, determining absolute band edge positions, and kinetic effects arising from the chemical environment.

This thesis addresses the question how electrochemical hole injection can be influenced. Therefore, the aspects of the binding group of the surface ligands attached to the NCs, the ligand density, the influence of inductive effects mediated by organic ligands, and electronic coupling of NCs are investigated. CsPbBr₃ NCs are chosen as a model system since they show the highest stability so far. The following section summarizes the findings of the chapters briefly and gives an outlook on possible research for improving further the electronic properties of LHPs in LEDs. The outlook is graphically summarized in Figure 6.1.

In chapter 2, the fundamentals of NCs in general, LHP NCs, and SEC are introduced. Thereby, the influence of the ligand shell on stability and optoelectronic properties are highlighted. In addition, the SEC setup at the University of Tübingen with the possibility of spatial resolution is demonstrated.

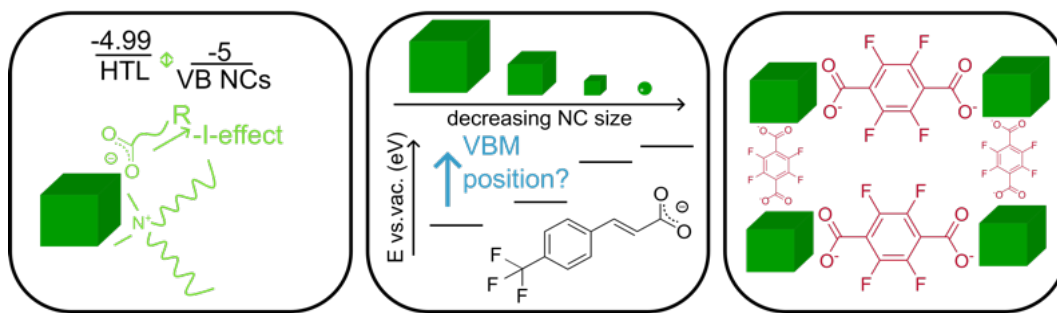


Figure 6.1: Future modification on LHP NCs for improved performance in LEDs. **Chapter 3:** Shifting the VB edge close to the HOMO of PTAA (on the left), **Chapter 4:** Size dependent VB shift with electron withdrawing surface ligands (in the center), and **Chapter 5:** NCs interconnected with tetrafluoroterephthalic acid self-assembled into a SC (on the right).

The impact of ligand density and ligand binding groups on hole injection into LHP NCs is shown in chapter 3. Here, the onset potential of hole injection of

as-synthesized NCs (OA/OAm) is compared to DDABr covered NCs with two ligand densities after precipitation of the NCs. The spectroelectrochemical results indicate a facilitated hole transfer to the DDABr covered NCs. As the ligand density is reduced, electron withdrawal requires a higher applied potential for both of the surface ligands. The hole injection potential is correlated to the VB edge position by UPS and DFT calculations. With the knowledge of the higher VB position, the higher EQE, resulting from increased charge carrier balance in DDABr covered NCs, can be explained.

Outlook. The absolute positions show an VB offset of 0.1 eV (UPS) and 0.08 eV (PL SEC) for DDABr on the NC surface. This value could be further reduced and aligned to the -4.99 eV of the HOMO of PTAA by introducing electron withdrawing ligands to the NC core in combination with DDA⁺.

Chapter 4 uses CA derivatives with electron withdrawing and donating functionalities as organic surface ligands of NCs. Within this work, the influence of such inductive effects on the electronic structure of the NCs is investigated. Ligand exchange protocols from oleate covered NCs to cinnamate-covered NCs are established and the exchange is verified by ¹H NMR spectroscopy. SEC in PL reveals a lower hole injection potential for electron withdrawing compared to electron donating ligands. The performance of the modified NCs is also tested in LEDs and hole-only devices. In hole-only devices, the current is increased for electron withdrawing ligands compared to electron donating ones. This result supports the SEC PL findings. The LEDs show a luminance onset comparable to ligand stripped NCs, while the EQE reveals no trap filling. Therefore, the charge injection into CA covered NCs is facilitated, despite many ligands on the surface. Finally, the conclusion is drawn that a kinetic effect is probably contributing to the hole injection potential during SEC PL and in devices. The strength of the kinetic effect depends on the inductive effect of the ligand.

Outlook. This work uses NCs with a size of >8 nm, being larger than the exciton Bohr radius. Consequently, the question arises whether the impact of the ligands becomes more pronounced in the quantum-confined regime (3-7 nm). The influence of ligands on the electronic structure for quantum confined CdSe NCs is known.³²⁰ Therefore, investigating this influence with CACF₃ as strong electron withdrawing ligand would be of interest. The shift of the VB depending on the NC size could either result in a VB shift towards PTAA or further away.

Chapter 5 reports on spatially resolved SEC of perovskite NC supercrystals for the first time. Therefore, self-assembled SCs are formed from CsPbBr₃ NCs.

The SCs are spectroscopically characterized before and after the addition of the electrolyte solution. The comparison reveals a high stability of the SCs against the electrolyte solution. During SEC, single spectra are recorded at different positions throughout the SC at every potential step. The single spectra show a gradual increase in PL intensity starting on the edges of the SC going to the center. This increase in PL is coinciding with electrochemical hole injection. The chapter shows how SC charging influences the PL intensity and that electrochemical doping does not start degradation processes accompanied with an irreversible PL bleach.

Outlook. In order to determine if charge transport is hindered going to the center of the SC and to further facilitate charge transfer in the structure, the NCs in the SC can be interconnected with organic molecules. This idea is known from other semiconductor NCs to achieve efficient charge transport in photodetectors or field effect transistors.³²¹ Due to crosslinking of LHP NCs with tetrafluoroterephthalic acid, electronic coupling might be further enhanced, resulting in a higher stability of the SC and homogeneous PL brightening.

This thesis shows how the electrochemical hole injection can be varied by 0.3 eV by the surface chemistry on CsPbBr₃ NCs. The VB alignment of NCs and HTL plays an important role for charge carrier balance in LEDs, contributing to an increase of EQE. Therefore, the VB position or hole injection potential of the NCs should be close to the HOMO of PTAA at -4.99 eV. This can be achieved by using DDABr as binding group to the NCs. Furthermore, electron withdrawing ligands can be used for reducing the hole injection potential. Ideally, the NCs should be covered by a combination of both charges, so that the ligands contribute to stability and charge carrier balance. The thesis also shows that the reduced stability can be overcome by crystallizing NCs into SCs. This approach can enhance the stability even with dynamically binding ligands.

In summary, this thesis highlights possible future modifications to achieve charge carrier balance, reduced onset potentials for hole injection, and stability under electrical bias. All these factors need to be considered when building efficient LEDs that may be incorporated in future QLED TVs.

7 Appendix

Chemical Structures.

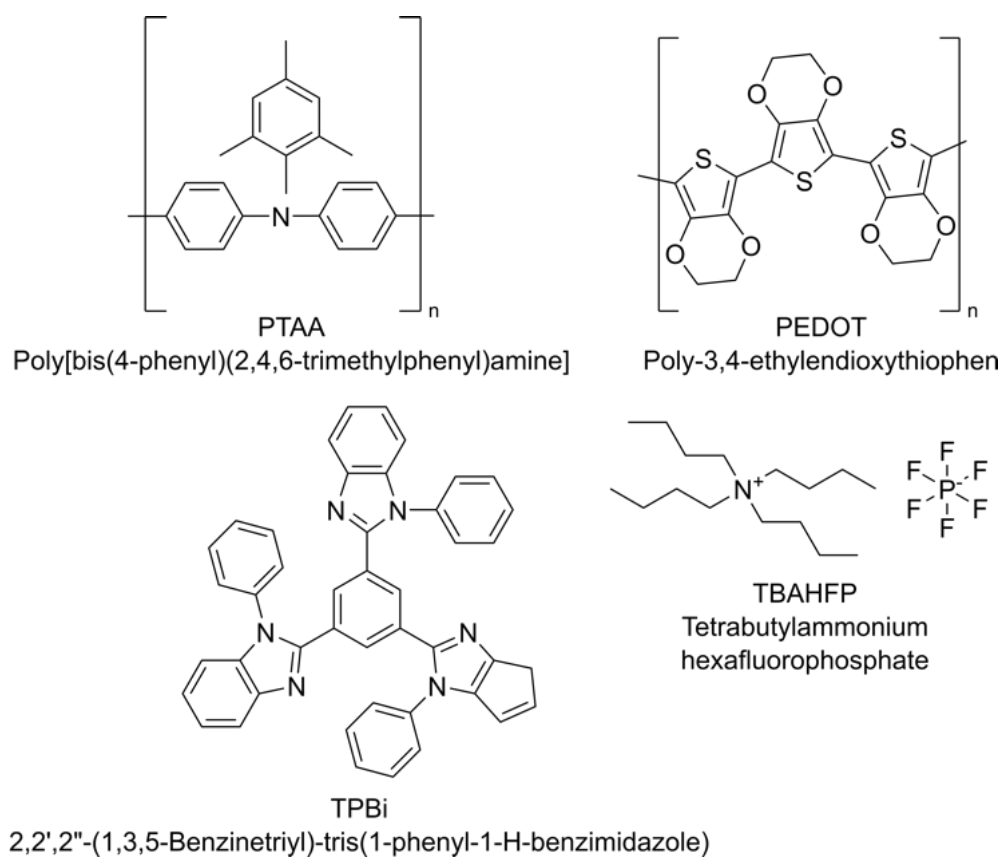


Figure 7.1: Chemical structures and full names of PTAA, PEDOT, TPBi, and TBAHFP.

List of Tables

2.1	Proportionality of DOS to energy.	10
3.1	PLQY of DDABr and OA/OAm NCs.	67
3.2	Lifetimes and decay rates extracted from TRPL in solution.	68
3.3	Lifetimes and decay rates extracted from TRPL in solution.	68
3.4	Relative atomic ratios calculated by XPS spectra.	73
4.1	PL characterization of CA-R covered NCs.	94
4.2	Determined onset potentials during SEC PL for statistics.	100
4.3	PL characteristics of CA-R/OAm NCs in solution.	103
4.4	Fitting parameters of time-resolved PL.	104
4.5	EL characteristics of CA-R/OAm LEDs.	107
4.6	Calculated absorption excitation energies.	108
5.1	Determined ligands per NC by the integrals from quantitative NMR spectroscopy.	124
5.2	Fitting parameters of time-resolved PL.	137

List of Figures

1.1	Introduction of CsPbBr ₃ NCs in LEDs.	2
1.2	Structure of this cumulative thesis.	5
2.1	Electronic structures of nanomaterials.	8
2.2	Density of energetic states in nanomaterials.	9
2.3	Schematic description NC nucleation.	11
2.4	Surface chemistry of NCs.	13
2.5	Energetic trap removal on core/shell CdSe/CdS heterostructures. . .	14
2.6	Characterization of CsPbBr ₃ NCs.	17
2.7	Defect tolerance in LHP NC.	18
2.8	Synthesis of LHP NCs.	19
2.9	Shapes of LHP nanostructures.	20
2.10	Surface chemistry of LHP NCs.	21
2.11	Probing the organic surface of LHP NCs.	23
2.12	Ligand exchange on LHP surfaces.	26
2.13	Assembly and superfluorescence of SCs.	28
2.14	LED energetic and physical setup.	29
2.15	NC LED performance.	30
2.16	Basics of cyclic voltammetry.	33
2.17	PL SEC basics.	35
2.18	SEC on NCs.	37
2.19	Spectroelectrochemical setup at the University of Tübingen.	38
2.20	State-of-the-art SEC on CsPbBr ₃	40
3.1	Scheme of OA, OAm, and DDABr.	45
3.2	Interparticle distance of DDABr and OA/OAm covered NCs by TEM. .	47
3.3	¹ H NMR spectroscopy on DDABr ligand exchange on OA/OAm-covered NCs.	48
3.4	Exemplary SEC PL study on once washed DDABr covered NCs and summary of determined VB positions by SEC PL.	50
3.5	UPS spectra on DDABr and OA/OAm NCs.	51
3.6	Hole-only device comparison of DDABr to OA/OAm covered NCs. . .	52
3.7	Theoretical calculation of different (OA/OAm, DDABr) NC passivation. .	54
3.8	Calculated MO energies of OA/OAm, DDABr NC passivations. . . .	56
3.9	LED performance comparison of polar and non-polar ETL with OA/OAm NCs.	58
3.10	Comparison of LED performance of OA/OAm and DDABr covered NCs.	59

3.11 Qualitative and quantitative ^1H NMR spectroscopy of once and twice ligand stripped NCs.	66
3.12 TRPL of DDABr and OA/OAm covered NCs.	68
3.13 Photobleach of DDABr and OA/OAm NCs in PC/TBAHFP.	69
3.14 Reference measurement of Fc/Fc^+ in PC/TBAHFP.	70
3.15 SEC PL on once ligand stripped OA/OAm NCs.	70
3.16 SEC PL on twice ligand stripped OA/OAm NCs.	71
3.17 SEC PL on twice ligand stripped DDABr NCs.	72
3.18 XPS survey spectra of native and DDABr NCs.	73
3.19 XPS core levels of the individual elements in native and DDABr NCs.	73
3.20 DFT calculations on Pb^{2+} and Cs^+ as binding site.	74
3.21 Calculation of GSP from contact potential measurements by Kelvin probe.	74
3.22 LED characterization of non-altered and once washed OA/OAm NCs.	75
3.23 EL of ETL and HTL.	75
3.24 Device operational lifetime of native and DDABr NC PeLEDs.	76
4.1 Characterization ligand exchange OA NCs to CA-R NCs.	81
4.2 SEC PL on CACF_3 -covered NCs.	82
4.3 SEC PL and summary of SEC PL data on CA-R covered NCs.	83
4.4 Performance of CA-R-covered NCs in LEDs and hole-only devices.	84
4.5 Characterization of CAH covered NCs.	93
4.6 Characterization of CAOMe covered NCs.	93
4.7 Characterization of $\text{CAN}(\text{Me})_2$ covered NCs.	94
4.8 Zoomed-in ^1H NMR spectra of CA-R covered NCs.	95
4.9 Full ^1H NMR spectra of CA-R covered NCs.	96
4.10 ^1H NMR spectrum of OA covered NCs.	96
4.11 Stability of NCs in electrolyte solution.	97
4.12 Reference measurements of Fc/Fc^+ in SEC PL cell.	98
4.13 Schematic of the used SEC cell.	98
4.14 2 nd example of SEC PL on CACF_3 covered NCs.	99
4.15 2 nd example of SEC PL on CAH covered NCs.	99
4.16 2 nd example of SEC PL on CAOMe covered NCs.	100
4.17 SEC PL on $\text{CAN}(\text{Me})_2$ NCs.	101
4.18 CV of CAs.	101
4.19 Characterization of OA/OAm covered NCs.	102
4.20 PL and absorbance spectra of CAR/OAm exchanged NCs.	102
4.21 SEM cross-section NC LEDs.	103
4.22 Time-resolved PL of CA-R/OAm exchanged NCs.	104
4.23 jVL and EQE of different LED pixels.	105
4.24 Maximum EQE of CA-R/OAm LEDs.	105
4.25 Performance of OA/OAm NC LED.	106
4.26 Electroluminescence of CA-R/OAm-covered NC LEDs.	106
4.27 Calculated MO energies with 12 CAs attached to NCs.	107
4.28 Calculated MO energies of CA-R covered NCs with Cs^+ and Pb^{2+} attachement.	108

