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Investigation of photoinduced electron
transfer from CdSe-CdS and FAPbBr₃
nanocrystal assemblies to molecular
acceptors

(CdSe-CdS および FAPbBr₃ ナノ結晶集合体か
ら分子受容体への光誘起電子移動の研究)

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Abstract

Luminescent materials, including halide perovskites (HPs) and chalcogenide quantum dots (QD), are being extensively researched as potential sources of considerable power for future energy requirements. These materials offer great luminosity, stability, and a longer lifetime, making them useful for future energy savings. Among its many features, the ability to promote photoinduced electron transport is essential since it plays a crucial role in device fabrication and operation. This thesis focuses on photoinduced electron transfer from HP nanocrystals and chalcogenide QDs assemblies to designated acceptor molecules. The study aims to understand better how these materials interact with acceptors and how their structural and electrical features affect electron transfer efficiency. The thesis is divided into five chapters to provide a full overview of the topic. Each chapter expands on the previous knowledge by thoroughly examining the materials, synthesis processes, instrumental methodologies, and experimental results, finally providing insights into the role of these illuminating materials in device fabrication applications.

Chapter 1 addresses the distinctive properties of PNCs and chalcogenide QDs and the photoinduced electron transfer process of these two materials. First, I define the class of luminous nanomaterials and the quantum confinement effect. Then, I report different synthesis methods for PNCs and chalcogenide QDs and how temperature and environment influence their size and shape. The film preparation of HPs and their assembly are also explained in detail. I explain absorption and emission properties and how size and shape affect absorption and luminescence abilities. I also provide numerous examples of how charge carrier features affect photoinduced electron transport. The chapter concludes with the research objectives and highlights the applications of these materials in solar cells, PeLEDs, and Q-LEDs.

Chapter 2 of this thesis overviews preparation methodologies of PNCs and chalcogenide QDs and the instrumental procedures used during this research. It begins with a detailed explanation of the synthesis procedures for PNCs and co-aggregated assemblies. I also describe how I construct the mesoscopic semiconductor assemblies. After that, the chapter examines the different tools I used in the study. Each instrument's underlying theoretical ideas and basic operating principles are fully described, providing insights into how they function and relate to the experiment's goals. This chapter provides a basic overview of the techniques and resources used to support the thesis's

findings. The optical characteristics and charge transfer process were examined using Quantaaurus tau (Q-Tau), fluorescence spectroscopy, and UV-visible spectroscopy system. In contrast, the interfacial electron transport in the film state was measured using a time-resolved picosecond (ps-system).

Chapter 3 focuses on the electron transfer from PNCs and their assemblies to specific acceptor molecules. 7,8,8-Tetracyanoquinodimethane (TCNQ), fullerene (C_{60}), and a functionalized fullerene (C_{60} -RCOOH) ligand were selected as the acceptor molecules due to their high electron affinity in this chapter. The electron transfer to the acceptor in PNCs did not show effective quenching due to the long chain ligand and the abundance of free ligands. However, the development of assemblies was essential for promoting electron transfer. The study was performed in both the solution and the film state to have a deeper understanding. FAPbBr₃ assemblies and co-aggregated assemblies of FAPbBr₃ and acceptor molecules were prepared to investigate the dynamics. The assemblies showed a significant electron transfer efficiency compared to single nanocrystals in both solution and film state. In isolated NC, the charge carriers are confined within a single particle due to quantum confinement, which hinders their carrier diffusion. However, when closely packed within an assembly, they enable charge carriers that increase their carrier diffusion length and lifetime. These results demonstrate the critical role that structural organization plays in maximizing the electron transport characteristics of materials based on HPs.

The experiments, results, and discussion in Chapter 4 are based on motivation from Chapter 3. I prepared a chalcogenide material-based assembly to investigate its electron transfer capabilities further. In this study, I selected well-established core and shell QD (CdSe/CdS) as the central unit of the assembly due to their exceptional optical properties, which make them highly suitable for device fabrication. As a cross-linker molecule, the CdSe/CdS assembly was prepared using the 1,6-hexanedithiol. A controlled ratio was followed to prepare the assembly. This controlled construction method allows us to analyze photoinduced electron transfer processes with remarkable accuracy, providing information about the assembly structure and electron transfer efficiency.

In Chapter 5, I investigated a bio-inspired technique that employs a novel method to generate water-soluble quantum dot assemblies of mesoscopic size. This novel concept highlights the diversity of assembly processes and creates new opportunities for biocompatible optoelectronic applications. In this study, the CdSe/CdS was functionalized with -COOH and made a large

aggregate following an amide condensation reaction using DMTMM and a significant quantity of mono lysine. Then, trypsin was used as an amide bond cleaver to make small assemblies. Surprisingly, the mesoscopic assemblies were formed with good dispersity. The STEM and the DLS data confirmed the assembly formation. These studies aim to define fundamental design principles for controlled nanocrystal assembly creation and better understand how assembly architecture affects electron transfer processes. This study raises the possibility of a contribution to future optoelectronic devices.

In summary, this thesis explores the assembly formation of perovskite materials and chalcogenide QDs. These assemblies showed exceptional uniformity and good distribution in the solution and the film state, showcasing their potentiality for practical applications. However, the study explores electron transfer dynamics to these assemblies, demonstrating their exceptional efficiency. Their potential as essential parts of optoelectronic devices, where effective charge transfer is crucial to functionality, is highlighted by their excellent electron transfer efficiency. The results reported in this thesis provide prospective avenues for developing cutting-edge optoelectronics technology and substantially contribute to our understanding of material interactions.

List of Abbreviations

ATR	Attenuated total reflectance
APD	Avalanche Photodiode
BNS	Biocatalytic nanoparticle shaping
C ₆₀	Buckminster fullerene
CBM	Conduction band minimum
CsBr	Caesium bromide
Ca	Centred around
°C	Degree Celsius
CCD	Charge-Coupled Device
CB	Conduction band
DMF	<i>N, N</i> -dimethylformamide
DLS	Dynamic light scattering
DMSO	Dimethyl sulfoxide
DM-TMM	4-(4,6-Dimethoxy-1,3,5-triazine-2-yl)-4-methylmorpholinium
ETL	Electron transport layer
E _{RED}	Reduction potential
ESI-MS	Electrospray ionization mass spectrometry
EDTA	Ethylenediamine tetraacetic acid
FA	Formamidinium
FABr	Formamidinium bromide
FTO	Fluorine-doped tin oxide
FT-IR	Fourier-transform infrared spectroscopy
fs	Femtosecond
FWHM	Full width at half maximum
g	Gram
GBL	Gamma-butyrolactone
h	Hour
HTL	Hole transport layer
HAD	Hexadecyl amine

HEPES	4-(2-Hydroxyethyl) piperazine-1-ethane sulfonic acid
HDT	1,6-hexanedithiol
HUMO	Highest unoccupied molecular orbital
HI	Hot injection
ITO	Indium tin oxide
K_{et}	Rate constant of electron transfer
K_1	Monomolecular recombination rate constant
K_3	Auger recombination rate constant
K_2	Bimolecular recombination rate constant
K_r	Rate constant of radiative relaxation
K_{nr}	Rate constant of nonradiative relaxation
K_B	Boltzmann's constant
K_{SV}	Stern-Volmer constant
LARP	Ligand-assisted reprecipitation
L_D	Diffusion length
LUMO	Lowest unoccupied molecular orbital
LED	Light emitting diode
MA	Methylammonium
MHz	Megahertz
Min	Minute
μM	Micromolar
μm	Micrometre
mL	Millilitre
mmol	Millimole
NIR	Near Infrared
NMR	Nuclear magnetic resonance
nm	Nanometre
ns	Nanosecond
PET	Photoinduced electron transfer
PL	Photoluminescence
PLQY	Photoluminescence quantum yield

PCBM-C ₆₁	[6, 6]-phenyl C ₆₁ butyric acid methyl ester
PeLED	Perovskite-based light-emitting diode
PEG	Polyethylene glycol
PCE	Power conversion efficiency
PNC	Perovskite nanocrystal
PSC	Perovskite solar cell
PDDA	Poly (diallyl dimethylammonium chloride)
PDI	Polydispersity index
RF	Refractive index
R _A	Ionic radii of ion A
R _B	Ionic radii of ion B
R _X	Ionic radii of ion X
s	Second
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscope
SOC	Spin-orbit coupling
SV	Stern-Volmer
T	Temperature
τ_{avg}	Average photoluminescence lifetime
TA	Transient absorption
TEM	Transmission electron microscopy
TCNB	1,2,4,5-tetracyanobenzene
TCNQ	7,7,8,8-tetracyanoquinodimethane
TBAI	Tetra-n-butylammonium iodide
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TOPO	Trioctylphosphine oxide
TCSPC	Time-correlated single photon counting system
UV	Ultraviolet
VBM	Valence band maximum
Vis	Visible

V	Voltage
VB	Valence band
QD	Quantum dot
QDSC	Quantum dot solar cell
λ	Wavelength

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Chapter 1

Introduction

1.1 Abstract

Luminescent nanomaterials constitute an important class of semiconductor materials that have gained overwhelming interest in several applications, including LEDs, optical detectors, photovoltaics, and display technologies. In this respect, halide perovskite NCs and chalcogenide QDs are becoming the most important. These semiconductor materials have gained considerable interest across a broad spectrum of next-generation optoelectronic devices owing to their superior photoluminescence, high absorption coefficients, and efficient charge carrier dynamics. Despite these advantages, the future of perovskite-based optoelectronics and photovoltaics squarely depends on furthering the understanding of the interfacial charge transfer-long-range carrier diffusion processes. Only when these challenges are met can their full commercial and industrial potential be realized. This chapter has been outlined through a succinct account of the history, basic structure, morphology, synthesis routes of both systems in comparison to one another, and key optical and electronic properties of photoinduced charge carriers; the emphasis has been on explaining mechanisms of quantum confinement contribution to electronic and optical property tuning. Several techniques are introduced in this chapter to synthesize materials with correct, controlled sizes and shapes: perovskite nanocrystals (PNCs) and quantum dots (QDs) using the bottom-up process of solution-phase synthesis, hot injection, or ligand-assisted reprecipitation; describing self-assembly techniques necessary to make thin films from such building blocks as part of any device application. The second part will cover the charge carrier dynamics mechanism: the charge carrier behavior in the film state. In this context, interfacial charge transfer, recombination pathways, and long-range carrier diffusion will be mainly presented as relevant to performance optimization concerning optoelectronic and photovoltaic devices. Next, this chapter will focus on different applications of halide perovskite NCs and chalcogenide QDs to diverse applications encompassing high-efficiency solar cells, brilliant light-emitting devices, photodetectors, and bioimaging. It has also explained various examples

of versatility and adaptability in diverse technological fields of those materials. The chapter ends with the motivation for this research and the details of the particular aims of this thesis.

1.2 General Introduction

1.2.1 Luminescent semiconductor nanocrystals and quantum dots

QDs of semiconductors are brightly emitting nanoparticles employed in diverse applications such as LEDs, displays, solar cells, bioimaging, and optical detection.^{1–}

⁶ These materials might be broadly divided into various categories according to their chemical composition:

Metal chalcogenides are classified as:

- II-VI compounds: MX ($M=Zn, Cd, Hg$; $X=S, Se, Te$)
- III-V compounds: MX ($M=Al, Ga, In$; $X=N, P, As$)
- III-VI compounds: M_2X_3 ($M=In$; $X=S, Se, Te$)
- IV-VI compounds: MX/MX_2 ($M=Pb/Sn$; $X=S, Se, Te$)

Metal halides and halide perovskites include:

- Simple metal halides: MX ($M=Cu/Ag$; $X=Cl, Br, I$)
- Perovskite structures: AMX_3 ($A=Cs/MA/FA$, $M=Pb/Sn$, $X=Cl/Br/I$)
- Complex structures: $A_3Bi_2X_9$, A_2BBiX_6 ($A=Rb/Cs/MA$, $B=Na/Mg/K/Zn/Ag$, $X=Cl/Br/I$)

These materials' distinctive photonic and electronic characteristics, which may be precisely adjusted through composition control and quantum confinement impacts have attracted a lot of attention. Their well-established synthesis techniques and diverse surface chemistry enable the creation of outstanding performance in optical-electronic devices and biological applications.

The manipulation of size, structure, and composition of these nanomaterials enables accurate bandgap engineering, allowing the wavelength of emission to be changed from ultraviolet to infrared. This adjustability, along with strong photoluminescence quantum yields and outstanding photostability, qualifies them for next-generation optoelectronic applications.

1.2.2 The structure of halide perovskites

The Russian mineralogist Lev Perovski is honored with the names of perovskite structures. The term "perovskite" was first used to refer to CaTiO_3 , a mineral that a German scientist called Gustav Rose found in the Ural Mountains in 1839.⁷ In time, the definition was widened to cover compounds with a similar structure. 3D perovskites have the general chemical formula ABX_3 , where A can be either an inorganic cation like Cs^+ or an organic cation like MA^+ (CH_3NH_3^+) or FA^+ ($\text{NH}_2\text{C}=\text{NH}_2^+$). B stands for a cation of a divalent metal. X refers to halide ions: I^- , Br^- , or Cl^- .⁸ 3D lead-based perovskites' structure (Figure 1.1) is schematically composed of lead-centered octahedra, PbX_6 , sharing a vertex. This provides a framework with the A cations filling in the holes between the octahedra. The size of the A cation is critical and is constrained by the gaps created between the corner-sharing octahedra.

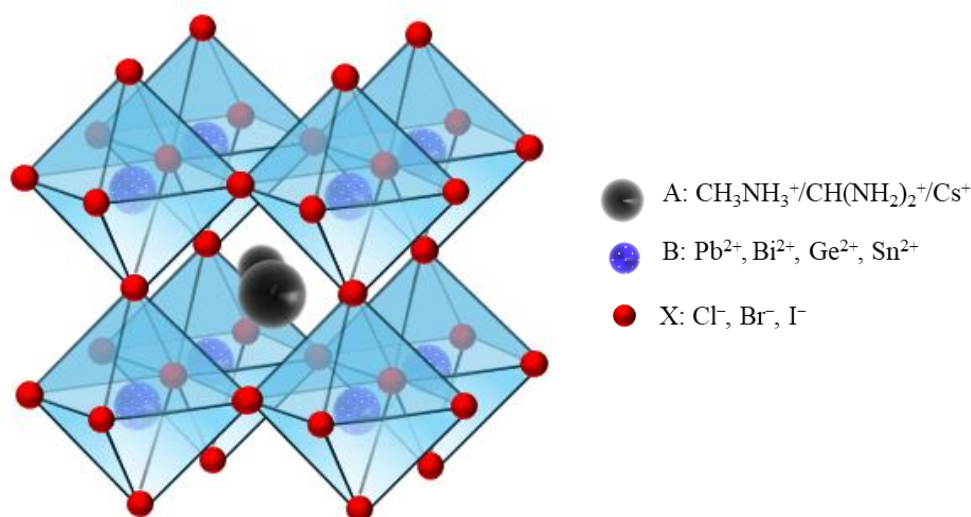


Figure 1.1 A unit cell of halide perovskite.

The geometrical criteria are some of the most important factors governing the stability and feasibility of perovskite structure formation. In other words, certain relationships must be satisfied among the ionic radii of A, B, and X ions, expressed as R_A , R_B , and R_X , respectively.

$$(R_A + R_X) = t\sqrt{2}(R_B + R_X)$$

The octahedral factor ($\mu = R_B/R_X$) indicates the stability of the structure, whereas the Goldschmidt tolerance factor (t) forecasts whether the mixture can form a stable

perovskite framework.⁹ Typically, a perovskite structure might be stable if $0.813 \leq t \leq 1.107$ and $0.442 \leq \mu \leq 0.895$. It is relatively low, particularly for materials with heavier halides, where the forecast accuracy falls to 60% or below (51% for chlorides, 56% for bromides, and 33% for iodides). τ was presented as a new tolerance factor and is defined as follows:

$$\tau = \frac{r_X}{r_B} - n_A \left(n_A - \frac{r_A/r_B}{\ln(r_A/r_B)} \right)$$

Where r_i is the ionic radius of ion I and n_A is the oxidation state of A. The substance is a perovskite if τ is less than 4.18.

The size of the A cation has significance in the phenomenon of 3D perovskites. The size of the A component should be as small as possible to ensure structural stability and proper integration in the lattice. The limitation in size helps to maintain the geometric compatibility required to form a robust perovskite structure.

1.2.3 The structure of the chalcogenide quantum dots

Chalcogenide QDs are nanoscale semiconductor particles based on materials containing chalcogen elements (oxygen, sulfur, selenium, or tellurium) combined with metals such as cadmium, lead, or indium.^{9,10} The special structure and properties of QDs result from the quantum confinement effect, which seriously affects their optical and electronic properties compared to the bulk material. The core of chalcogenide QDs is with a nanocrystal structure made up of semiconductor material, enveloped by an outer shell made from another material. In such a structure, the optical and electronic properties are improved, hence enhancing the performance and stability of QDs in respective applications. The core of the QDs is defined by its central region, which is made of semiconductor materials like CdSe, PbS, or InP. The emission wavelength is one of the primary optical and electrical characteristics that it regulates through the quantum confinement effect.¹¹ The smaller the core, the higher the energy (blue-shifted) the emission, the larger the core, the lower the energy (red-shifted) the emission. A shell, typically made from a second semiconductor material like ZnS, ZnSe, or CdS, covers the core. The shell acts as a protective layer to the core from environmental degradations like oxidation or photodegradation. It also passivates the surface of the core, reducing

nonradiative recombination and hence increasing quantum yield (QY). The general structure is shown in Figure 1.2,

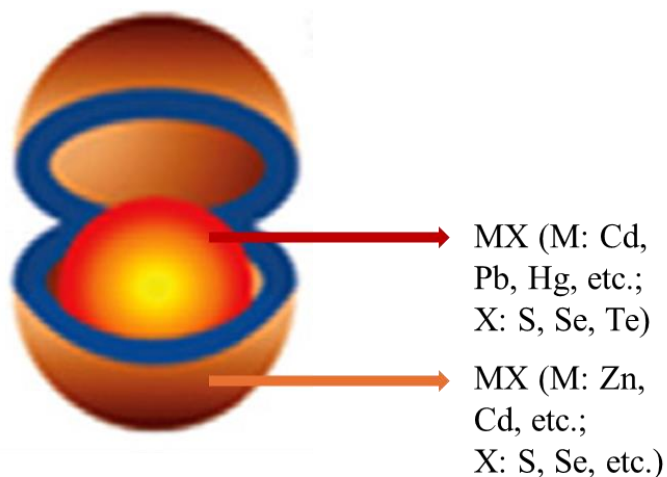


Figure 1.2 General structure of the metal chalcogenide (core-shell)

Organic molecules or polymers coat the surface of the shell to stabilize the QD in solution and enhance compatibility with the surrounding medium. Ligands can also affect the solubility and processability of the QDs. In type I structures, the shell material possesses a larger band gap compared to the core, confining electrons and holes within the core and enhancing luminescence efficiency. An example of this is CdSe/ZnS QDs. In type II structures, the shell's conduction band minimum is lower than the core's, or its valence band maximum is higher.¹² This results in a spatial distinction between electrons and holes, leading to longer exciton lifetimes and red-shifted emission. For example, CdTe/CdSe QDs. There is a gradual variation in composition from the core to the shell, which minimizes lattice mismatch and enhances structural stability. Example: CdSe/ZnSe QDs with a composition gradient alloy shell. In an inverted core-shell, the core material should have a higher bandgap than the shell for carriers to be confined in the shell. Example: ZnSe/CdSe QDs. Shell passivation reduces the surface defects serving as nonradiative recombination sites. The shell protects the core from chemical and photochemical degradation. Tuning of core-shell materials allows the optical and electronic properties to be precisely tuned.⁵

1.2.4 Background of Quantum Confinement

Quantum confinement, commonly known as the 'particle-in-a-box' problem, was first theoretically stated in the 1930s by physicist Herbert Fröhlich who first proposed that the macroscopic dimensions of a small particle can determine material properties.¹³

Fröhlich investigated the repercussions of the Schrödinger equation, which states that when particles get exceedingly small, there is less space for the material's electrons, causing the electrons to be pressed together. In the decades following Fröhlich's initial work, the understanding of quantum size effects evolved significantly. Researchers were able to develop nanostructures in the 1970s and show that size did affect their optical characteristics.

The first experimental realization of quantum confinement in semiconductor nanoparticles, such as quantum dots, quantum wires, and quantum wells, occurred in 1980. Because of the confinement of charge carriers, these structures displayed distinct energy levels. A key idea in materials science and nanotechnology nowadays is quantum confinement. Numerous uses in electronic devices, photographic science, and quantum computation have resulted from the exact regulation of the form and structure of nanoparticles made feasible by advancements in manufacturing techniques. Quantum confinement in semiconductors is the phenomenon whereby materials' electronic and visible properties change as they approach the nanoscale, often below the exciton Bohr radius. This occurrence has a major effect on the behavior of materials, leading to different energy levels and size-dependent band gaps. Quantum confinement has been shown in several experimental investigations in diverse semiconductor nanostructures. One of the best-studied systems for observing quantum confinement phenomena is CdS QDs. One of the earliest theoretical and experimental proofs of quantum confinement in CdS QDs was given by Brus (1984).¹⁴ Murray et al. (1993) synthesized semiconductor nanocrystals of varying sizes and observed clear size-dependent shifts in absorption edge in ultraviolet and luminescence spectra.¹⁵ Efros and Efros (1982) theoretically predicted and experimentally confirmed discrete excitonic states in the semiconductor sphere.¹⁶ Alivisatos et al. demonstrated size-regulated preparation of different sizes of semiconductors, resulting in a continuous range of tunable emission colors.¹⁷ Peng and Peng (2001) improved synthetic techniques to produce highly stable semiconductor QDs

with tunable QYs.¹⁸ Together, these investigations show that quantum confinement effects cause substantial alterations in the electrical and optical characteristics of semiconductor materials as they are reduced to nanoscale dimensions.