4.29	SEC PL on insulating OA/OAM covered NCs.	109
4.30	SEC PL on ligand stripped OA covered NCs.	109
5.1	Characterization of CsPbBr ₃ NCs and their self-assembled SCs. . . .	114
5.2	Stability of CsPbBr ₃ SCs against the electrolyte solution.	116
5.3	SEC PL on CsPbBr ₃ SC.	118
5.4	Spectral mapping of SC sample before and after SCV.	120
5.5	Full ¹ H NMR spectra of exchanged lecithin NCs.	124
5.6	SEM of as-synthesized and exchanged NCs.	125
5.7	Light microscopy in the dark-field mode of SCs.	125
5.8	SEM of tilted SC.	126
5.9	Photographs of SEC PL cell.	126
5.10	CV of Fc/Fc ⁺ in PC/TBAHFP in SEC PL cell.	126
5.11	Single PL spectra extracted from spectral maps with and without ES. .	127
5.12	SEC PL on SC with bromide oxidation leading to complete dissolution. .	128
5.13	SCV and CV including bromide oxidation from solution.	128
5.14	All spectra recorded during SCV.	129
5.15	Peak PL intensity edge positions.	130
5.16	Peak PL intensity center positions.	130
5.17	Intensity map of probed SCs, spectra, and SCV.	131
5.18	PL intensity trace during SCV from 0.03-0.63 V for edge positions. . .	132
5.19	PL intensity trace during SCV from 0.03-0.63 V for center positions. .	132
5.20	Summary of onset potentials depending on position in SC.	133
5.21	Photograph of SEC absorbance cell.	133
5.22	Fc/Fc ⁺ reference in SEC absorbance cell.	134
5.23	Background absorbance SEC cell.	134
5.24	SCV Absorbance SEC of NC thin-film.	135
5.25	Absorbance SEC at constant potential.	135
5.26	Spectral mapping of another SC sample.	136
5.27	Time-resolved PL in SCs.	137
5.28	Statistics PL brightening.	138
5.29	Edge brightening of SCs.	138
6.1	Future modification of LHP NCs for improved performance in LEDs. .	139
7.1	Chemical structures and full names of PTAA, PEDOT, TPBi, and TBAHFP.	143

A List of Scholarly Contributions

Publications included in this thesis.

- Roshini Jayabalan, Girish K. Hanumantharaju, **Theresa Hettiger**, Arup Sarkar, Fengshuo Zu, Aladin Ullrich, Anna Abfalterer, Alexander S. Urban, Norbert Koch, Denis Andrienko, Marcus Scheele, and Wolfgang Brütting. Optimizing Carrier Balance in CsPbBr₃ Nanocrystal LEDs: The Role of Alkyl Ligands and Polar Electron Transport Layers. *Adv. Optical Mater.* 2025, 13, 28: e01361. <https://doi.org/10.1002/adom.202501361>
- **Theresa Hettiger**, Roshini Jayabalan, Arup Sarkar, Jonas L. Hiller, Max Nuss Hör, Denis Andrienko, Wolfgang Brütting, and Marcus Scheele. Impact of Ligand-Mediated Inductive Effects on Electrochemical p-Doping of CsPbBr₃ Nanocrystals. *ACS Energy Lett.* 2026, 11, 1, 567–572 . <https://doi.org/10.1021/acsenergylett.5c03184>
- **Theresa Hettiger**, Jonas L. Hiller, Richard Hodak, Martin Eberle, Alfred J. Meixner, and Marcus Scheele. Spatial Mapping of Electrochemical Hole-Injection into Supercrystals of Perovskite Nanocrystals. *Nano Lett.* (2026) 26 (29): 9403–9409. <https://doi.org/10.1021/acs.nanolett.6c01326>

Peer-reviewed publications not included in this thesis.

- Serhii Medvedko, Markus Ströbele, Maike Fechter, Antonia Fischer, **Theresa Hettiger**, Paul Idzko, Marcus Scheele, and J. Philipp Wagner. Synthesis of Thiourea and Thioamide S-Oxides via SO Transfer from a Thiirane S-Oxide onto N-Heterocyclic Carbenes. *Org. Lett.* 2024, 26, 27, 5868–5872. <https://doi.org/10.1021/acs.orglett.4c02253>
- Johannes Schöntag, **Theresa Hettiger**, William Roberts, Marcus Scheele, Markus Ströbele, and Holger F. Bettinger. Rearrangement Cascade Initiated by Nucleophilic Benzyne Attack on 3,6-Di(2-pyridyl)-1,2-diazines. *ACS Org. Inorg. Au* 2025, 5, 2, 97–104. <https://doi.org/10.1021/acsorginorgau.4c00070>

- Jonas L. Hiller, Robert Thalwitzer, Ata Bozkurt, Ross Ewan Carter, **Theresa Hettiger**, Markus Fröhlich, Richard Hodak, Matheus Gomes Ferreira, Martin Eberle, Ekaterina Kneschaurek, Gerard N. Hinsley, Bihan Wang, Kuan Hoon Ngoi, Elke Nadler, Wojciech Roseker, Fabian Westermeier, Michael Sprung, Dmitry Baranov, Jannika Lauth, Frank Schreiber, Ivan A. Vartanyants, Marcus Scheele, and Ivan A. Zaluzhnyy.
How Antisolvent-Induced Ligand Stripping Shapes CsPbX₃ Nanocrystals and Their Assemblies.
Nano Lett. 2026, 26, 8, 2955–2963.
<https://doi.org/10.1021/acs.nanolett.5c06380>

Contributed talks and posters to scientific conferences

- Poster presentation at Bunsentagung **2023**, Deutsche Bunsen-Gesellschaft, in Berlin.
Awarded with a poster prize by the audience.
- Invited talk at Bunsentagung **2024**, Deutsche Bunsen-Gesellschaft in Aachen.
Modifying the Electronic Structure of CsPbBr₃ Nanocrystals by Ligand Exchange with Cinnamic Acid Derivatives.
- Poster presentation at Materials for Sustainable Development Conference Spring **2024**, nanoGe, in Barcelona.
Awarded with a poster prize of the #PEROQUANT symposium.
- Talk at Materials for Sustainable Development Conference Spring **2025**, nanoGe, in Sevilla.
Ligand-Driven Shifts of the Electronic Properties of CsPbBr₃ Nanocrystals.
- Talk at Bunsentagung **2025**, Deutsche Bunsen-Gesellschaft, in Leipzig.
Optimizing CsPbBr₃ Nanocrystals for LEDs: Spectroelectrochemical Study of Ligand Effects.
- Talk at PerFunPro Conference **2025**, nanoGe, in Konstanz.
Influences of Ligands on p-Doping of CsPbBr₃ Nanocrystals.

In addition, I presented my work at two SPP conferences (in Bonn **2023** and Stuttgart **2024**) on a poster and in a shared talk with my collaborators from the University of Augsburg. I also participated at the international workshop on "Chemical Coding at the Atomic Scale: Designing Hybrid and Quantum Nanostructures for Applications in Optical Biosensing, Light Harvesting, Chiral Catalysis, and More" **2024** in Dresden and presented my work on a poster.

Contributions to other theses.

- Roshini Jayabalan. Ph.D. Thesis.
- Jonas Hiller, Ph.D. Thesis.
- Anna-Lena Renz, Master and Ph.D. Thesis.
- Martin Eberle, Master Thesis.
- Johannes Schöntag. Ph.D. Thesis.
- Serhii Medvedko, Ph.D. Thesis.
- Anqi Shen, Ph.D. Thesis.

Supervision of practical courses.

- Jannik Allnach, Lab practical and Bachelor Thesis, Nano-Science (2022).
"Ligand Exchange on CsPbBr₃ Nanocrystals with Cinnamic Acid Derivatives."
- Melena Groß, Lab practical Master Nano-Science (2023).
"Ligand Exchange on CsPbBr₃ Nanocrystals with Cinnamic Acid."
- Max Nuss Hör, Lab practical Master chemistry (2024). "Investigations of the synthesis as well as ligand exchange on CsPbBr₃ nanoparticles and their properties."

B Declaration of Contribution

In the following, my contributions to the publications included in this thesis are stated.

Optimizing Carrier Balance in CsPbBr₃ Nanocrystal LEDs: The Role of Alkyl Ligands and Polar Electron Transport Layers⁴⁵

preparation of NMR samples, data evaluation and interpretation; conceptualization and recording of SEC PL experiments; data interpretation; preparation of NMR and SEC PL figures; writing of draft on SEC PL and NMR

Estimated contribution of my own: ~ 11%

Impact of Ligand-Mediated Inductive Effects on Electrochemical p-Doping of CsPbBr₃ Nanocrystals⁴⁶

conceptualization; NC synthesis; ligand exchange; NC characterization; NMR spectroscopy; SEC PL study on exchanged NCs; data evaluation; data interpretation; discussion; writing of original draft; preparation of all figures; answering to reviewer questions; editing and rewriting of the reviewed draft

Estimated contribution of my own: ~ 75%

Spatial Mapping of Electrochemical Hole Injection into Supercrystals of Perovskite Nanocrystals⁴⁷

original idea; conceptualization; NC synthesis; ligand exchange; NC characterization; SEM and NMR evaluation; SC crystallization; optical characterization; SEC PL study; data interpretation and visualization; discussion; writing of original draft; preparation of figures

Estimated contribution of my own: ~ 65%

C Acknowledgements

I would like to thank Prof. Dr. Marcus Scheele for his continuous support throughout my work as PhD student. He supported my work in critically reviewing and coming up with new ideas, which shaped the project. Thank you for giving me the opportunity to work on this project and supporting my own development, i.e. encouraging scientific discourse with project partners and at conferences.

I want to thank apl. Prof. Dr. Heiko Peisert for being the second reviewer of this thesis.

I am grateful to have Jonas Hiller as a friend and colleague. His work on the spectroelectrochemical cell paved the way to SEC on NCs within this cumulative thesis. He encouraged me throughout the years, gave me advice on how to prepare manuscripts, and listened to many ideas.

I would like to thank Roshini Jayabalan and Dr. Arup Sarkar for their contributions to this work. Within the priority program: *Perovskite semiconductors: from fundamentals to devices* of the Deutsche Forschungsgemeinschaft, we aimed on collaborating: me fabricating NCs, Arup supporting from the theory side, and Roshini building devices. I am grateful to Roshini for showing me LED fabrication in Augsburg and for being patient with me and my NCs. I also want to thank the PIs in the project: Prof. Dr. Wolfgang Brütting and Dr. Denis Andrienko. Their critical reviewing resulted in an improvement of this work.

Thank you to Dr. Jan Wahl, Dr. Christopher Kirsch and Kai Wurst, who all three introduced me to chemical and electrochemical setups. Their work and knowledge paved the way to the work I did. I am grateful for the scientific discussions and their support.

I also want to thank the whole working group for the fun time we spent at lunch breaks and at group workshops. I am grateful for constructive discussions, material and ideas: Ata Bozkurt, Lars Eckhardt, Philipp Frech, Philipp Haizmann, Richard Hodak, Eric Juriatti, Dr. Andre Maier, Mario Martin, Patrick Michel, William Roberts, Dr. Christine Schedel, Dr. Fabian Strauß, Robert Thalwitzer, Tim Werz, and Sophia Westendorf. I am especially grateful to Tim and Fabian, who supported me during rough times in the lab.

Then, I would like to thank the members of the work group Lauth: Leon Biesterfeld, Markus Fröhlich, and Onno Strolka. I enjoyed the time discussing figures, synthesis questions, and at conferences.

A special thanks goes to my sister Christina and Leon for proofreading this thesis.

I am grateful for all the support I received from my parents, my (former) housemates, and all my friends.

Bibliography

- (1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *Journal of the American Chemical Society* **1993**, *115*, 8706–8715.
- (2) Rossetti, R.; Nakahara, S.; Brus, L. E. Quantum Size Effects in the Redox Potentials, Resonance Raman Spectra, and Electronic Spectra of CdS Crystallites in Aqueous Solution. *The Journal of Chemical Physics* **1983**, *79*, 1086–1088.
- (3) Ekimov, A. I.; Onushchenko, A. A. Quantum Size Effect in Three-Dimensional Microscopic Semiconductor Crystals. *JETP Letters* **2023**, *118*, S15–S17.
- (4) Nobel Prize Outreach 2025 Nobel Prize in Chemistry 2023, <https://www.nobelprize.org/prizes/chemistry/2023/press-release/>, Press Release, 2023.
- (5) Rogach, A. L.; Franzl, T.; Klar, T. A.; Feldmann, J.; Gaponik, N.; Lesnyak, V.; Shavel, A.; Eychmüller, A.; Rakovich, Y. P.; Donegan, J. F. Aqueous Synthesis of Thiol-Capped CdTe Nanocrystals: State-of-the-Art. *The Journal of Physical Chemistry C* **2007**, *111*, 14628–14637.
- (6) Qu, L.; Peng, X. Control of Photoluminescence Properties of CdSe Nanocrystals in Growth. *Journal of the American Chemical Society* **2002**, *124*, 2049–2055.
- (7) De Mello Donegá, C.; Hickey, S. G.; Wuister, S. F.; Vanmaekelbergh, D.; Meijerink, A. Single-Step Synthesis to Control the Photoluminescence Quantum Yield and Size Dispersion of CdSe Nanocrystals. *The Journal of Physical Chemistry B* **2003**, *107*, 489–496.
- (8) McDonald, S. A.; Konstantatos, G.; Zhang, S.; Cyr, P. W.; Klem, E. J. D.; Levina, L.; Sargent, E. H. Solution-Processed PbS Quantum Dot Infrared Photodetectors and Photovoltaics. *Nature Materials* **2005**, *4*, 138–142.
- (9) Klepzig, L. F.; Biesterfeld, L.; Romain, M.; Niebur, A.; Schlosser, A.; Hübner, J.; Lauth, J. Colloidal 2D PbSe Nanoplatelets with Efficient Emission Reaching the Telecom O-, E- and S-band. *Nanoscale Advances* **2022**, *4*, 590–599.
- (10) García De Arquer, F. P.; Talapin, D. V.; Klimov, V. I.; Arakawa, Y.; Bayer, M.; Sargent, E. H. Semiconductor Quantum Dots: Technological Progress and Future Challenges. *Science* **2021**, *373*, eaaz8541.

-
- (11) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chemical Reviews* **2010**, *110*, 389–458.
- (12) Wu, Z.; Troll, J.; Jeong, H.-H.; Wei, Q.; Stang, M.; Ziemssen, F.; Wang, Z.; Dong, M.; Schnichels, S.; Qiu, T.; Fischer, P. A Swarm of Slippery Micropropellers Penetrates the Vitreous Body of the Eye. *Science Advances* **2018**, *4*, eaat4388.
- (13) Liang, Z.; Zhang, B.; Yi, S.; Sun, K.; Pei, G.; Shang, Y.; Liu, X.; Ren, S.; Liu, P.; Zhao, J. Promising Advances in Physically Propelled Micro/Nanoscale Robots. *Nano Materials Science* **2025**, *7*, 582–598.
- (14) Hsu, J. C.; Nieves, L. M.; Betzer, O.; Sadan, T.; Noël, P. B.; Popovtzer, R.; Cormode, D. P. Nanoparticle Contrast Agents for X-ray Imaging Applications. *WIREs Nanomedicine and Nanobiotechnology* **2020**, *12*, e1642.
- (15) Giljohann, D. A.; Seferos, D. S.; Daniel, W. L.; Massich, M. D.; Patel, P. C.; Mirkin, C. A. Gold Nanoparticles for Biology and Medicine. *Angewandte Chemie International Edition* **2010**, *49*, 3280–3294.
- (16) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor Nanocrystals as Fluorescent Biological Labels. *Science* **1998**, *281*, 2013–2016.
- (17) Yoon, W.; Boercker, J. E.; Lumb, M. P.; Placencia, D.; Foos, E. E.; Tischler, J. G. Enhanced Open-Circuit Voltage of PbS Nanocrystal Quantum Dot Solar Cells. *Scientific Reports* **2013**, *3*, 2225.
- (18) Carey, G. H.; Abdelhady, A. L.; Ning, Z.; Thon, S. M.; Bakr, O. M.; Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Chemical Reviews* **2015**, *115*, 12732–12763.
- (19) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H.-J.; Bawendi, M. G. Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots. *Science* **2000**, *290*, 314–317.
- (20) Klimov, V. I.; Ivanov, S. A.; Nanda, J.; Achermann, M.; Bezel, I.; McGuire, J. A.; Piryatinski, A. Single-Exciton Optical Gain in Semiconductor Nanocrystals. *Nature* **2007**, *447*, 441–446.
- (21) Sadeghi, S.; Khabbaz Abkenar, S.; Ow-Yang, C. W.; Nizamoglu, S. Efficient White LEDs Using Liquid-state Magic-sized CdSe Quantum Dots. *Scientific Reports* **2019**, *9*, 10061.
- (22) Bourzac, K. Quantum Dots Go on Display. *Nature* **2013**, *493*, 283–283.
- (23) Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulović, V. Emergence of Colloidal Quantum-Dot Light-Emitting Technologies. *Nature Photonics* **2013**, *7*, 13–23.
- (24) Wood, V.; Bulović, V. Colloidal Quantum Dot Light-Emitting Devices. *Nano Reviews* **2010**, *1*, 5202.
- (25) Reiss, P.; Bleuse, J.; Pron, A. Highly Luminescent CdSe/ZnSe Core/Shell Nanocrystals of Low Size Dispersion. *Nano Letters* **2002**, *2*, 781–784.

- (26) Wang, X.; Yu, J.; Chen, R. Optical Characteristics of ZnS Passivated CdSe/CdS Quantum Dots for High Photostability and Lasing. *Scientific Reports* **2018**, *8*, 17323.
- (27) Lin, K. et al. Perovskite Light-Emitting Diodes with External Quantum Efficiency Exceeding 20 per Cent. *Nature* **2018**, *562*, 245–248.
- (28) Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P. Essentially Trap-Free CsPbBr₃ Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *Journal of the American Chemical Society* **2017**, *139*, 6566–6569.
- (29) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Letters* **2015**, *15*, 3692–3696.
- (30) Akkerman, Q. A.; Valerio D’Innocenzo; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. *Journal of the American Chemical Society* **2015**, *137*, 10276–10281.
- (31) Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V. Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, I). *Nano Letters* **2015**, *15*, 5635–5640.
- (32) Zhao, Y.; Choi, B.-H.; Kim, E.; Zeng, Q.; Lee, T.-W. Advancing Perovskite Nanocrystals for High-Resolution LED Displays. *Communications Materials* **2025**, *6*, 281.
- (33) Park, J. H.; Lee, A.-y.; Yu, J. C.; Nam, Y. S.; Choi, Y.; Park, J.; Song, M. H. Surface Ligand Engineering for Efficient Perovskite Nanocrystal-Based Light-Emitting Diodes. *ACS Applied Materials & Interfaces* **2019**, *11*, 8428–8435.
- (34) Li, G.; Huang, J.; Zhu, H.; Li, Y.; Tang, J.-X.; Jiang, Y. Surface Ligand Engineering for Near-Unity Quantum Yield Inorganic Halide Perovskite QDs and High-Performance QLEDs. *Chemistry of Materials* **2018**, *30*, 6099–6107.
- (35) De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, *10*, 2071–2081.
- (36) Chiba, T.; Hoshi, K.; Pu, Y.-J.; Takeda, Y.; Hayashi, Y.; Ohisa, S.; Kawata, S.; Kido, J. High-Efficiency Perovskite Quantum-Dot Light-Emitting Devices by Effective Washing Process and Interfacial Energy Level Alignment. *ACS Applied Materials & Interfaces* **2017**, *9*, 18054–18060.

-
- (37) De Trizio, L.; Infante, I.; Manna, L. Surface Chemistry of Lead Halide Perovskite Colloidal Nanocrystals. *Accounts of Chemical Research* **2023**, *56*, 1815–1825.
- (38) Sun, S.-Q.; Hua, X.-C.; Liu, Q.-W.; Wang, T.-T.; Luo, W.; Zhang, Y.-J.; Liao, L.-S.; Fung, M.-K. Influence of a Lecithin Additive on the Performance of All-Inorganic Perovskite Light-Emitting Diodes. *Journal of Materials Chemistry C* **2019**, *7*, 2905–2910.
- (39) Deng, C.; Fu, T.; Huang, Q.; Fu, Z.; Lu, Y. Enhancing the Quantum Yield and Stability of CsPbBr₃ Quantum Dots with Zwitterionic Ligand Post-Treatment. *Journal of Luminescence* **2024**, *267*, 120395.
- (40) Fiuza-Maneiro, N.; Sun, K.; López-Fernández, I.; Gómez-Graña, S.; Müller-Buschbaum, P.; Polavarapu, L. Ligand Chemistry of Inorganic Lead Halide Perovskite Nanocrystals. *ACS Energy Letters* **2023**, *8*, 1152–1191.
- (41) Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; Ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C.-J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Letters* **2018**, *3*, 641–646.
- (42) Milanese, S.; De Giorgi, M. L.; Morello, G.; Bodnarchuk, M. I.; Anni, M. Role of the Capping Ligand in CsPbBr₃ Nanocrystals Amplified Spontaneous Emission Properties. *ACS Applied Nano Materials* **2025**, *8*, 3964–3973.
- (43) Yu, D.; Wang, C.; Guyot-Sionnest, P. *N*-Type Conducting CdSe Nanocrystal Solids. *Science* **2003**, *300*, 1277–1280.
- (44) Guyot-Sionnest, P.; Wang, C. Fast Voltammetric and Electrochromic Response of Semiconductor Nanocrystal Thin Films. *The Journal of Physical Chemistry B* **2003**, *107*, 7355–7359.
- (45) Jayabalan, R.; Hanumantharaju, G. K.; Hettiger, T.; Sarkar, A.; Zu, F.; Ullrich, A.; Abfalterer, A.; Urban, A. S.; Koch, N.; Andrienko, D.; Scheele, M.; Brütting, W. Optimizing Carrier Balance in CsPbBr₃ Nanocrystal LEDs: The Role of Alkyl Ligands and Polar Electron Transport Layers. *Advanced Optical Materials* **2025**, e01361.
- (46) Hettiger, T.; Jayabalan, R.; Sarkar, A.; Hiller, J. L.; Nuss Hör, M.; Andrienko, D.; Brütting, W.; Scheele, M. Impact of Ligand-Mediated Inductive Effects on Electrochemical p-Doping of CsPbBr₃ Nanocrystals. *ACS Energy Letters* **2026**, *11*, 567–572.
- (47) Hettiger, T.; Hiller, J. L.; Hodak, R.; Eberle, M.; Meixner, A. J.; Scheele, M. Spatial Mapping of Electrochemical Hole Injection into Supercrystals of Perovskite Nanocrystals. *Nano Letters* **2026**, *26*, 9403–9409.
- (48) Houtepen, A. J.; Sargent, E. H.; Infante, I.; Owen, J. S.; Green, P. B.; Schaller, R. D.; Bals, S.; Zeiske, S.; Stöferle, T.; Hens, Z. Colloidal Quantum Dots for Optoelectronics. *Nature Reviews Methods Primers* **2025**, *5*, 42.

- (49) Böer, K. W.; Pohl, U. W., *Semiconductor Physics*; Springer International Publishing: Cham, 2018.
- (50) In *Statistik, Festkörper, Materialien*; De Gruyter: 2021, pp 125–342.
- (51) Yu, P. Y.; Cardona, M., *Fundamentals of Semiconductors: Physics and Materials Properties*; Graduate Texts in Physics; Springer Berlin Heidelberg: Berlin, Heidelberg, 2010.
- (52) Nirmal, M.; Brus, L. Luminescence Photophysics in Semiconductor Nanocrystals. *Accounts of Chemical Research* **1999**, *32*, 407–414.
- (53) *Nanoparticles: Workhorses of Nanoscience*; De Mello Donega, C., Ed.; Springer Nature Switzerland: Cham, 2024.
- (54) Donegá, C. D. M. Synthesis and Properties of Colloidal Heteronanocrystals. *Chem. Soc. Rev.* **2011**, *40*, 1512–1546.
- (55) Norris, D. J.; Bawendi, M. G. Measurement and Assignment of the Size-Dependent Optical Spectrum in CdSe Quantum Dots. *Physical Review B* **1996**, *53*, 16338–16346.
- (56) Al L Efros; A L Efros Interband Absorption of Light in a Semiconductor Sphere. **1982**, *16*, 772–775.
- (57) Weller, H. Colloidal Semiconductor Q-Particles: Chemistry in the Transition Region Between Solid State and Molecules. *Angewandte Chemie International Edition in English* **1993**, *32*, 41–53.
- (58) Brus, L. Electronic Wave Functions in Semiconductor Clusters: Experiment and Theory. *The Journal of Physical Chemistry* **1986**, *90*, 2555–2560.
- (59) Kippeny, T.; Swafford, L. A.; Rosenthal, S. J. Semiconductor Nanocrystals: A Powerful Visual Aid for Introducing the Particle in a Box. *Journal of Chemical Education* **2002**, *79*, 1094.
- (60) Chen, Z.; Manian, A.; Widmer-Cooper, A.; Russo, S. P.; Mulvaney, P. Semiconductor Quantum Dots in the Cluster Regime: Focus Review. *Chemical Reviews* **2025**, *125*, 4359–4396.
- (61) Wise, F. W. Lead Salt Quantum Dots: The Limit of Strong Quantum Confinement. *Accounts of Chemical Research* **2000**, *33*, 773–780.
- (62) Murphy, J. E.; Beard, M. C.; Norman, A. G.; Ahrenkiel, S. P.; Johnson, J. C.; Yu, P.; Mičić, O. I.; Ellingson, R. J.; Nozik, A. J. PbTe Colloidal Nanocrystals: Synthesis, Characterization, and Multiple Exciton Generation. *Journal of the American Chemical Society* **2006**, *128*, 3241–3247.
- (63) Fox, M., *Optical Properties of Solids*, 2nd ed; Oxford Master Series in Condensed Matter Physics v. 3; Oxford University Press: Oxford ; New York, 2010.
- (64) Alivisatos, A. P. Perspectives on the Physical Chemistry of Semiconductor Nanocrystals. *The Journal of Physical Chemistry* **1996**, *100*, 13226–13239.