Similar to conventional semiconductor QDs like CdSe, perovskite QDs, particularly those based on lead halides have shown quantum confinement effects. This quantum confinement results in a significant size-dependent bandgap that allows for tunable emission wavelengths.

Protesescu et al. (2015) prepared CsPbBr₃ nanocrystals and found that when nanocrystals' sizes decreased from large to nanosize, there was a noticeable shift in the spectrum of light emission and absorption.¹⁹ When the perovskite QDs' size decreases, their electronic states split into discrete energy levels. Becker et al. (2018) studied CsPbBr₃ QDs using single-particle spectroscopy and found evidence of discrete excitonic transitions.²⁰ Zhang et al. (2018) synthesized CH₃NH₃PbX₃ (X = Cl, I, Br) PNCs and demonstrated that the emission of light wavelength changed by adjusting the halide content and managing the dimension of QDs.²¹ The quantum confinement in these QDs results in narrow and stable photoluminescence (PL) peaks. Kovalenko et al. (2017) found that CsPbBr₃ QDs produce stable, narrow-band emission over time.²² These results make perovskite QDs attractive options for use in optical devices.

1.3 Synthesis of halide perovskites and chalcogenide quantum dots

1.3.1 Preparation of halide perovskite nanocrystals and quantum dots

Numerous efforts have been made to develop a straightforward and reliable synthesis process for PNCs. The growth process is the framework for the broad classification of these synthesis techniques into "top-down" and "bottom-up" approaches. Heat-up, reprecipitation, and in situ synthesis are the three primary categories into which the bottom-up techniques are grouped further. Hot injection (HI) and ligand-assisted reprecipitation (LARP) approaches have become the most used synthesis methods among those shown in Figure 1.3. Figure 1.3(a) illustrates the HI synthesis process, which involves dissolving PbX₂ with ligands in 1-octadecene, followed by heating the mixture to a high temperature under an argon atmosphere. Subsequently, pre-prepared Cs-oleate is injected into the solution, and the reaction is rapidly quenched by cooling in a cold water bath.

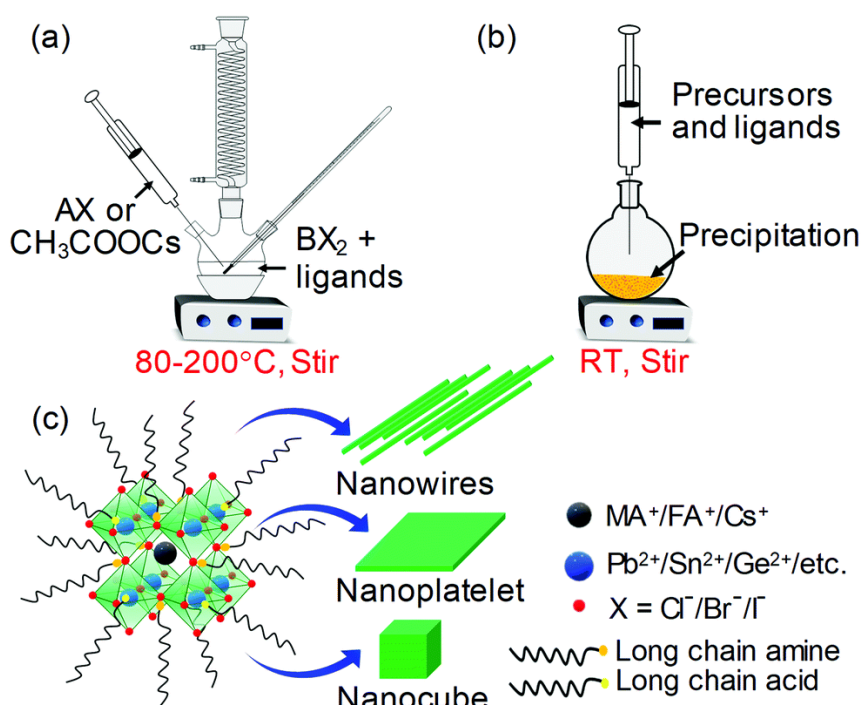


Figure 1.3 (a, b) PNCs are produced through the hot-injection method and the LARP technique, respectively. (c) Ligand-capped PNCs display a variety of morphologies.²³

The hot injection strategy requires precise control of precursor concentrations, injection temperature, reaction duration, and precursor-to-surfactant ratio to regulate size distribution and morphology.^{8,24,25} This approach indeed plays a significant role in exercising very precise control over synthesis through effective decoupling of the nucleation and growth phases. The possibility of separating these two most important stages allows the opportunity to control the conditions whereby PNCs could be formed to ensure their sizes remain small and uniform. This technique consequently reduces undesirable aggregations and overgrowths; hence, PNCs of a very narrow size distribution can be achieved very important factor to retain their valuable optical and electronic properties. Among the most important results obtained so far in this field is that published by Protesescu et al. in 2015, they developed a colloidal synthesis technique to prepare cesium lead halide PNCs (CsPbX_3). CsPbX_3 PNCs were successfully synthesized by injecting Cs-oleate into a heated solution (140–200 °C) that contained PbX_2 , salts, alkyl amines, and fatty acids dispersed in octadecene. Their findings demonstrated that changing the reaction temperature and ligand ratios affected the size of the PNCs. The use of several halide salts (Cl^- , Br^- , and I^-) enabled tunable emission colors across the visible spectrum.²⁶ Udayabhaskararao et al. described a two-step growth mechanism in a

follow-up study in 2017.²⁷ They tracked the CsPbX₃ PNC growth using electron microscopy, observing the seed generation of Pb⁰ NCs followed by CsPbX₃ nucleation.

The LARP (Ligand-Assisted Reprecipitation) approach is a simple and cost-effective way to create colloidal PNCs.^{22,23} By supersaturating precursors in a solvent, a nonequilibrium condition is generated, causing PNCs to precipitate. These PNCs are stabilized by capping with long-chain acid or amine ligands. Adjusting the temperature, adding a subpar solvent, or letting the solvent evaporate can all cause supersaturation. Zhang and colleagues (2015) presented the LARP approach for PNC synthesis.²¹ To produce colloidal MAPbBr₃ PNCs, they dissolved ligands (alkyl amine and carboxylic acid) and precursors (PbBr₂ and MABr) in DMF. The precursor solution was then introduced into toluene at room temperature under constant stirring and finally got the crystals a yellow solid.

1.3.2 Preparation of thin films

Films of halide perovskites are employed as working layers in light emitters and energy harvesters. The stability and surface chemistry of the perovskite layers largely dictate the devices' optical and electrical characteristics.^{28–30} Although extensive research has been conducted, many aspects of the crystallization process and surface properties of perovskite thin films remain unresolved.

Several deposition techniques have been conducted for the production of homogeneous high-quality thin films with different advantages and suitable conditions for target applications. Among these, the most common deposition methods are spin coating, doctor-blade coating, drop-casting, and spray coating, each of these techniques presents huge differences in operational principles, scalability, and film qualities. These methods can produce these perovskite films in one or two steps by depositing their precursor solutions (Figure 1.4).³¹ A highly luminous polycrystalline film can be created by depositing precursor salts in DMF, GBL, or DMSO, followed by drying and annealing.³² Perovskites will be aided in nucleation and growth by the solvents' temperatures and low pressures. The settings utilized to prepare perovskite thin films have a significant impact on the crystallization process. Sequential deposition can produce films of excellent quality by first applying the first precursor mixture to a surface, drying it, and then applying, drying, and annealing a second precursor solution.³³

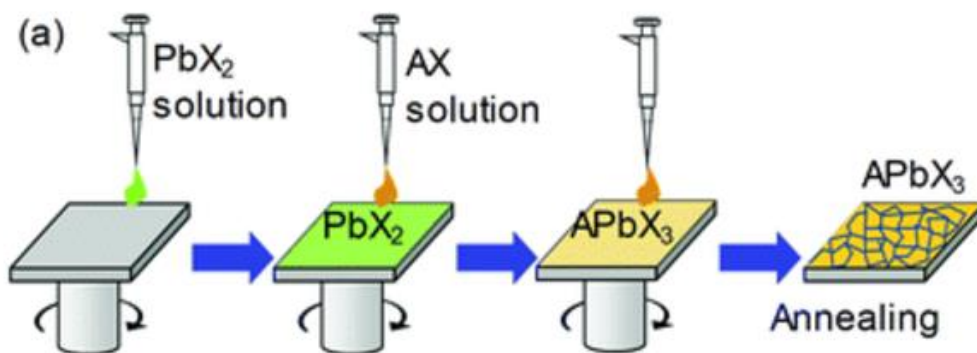


Figure 1.4 General methods for synthesizing perovskite films. (a) Sequential deposition of the precursor solution.²³

Among the most important challenges for preparing high-quality perovskite thin films, the shape control of produced nanoparticles is a key challenge. The shape and size of nanoparticles are considered to be very important factors that seriously influence optical, electronic, and structural properties in perovskite materials, highly related to the device performance. The diffusion of charge carriers occurs in PNC thin films with densely packed nanocrystals, resulting in a loss in quantum confinement. The enhanced dielectric screening in these films helps excitons dissociate into free carriers, allowing them to move.³⁴

Therefore, it is crucial to fabricate these dense nano-structures to learn more about the diffusion and migration of charge carriers. These assemblies are prepared utilizing simple spin-coating and drop-casting techniques for making ligand-assisted self-assembled films. For example, a double-stage spin-coating method can be used to deposit PNCs suspended in toluene onto a material to create highly luminous nanocrystalline films, first at low speed (100 rpm for one min) followed by high speed (1000 rpm for three min).³⁵

1.3.3 Synthesis of chalcogenide quantum dots

In the current period, there were various preparation methods were reported, including sol-gel, co-precipitation, microemulsion, facile, and other approaches. The sort of synthesis process is generally determined by the desired application and specific material requirements, as each methodology has distinct advantages and limits. In some cases, one method may work well, while in others, the same procedure may not be suitable due to differences in conditions and basic materials employed. The choice of the method of QD synthesis is a crucial step that directly influences the quality, size, shape, and functionality of the key parameters for specific applications of QDs. Additionally, precursors, such as metal salts, organic ligands, or solvents, critically account for the synthesis strategy or conditions to control QDs in synthesis. QDs are typically synthesized using one of two fundamental strategies, top-down or bottom-up methods, each with distinct mechanisms, advantages, and limitations.