-
- (65) Edvinsson, T. Optical Quantum Confinement and Photocatalytic Properties in Two-, One- and Zero-Dimensional Nanostructures. *Royal Society Open Science* **2018**, *5*, 180387.
- (66) Novoselov, K. S.; Geim, A. K.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- (67) Huang, Y. et al. Universal Mechanical Exfoliation of Large-Area 2D Crystals. *Nature Communications* **2020**, *11*, 2453.
- (68) Protesescu, L.; Yakunin, S.; Nazarenko, O.; Dirin, D. N.; Kovalenko, M. V. Low-Cost Synthesis of Highly Luminescent Colloidal Lead Halide Perovskite Nanocrystals by Wet Ball Milling. *ACS Applied Nano Materials* **2018**, *1*, 1300–1308.
- (69) Xing, T.; Sunarso, J.; Yang, W.; Yin, Y.; Glushenkov, A. M.; Li, L. H.; Howlett, P. C.; Chen, Y. Ball Milling: A Green Mechanochemical Approach for Synthesis of Nitrogen Doped Carbon Nanoparticles. *Nanoscale* **2013**, *5*, 7970.
- (70) Hines, M.; Scholes, G. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Advanced Materials* **2003**, *15*, 1844–1849.
- (71) Weidman, M. C.; Beck, M. E.; Hoffman, R. S.; Prins, F.; Tisdale, W. A. Monodisperse, Air-Stable PbS Nanocrystals *via* Precursor Stoichiometry Control. *ACS Nano* **2014**, *8*, 6363–6371.
- (72) Peng, Z. A.; Peng, X. Formation of High-Quality CdTe, CdSe, and CdS Nanocrystals Using CdO as Precursor. *Journal of the American Chemical Society* **2001**, *123*, 183–184.
- (73) LaMer, V. K.; Dinegar, R. H. Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *Journal of the American Chemical Society* **1950**, *72*, 4847–4854.
- (74) Keller, D.; Dachraoui, W.; Henninen, T. R.; Erni, R. Towards an Improved, Empirically Derived Model Describing Real Nucleation and Particle Growth Reactions at the Atomic Level. *Philosophical Magazine* **2025**, *105*, 1567–1605.
- (75) de Mello Donegá, C.; Liljeroth, P.; Vanmaekelbergh, D. Physicochemical Evaluation of the Hot-Injection Method, a Synthesis Route for Monodisperse Nanocrystals. *Small* **2005**, *1*, 1152–1162.
- (76) Shevchenko, E. V.; Talapin, D. V.; Schnablegger, H.; Kornowski, A.; Festin, Ö.; Svedlindh, P.; Haase, M.; Weller, H. Study of Nucleation and Growth in the Organometallic Synthesis of Magnetic Alloy Nanocrystals: The Role of Nucleation Rate in Size Control of CoPt₃ Nanocrystals. *Journal of the American Chemical Society* **2003**, *125*, 9090–9101.
- (77) Kwon, S. G.; Hyeon, T. Formation Mechanisms of Uniform Nanocrystals via Hot-Injection and Heat-Up Methods. *Small* **2011**, *7*, 2685–2702.

- (78) Kim, J. Y.; Voznyy, O.; Zhitomirsky, D.; Sargent, E. H. 25th Anniversary Article: Colloidal Quantum Dot Materials and Devices: A Quarter-Century of Advances. *Advanced Materials* **2013**, *25*, 4986–5010.
- (79) Volmer, M.; Weber, . Keimbildung in Übersättigten Gebilden. *Zeitschrift für Physikalische Chemie* **1926**, *119U*, 277–301.
- (80) Oxtoby, D. W. Nucleation of First-Order Phase Transitions. *Accounts of Chemical Research* **1998**, *31*, 91–97.
- (81) Polte, J. Fundamental Growth Principles of Colloidal Metal Nanoparticles – a New Perspective. *CrystEngComm* **2015**, *17*, 6809–6830.
- (82) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chemical Reviews* **2014**, *114*, 7610–7630.
- (83) Peng, X.; Wickham, J.; Alivisatos, A. P. Kinetics of II-VI and III-V Colloidal Semiconductor Nanocrystal Growth: “Focusing” of Size Distributions. *Journal of the American Chemical Society* **1998**, *120*, 5343–5344.
- (84) Yin, Y.; Alivisatos, A. P. Colloidal Nanocrystal Synthesis and the Organic–Inorganic Interface. *Nature* **2005**, *437*, 664–670.
- (85) Knüsel, P. N.; Riedinger, A.; Rossinelli, A. A.; Ott, F. D.; Mule, A. S.; Norris, D. J. Experimental Evidence for Two-Dimensional Ostwald Ripening in Semiconductor Nanoplatelets. *Chemistry of Materials* **2020**, *32*, 3312–3319.
- (86) Xu, L.; Liang, H.-W.; Yang, Y.; Yu, S.-H. Stability and Reactivity: Positive and Negative Aspects for Nanoparticle Processing. *Chemical Reviews* **2018**, *118*, 3209–3250.
- (87) Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V. The Surface Science of Nanocrystals. *Nature Materials* **2016**, *15*, 141–153.
- (88) Houtepen, A. J.; Hens, Z.; Owen, J. S.; Infante, I. On the Origin of Surface Traps in Colloidal II–VI Semiconductor Nanocrystals. *Chemistry of Materials* **2017**, *29*, 752–761.
- (89) Voznyy, O.; Thon, S. M.; Ip, A. H.; Sargent, E. H. Dynamic Trap Formation and Elimination in Colloidal Quantum Dots. *The Journal of Physical Chemistry Letters* **2013**, *4*, 987–992.
- (90) Baker, D. R.; Kamat, P. V. Tuning the Emission of CdSe Quantum Dots by Controlled Trap Enhancement. *Langmuir* **2010**, *26*, 11272–11276.
- (91) Smith, A. M.; Nie, S. Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering. *Accounts of Chemical Research* **2010**, *43*, 190–200.
- (92) Brandt, R. E.; Poindexter, J. R.; Gorai, P.; Kurchin, R. C.; Hoye, R. L. Z.; Nienhaus, L.; Wilson, M. W. B.; Polizzotti, J. A.; Sereika, R.; Žaltauskas, R.; Lee, L. C.; MacManus-Driscoll, J. L.; Bawendi, M.; Stevanović, V.; Buonassisi, T. Searching for “Defect-Tolerant” Photovoltaic Materials: Combined Theoretical and Experimental Screening. *Chemistry of Materials* **2017**, *29*, 4667–4674.

-
- (93) Green, M. A New Approach to the Formal Classification of Covalent Compounds of the Elements. *Journal of Organometallic Chemistry* **1995**, *500*, 127–148.
- (94) Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* **2013**, *135*, 18536–18548.
- (95) De Roo, J.; De Keukeleere, K.; Hens, Z.; Van Driessche, I. From Ligands to Binding Motifs and beyond; the Enhanced Versatility of Nanocrystal Surfaces. *Dalton Transactions* **2016**, *45*, 13277–13283.
- (96) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility. *Journal of the American Chemical Society* **1997**, *119*, 7019–7029.
- (97) Kirkwood, N.; Monchen, J. O. V.; Crisp, R. W.; Grimaldi, G.; Bergstein, H. A. C.; Du Fossé, I.; Van Der Stam, W.; Infante, I.; Houtepen, A. J. Finding and Fixing Traps in II–VI and III–V Colloidal Quantum Dots: The Importance of Z-Type Ligand Passivation. *Journal of the American Chemical Society* **2018**, *140*, 15712–15723.
- (98) Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. Improved Performance and Stability in Quantum Dot Solar Cells through Band Alignment Engineering. *Nature Materials* **2014**, *13*, 796–801.
- (99) Dong, A.; Jiao, Y.; Milliron, D. J. Electronically Coupled Nanocrystal Superlattice Films by *in Situ* Ligand Exchange at the Liquid–Air Interface. *ACS Nano* **2013**, *7*, 10978–10984.
- (100) Michel, P.; Martin, M.; Hiller, J. L.; Scheele, M. Effects of Ethylenediamine on the Intrinsic Photoresponse of PbS Quantum Dots. *Nanoscale* **2025**, *17*, 25297–25304.
- (101) Klem, E. J. D.; Shukla, H.; Hinds, S.; MacNeil, D. D.; Levina, L.; Sargent, E. H. Impact of Dithiol Treatment and Air Annealing on the Conductivity, Mobility, and Hole Density in PbS Colloidal Quantum Dot Solids. *Applied Physics Letters* **2008**, *92*, 212105.
- (102) Luther, J. M.; Law, M.; Song, Q.; Perkins, C. L.; Beard, M. C.; Nozik, A. J. Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol. *ACS Nano* **2008**, *2*, 271–280.
- (103) Moody, I. S.; Stonas, A. R.; Lonergan, M. C. PbS Nanocrystals Functionalized with a Short-Chain, Ionic, Dithiol Ligand. *The Journal of Physical Chemistry C* **2008**, *112*, 19383–19389.
- (104) André, A.; Weber, M.; Wurst, K. M.; Maiti, S.; Schreiber, F.; Scheele, M. Electron-Conducting PbS Nanocrystal Superlattices with Long-Range Order Enabled by Terthiophene Molecular Linkers. *ACS Applied Materials & Interfaces* **2018**, *10*, 24708–24714.

- (105) Choi, J. J.; Luria, J.; Hyun, B.-R.; Bartnik, A. C.; Sun, L.; Lim, Y.-F.; Marohn, J. A.; Wise, F. W.; Hanrath, T. Photogenerated Exciton Dissociation in Highly Coupled Lead Salt Nanocrystal Assemblies. *Nano Letters* **2010**, *10*, 1805–1811.
- (106) Lauth, J.; Grimaldi, G.; Kinge, S.; Houtepen, A. J.; Siebbeles, L. D. A.; Scheele, M. Ultrafast Charge Transfer and Upconversion in Zinc β -Tetraaminophthalocyanine-Functionalized PbS Nanostructures Probed by Transient Absorption Spectroscopy. *Angewandte Chemie* **2017**, *129*, 14249–14253.
- (107) Wahl, J.; Engelmayer, M.; Mandal, M.; Naujoks, T.; Haizmann, P.; Maier, A.; Peisert, H.; Andrienko, D.; Brütting, W.; Scheele, M. Porphyrin Functionalization of CsPbBr₂/SiO₂ Core–Shell Nanocrystals Enhances the Stability and Efficiency in Electroluminescent Devices. *Advanced Optical Materials* **2022**, *10*, 2101945.
- (108) Kumar, K.; Hiller, J.; Bender, M.; Nosrati, S.; Liu, Q.; Edelmann, M.; Maier, S.; Rammler, T.; Wackenhut, F.; Meixner, A. J.; Braun, K.; Bunz, U. H. F.; Scheele, M. Periodic Fluorescence Variations of CdSe Quantum Dots Coupled to Aryleneethynylenes with Aggregation-Induced Emission. *ACS Nano* **2021**, *15*, 480–488.
- (109) Rose, G. De Novis Quibusdam Fossilibus Quae in Montibus Uraliis Inveniuntur, Ph.D. Thesis, Berolina, 1839.
- (110) Journal Für Praktische Chemie : Practical Applications and Applied Chemistry ; Covering All Aspects of Applied Chemistry. 19. 1840. **1840**.
- (111) Barth, T. F. W. Die Kristallstruktur von Perowskit Und Verwandten Verbindungen. **1925**, *3*, 201–216.
- (112) Goldschmidt, V. M. Die Gesetze der Krystallochemie. *Die Naturwissenschaften* **1926**, *14*, 477–485.
- (113) Bohm, J.; Klimm, D.; Mühlberg, M.; Winkler, B., *Einführung in die Kristallographie*, 20. überarbeitete Auflage; Kleber, W., Ed.; De Gruyter Studium; De Gruyter: Berlin, 2021.
- (114) Jung, M.-C.; Lee, K.-W.; Pickett, W. E. Perovskite ThTa₂N₃ : A Large-Thermopower Topological Crystalline Insulator. *Physical Review B* **2018**, *97*, 121104.
- (115) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society* **2009**, *131*, 6050–6051.
- (116) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, *338*, 643–647.

- (117) Oga, H.; Saeki, A.; Ogomi, Y.; Hayase, S.; Seki, S. Improved Understanding of the Electronic and Energetic Landscapes of Perovskite Solar Cells: High Local Charge Carrier Mobility, Reduced Recombination, and Extremely Shallow Traps. *Journal of the American Chemical Society* **2014**, *136*, 13818–13825.
- (118) Schmidt, L. C.; Pertegás, A.; González-Carrero, S.; Malinkiewicz, O.; Agouram, S.; Mínguez Espallargas, G.; Bolink, H. J.; Galian, R. E.; Pérez-Prieto, J. Nontemplate Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoparticles. *Journal of the American Chemical Society* **2014**, *136*, 850–853.
- (119) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (120) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *The Journal of Physical Chemistry B* **1997**, *101*, 9463–9475.
- (121) Brandt, R. E.; Stevanović, V.; Ginley, D. S. Identifying Defect-Tolerant Semiconductors with High Minority-Carrier Lifetimes: Beyond Hybrid Lead Halide Perovskites. *MRS Communications* **2015**, *5*, 265–275.
- (122) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nature Materials* **2018**, *17*, 394–405.
- (123) Kang, J.; Wang, L.-W. High Defect Tolerance in Lead Halide Perovskite CsPbBr_3 . *The Journal of Physical Chemistry Letters* **2017**, *8*, 489–493.
- (124) Hines, M. A.; Guyot-Sionnest, P. Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals. *The Journal of Physical Chemistry* **1996**, *100*, 468–471.
- (125) Zhu, H.; Miyata, K.; Fu, Y.; Wang, J.; Joshi, P. P.; Niesner, D.; Williams, K. W.; Jin, S.; Zhu, X.-Y. Screening in Crystalline Liquids Protects Energetic Carriers in Hybrid Perovskites. *Science* **2016**, *353*, 1409–1413.
- (126) Otero-Martínez, C.; García-Lojo, D.; Pastoriza-Santos, I.; Pérez-Juste, J.; Polavarapu, L. Dimensionality Control of Inorganic and Hybrid Perovskite Nanocrystals by Reaction Temperature: From No-Confinement to 3D and 1D Quantum Confinement. *Angewandte Chemie* **2021**, *133*, 26881–26888.
- (127) Dong, Y.; Qiao, T.; Kim, D.; Parobek, D.; Rossi, D.; Son, D. H. Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite Quantum Dots via Thermodynamic Equilibrium. *Nano Letters* **2018**, *18*, 3716–3722.
- (128) Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahne, R.; De Trizio, L.; Manna, L. Benzoyl Halides as Alternative Precursors for the Colloidal Synthesis of Lead-Based Halide Perovskite Nanocrystals. *Journal of the American Chemical Society* **2018**, *140*, 2656–2664.