The strategy of this method creates nanoparticles (NPs) by breaking down bigger units into smaller ones, which are then transformed into nanometric scale particles. As illustrated in Figure 1.5, this approach is used in a variety of processes, including laser ablation by Amendola and Meneghetti, 2009³⁶ and Hulteen et al., 1999³⁷; ball milling by Cundy and Liversidge, 1995³⁸; and Liversidge-Merisko et al., 2003³⁹, nanolithography, sputtering, and thermal control (Bikiaris and Chrissafis, 2011⁴⁰). However, the primary drawbacks of this method are the inclusion of contaminants and structural flaws through patterning during the formation of QDs.⁴¹

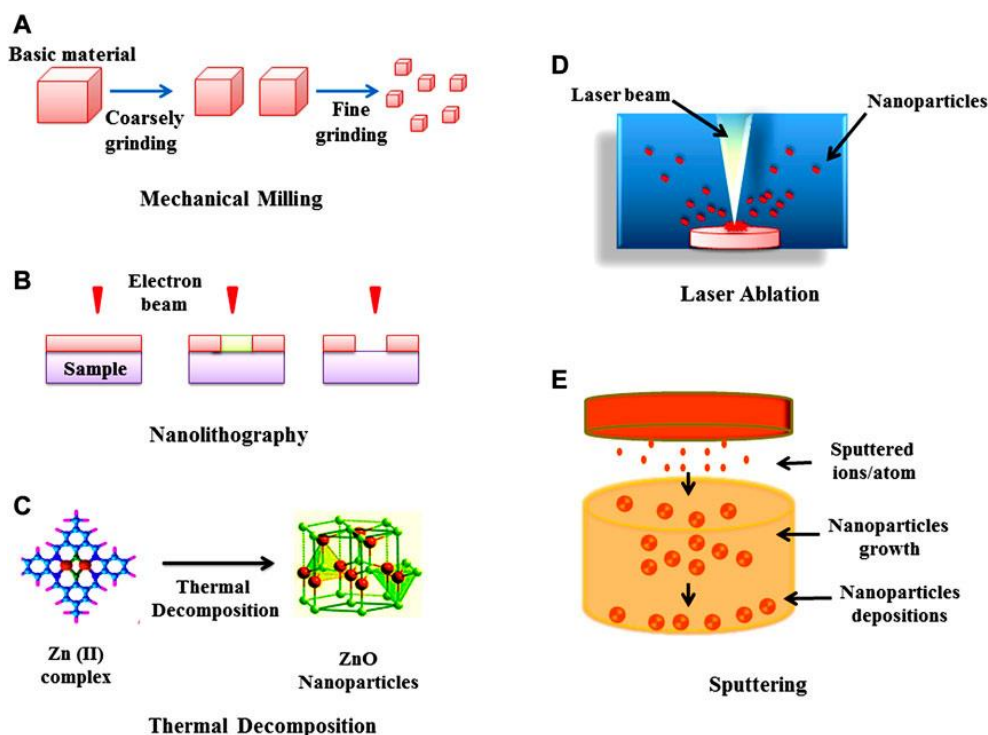


Figure 1.5 Nanoparticle synthesis via a top-down approach, (A) mechanical milling (B) nanolithography (C) thermal decomposition, (D) laser ablation, and (E) sputtering.⁴²

The bottom-up approach, often referred to as the self-assembly strategy, constructs nanostructures by assembling fundamental units into larger, stable configurations through the controlled influence of nanoscale physical forces. Using this method, nanostructures are created by additional self-assembly once the required material is reduced in size. Self-assembly relies on nanoscale physical forces to transform basic units into larger, uniform structures. The creation of nanostructured particles from colloidal dispersions and the development of QDs through epitaxial growth serve as common examples. This method combines a variety of laboratory-based techniques, often referred to as colloidal techniques such as the sol-gel method, ion-exchange reactions, hot injection, co-precipitation, and hydrothermal techniques.

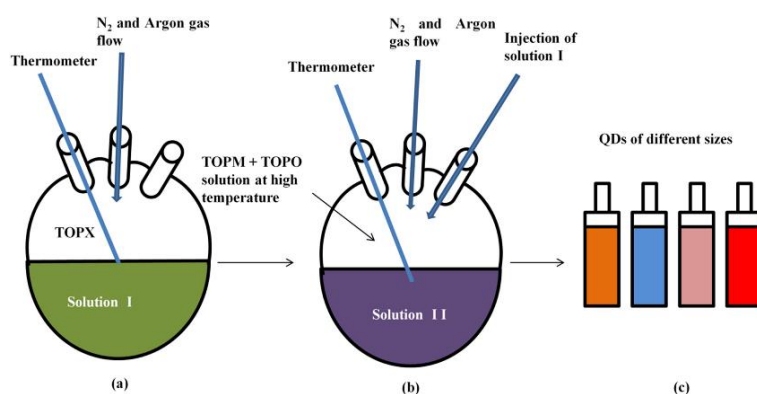


Figure 1.6 The hot-injection technique (a) TOPX (TOPSe, TOPS, or TOPTe) is present in solution I. (b) TOPO solution and TOPM (TOPCd) at elevated temperatures (often above 200 °C) are present in solution II. (c) little aliquots of QDs of varying sizes were collected at various times.

The standard process for preparing QDs, which involves heating particular organic solvents and adding precursors, was developed in 1993 by Murray et al.¹⁵ To make the Se and Cd solutions, Se and $\text{Cd}(\text{CH}_3)_2$ are mixed with tri-*n*-octylphosphine (TOP) solutions, as shown in the schematic design of Figure 1.6. In a batch reactor, these solutions are swiftly poured into a heated trioctylphosphine oxide (TOPO) solution in an inert environment.¹⁵ By acting as a high boiling solvent and stabilizing ingredient, TOPO enables the mixture for gain raised temperatures (at 320 °C). TOPO acts as both a protector and a solvent with a high boiling point, allowing the solution to reach reaction temperatures of as high as 320 °. By regulating the growth temperature, QDs of various sizes, ranging from 1.5 to 11.5 nm, could be produced. However, the reactant $\text{Cd}(\text{CH}_3)_2$ is exceedingly toxic, costly, and explosive, making this approach unsuitable for QD synthesis in large amounts. Peng et al. devised an eco-friendly approach for hot-injection QD synthesis, which marked a significant development. This technology substituted the very toxic and expensive $\text{Cd}(\text{CH}_3)_2$ with the more cost-effective and less hazardous CdO to create CdSe nanocrystals, resulting in high-quality QDs without compromising performance.^{18,43} It is widely recognized that octadecene (ODE), a non-coordinating solvent, can serve as an alternative to TOPO, a coordinating solvent.^{44,45} After the synthesis parameters are optimized, the final QDs' quality does not decline.⁴⁶

Deng et al. made the manufacture of CdSe QDs more environmentally friendly and cost-effective by using oleic acid and liquid paraffin as reaction conditions rather than

standard TOP/TOPO.⁴⁷ Through the careful selection of precursors and optimization of synthesis parameters, the hot-injection method has been adapted for the production of various semiconductor QDs.^{48,49}

Initially, researchers focused on single nanoparticles since they had significantly better qualities than materials in bulk size. The discovery was that in 1980, semiconductor particles that are sandwiched, composite, or heterogeneous are more effective.^{50–52} The evolution of core/shell structures marked a crucial milestone in the early 1990s. To enhance the characteristics of these semiconductor materials, researchers created semiconductor nanoparticles with several layers. The term "core/shell" was introduced to describe nanoparticles consisting of two primary components: the core, which is the inner material, and the shell, which forms the outer layer.^{53–55} Figure 1.7 shows a schematic of some core/shell structure types. Of the many different core/shell nanostructures the most common are spherical core/shell nanoparticles. Figure 1.7a where a spherical core particle is completely enclosed within a shell composed of another material.

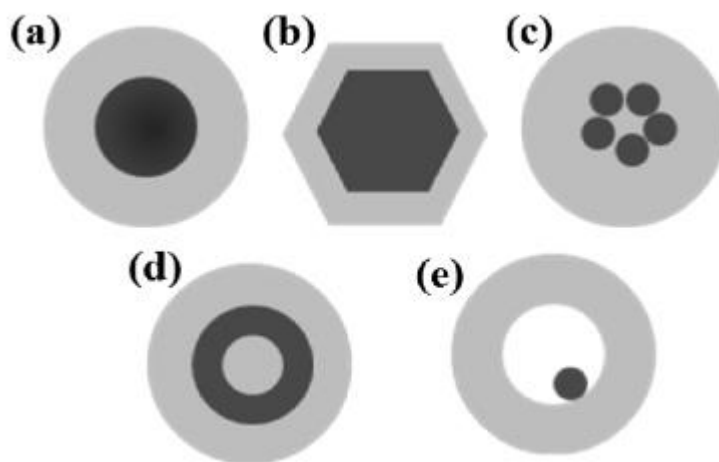


Figure 1.7 Various nanoparticles with core/shell are shown. (a) Nanoparticles with a spherical core and shell; (b) Nanoparticles with a hexagonal core and shell; (c) nanomatryushka material; (d) moveable core within hollow shell material; and (e) several tiny core components covered in a single shell.⁵⁶

A combination of the two techniques can also be applied to maintain precise and constant shell thickness. For instance, the top-down method is used to create core particles, and the bottom-up method is used to coat them. The overall luminescence of the freshly

prepared colloid is enhanced when zinc cations are adsorbed onto the sulfur-enriched surfaces of CdS particles, forming a pseudo-ZnS shell, as was noted as early as 1982.⁵⁷ Henglein and colleagues later carried out more detailed studies, showing that aqueous CdS/Cd(OH)₂ samples can achieve a QY of 50% at room temperature and display significantly greater resistance to photo-anodic corrosion compared to uncoated CdS particles.⁵¹ ZnS⁵³ and ZnSe⁵⁸ shells were successfully deposited onto CdSe in 1990 by White and colleagues, and Brus and colleagues using the inverse micelle technique.