- (129) Yassitepe, E. et al. Amine-Free Synthesis of Cesium Lead Halide Perovskite Quantum Dots for Efficient Light-Emitting Diodes. *Advanced Functional Materials* **2016**, *26*, 8757–8763.
- (130) Akkerman, Q. A.; Nguyen, T. P. T.; Boehme, S. C.; Montanarella, F.; Dirin, D. N.; Wechsler, P.; Beiglböck, F.; Rainò, G.; Erni, R.; Katan, C.; Even, J.; Kovalenko, M. V. Controlling the Nucleation and Growth Kinetics of Lead Halide Perovskite Quantum Dots. *Science* **2022**, *377*, 1406–1412.
- (131) Akkerman, Q. A. Spheroidal Cesium Lead Chloride–Bromide Quantum Dots and a Fast Determination of Their Size and Halide Content. *Nano Letters* **2022**, *22*, 8168–8173.
- (132) Imran, M.; Ijaz, P.; Baranov, D.; Goldoni, L.; Petralanda, U.; Akkerman, Q.; Abdelhady, A. L.; Prato, M.; Bianchini, P.; Infante, I.; Manna, L. Shape-Pure, Nearly Monodispersed CsPbBr₃ Nanocubes Prepared Using Secondary Aliphatic Amines. *Nano Letters* **2018**, *18*, 7822–7831.
- (133) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires. *Journal of the American Chemical Society* **2015**, *137*, 9230–9233.
- (134) Shamsi, J.; Dang, Z.; Bianchini, P.; Canale, C.; Di Stasio, F.; Brescia, R.; Prato, M.; Manna, L. Colloidal Synthesis of Quantum Confined Single Crystal CsPbBr₃ Nanosheets with Lateral Size Control up to the Micrometer Range. *Journal of the American Chemical Society* **2016**, *138*, 7240–7243.
- (135) Zhang, D.-M.; Zu, K.-L.; Yu, M.-B.; Chen, N.; Hu, J.-T.; Dong, Q.-L.; Shi, C.-S.; Wang, D.-K.; Ding, H.-Y.; Leng, M.; Zhao, Y.-B.; Lu, Z.-H. Deep Blue CsPbBr₃ Quantum Wires with Tailored Shapes. *The Journal of Physical Chemistry Letters* **2024**, *15*, 7892–7900.
- (136) Imran, M.; Di Stasio, F.; Dang, Z.; Canale, C.; Khan, A. H.; Shamsi, J.; Brescia, R.; Prato, M.; Manna, L. Colloidal Synthesis of Strongly Fluorescent CsPbBr₃ Nanowires with Width Tunable down to the Quantum Confinement Regime. *Chemistry of Materials* **2016**, *28*, 6450–6454.
- (137) Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P.; Alivisatos, A. P. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *Journal of the American Chemical Society* **2015**, *137*, 16008–16011.
- (138) Akkerman, Q. A.; Motti, S. G.; Srimath Kandada, A. R.; Mosconi, E.; D’Innocenzo, V.; Bertoni, G.; Marras, S.; Kamino, B. A.; Miranda, L.; De Angelis, F.; Petrozza, A.; Prato, M.; Manna, L. Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *Journal of the American Chemical Society* **2016**, *138*, 1010–1016.

-
- (139) Bohn, B. J.; Tong, Y.; Gramlich, M.; Lai, M. L.; Döblinger, M.; Wang, K.; Hoye, R. L. Z.; Müller-Buschbaum, P.; Stranks, S. D.; Urban, A. S.; Polavarapu, L.; Feldmann, J. Boosting Tunable Blue Luminescence of Halide Perovskite Nanoplatelets through Postsynthetic Surface Trap Repair. *Nano Letters* **2018**, *18*, 5231–5238.
- (140) Sun, S.; Yuan, D.; Xu, Y.; Wang, A.; Deng, Z. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals *via* Re-precipitation Process at Room Temperature. *ACS Nano* **2016**, *10*, 3648–3657.
- (141) Pan, A.; He, B.; Fan, X.; Liu, Z.; Urban, J. J.; Alivisatos, A. P.; He, L.; Liu, Y. Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr₃ Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors. *ACS Nano* **2016**, *10*, 7943–7954.
- (142) Bodnarchuk, M. I.; Boehme, S. C.; Ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; Infante, I. Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Letters* **2019**, *4*, 63–74.
- (143) Hens, Z. Ligands on Nanocrystal Surfaces, the ¹H Nuclear Magnetic Resonance Fingerprint. *Accounts of Chemical Research* **2023**, *56*, 1623–1633.
- (144) De Roo, J. The Surface Chemistry of Colloidal Nanocrystals Capped by Organic Ligands. *Chemistry of Materials* **2023**, *35*, 3781–3792.
- (145) De Roo, J.; Yazdani, N.; Drijvers, E.; Lauria, A.; Maes, J.; Owen, J. S.; Van Driessche, I.; Niederberger, M.; Wood, V.; Martins, J. C.; Infante, I.; Hens, Z. Probing Solvent–Ligand Interactions in Colloidal Nanocrystals by the NMR Line Broadening. *Chemistry of Materials* **2018**, *30*, 5485–5492.
- (146) De Roo, J.; Justo, Y.; De Keukeleere, K.; Van den Broeck, F.; Martins, J. C.; Van Driessche, I.; Hens, Z. Carboxylic-Acid-Passivated Metal Oxide Nanocrystals: Ligand Exchange Characteristics of a New Binding Motif. *Angewandte Chemie International Edition* **2015**, *54*, 6488–6491.
- (147) Kessler, M. L.; Starr, H. E.; Knauf, R. R.; Rountree, K. J.; Dempsey, J. L. Exchange Equilibria of Carboxylate-Terminated Ligands at PbS Nanocrystal Surfaces. *Physical Chemistry Chemical Physics* **2018**, *20*, 23649–23655.
- (148) Hens, Z.; Martins, J. C. A Solution NMR Toolbox for Characterizing the Surface Chemistry of Colloidal Nanocrystals. *Chemistry of Materials* **2013**, *25*, 1211–1221.
- (149) Fritzinger, B.; Moreels, I.; Lommens, P.; Koole, R.; Hens, Z.; Martins, J. C. In Situ Observation of Rapid Ligand Exchange in Colloidal Nanocrystal Suspensions Using Transfer NOE Nuclear Magnetic Resonance Spectroscopy. *Journal of the American Chemical Society* **2009**, *131*, 3024–3032.
- (150) Hassinen, A.; Martins, J. C.; Hens, Z. In *Nanoparticles*, De Mello Donega, C., Ed.; Springer Nature Switzerland: Cham, 2024, pp 287–307.

- (151) Ravi, V. K.; Santra, P. K.; Joshi, N.; Chugh, J.; Singh, S. K.; Rensmo, H.; Ghosh, P.; Nag, A. Origin of the Substitution Mechanism for the Binding of Organic Ligands on the Surface of CsPbBr₃ Perovskite Nanocubes. *The Journal of Physical Chemistry Letters* **2017**, *8*, 4988–4994.
- (152) Ten Brinck, S.; Infante, I. Surface Termination, Morphology, and Bright Photoluminescence of Cesium Lead Halide Perovskite Nanocrystals. *ACS Energy Letters* **2016**, *1*, 1266–1272.
- (153) Smock, S. R.; Williams, T. J.; Brutchey, R. L. Quantifying the Thermodynamics of Ligand Binding to CsPbBr₃ Quantum Dots. *Angewandte Chemie International Edition* **2018**, *57*, 11711–11715.
- (154) Smock, S. R.; Chen, Y.; Rossini, A. J.; Brutchey, R. L. The Surface Chemistry and Structure of Colloidal Lead Halide Perovskite Nanocrystals. *Accounts of Chemical Research* **2021**, *54*, 707–718.
- (155) Krieg, F.; Ong, Q. K.; Burian, M.; Rainò, G.; Naumenko, D.; Amenitsch, H.; Süess, A.; Grotevent, M. J.; Krumeich, F.; Bodnarchuk, M. I.; Shorubalko, I.; Stellacci, F.; Kovalenko, M. V. Stable Ultraconcentrated and Ultradilute Colloids of CsPbX₃ (X = Cl, Br) Nanocrystals Using Natural Lecithin as a Capping Ligand. *Journal of the American Chemical Society* **2019**, *141*, 19839–19849.
- (156) Imran, M.; Ijaz, P.; Goldoni, L.; Maggioni, D.; Petralanda, U.; Prato, M.; Almeida, G.; Infante, I.; Manna, L. Simultaneous Cationic and Anionic Ligand Exchange For Colloidally Stable CsPbBr₃ Nanocrystals. *ACS Energy Letters* **2019**, *4*, 819–824.
- (157) Pan, J. et al. Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering. *Advanced Materials* **2016**, *28*, 8718–8725.
- (158) De, A.; Mondal, N.; Samanta, A. Hole Transfer Dynamics from Photoexcited Cesium Lead Halide Perovskite Nanocrystals: 1-Aminopyrene as Hole Acceptor. *The Journal of Physical Chemistry C* **2018**, *122*, 13617–13623.
- (159) Morad, V. et al. Designer Phospholipid Capping Ligands for Soft Metal Halide Nanocrystals. *Nature* **2024**, *626*, 542–548.
- (160) Berezovska, Y.; Sabisch, S.; Bernasconi, C.; Sahin, Y.; Bertolotti, F.; Guagliardi, A.; Bodnarchuk, M. I.; Dirin, D. N.; Kovalenko, M. V. Tightly yet Dynamically Bound Aliphatic Guanidinium Ligands for Lead Halide Perovskite Nanocrystals. *Journal of the American Chemical Society* **2025**, *147*, 35446–35455.
- (161) Zhang, C.; Wan, Q.; Wang, B.; Zheng, W.; Liu, M.; Zhang, Q.; Kong, L.; Li, L. Surface Ligand Engineering toward Brightly Luminescent and Stable Cesium Lead Halide Perovskite Nanoplatelets for Efficient Blue-Light-Emitting Diodes. *The Journal of Physical Chemistry C* **2019**, *123*, 26161–26169.

-
- (162) Dai, J.; Roshan, H.; De Franco, M.; Goldoni, L.; De Boni, F.; Xi, J.; Yuan, F.; Dong, H.; Wu, Z.; Di Stasio, F.; Manna, L. Partial Ligand Stripping from CsPbBr₃ Nanocrystals Improves Their Performance in Light-Emitting Diodes. *ACS Applied Materials & Interfaces* **2024**, *16*, 11627–11636.
- (163) Luo, X.; Lai, R.; Li, Y.; Han, Y.; Liang, G.; Liu, X.; Ding, T.; Wang, J.; Wu, K. Triplet Energy Transfer from CsPbBr₃ Nanocrystals Enabled by Quantum Confinement. *Journal of the American Chemical Society* **2019**, *141*, 4186–4190.
- (164) Luo, X.; Han, Y.; Chen, Z.; Li, Y.; Liang, G.; Liu, X.; Ding, T.; Nie, C.; Wang, M.; Castellano, F. N.; Wu, K. Mechanisms of Triplet Energy Transfer across the Inorganic Nanocrystal/Organic Molecule Interface. *Nature Communications* **2020**, *11*, 28.
- (165) Ma, J.; Fang, C.; Chen, C.; Jin, L.; Wang, J.; Wang, S.; Tang, J.; Li, D. Chiral 2D Perovskites with a High Degree of Circularly Polarized Photoluminescence. *ACS Nano* **2019**, *13*, 3659–3665.
- (166) Babu, R.; Heger, J. E.; Dutta, T.; Hu, X.; Pradhan, N.; Müller-Buschbaum, P.; Gómez-Graña, S.; Polavarapu, L. Chiral Molecules in Action: Chemistry of Chiral Perovskite and Perovskite-Inspired Materials. *ACS Energy Letters* **2025**, *10*, 5703–5721.
- (167) Kroupa, D. M.; Vörös, M.; Brawand, N. P.; McNichols, B. W.; Miller, E. M.; Gu, J.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C. Tuning Colloidal Quantum Dot Band Edge Positions through Solution-Phase Surface Chemistry Modification. *Nature Communications* **2017**, *8*, 15257.
- (168) Kirsch, C.; Naujoks, T.; Haizmann, P.; Frech, P.; Peisert, H.; Chassé, T.; Brütting, W.; Scheele, M. Zwitterionic Carbazole Ligands Enhance the Stability and Performance of Perovskite Nanocrystals in Light-Emitting Diodes. *ACS Applied Materials & Interfaces* **2023**, *15*, 32744–32752.
- (169) Vanmaekelbergh, D. Self-Assembly of Colloidal Nanocrystals as Route to Novel Classes of Nanostructured Materials. *Nano Today* **2011**, *6*, 419–437.
- (170) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. Self-Organization of CdSe Nanocrystallites into Three-Dimensional Quantum Dot Superlattices. *Science* **1995**, *270*, 1335–1338.
- (171) Talapin, D. V.; Shevchenko, E. V.; Kornowski, A.; Gaponik, N.; Haase, M.; Rogach, A. L.; Weller, H. A New Approach to Crystallization of CdSe Nanoparticles into Ordered Three-Dimensional Superlattices. *Advanced Materials* **2001**, *13*, 1868.
- (172) Wang, R. Y.; Feser, J. P.; Lee, J.-S.; Talapin, D. V.; Segalman, R.; Majumdar, A. Enhanced Thermopower in PbSe Nanocrystal Quantum Dot Superlattices. *Nano Letters* **2008**, *8*, 2283–2288.

- (173) Boneschanscher, M. P.; Evers, W. H.; Geuchies, J. J.; Altantzis, T.; Goris, B.; Rabouw, F. T.; Van Rossum, S. A. P.; Van Der Zant, H. S. J.; Siebbeles, L. D. A.; Van Tendeloo, G.; Swart, I.; Hilhorst, J.; Petukhov, A. V.; Bals, S.; Vanmaekelbergh, D. Long-Range Orientation and Atomic Attachment of Nanocrystals in 2D Honeycomb Superlattices. *Science* **2014**, *344*, 1377–1380.
- (174) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors. *Science* **1999**, *286*, 945–947.
- (175) Tong, Y.; Yao, E.-P.; Manzi, A.; Bladt, E.; Wang, K.; Döblinger, M.; Bals, S.; Müller-Buschbaum, P.; Urban, A. S.; Polavarapu, L.; Feldmann, J. Spontaneous Self-Assembly of Perovskite Nanocrystals into Electronically Coupled Supercrystals: Toward Filling the Green Gap. *Advanced Materials* **2018**, *30*, 1801117.
- (176) Baranov, D.; Toso, S.; Imran, M.; Manna, L. Investigation into the Photoluminescence Red Shift in Cesium Lead Bromide Nanocrystal Superlattices. *The Journal of Physical Chemistry Letters* **2019**, *10*, 655–660.
- (177) Lan, X.; Chen, M.; Hudson, M. H.; Kamysbayev, V.; Wang, Y.; Guyot-Sionnest, P.; Talapin, D. V. Quantum Dot Solids Showing State-Resolved Band-like Transport. *Nature Materials* **2020**, *19*, 323–329.
- (178) Tang, Y.; Gomez, L.; Lesage, A.; Marino, E.; Kodger, T. E.; Meijer, J.-M.; Kolpakov, P.; Meng, J.; Zheng, K.; Gregorkiewicz, T.; Schall, P. Highly Stable Perovskite Supercrystals via Oil-in-Oil Templating. *Nano Letters* **2020**, *20*, 5997–6004.
- (179) Boehme, S. C. et al. Strongly Confined CsPbBr₃ Quantum Dots as Quantum Emitters and Building Blocks for Rhombic Superlattices. *ACS Nano* **2023**, *17*, 2089–2100.
- (180) Boles, M. A.; Engel, M.; Talapin, D. V. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. *Chemical Reviews* **2016**, *116*, 11220–11289.
- (181) Bertolotti, F.; Vivani, A.; Ferri, F.; Anzini, P.; Cervellino, A.; Bodnarchuk, M. I.; Nedelcu, G.; Bernasconi, C.; Kovalenko, M. V.; Masciocchi, N.; Guagliardi, A. Size Segregation and Atomic Structural Coherence in Spontaneous Assemblies of Colloidal Cesium Lead Halide Nanocrystals. *Chemistry of Materials* **2022**, *34*, 594–608.
- (182) Clark, D. E.; Lumsargis, V. A.; Blach, D. D.; Zhu, K.; Shumski, A. J.; Yao, L.; Chen, Q.; Huang, L.; Li, C. W. Quantifying Structural Heterogeneity in Individual CsPbBr₃ Quantum Dot Superlattices. *Chemistry of Materials* **2022**, *34*, 10200–10207.
- (183) Rainò, G.; Becker, M. A.; Bodnarchuk, M. I.; Mahrt, R. F.; Kovalenko, M. V.; Stöferle, T. Superfluorescence from Lead Halide Perovskite Quantum Dot Superlattices. *Nature* **2018**, *563*, 671–675.

-
- (184) Kalt, H.; Klingshirn, C. F. In *Semiconductor Optics 2*; Springer International Publishing: Cham, 2024, pp 519–538.
- (185) Liu, A.; Bi, C.; Guo, R.; Zhang, M.; Qu, X.; Tian, J. Electroluminescence Principle and Performance Improvement of Metal Halide Perovskite Light-Emitting Diodes. *Advanced Optical Materials* **2021**, *9*, 2002167.
- (186) Sutherland, B. R.; Sargent, E. H. Perovskite Photonic Sources. *Nature Photonics* **2016**, *10*, 295–302.
- (187) Cao, M.; Xu, Y.; Li, P.; Zhong, Q.; Yang, D.; Zhang, Q. Recent Advances and Perspectives on Light Emitting Diodes Fabricated from Halide Metal Perovskite Nanocrystals. *Journal of Materials Chemistry C* **2019**, *7*, 14412–14440.
- (188) Jang, E.; Jang, H. Review: Quantum Dot Light-Emitting Diodes. *Chemical Reviews* **2023**, *123*, 4663–4692.
- (189) Chiba, T.; Hayashi, Y.; Ebe, H.; Hoshi, K.; Sato, J.; Sato, S.; Pu, Y.-J.; Ohisa, S.; Kido, J. Anion-Exchange Red Perovskite Quantum Dots with Ammonium Iodine Salts for Highly Efficient Light-Emitting Devices. *Nature Photonics* **2018**, *12*, 681–687.
- (190) Schlaf, R.; Parkinson, B. A.; Lee, P. A.; Nebesny, K. W.; Jabbour, G.; Kipplen, B.; Peyghambarian, N.; Armstrong, N. R. Photoemission Spectroscopy of LiF Coated Al and Pt Electrodes. *Journal of Applied Physics* **1998**, *84*, 6729–6736.
- (191) Wang, J.; Liu, J.; Huang, S.; Wu, X.; Shi, X.; Chen, C.; Ye, Z.; Lu, J.; Su, Y.; He, G.; Zheng, Y. High Efficiency Green Phosphorescent Organic Light-Emitting Diodes with a Low Roll-off at High Brightness. *Organic Electronics* **2013**, *14*, 2854–2858.
- (192) Song, J.; Li, J.; Li, X.; Xu, L.; Dong, Y.; Zeng, H. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX_3). *Advanced Materials* **2015**, *27*, 7162–7167.
- (193) Dong, Y. et al. Bipolar-Shell Resurfacing for Blue LEDs Based on Strongly Confined Perovskite Quantum Dots. *Nature Nanotechnology* **2020**, *15*, 668–674.
- (194) Wan, Q.; Zheng, W.; Zou, C.; Carulli, F.; Zhang, C.; Song, H.; Liu, M.; Zhang, Q.; Lin, L. Y.; Kong, L.; Li, L.; Brovelli, S. Ultrathin Light-Emitting Diodes with External Efficiency over 26% Based on Resurfaced Perovskite Nanocrystals. *ACS Energy Letters* **2023**, *8*, 927–934.
- (195) Lu, M.; Zhang, Y.; Wang, S.; Guo, J.; Yu, W. W.; Rogach, A. L. Metal Halide Perovskite Light-Emitting Devices: Promising Technology for Next-Generation Displays. *Advanced Functional Materials* **2019**, *29*, 1902008.
- (196) Brütting, W.; Frischeisen, J.; Schmidt, T. D.; Scholz, B. J.; Mayr, C. Device Efficiency of Organic Light-emitting Diodes: Progress by Improved Light Outcoupling. *physica status solidi (a)* **2013**, *210*, 44–65.

- (197) Sun, S.-Q.; Tai, J.-W.; He, W.; Yu, Y.-J.; Feng, Z.-Q.; Sun, Q.; Tong, K.-N.; Shi, K.; Liu, B.-C.; Zhu, M.; Wei, G.; Fan, J.; Xie, Y.-M.; Liao, L.-S.; Fung, M.-K. Enhancing Light Outcoupling Efficiency via Anisotropic Low Refractive Index Electron Transporting Materials for Efficient Perovskite Light-Emitting Diodes. *Advanced Materials* **2024**, *36*, 2400421.
- (198) Baumgärtel, H., *Electrochemistry: A Guide for Newcomers*; De Gruyter: Berlin Boston, 2019.
- (199) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. *Journal of Chemical Education* **2018**, *95*, 197–206.
- (200) Speiser, B. Elektroanalytische Methoden I: Elektrodenreaktionen Und Chronoamperometrie. *Chemie in unserer Zeit* **1981**, *15*, 21–26.
- (201) Kurzweil, P., *Angewandte Elektrochemie: Grundlagen, Messtechnik, Elektroanalytik, Energiewandlung, technische Verfahren*; Springer Fachmedien Wiesbaden: Wiesbaden, 2020.
- (202) Heinze, J. Cyclic Voltammetry—"Electrochemical Spectroscopy". New Analytical Methods (25). *Angewandte Chemie International Edition in English* **1984**, *23*, 831–847.
- (203) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. Ferrocene as an Internal Standard for Electrochemical Measurements. *Inorganic Chemistry* **1980**, *19*, 2854–2855.
- (204) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Advanced Materials* **2011**, *23*, 2367–2371.
- (205) Faulkner, L. L.; Bard, A. J., *Electrochemical Methods and Applications*, 2nd ed; Wiley: New Yor, 2001.
- (206) Houtepen, A. J.; Vanmaekelbergh, D. Orbital Occupation in Electron-Charged CdSe Quantum-Dot Solids. *The Journal of Physical Chemistry B* **2005**, *109*, 19634–19642.
- (207) Wehrenberg, B. L.; Guyot-Sionnest, P. Electron and Hole Injection in PbSe Quantum Dot Films. *Journal of the American Chemical Society* **2003**, *125*, 7806–7807.
- (208) Boehme, S. C.; Azpiroz, J. M.; Aulin, Y. V.; Grozema, F. C.; Vanmaekelbergh, D.; Siebbeles, L. D.; Infante, I.; Houtepen, A. J. Density of Trap States and Auger-mediated Electron Trapping in CdTe Quantum-Dot Solids. *Nano Letters* **2015**, *15*, 3056–3066.
- (209) Pinchetti, V.; Lorenzon, M.; McDaniel, H.; Lorenzi, R.; Meinardi, F.; Klimov, V. I.; Brovelli, S. Spectro-Electrochemical Probing of Intrinsic and Extrinsic Processes in Exciton Recombination in I-III-VI₂ Nanocrystals. *Nano Letters* **2017**, *17*, 4508–4517.

-
- (210) Grimaldi, G.; Geuchies, J. J.; Van Der Stam, W.; Du Fossé, I.; Brynjarsson, B.; Kirkwood, N.; Kinge, S.; Siebbeles, L. D.; Houtepen, A. J. Spectroscopic Evidence for the Contribution of Holes to the Bleach of Cd-Chalcogenide Quantum Dots. *Nano Letters* **2019**, *19*, 3002–3010.
- (211) Hickey, S. G.; Riley, D. Intensity Modulated Photocurrent Spectroscopy Studies of CdS Nanoparticle Modified Electrodes. *Electrochimica Acta* **2000**, *45*, 3277–3282.
- (212) Spittel, D.; Poppe, J.; Meerbach, C.; Ziegler, C.; Hickey, S. G.; Eychmüller, A. Absolute Energy Level Positions in CdSe Nanostructures from Potential-Modulated Absorption Spectroscopy (EMAS). *ACS Nano* **2017**, *11*, 12174–12184.
- (213) Westendorf, S.; Li, S.; Michel, P.; Hu, B.; Scheele, M. Spectroelectrochemistry with Hydrogen-Doped Indium Oxide Electrodes Monitors Electron and Hole Injection into PbS Quantum Dots. *Nanoscale* **2025**, *17*, 7202–7210.
- (214) Boehme, S. C.; Vanmaekelbergh, D.; Evers, W. H.; Siebbeles, L. D. A.; Houtepen, A. J. In Situ Spectroelectrochemical Determination of Energy Levels and Energy Level Offsets in Quantum-Dot Heterojunctions. *The Journal of Physical Chemistry C* **2016**, *120*, 5164–5173.
- (215) Grimaldi, G.; Van Den Brom, M. J.; Du Fossé, I.; Crisp, R. W.; Kirkwood, N.; Gudjonsdottir, S.; Geuchies, J. J.; Kinge, S.; Siebbeles, L. D. A.; Houtepen, A. J. Engineering the Band Alignment in QD Heterojunction Films via Ligand Exchange. *The Journal of Physical Chemistry C* **2019**, *123*, 29599–29608.
- (216) Van Der Stam, W.; Du Fossé, I.; Grimaldi, G.; Monchen, J. O. V.; Kirkwood, N.; Houtepen, A. J. Spectroelectrochemical Signatures of Surface Trap Passivation on CdTe Nanocrystals. *Chemistry of Materials* **2018**, *30*, 8052–8061.
- (217) Boehme, S. C.; Wang, H.; Siebbeles, L. D.; Vanmaekelbergh, D.; Houtepen, A. J. Electrochemical Charging of CdSe Quantum Dot Films: Dependence on Void Size and Counterion Proximity. *ACS Nano* **2013**, *7*, 2500–2508.
- (218) Hiller, Jonas *Spectroelectrochemistry of CdSe Quantum Dots*; Research Report; Tübingen, 2021.
- (219) Murphy, D. B.; Davidson, M. W., *Fundamentals of Light Microscopy and Electronic Imaging*, 2nd ed; Wiley-Blackwell: Hoboken, N.J, 2013.
- (220) Samu, G. F.; Scheidt, R. A.; Kamat, P. V.; Janáky, C. Electrochemistry and Spectroelectrochemistry of Lead Halide Perovskite Films: Materials Science Aspects and Boundary Conditions. *Chemistry of Materials* **2018**, *30*, 561–569.
- (221) Mulder, J. T.; Du Fossé, I.; Alimoradi Jazi, M.; Manna, L.; Houtepen, A. J. Electrochemical P-Doping of CsPbBr₃ Perovskite Nanocrystals. *ACS Energy Letters* **2021**, *6*, 2519–2525.