1.4 Photophysical properties of chalcogenide nanocrystals and quantum dots

1.4.1 Optical properties of halide perovskites

The [PbX₆]⁴⁻ octahedra in lead halide perovskites make a strong contribution to the band-edge electronic structure, which plays a decisive role in classifying these materials as direct bandgap semiconductors.^{59–62} Figure 1.8, sigma (σ^*) and pi (π^*) antibonding orbitals of the conduction band minimum (CBM) arise from the hybridization of the s- and p-orbitals of the halogen with the 6p-orbitals of lead. By comparison, the VBM is primarily composed of s- and p-orbitals of the halogens and 6s- and 6p-orbitals of Pb. It thus follows that the bandgap and optical properties are defined by the [PbX₆]⁴⁻ octahedral framework. While the composition of the halogen changes from chlorine to bromine and further to iodine, the contribution of the halide p-orbitals increases to the VBM. An enhanced orbital mixing between the halide p-orbitals and the Pb s-orbital results in a systematic reduction of the optical bandgap energy (E_g) in the order of I < Br < Cl.^{59,63} Figure 1.10B shows that the PL of perovskites can be precisely modulated within the UV-visible to near-infrared spectrum by changing the halogen composition via anion exchange, thus offering variable optical properties for different applications.

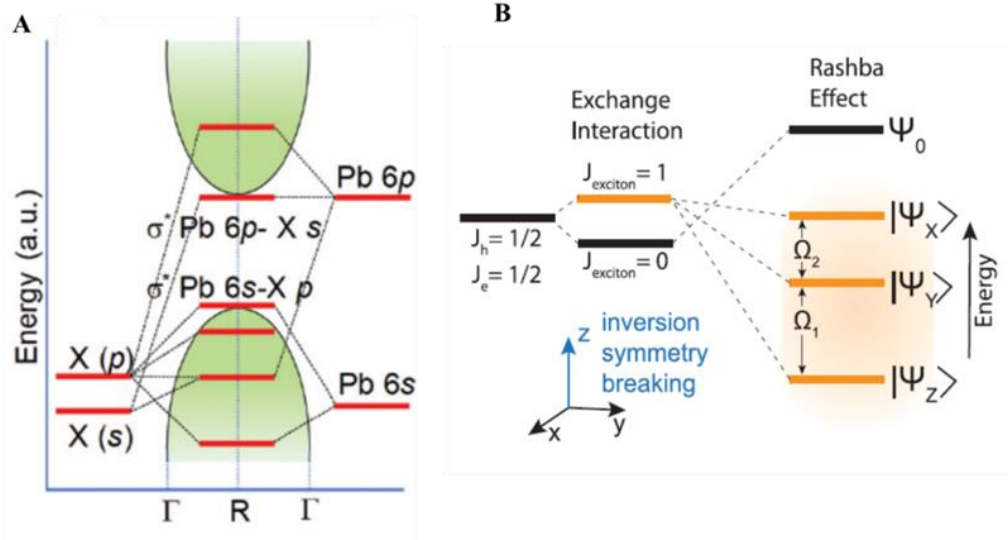


Figure 1.8 (A) Depicts the band-edge states of lead halide perovskites, emphasizing the role of spin-orbit coupling and the total angular momentum associated with the electron states. Adapted from Chouhan et al.¹⁹ and Utzat et al. (B).⁶⁴

Spin-orbital coupling (SOC), which results from the mixing of orbital-angular momentum (p , d , and f orbital electron motion) and spin-angular momentum (electrons rotate either clockwise or anticlockwise around their axis) affects the optical bandgap in lead halide perovskites.^{61,62,65} SOC significantly lowers optical bandgap energies in lead halide perovskites by splitting the three-fold degenerate CBM into higher-energy quadruplet states and lower-energy doublet spin-orbit split-off states. The perovskites' optical properties are influenced by SOC through CBM modification, which is linked to the octahedral tilting and the compositions of the cations positioned at the A-site and B-site.^{65–68} A decrease in the Pb-X-Pb dihedral angle from its optimum value (180°) causes an octahedral tilt when the size of the A-site cation's size shrinks from a bigger FA^+ to a smaller Cs^+ .^{59,65,66} The lead halide perovskites' crystal structures with and without octahedral tilting are depicted in Figure 1.9.

Halide perovskites are generally characterized by their direct bandgap nature. Recent research suggests that the noncentrosymmetric lattice structure in halide perovskites may lead to Rashba or Dresselhaus band splitting.⁶⁹ Quantum confinement is normally weak in perovskites due to their rather large exciton Bohr radius, providing a means whereby electronic and optical properties remain unaltered with nanoscale reduction in size. This interaction gives rise to excitonic states characterized by total angular momentum

quantum numbers (J) of 0 or 1. These states are created by the so-called Rashba effect, which is a consequence of the loss of inversion symmetry in the perovskite crystal lattice. In detail, the Rashba effect arises from the interplay between spin-orbit coupling and an asymmetry of the crystal electric field concerning the spatial coordinate; this interplay gives rise to a splitting of energy levels depending on the spin and momentum of electrons. The heavy nucleus of lead creates strong momentum-dependent interactions, resulting in spin-orbit interaction that divides the exciton levels into singlet and triplet states.⁷⁰ More precisely, Figure 1.8B presents how the band edge for perovskites has further split into three discrete triplet states, which, in turn, appears under the action of the angular momentum projections driven by the Rashba effect.

Additionally, spin-orbit coupling (SOC) in perovskite materials modifies the optical characteristics through CBM manipulation. The structural configuration of lead halide perovskites is, in particular, quite heavily influenced by the size of A-site cations within the crystal lattice. The cations occupy the central voids between the corner-sharing PbX_6 octahedra and vital importance to stabilize the lattice structure and thus dictate the overall geometry. As the ionic radius of the A-site cation decreases, the spatial constraints within the lattice change, leading to a progressive reduction in the Pb-X-Pb dihedral angle, which defines the angle formed by the bonds between lead and halogen atoms across adjacent octahedra. Larger A-site cations, such as formamidinium ($\text{CH}(\text{NH}_2)_2^+$, FA^+), accommodate a near-linear alignment of the Pb-X-Pb bonds with a dihedral angle close to 180° . However, as smaller cations like methylammonium (CH_3NH_3^+ , MA^+) and cesium (Cs^+) replace FA^+ , the dihedral angle reduces significantly due to increased tilting of the PbX_6 octahedra. This is attributed to the decreasing size of the A-site cations, which induce greater distortion in the crystal lattice for structural stability. Specifically, for FA^+ , the Pb-X-Pb dihedral angle is close to 180° , giving a negligible tilting and thus a more symmetric arrangement of the octahedra; for MA^+ , this angle decreases to approximately 163° , showing noticeable tilting in the octahedral geometry. In the case of Cs^+ , this angle is further reduced to about 153° , reflecting an important tilting and more distorted lattice configuration. Figure 1.9 provides a structure of these structural changes visually. It shows the PbX_6 octahedral structure: without tilt (FA^+) and with tilt in MA^+ and Cs^+ . The latter indicates that the reduction of this dihedral angle depends upon the size of the A-site cation from virtually unchanged 180° for FA^+ to very strongly tilted structures for

smaller cations, such as MA^+ and Cs^+ . This tilting has a great impact on the electronic and optical properties of the material. Changes in the Pb-X-Pb angle affect the orbital overlap between lead and halogen atoms, which alters the bandwidth of the conduction and valence bands. This tilting thus affects the bandgap energy and charge transport properties of perovskites, besides photophysical behavior, rendering the kind of A-site cation important to adapt these materials to particular requirements for photovoltaic or light-emitting diodes and other optoelectronic applications.

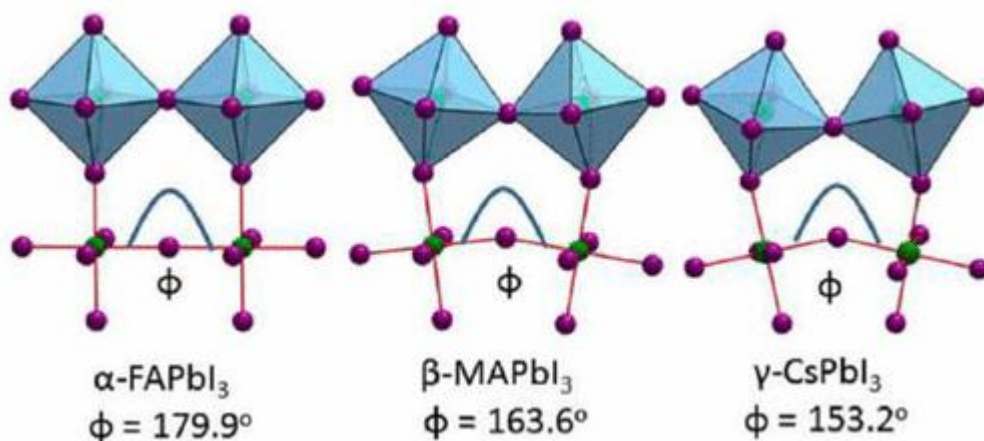


Figure 1.9 The structural configuration of halide perovskites undergoes notable deformations that are closely tied to the size of the A-site cation. Adapted from the work of Manser et al.⁵⁹

In general, the tilting of PbX_6 octahedra in halide perovskites largely influences the electronic structure due to a change in the SOC strength. The SOC is an important factor in defining band-edge electronic properties and depends strongly on the orbital overlap between Pb and X atoms within the perovskite lattice. On the tilting of PbX_6 octahedra, the orbital overlap reduces due to the distortion in bond angles, specifically the Pb-X-Pb dihedral angle. This reduction in orbital overlap leads to a decreased contribution of the Pb orbitals to the band-edge states. Since the SOC strength is directly related to the mixing of Pb's heavy 6s and 6p orbitals with the halogen orbitals, the weakening of SOC changes the band structure. With this effect of reduced SOC, in particular, the strength translates to an expanded bandgap by a shift in CBM upwards and a shift in VBM downward. Modifications within the bandgap bring immediate effects on optical properties. Consequently, the absorption and PL spectra of the material blue shift due to the

expansion of the bandgap. This effect is graphically portrayed in Figure 1.10, showing how such tilting of octahedra, the SOC strength, and spectral shifts are all connected.