- (222) Mulder, J. T.; Monchen, J. O. V.; Vogel, Y. B.; Lin, C. T.; Drago, F.; Caselli, V. M.; Saikumar, N.; Savenije, T. J.; Houtepen, A. J. Orthogonal Electrochemical Stability of Bulk and Surface in Lead Halide Perovskite Thin Films and Nanocrystals. *Journal of the American Chemical Society* **2024**, *146*, 24415–24425.
- (223) Cohen, T. A.; Sharp, D.; Kluherz, K. T.; Chen, Y.; Munley, C.; Anderson, R. T.; Swanson, C. J.; De Yoreo, J. J.; Luscombe, C. K.; Majumdar, A.; Gamelin, D. R.; Mackenzie, J. D. Direct Patterning of Perovskite Nanocrystals on Nanophotonic Cavities with Electrohydrodynamic Inkjet Printing. *Nano Letters* **2022**, *22*, 5681–5688.
- (224) Lee, S. Y.; Lee, G.; Kim, D. Y.; Jang, S. H.; Choi, I.; Park, J.; Park, H.-K.; Jung, J. W.; Cho, K. H.; Choi, J. Investigation of High-Performance Perovskite Nanocrystals for Inkjet-Printed Color Conversion Layers with Superior Color Purity. *APL Photonics* **2021**, *6*, 056104.
- (225) Ye, T.; Jia, S.; Wang, Z.; Cai, R.; Yang, H.; Zhao, F.; Tan, Y.; Sun, X.; Wu, D.; Wang, K. Fabrication of Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes via Inkjet Printing. *Micromachines* **2022**, *13*, 983.
- (226) Shibata, M.; Sakai, Y.; Yokoyama, D. Advantages and Disadvantages of Vacuum-Deposited and Spin-Coated Amorphous Organic Semiconductor Films for Organic Light-Emitting Diodes. *Journal of Materials Chemistry C* **2015**, *3*, 11178–11191.
- (227) Mohamed, W. A. A.; Abd El-Gawad, H.; Mekkey, S.; Galal, H.; Handal, H.; Mousa, H.; Labib, A. Quantum Dots Synthetization and Future Prospect Applications. *Nanotechnology Reviews* **2021**, *10*, 1926–1940.
- (228) Huang, H.; Bodnarchuk, M. I.; Kershaw, S. V.; Kovalenko, M. V.; Rogach, A. L. Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance. *ACS Energy Letters* **2017**, *2*, 2071–2083.
- (229) Aldakov, D.; Reiss, P. Safer-by-Design Fluorescent Nanocrystals: Metal Halide Perovskites vs Semiconductor Quantum Dots. *The Journal of Physical Chemistry C* **2019**, *123*, 12527–12541.
- (230) Du Fossé, I.; Mulder, J. T.; Almeida, G.; Spruit, A. G. M.; Infante, I.; Grozema, F. C.; Houtepen, A. J. Limits of Defect Tolerance in Perovskite Nanocrystals: Effect of Local Electrostatic Potential on Trap States. *Journal of the American Chemical Society* **2022**, *144*, 11059–11063.
- (231) Choi, J.; Kim, B. H. Ligands of Nanoparticles and Their Influence on the Morphologies of Nanoparticle-Based Films. *Nanomaterials* **2024**, *14*, 1685.
- (232) Richter, J. M.; Abdi-Jalebi, M.; Sadhanala, A.; Tabachnyk, M.; Rivett, J. P.; Pazos-Outón, L. M.; Gödel, K. C.; Price, M.; Deschler, F.; Friend, R. H. Enhancing Photoluminescence Yields in Lead Halide Perovskites by Photon Recycling and Light Out-Coupling. *Nature Communications* **2016**, *7*, 13941.

- (233) Kumar, S.; Jagielski, J.; Marcato, T.; Solari, S. F.; Shih, C.-J. Understanding the Ligand Effects on Photophysical, Optical, and Electroluminescent Characteristics of Hybrid Lead Halide Perovskite Nanocrystal Solids. *The Journal of Physical Chemistry Letters* **2019**, *10*, 7560–7567.
- (234) Shynkarenko, Y.; Bodnarchuk, M. I.; Bernasconi, C.; Berezovska, Y.; Verteletskyi, V.; Ochsenbein, S. T.; Kovalenko, M. V. Direct Synthesis of Quaternary Alkylammonium-Capped Perovskite Nanocrystals for Efficient Blue and Green Light-Emitting Diodes. *ACS Energy Letters* **2019**, *4*, 2703–2711.
- (235) Zaccaria, F.; Zhang, B.; Goldoni, L.; Imran, M.; Zito, J.; Van Beek, B.; Lauciello, S.; De Trizio, L.; Manna, L.; Infante, I. The Reactivity of CsPbBr₃ Nanocrystals toward Acid/Base Ligands. *ACS Nano* **2022**, *16*, 1444–1455.
- (236) Sun, S.; Huang, P.; Wu, X.-g.; Chen, C.; Hu, X.; Bai, Z.; Pushkarev, A.; Zhong, H. Ligand Exchange-Induced Shape Transformation of CsPbBr₃ Nanocrystals Boosts the Efficiency of Perovskite Light-Emitting Diodes. *The Journal of Physical Chemistry C* **2024**, *128*, 3602–3608.
- (237) Uribe-Vegas, P. et al. The Role of Alkylammonium Bromides on the Surface Passivation of Stable Alcohol-Dispersed CsPbX₃ Nanocrystals and on the Stability Enhancement in Light-Emitting Applications. *Advanced Optical Materials* **2024**, *12*, 2401475.
- (238) Hung, W.-K.; Tseng, Y.-H.; Lin, C.-C.; Chen, S.-A.; Hsu, C.-H.; Li, C.-F.; Chen, Y.-J.; Tseng, Z.-L. Anion-Exchange Blue Perovskite Quantum Dots for Efficient Light-Emitting Devices. *Nanomaterials* **2022**, *12*, 3957.
- (239) Yang, S.; Bi, C.; Tian, J. Highly Pure White Light-Emitting Single-Component Perovskite Colloidal Quantum Dots. *The Journal of Physical Chemistry C* **2021**, *125*, 18810–18816.
- (240) Xue, J.; Wang, R.; Yang, Y. The Surface of Halide Perovskites from Nano to Bulk. *Nature Reviews Materials* **2020**, *5*, 809–827.
- (241) Tian, H.; Liu, Y.; Jiang, F.-L. Chemical Instability of CsPbBr₃ Nanocrystals and the Reversible Transformation between CsPbBr₃ and Cs₄PbBr₆ Nanocrystals as Driven by Synthetic Precursors. *Chemistry of Materials* **2024**, *36*, 8949–8964.
- (242) Ashokan, A.; Mulvaney, P. Spectroelectrochemistry of Colloidal CdSe Quantum Dots. *Chemistry of Materials* **2021**, *33*, 1353–1362.
- (243) Cohen, A. V.; Egger, D. A.; Rappe, A. M.; Kronik, L. Breakdown of the Static Picture of Defect Energetics in Halide Perovskites: The Case of the Br Vacancy in CsPbBr₃. *The Journal of Physical Chemistry Letters* **2019**, *10*, 4490–4498.
- (244) Naujoks, T.; Jayabalan, R.; Kirsch, C.; Zu, F.; Mandal, M.; Wahl, J.; Waibel, M.; Opitz, A.; Koch, N.; Andrienko, D.; Scheele, M.; Brütting, W. Quantum Efficiency Enhancement of Lead-Halide Perovskite Nanocrystal LEDs by Organic Lithium Salt Treatment. *ACS Applied Materials & Interfaces* **2022**, *14*, 28985–28996.

- (245) Köhler, A.; Bässler, H. In John Wiley & Sons, Ltd: 2015, pp 307–388.
- (246) Futscher, M. H.; Gangishetty, M. K.; Congreve, D. N.; Ehrler, B. Quantifying Mobile Ions and Electronic Defects in Perovskite-Based Devices with Temperature-Dependent Capacitance Measurements: Frequency vs Time Domain. *The Journal of Chemical Physics* **2020**, *152*, 044202.
- (247) Kühne, T. D. et al. CP2K: An Electronic Structure and Molecular Dynamics Software Package - Quickstep: Efficient and Accurate Electronic Structure Calculations. *The Journal of Chemical Physics* **2020**, *152*, 194103.
- (248) Lapkin, D. et al. Spatially Resolved Fluorescence of Caesium Lead Halide Perovskite Supercrystals Reveals Quasi-Atomic Behavior of Nanocrystals. *Nature Communications* **2022**, *13*, 892.
- (249) Wei, S.; Yang, Y.; Kang, X.; Wang, L.; Huang, L.; Pan, D. Room-Temperature and Gram-Scale Synthesis of CsPbX₃ (X = Cl, Br, I) Perovskite Nanocrystals with 50–85% Photoluminescence Quantum Yields. *Chemical Communications* **2016**, *52*, 7265–7268.
- (250) Voznyy, O. Mobile Surface Traps in CdSe Nanocrystals with Carboxylic Acid Ligands. *The Journal of Physical Chemistry C* **2011**, *115*, 15927–15932.
- (251) Cosseddu, S.; Pascazio, R.; Giansante, C.; Manna, L.; Infante, I. Ligand Dynamics on the Surface of CdSe Nanocrystals. *Nanoscale* **2023**, *15*, 7410–7419.
- (252) Shen, C.; Fang, S.; Zhang, J.; Liang, X.; Su, C.; Qing, J.; Cai, W.; Luo, Y.; Yang, R.; Hou, L. High Performance and Stable Pure-Blue Quasi-2D Perovskite Light-Emitting Diodes by Multifunctional Zwitterionic Passivation Engineering. *Advanced Photonics* **2024**, *6*, DOI: 10.1117/1.AP.6.2.026002.
- (253) Guo, K.; Ren, L.; Chen, C.; Tang, Z.; Niu, X.; Kong, L.; Xue, T.; Ding, L.; Wang, S.; Zhang, F.; Yang, X. High-Brightness Blue Perovskite Light-Emitting Diodes With Low Efficiency Roll-Off Enabled by Dual-ETL and Hole Transport Regulation. *Advanced Optical Materials* **2025**, *13*, 2403483.
- (254) Noguchi, Y.; Tanaka, Y.; Ishii, H.; Brütting, W. Understanding Spontaneous Orientation Polarization of Amorphous Organic Semiconducting Films and Its Application to Devices. *Synthetic Metals* **2022**, *288*, 117101.
- (255) Hofmann, A.; Cakaj, A.; Kolb, L.; Noguchi, Y.; Brütting, W. Enhancement of Spontaneous Orientation Polarization in Glassy Organic Semiconductor Mixtures. *The Journal of Physical Chemistry B* **2025**, *129*, 779–787.
- (256) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *The Journal of Chemical Physics* **2007**, *127*, 114105.
- (257) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Physical Review B* **1996**, *54*, 1703–1710.
- (258) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77*, 3865–3868.

- (259) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *The Journal of Chemical Physics* **2010**, *132*, 154104.
- (260) Shamsi, J.; Kubicki, D.; Anaya, M.; Liu, Y.; Ji, K.; Frohna, K.; Grey, C. P.; Friend, R. H.; Stranks, S. D. Stable Hexylphosphonate-Capped Blue-Emitting Quantum-Confined CsPbBr₃ Nanoplatelets. *ACS Energy Letters* **2020**, *5*, 1900–1907.
- (261) Chen, R.; Wang, Z.; Pang, T.; Teng, Q.; Li, C.; Jiang, N.; Zheng, S.; Zhang, R.; Zheng, Y.; Chen, D.; Yuan, F. Ultra-Narrow-Bandwidth Deep-Red Electroluminescence Based on Green Plant-Derived Carbon Dots. *Advanced Materials* **2023**, *35*, 2302275.
- (262) Wang, F.; Hu, J.; Cao, X.; Yang, T.; Tao, Y.; Mei, L.; Zhang, X.; Huang, W. A Low-Cost Phenylbenzimidazole Containing Electron Transport Material for Efficient Green Phosphorescent and Thermally Activated Delayed Fluorescent OLEDs. *Journal of Materials Chemistry C* **2015**, *3*, 5533–5540.
- (263) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chemical Reviews* **2019**, *119*, 3296–3348.
- (264) Liu, Y. et al. Efficient Blue Light-Emitting Diodes Based on Quantum-Confined Bromide Perovskite Nanostructures. *Nature Photonics* **2019**, *13*, 760–764.
- (265) Liu, X.-K.; Xu, W.; Bai, S.; Jin, Y.; Wang, J.; Friend, R. H.; Gao, F. Metal Halide Perovskites for Light-Emitting Diodes. *Nature Materials* **2021**, *20*, 10–21.
- (266) Wu, Y.; Chen, D.; Zou, G.; Liu, H.; Zhu, Z.; Rogach, A. L.; Yip, H.-L. Strategies for Stabilizing Metal Halide Perovskite Light-Emitting Diodes: Bulk and Surface Reconstruction of Perovskite Nanocrystals. *ACS Nano* **2025**, *19*, 9740–9759.
- (267) Kim, J. Y.; Lee, J.-W.; Jung, H. S.; Shin, H.; Park, N.-G. High-Efficiency Perovskite Solar Cells. *Chemical Reviews* **2020**, *120*, 7867–7918.
- (268) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chemical Reviews* **2019**, *119*, 3036–3103.
- (269) Quan, L. N.; García De Arquer, F. P.; Sabatini, R. P.; Sargent, E. H. Perovskites for Light Emission. *Advanced Materials* **2018**, *30*, 1801996.
- (270) Yan, F.; Tan, S. T.; Li, X.; Demir, H. V. Light Generation in Lead Halide Perovskite Nanocrystals: LEDs, Color Converters, Lasers, and Other Applications. *Small* **2019**, *15*, 1902079.