Octahedral tilting may arise from a change in the structure of the crystal from cube to square or different phases. Additionally, the perovskite lattice is sensitive to temperature,^{71,72} pressure,^{73,74} which results in this crystal phase shift and octahedral tilt. As a result, these variables affect the band-edge electrical structure, which in turn affects the E_g values and, ultimately, the optical characteristics of these materials. In addition to octahedral symmetry and chemical composition, quantum-size effects or quantum confinement also affect lead halide perovskite's optical properties.^{19,75–77}

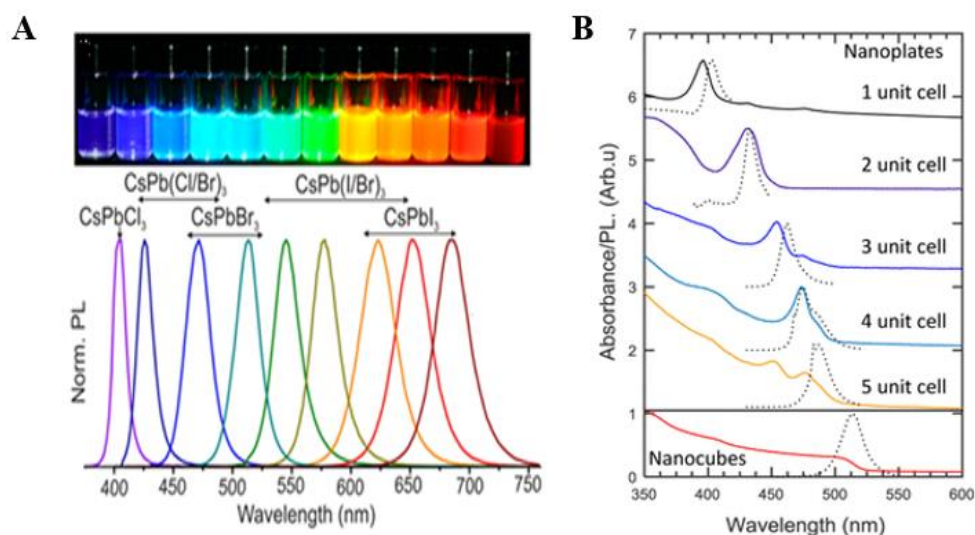


Figure 1.10 (A) Colloidal CsPbBr₃ PNCs dissolved in toluene show brilliant PL upon excitation by UV light, (B) PL spectra of CsPbBr₃ PNCs after undergoing halide ion exchange to tune their emissive wavelengths, (C) The corresponding UV-vis absorption and PL spectra show excellent light absorption and efficient radiative recombination for halide-exchanged CsPbBr₃ PNCs. These data, adapted from the referenced study, (A, C) Protescu et al.¹⁹ and (B) Bekenstein et al.⁷⁵

The quantum confinement effect, when the size of a material approaches the exciton Bohr radius, has more and more significant influence, and thus it has caused a blue shift of PL bands and absorption edges. For nanostructures, where the dimensions are reduced to this scale, the increased spatial confinement of charge carriers raises their energy by the restriction of their movement. It leads to bandgap widening, shifting the material to absorb and emit light at shorter wavelengths, hence a blue shift in its optical spectra. The

change of CsPbBr₃ PNCs from 3D nanocubes to 2D nanoplatelets is an example of this effect. Transitioning from a three-dimensional (3D) geometry into a two-dimensional (2D) geometry reduces the dimensionality of quantum confinement, thereby further constricting the motion of charge carriers.⁷⁵ In nanocubes, confinement is along all three spatial dimensions, while in nanoplatelets, the confinement is essentially along the thickness dimension, significantly changing the electronic and optical properties.

1.4.2 Optical properties of chalcogenide quantum dots

Well-designed QDs have a small diameter (between 2 and 20 nm), which allows them to have unique electrical characteristics, good photostability, and exceptional brightness with high PLQY.⁷⁸ In QDs, the excitons are firmly contained in three dimensions and bound by Coulomb interactions. The confinement effect, which is determined by size and form, influences the optoelectronic properties of the materials⁷⁹

In addition, when the size of particles in a material is decreased down to the nanoscale, some remarkable changes in its electronic and optical properties show up as a result of the quantum confinement effect. It arises when the size of a particle becomes comparable to, or less than, the natural size of an exciton described by the Bohr radius. This confinement spatially confines the charge carriers-electrons thereby reducing the energy states to discrete rather than the continuous bands found in bulk. This confinement increases the interband energy and thus broadens the bandgap; the consequence is the shift in the optical absorption and emission to higher energies-short wavelengths. In 1990, Luis Brus and Moungi Bawendi first realized the basic concept of quantum confinement and its effect on optical absorption in QDs.⁸⁰ They were able to determine how the decrease in the size of the particle modifies the electronic structure by molecular orbital calculations, giving rise to size-dependent optical properties. Their work provided essential insight into how QDs behave differently from their bulk counterparts.

CdX QDs show narrow Gaussian emission spectra and a wide and continuous excitation range. The first exciton peak is 15–30 nm less than the PL peak, and additional

excitonic peaks emerge at shorter wavelengths.^{81,82} These QDs show broad absorption when excited above their band-edge states. Figure 1.11 displays the PL and absorption.

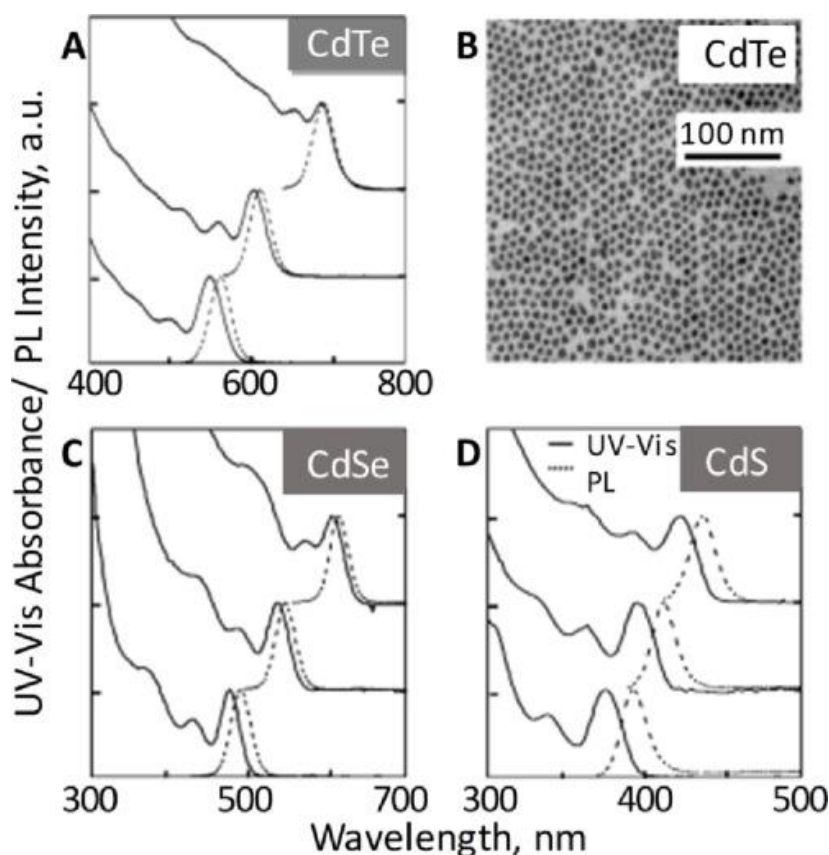


Figure 1.11 PL and absorption spectra of (A) CdTe, (B) CdSe, and (D) CdS QD illustrate spectral redshifts caused by the crystals' size changes over time. Reprinted from Ref.⁸³

The PL intensities of QDs are determined by the relative states of the valence band (VB) and conduction band (CB), as well as the core and shell band gaps. Excitons are confined within the core by shells with larger bandgaps, and the PL wavelength is decided by the core's energy gap. CdSe/CdS, CdTe/CdS, and CdSe/ZnS are examples of such types of QDs.⁸⁴ However, the core's surface activity is reduced by the thickness of the shells. As observed in ZnS/CdSe and CdS/CdSe QDs, the excitons on the shell are somewhat confined when a narrow bandgap material is coated over a broad bandgap core material. Even though such techniques have shown an improved ability to resist photobleaching, the PLQYs were low. These issues might be resolved by covering the surface with a material with a broad bandgap.

To restrict carriers on the shell and core, staggered-type QDs are designed with the core of VB and CB at a smaller or larger state than the shell. This structure effectively facilitates electron and hole separation, extends decay times, and enhances wavelength tunability. CdTe/CdSe, CdS/ZnSe, ZnTe/ZnSe, and CdSe/ZnSe, ZnTe/CdS, CdTe/CdS, are a few examples of this type. The application of additional multi-shell coatings enhances the physical and photonic characteristics of QDs, such as their bandgap, PLQY, PL lifetime, and PL wavelength.^{79,85,86}

1.5 Charge carrier properties

Photoexcitation produces excitons (bound electron-hole pairs) due to strong Coulomb interactions. Exciton binding energy depends on size, with smaller QDs having higher binding energy due to stronger confinement. At room temperature, QDs with low exciton binding energy can dissociate into free electrons and holes. Carrier mobility is usually limited in isolated QD systems because of quantum confinement and scattering at the borders. In well-assembled QD films, where electrical coupling between QDs is improved, electron and hole mobility can rise. Because of faster recombination and more overlap between the electron and hole wavefunctions, smaller QDs have shorter carrier lifetimes. To determine the diffusion length (L_D) of charge carriers in a material, we can use the relationship between the charge carrier lifetime (τ) and the diffusion coefficient (D), as shown in Equation (1),

$$L_D = \tau D \dots\dots\dots(1)$$

This equation, again, points out that the diffusion length is directly related to the charge carrier lifetime and the diffusion coefficient. Here, τ is the lifetime of a carrier, being an electron or hole, while the diffusion coefficient, D , is defined by the speed at which carriers diffuse through a material. The relation by Einstein provides a link between the diffusion coefficient, D , and carrier mobility, μ , under field-free conditions expressed in equation (2),

$$\mu = Dq/k_B T \dots\dots\dots(2)$$

Where q is the electronic charge, k_B is Boltzmann's constant, and T is temperature. This relationship shows that the diffusion coefficient can be expressed in terms of carrier

mobility, which is a measure of the speed at which charge carriers move under an electric field.

By substituting the expression for D from Equation (2) into Equation (1), one can calculate the diffusion length (LD) if the charge carrier mobility (μ), temperature (T), and charge carrier lifetime (τ) are known. This relationship allows us to gain insight into the behavior of charge carriers in materials, such as semiconductors or perovskites, which are critical for applications in solar cells, light-emitting devices, and sensors.

Charge carrier recombination, which refers to the process in which an electron and a hole recombine, releasing energy, can be modeled by a differential equation that accounts for the rate of change in carrier concentration (n) over time. The recombination dynamics are governed by several processes, including third-order, second-order, and first-order recombination, as described by equation (3),

$$dn/dt = -k_3n^3 - k_2n^2 - k_1n \dots (3)$$

In this equation, n represents the concentration of total charge carriers (electrons and holes), and k_1 , k_2 , and k_3 are the rate constants for first-order, second-order, and third-order recombination processes, respectively. The rate of change of n is negative, indicating that as time progresses, the carrier concentration decreases due to recombination.