- (271) Li, M.; Liu, M.; Qi, F.; Lin, F. R.; Jen, A. K.-Y. Self-Assembled Monolayers for Interfacial Engineering in Solution-Processed Thin-Film Electronic Devices: Design, Fabrication, and Applications. *Chemical Reviews* **2024**, *124*, 2138–2204.
- (272) Li, C.; Ganesan, P.; Li, Y.; Tang, S.; Wang, Y.; Liu, C.; Liang, L.; Yu, Y.; Yusoff, A. R. B. M.; Grätzel, M.; Gao, P. Synergistic Electron-Deficient Surface Engineering: A Key Factor in Dictating Electron Carrier Extraction for Perovskite Photovoltaics. *Journal of the American Chemical Society* **2025**, *147*, 25738–25749.
- (273) Yuan, L.; Xue, Q.; Wang, F.; Li, N.; Waterhouse, G. I. N.; Brabec, C. J.; Gao, F.; Yan, K. Perovskite Solar Cells and Light Emitting Diodes: Materials Chemistry, Device Physics and Relationship. *Chemical Reviews* **2025**, *125*, 5057–5162.
- (274) Teale, S.; Degani, M.; Chen, B.; Sargent, E. H.; Grancini, G. Molecular Cation and Low-Dimensional Perovskite Surface Passivation in Perovskite Solar Cells. *Nature Energy* **2024**, *9*, 779–792.
- (275) Schulz, P.; Edri, E.; Kirmayer, S.; Hodes, G.; Cahen, D.; Kahn, A. Interface Energetics in Organo-Metal Halide Perovskite-Based Photovoltaic Cells. *Energy & Environmental Science* **2014**, *7*, 1377.
- (276) Burrell, J. M.; Adhikari, B.; Abiodun, S. L.; Greytak, A. B. Constructing Lead Halide Perovskite Nanocrystal Surfaces. *ACS Energy Letters* **2025**, 4158–4183.
- (277) Alam, A.; Li, Y.; Ning, F.; Li, T.; Wang, Y. Enhancing the Optical Properties and Stability of CsPbBr₃ Quantum Dots through Ligand Modification, Encapsulation, and Interaction with a Superhydrophobic Polymer. *ACS Applied Materials & Interfaces* **2025**, *17*, 17026–17035.
- (278) Grisorio, R.; Di Clemente, M. E.; Fanizza, E.; Allegretta, I.; Altamura, D.; Striccoli, M.; Terzano, R.; Giannini, C.; Irimia-Vladu, M.; Suranna, G. P. Exploring the Surface Chemistry of Cesium Lead Halide Perovskite Nanocrystals. *Nanoscale* **2019**, *11*, 986–999.
- (279) Chen, Y.; Smock, S. R.; Flintgruber, A. H.; Perras, F. A.; Brutchey, R. L.; Rossini, A. J. Surface Termination of CsPbBr₃ Perovskite Quantum Dots Determined by Solid-State NMR Spectroscopy. *Journal of the American Chemical Society* **2020**, *142*, 6117–6127.
- (280) Tao, S.; Schmidt, I.; Brocks, G.; Jiang, J.; Tranca, I.; Meerholz, K.; Olthof, S. Absolute Energy Level Positions in Tin- and Lead-Based Halide Perovskites. *Nature Communications* **2019**, *10*, 2560.
- (281) Lu, H.; Zhu, X.; Miller, C.; San Martin, J.; Chen, X.; Miller, E. M.; Yan, Y.; Beard, M. C. Enhanced Photoredox Activity of CsPbBr₃ Nanocrystals by Quantitative Colloidal Ligand Exchange. *The Journal of Chemical Physics* **2019**, *151*, 204305.

- (282) Min, S.; Jeon, M.; Cho, J.; Bang, J. H.; Kamat, P. V. Spectroelectrochemical Insights into the Intrinsic Nature of Lead Halide Perovskites. *Nano Convergence* **2024**, *11*, 49.
- (283) Chiba, T.; Pu, Y.-J.; Miyazaki, R.; Nakayama, K.-i.; Sasabe, H.; Kido, J. Ultra-High Efficiency by Multiple Emission from Stacked Organic Light-Emitting Devices. *Organic Electronics* **2011**, *12*, 710–715.
- (284) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.
- (285) Zhang, F.; Zhong, H.; Chen, C.; Wu, X.-g.; Hu, X.; Huang, H.; Han, J.; Zou, B.; Dong, Y. Brightly Luminescent and Color-Tunable Colloidal $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{I}, \text{Cl}$) Quantum Dots: Potential Alternatives for Display Technology. *ACS Nano* **2015**, *9*, 4533–4542.
- (286) Frisch, M. J. et al. Gaussian 16 Revision C.01, 2016.
- (287) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *The Journal of Chemical Physics* **1993**, *98*, 5648–5652.
- (288) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *The Journal of Chemical Physics* **1988**, *89*, 2193–2218.
- (289) Kim, J. S.; Heo, J.-M.; Park, G.-S.; Woo, S.-J.; Cho, C.; Yun, H. J.; Kim, D.-H.; Park, J.; Lee, S.-C.; Park, S.-H.; Yoon, E.; Greenham, N. C.; Lee, T.-W. Ultra-Bright, Efficient and Stable Perovskite Light-Emitting Diodes. *Nature* **2022**, *611*, 688–694.
- (290) Kim, Y.-H.; Park, J.; Kim, S.; Kim, J. S.; Xu, H.; Jeong, S.-H.; Hu, B.; Lee, T.-W. Exploiting the Full Advantages of Colloidal Perovskite Nanocrystals for Large-Area Efficient Light-Emitting Diodes. *Nature Nanotechnology* **2022**, *17*, 590–597.
- (291) Liu, B.; Wang, L.; Gu, H.; Sun, H.; Demir, H. V. Highly Efficient Green Light-Emitting Diodes from All-Inorganic Perovskite Nanocrystals Enabled by a New Electron Transport Layer. *Advanced Optical Materials* **2018**, *6*, 1800220.
- (292) Dutt, V. G. V.; Akhil, S.; Singh, R.; Palabathuni, M.; Mishra, N. Year-Long Stability and Near-Unity Photoluminescence Quantum Yield of CsPbBr_3 Perovskite Nanocrystals by Benzoic Acid Post-treatment. *The Journal of Physical Chemistry C* **2022**, *126*, 9502–9508.

- (293) Liu, F.; Zhang, Y.; Ding, C.; Kobayashi, S.; Izuishi, T.; Nakazawa, N.; Toyoda, T.; Ohta, T.; Hayase, S.; Minemoto, T.; Yoshino, K.; Dai, S.; Shen, Q. Highly Luminescent Phase-Stable CsPbI₃ Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield. *ACS Nano* **2017**, *11*, 10373–10383.
- (294) Aneesha, S. L.; Xia, Y.; Okamoto, T.; Gaur, D.; Seth, S.; Hofkens, J.; Polavarapu, L.; Biju, V. From Halide Perovskite Nanocrystals to Supercrystals: Fundamentals and Applications. *Chemical Society Reviews* **2025**, *54*, 9585–9611.
- (295) Tang, Y.; Poonia, D.; Van Der Laan, M.; Timmerman, D.; Kinge, S.; Siebbeles, L. D. A.; Schall, P. Electronic Coupling of Highly Ordered Perovskite Nanocrystals in Supercrystals. *ACS Applied Energy Materials* **2022**, *5*, 5415–5422.
- (296) Vila-Liarte, D.; Feil, M. W.; Manzi, A.; Garcia-Pomar, J. L.; Huang, H.; Döblinger, M.; Liz-Marzán, L. M.; Feldmann, J.; Polavarapu, L.; Mihi, A. Templated-Assembly of CsPbBr₃ Perovskite Nanocrystals into 2D Photonic Supercrystals with Amplified Spontaneous Emission. *Angewandte Chemie International Edition* **2020**, *59*, 17750–17756.
- (297) Li, X.; Xue, Z.; Chen, X.; Qiao, X.; Mo, G.; Bu, W.; Guan, B.; Wang, T. Printable Assemblies of Perovskite Nanocubes on Meter-Scale Panel. *Science Advances* **2022**, *8*, eadd1559.
- (298) Zhang, C. et al. Pixelated Quantum-Dot Superlattice LEDs. *Nature* **2026**, DOI: 10.1038/s41586-026-10392-z.
- (299) Zheng, D. G.; Kim, D. H. Degradation Mechanisms of Perovskite Light-Emitting Diodes under Electrical Bias. *Nanophotonics* **2023**, *12*, 451–476.
- (300) Kong, L.; Zhang, X.; Zhang, C.; Wang, L.; Wang, S.; Cao, F.; Zhao, D.; Rogach, A. L.; Yang, X. Stability of Perovskite Light-Emitting Diodes: Existing Issues and Mitigation Strategies Related to Both Material and Device Aspects. *Advanced Materials* **2022**, *34*, 2205217.
- (301) Ung, T.; Giersig, M.; Dunstan, D.; Mulvaney, P. Spectroelectrochemistry of Colloidal Silver. *Langmuir* **1997**, *13*, 1773–1782.
- (302) Boehme, S. C.; Walvis, T. A.; Infante, I.; Grozema, F. C.; Vanmaekelbergh, D.; Siebbeles, L. D. A.; Houtepen, A. J. Electrochemical Control over Photoinduced Electron Transfer and Trapping in CdSe-CdTe Quantum-Dot Solids. *ACS Nano* **2014**, *8*, 7067–7077.
- (303) Jacobsson, T. J.; Edvinsson, T. A Spectroelectrochemical Method for Locating Fluorescence Trap States in Nanoparticles and Quantum Dots. *The Journal of Physical Chemistry C* **2013**, *117*, 5497–5504.
- (304) Galland, C.; Ghosh, Y.; Steinbrück, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H. Two Types of Luminescence Blinking Revealed by Spectroelectrochemistry of Single Quantum Dots. *Nature* **2011**, *479*, 203–207.

- (305) Vogel, Y. B.; Tao, R.; Chen, H.; Ferraresi, L. J.; Boehme, S. C.; Dirin, D. N.; Shorubalko, I.; Houtepen, A. J.; Kovalenko, M. V. Electrochemical Control over Electron Density of InAs Quantum Dots. *Journal of the American Chemical Society* **2026**, *148*, 3938–3943.
- (306) Samu, G. F.; Balog, Á.; De Angelis, F.; Meggiolaro, D.; Kamat, P. V.; Janáky, C. Electrochemical Hole Injection Selectively Expels Iodide from Mixed Halide Perovskite Films. *Journal of the American Chemical Society* **2019**, *141*, 10812–10820.
- (307) Xu, Z.; Kerner, R. A.; Berry, J. J.; Rand, B. P. Iodine Electrochemistry Dictates Voltage-Induced Halide Segregation Thresholds in Mixed-Halide Perovskite Devices. *Advanced Functional Materials* **2022**, *32*, 2203432.
- (308) Mathew, P. S.; Samu, G. F.; Janáky, C.; Kamat, P. V. Iodine (I) Expulsion at Photoirradiated Mixed Halide Perovskite Interface. *Should I Stay or Should I Go? ACS Energy Letters* **2020**, *5*, 1872–1880.
- (309) Hiller, J. L. et al. Mechanically Robust Supercrystals from Antisolvent-Induced Assembly of Perovskite Nanocrystals. *ACS Nano* **2025**, *19*, 26117–26126.
- (310) Hiller, J. L. et al. How Antisolvent-Induced Ligand Stripping Shapes CsPbX₃ Nanocrystals and Their Assemblies. *Nano Letters* **2026**, *26*, 2955–2963.
- (311) Wang, C.; Chesman, A. S. R.; Yin, W.; Frazer, L.; Funston, A. M.; Jasieniak, J. J. Facile Purification of CsPbX₃ (X = Cl⁻, Br⁻, I⁻) Perovskite Nanocrystals. *The Journal of Chemical Physics* **2019**, *151*, 121105.
- (312) Baitova, V. A.; Knyazeva, M. A.; Mukanov, I. A.; Tarasevich, A. O.; Naumov, A. V.; Son, A. G.; Kozyukhin, S. A.; Eremchev, I. Y. Evolution of the Luminescence Properties of Single CsPbBr₃ Perovskite Nanocrystals During Photodegradation. *JETP Letters* **2023**, *118*, 560–567.
- (313) Darmawan, Y. A.; Yamauchi, M.; Masuo, S. In Situ Observation of a Photodegradation-Induced Blueshift in Perovskite Nanocrystals Using Single-Particle Spectroscopy Combined with Atomic Force Microscopy. *The Journal of Physical Chemistry C* **2020**, *124*, 18770–18776.
- (314) Yuan, G.; Ritchie, C.; Ritter, M.; Murphy, S.; Gómez, D. E.; Mulvaney, P. The Degradation and Blinking of Single CsPbI₃ Perovskite Quantum Dots. *The Journal of Physical Chemistry C* **2018**, *122*, 13407–13415.
- (315) Fang, H.-H.; Adjokatse, S.; Wei, H.; Yang, J.; Blake, G. R.; Huang, J.; Even, J.; Loi, M. A. Ultrahigh Sensitivity of Methylammonium Lead Tribromide Perovskite Single Crystals to Environmental Gases. *Science Advances* **2016**, *2*, e1600534.
- (316) Wang, Y.; Ren, Y.; Zhang, S.; Wu, J.; Song, J.; Li, X.; Xu, J.; Sow, C. H.; Zeng, H.; Sun, H. Switching Excitonic Recombination and Carrier Trapping in Cesium Lead Halide Perovskites by Air. *Communications Physics* **2018**, *1*, 96.

- (317) Kim, S. H.; Heo, D. G.; Yim, S.-Y.; Lee, H. S. High-Quality and Stable Perovskite Nanocrystals with Enhanced Properties via Photo-Brightening. *Journal of Colloid and Interface Science* **2025**, *696*, 137872.
- (318) Godding, J. S.; Ramadan, A. J.; Lin, Y.-H.; Schutt, K.; Snaith, H. J.; Wenger, B. Oxidative Passivation of Metal Halide Perovskites. *Joule* **2019**, *3*, 2716–2731.
- (319) Lorenzon, M.; Sortino, L.; Akkerman, Q.; Accornero, S.; Pedrini, J.; Prato, M.; Pinchetti, V.; Meinardi, F.; Manna, L.; Brovelli, S. Role of Nonradiative Defects and Environmental Oxygen on Exciton Recombination Processes in CsPbBr₃ Perovskite Nanocrystals. *Nano Letters* **2017**, *17*, 3844–3853.
- (320) Bloom, B. P.; Zhao, L.-B.; Wang, Y.; Waldeck, D. H.; Liu, R.; Zhang, P.; Beratan, D. N. Ligand-Induced Changes in the Characteristic Size-Dependent Electronic Energies of CdSe Nanocrystals. *The Journal of Physical Chemistry C* **2013**, *117*, 22401–22411.
- (321) Steiner, A. M.; Lissel, F.; Fery, A.; Lauth, J.; Scheele, M. Prospects of Coupled Organic–Inorganic Nanostructures for Charge and Energy Transfer Applications. *Angewandte Chemie International Edition* **2021**, *60*, 1152–1175.