To understand carrier diffusion paths, the diffusion coefficients must be estimated. Crystal defects and local characteristics can both have a major impact on diffusion coefficients. For a single crystal, a wide range of local diffusion coefficients has been observed, ranging from 0.3 to 2 cm²s⁻¹, depending on trap density and crystal shape.⁸⁷ Diffusion lengths, mobility, and carrier lifetimes are the main factors influencing the monomolecular, bimolecular, and Augur recombination rates. Monomolecular recombination rates are influenced by trap states. Nevertheless, thin-film exciton recombination is not much aided by the low exciton binding energies. The fact that the exciton recombines with a trap in the band gap is widely known. As a result, monomolecular recombination rates have a direct correlation with the number of trap states.

Halide and B-site cation compositions influence charge carriers during bimolecular recombination.⁸⁸ This mechanism is dominant at modest charge carrier density. When the trap state concentration is low, the major relaxation pathway is radiative recombination.

Furthermore, In perovskite, auge-assisted recombination is dominant for elevated charge carrier ratios and excitation intensities. Langevin recombination, which occurs when excitons are inside their shared coulombic area, is generally encouraged by free carriers in low-mobility systems. The bimolecular recombination rate present in halide perovskites is essentially distinct from this recombination process. Consequently, halide perovskites have substantial carrier mobility for non-Langevin bimolecular recombination.^{23,87}

An accurate understanding of halide perovskites' charge carrier characteristics is essential for developing photovoltaic and optoelectronic applications. These materials have distant carrier diffusion, strong charge carrier movement, and longer charge carrier lifetimes. Charge transport converts photoexcited excitons to hot electric charge states, which dissociate into neutral charge carriers in less than 1 ps. There have been reports of a high number of charge carriers in halide perovskites. The lifetime is primarily governed by electron fractional distribution, electrostatic screening, exciton binding force, and exciton diffusion, among other factors. (Figure 1.12)

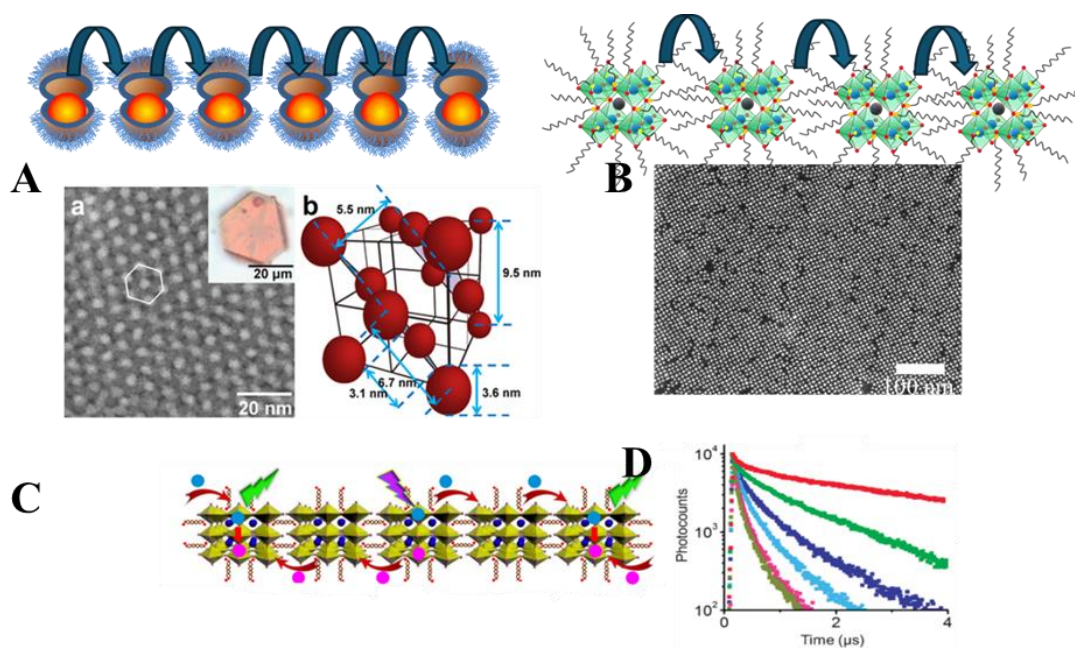


Figure 1.12 STEM images of (A) QD, (B) FAPbBr₃ QD, (C) Electron transfer (D) Time-resolved PLdecay of FAPbBr₃ PNCs film. Reproduced from (A) Yoon et al.⁸⁹ (B) Zhang et al.⁹⁰ (C, D) Nair et al.⁹¹

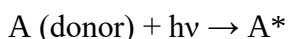
Due to their densely packed nature, the films of PNCs intrinsically possess several unique properties, which make them highly promising for further advanced optoelectronic applications. The high dielectric constants efficiently screen the Coulombic interactions between charge carriers and low exciton binding energies, thus promoting efficient separation of electron-hole pairs and enabling free carriers prerequisite for photovoltaic and light-emitting applications. Electron delocalization and hole localization are common phenomena in halide perovskites, which contribute to their remarkable charge transport properties. The mean free paths of electrons in these materials lie in the range of 10-30 nm, which suggests that electrons can travel for considerable distances without being scattered. These characteristics are very important for effective charge collection and transport in devices. High-resolution STEM and TEM images of densely packed PNC films confirm that interparticle distances are of the order of 1.6 nm. This distance is consistent with the thickness of the most commonly used surface ligands during the synthesis to stabilize the nanocrystals, such as oleic acid and oleylamine. While these ligands prevent aggregation and maintain colloidal stability, their presence also affects the optical and electronic properties of the films. The interparticle spacing induced by the ligands reduces exciton-to-free carrier conversion due to partial confinement of the excitons within individual PNCs.

In this context, the control of recombination dynamics of charge carriers becomes crucial. Radiative and nonradiative recombination processes have a great impact on the efficiency of PNC-based devices. The effective management of such dynamics requires a deep understanding of the distribution and behavior of charge carriers in densely packed PNC films. Optimization of ligand length, packing density, and the degree of electronic coupling between adjacent PNCs is necessary for better performance. A way to surmount these challenges requires intensive engineering of the composition and structure in PNC films for superior interparticle coupling while retaining stability, thereby enabling the designing of perovskite-based devices with superior efficiency, stability, and functionality across a wide gamut of applications in LED, photodetectors and solar cells.

1.6 The photoinduced electron transfer process

A basic process known as photoinduced electron transfer (PET) uses photoexcitation to transfer an electron from the donor to an acceptor (D-A).⁹² When light is absorbed, the donor molecule or substance becomes stimulated, allowing the passing of an electron to the acceptor more energy efficient. PET is essential for a variety of natural and artificial processes, including photosynthesis, photovoltaics, photocatalysis, and molecular sensing. Electron bands in materials and electron orbitals in molecules are two terminology often used to describe where electron transfer. To keep things simple, the description below will be expressed in terms of molecular level. It is possible to stimulate an electron in a ground state orbital to a higher energy orbit when a beam of light interacts with a molecule. An electron donor can replace the vacancy created in a ground state orbital by its excited state. It produces an electron that can be carried to an electron acceptor at a high-energy level. A photoexcited molecule can act as an oxidizing or reducing agent in these contexts.

Photoinduced oxidation



Photoinduced reduction

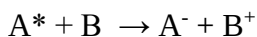


Figure 1.13 depicts the mechanism.

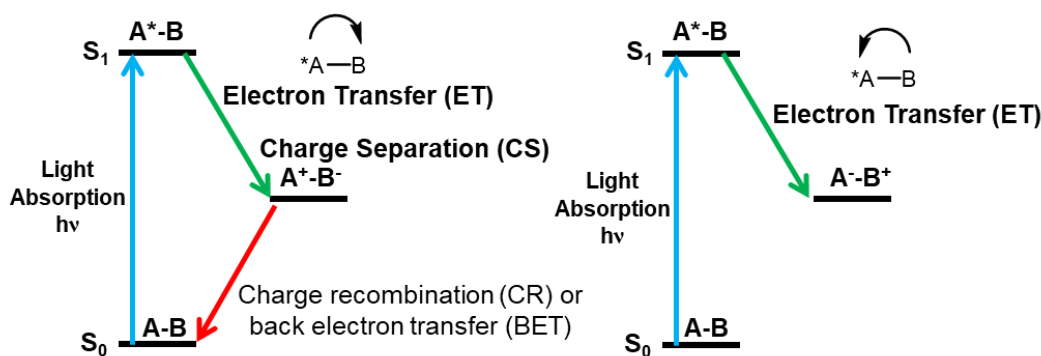
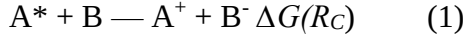


Figure 1.13 Charge transport dynamics in a donor-acceptor system (D-A) are shown schematically. Reproduced from⁹³

Both processes finally deliver an electron to a higher energy level at its previous location. When dealing with semiconductors, what is commonly called a charge-separated electron-hole pair. The reaction free energy (ΔG°) determines the rate of

electron transfer.⁹⁴ When an excited donor particle (D^*) and a ground-state acceptor particle are separated by R_C , the free-energy change for photoinduced electron transfer (1) is expressed as $\Delta G(R_C)$.



The Rehm-Weller and Marcus equations help estimate the formation of free energy⁹⁴ and predict the feasibility of electron transfer.

$$\Delta G_{et}^0 = E_{ox} - E_{RED} - E_{00} + C \quad (2)$$

Where E_{00} is the zero-zero transition energy, E_{ox} is the donor's oxidation potential, and E_{RED} is the acceptor reduction potential. Considering the solvent reorganization energy for the charge transfer state, the ΔG_{et}^0 can approximate employing the Marcus equation.

$$\Delta G_{et}^0 = E_{ox} - E_{RED} - E_{00} + e^2/2 \left(1/r_A + 1/r_D - 2/R_{cc} \right) \left(1/\epsilon_T - 1/\epsilon_{REF} \right) - e^2/\epsilon_{REF} R_{cc} \quad (3)$$

Where r_A is the effective radius of the donor, and r_D is the effective radius of an acceptor. ϵ_T and ϵ_{REF} are the dielectric constant of the solvent and reference solvent, respectively. R_{cc} is the center-to-center distance between the donor and acceptor. The negative ΔG_{et}^0 value indicates whether the PET is feasible or not.

1.6.1 Photoinduced electron transfer from halide perovskites

Perovskite QDs (PQDs), nanocrystals, and perovskite materials films show promise for solar cells. The efficiency of solar cell charge separation is impacted by variations in photoinduced electron transfer (PET) rates. Perovskite samples doped with electron donors or acceptors facilitate PET analysis and the effective harvesting of charge carriers. PET has hence created considerable interest in the donor-acceptor systems based on perovskites. The highly negative Gibbs energy changes of PET were theoretically calculated using the size of the donor-acceptor, redox potentials, and solvent dielectric constant. PET's dynamic nature is evidenced by a fall in the fluorescence, fluorescence (PL) lifetimes, and PL photocounts of donors as acceptor concentrations grow.⁹⁵ Because of their high absorption coefficients in the solar spectrum region, wide and adjustable PL color, long-range charge carrier diffusion, superior defect tolerance, and high PLQYs, halide perovskite QDs are appealing for use in optoelectronic technologies.^{76,90,96–98} The charge carrier extraction efficiency in perovskite-based solar cells improves power conversion efficiency. A variety of electron acceptors was used in the PET system,

including SnO_2 , (PCBM- C_{60}), TiO_2 , fullerene (C_{60}), and 7,7,8,8-tetracyanoquinodimethane (TCNQ) And 1,2,4,5-tetracyanobenzene (TCNB),^{95,99–103} Because of possible uses in solar cell technology, charge transport investigations is important in electron donor-acceptor (D-A) systems and recently gained a lot of attention. For instance, Jeong et al. observed that TCNQ was used as an electron acceptor in the experiment and PET was transferred quickly from the donor (electrode) to TCNQ. PET from the electrode to TCNQ and employed TCNQ as an electron scavenger in photoelectrochemical investigations.¹⁰⁴ Additionally, sandwiched multiple graphene/TCNQ electrodes were developed by Hsu et al. for photovoltaics, in which two graphene layers are connected by TCNQ molecules.¹⁰⁵ TCNQ's strong electron affinity contributed to its high PCE. In another group Wu and his colleagues demonstrated effective charge separation was found from perovskite materials to acceptors (phenothiazine and benzoquinone).¹⁰⁶ In a recent investigation, Long and associates claimed great efficiency for a PSC employing TiO_2 as the electron acceptor and showed quick interfacial charge separation.¹⁰⁷ In this case, the perovskite TiO_2 interface has a fast electron injection rate. This work provides a tiny time-domain account of interfacial electron transmission through simulation. Yang and associates used fullerene derivatives, including PCBM, as an electron transport layer in an inverted perovskite solar cell to achieve a power conversion efficiency (PCE) of 20.6%.¹⁰⁸ These PNC electron transfer systems were created with heterostructures and the distribution of D-A heterojunctions should be used to choose the best design.¹⁰⁹ The charge mobility at interfaces is shown by both the PL lifetime and transient absorption (TA) measurements when electron- and hole-accepting materials are present.⁸⁸ However, photogeneration, transfer of electrons, and distance-dependent movement in these junctions remain complex and need further investigation. Our lab team demonstrated how C_{60} affected the PL of the FAPbBr_3 PNCs film.¹¹⁰ It shows how moving carriers in PNC films are channeled into C_{60} . They discovered that interfacial electron transport in PNC-based D-A junctions is both diffusion-controlled and distance-dependent (Figure 1.14).

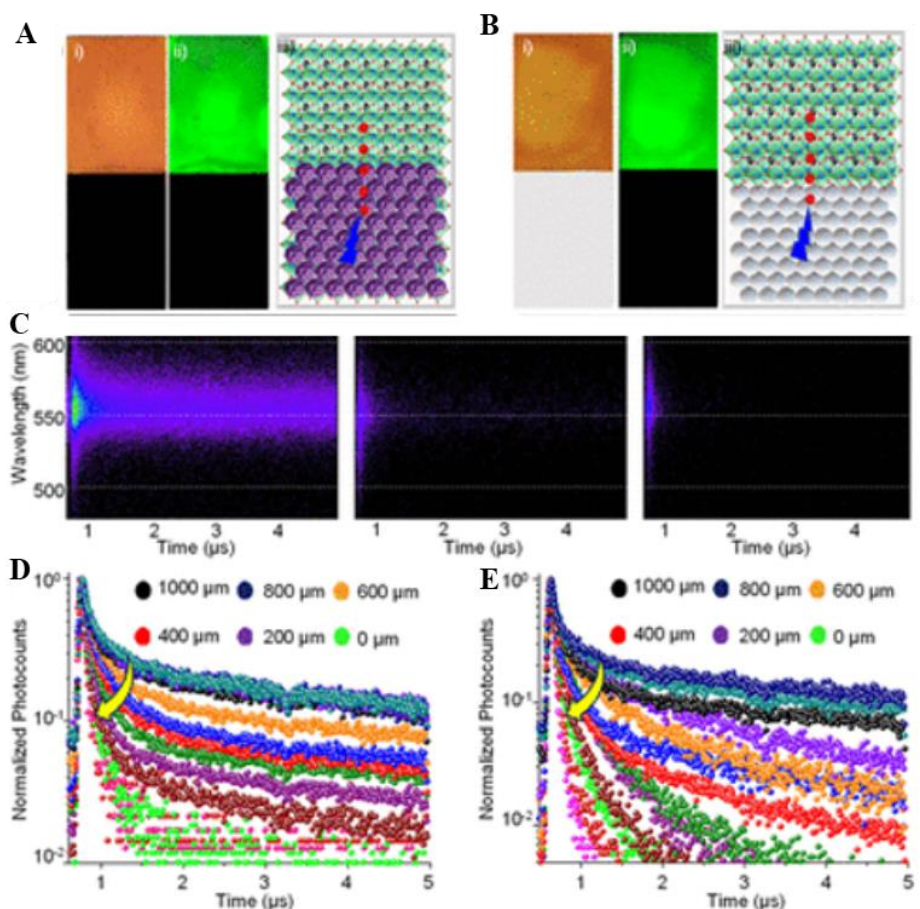


Figure 1.14 PL lifetime of donor-acceptor films based on distance. (A, B) Photographs and schematics of PNC films containing (A) FAPbBr₃:C₆₀ or (B) FAPbBr₃:TiO₂ interfaces under (i) room light and (ii) UV light. Photocount maps of FAPbBr₃:C₆₀/TiO₂ films were acquired at 1000 μm, 0 μm, and 0 μm from the FAPbBr₃:C₆₀ interface, respectively. Figures (D, E) show that The PL decay patterns of FAPbBr₃:C₆₀/TiO₂ films were explored from 1000 to -200 μm from the PNC.C₆₀ and PNC-TiO₂ interfaces.¹¹⁰

Most perovskite-based optoelectronic devices are not able to realize effective electron transfer because of many challenges from intrinsic properties of perovskite materials, interactions with adjacent layers, and structural quality of the films themselves often prohibit such processes. Such reductions in efficiency and stability make the elucidation of the underlying issues highly critical. One of the main issues is trap states, which are generated by defects in the perovskite crystal lattice. Such defects can occur in a few different forms, including interstitial atoms, vacancies, and grain boundaries. The trap states capture the charge carriers before they are effectively collected or utilized, causing

nonradiative recombination losses. This fact drastically reduces the overall efficiency of the device. The defects are particularly concentrated on the surfaces of perovskite films, where they act as recombination centers and inhibit electron extraction. These surface defects are more pronounced in polycrystalline films because of grain boundaries that introduce additional recombination sites or barriers to charge carrier movement. The most general polycrystalline perovskite films, obtained through device fabrication, are full of grain boundaries. Such grain boundaries disrupt electron transport by acting as recombination sites or as physical barriers to carrier transport. Further complications in charge transfer arise due to the presence of nonuniform grain sizes, originating from poorly controlled crystallization upon film deposition. The larger grains allow better pathways for charge carriers, while smaller ones increase the chances of recombination, thus leading to efficiency losses. That also depends on the proper alignment of energy levels between the conduction band of the perovskite material and that of the electron transport layer. Poorly matched energy levels create barriers for electron injection into the ETL, reducing efficiency in charge extraction. Such mismatches result in increased recombination and energy losses, hence reducing device performance. Poor contact with the ETL arising from nonuniform perovskite films introduces resistive losses and localized charge accumulation. This can be further propagated inhomogeneously, perhaps leading to the enhancement of recombination and, consequently, overall efficiency degradation. A uniform thickness and consistent morphology of grains are thus a very important property that has to be ensured for achieving efficient charge transport and minimal loss.

1.6.2 Photoinduced electron transfer from chalcogenide quantum dots

Because of their excellent photoemission properties and multifunctionality, chalcogenide QDs have attracted enormous attention in modern nanotechnology. Serving as photoelectrical conversion sources after optical excitation, these QDs may be useful in providing an avenue toward the development of advanced optoelectronic and photovoltaic systems. Upon light excitation, QDs form excitons, which are electron-hole pairs bound through Coulombic attraction.^{111,112} Eventually, the electron-hole pairs can be separated (Figure 1.15), which enables the newly created charge carriers to leave the nanoparticle and interact with the environment. Inorganic QDs during their synthesis and

subsequent processing are invariably coated with organic ligands to maintain colloidal stability. The nature of these surface ligands has a crucial role in modulating charge generation and its separation within the nanoparticles. The surface modifications may include secondary charge transfer pathways, charge carrier generation rates, and electron-hole recombination processes, whether radiative or nonradiative. All these factors together govern the photophysical behavior of QDs, which has implications in its applications like photovoltaics, photocatalysis, bioanalysis, LEDs, and QD-based cellular automata.

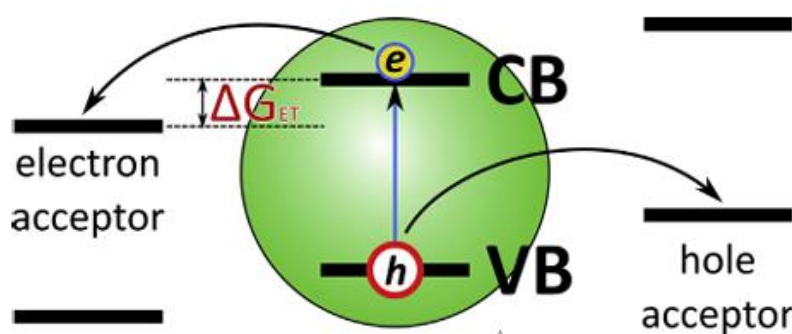


Figure 1.15 A schematic illustration of photo-induced charge transfer between a QD and charge acceptors is presented. Valence bands are denoted by VB and conduction bands by CB.¹¹³

Such an alignment is favorable for electron transfer when the energy level of the ligand's lowest unoccupied molecular orbital is at or lower than that of the QD core's CB edge. In this energetic configuration, photoexcitation would provide an electron in the conduction band of the QD with enough driving force to move onto the LUMO of the ligand acting as an electron acceptor. Various types of compounds, such as ethylene blue¹¹⁴ Rhodamine B (RhB)¹¹⁵ anthraquinone dyes¹¹⁶, viologen derivatives¹¹⁷, organometallic complexes of transition metals¹¹⁸ functionalized fullerenes¹¹⁹, carbon nanotubes¹²⁰, etc. The most relevant kinds of probe molecules for researching charge transfer on QD surfaces using optical spectroscopic methods.

To investigate how the gap between the electron acceptor and the QD affects the electron transfer rate put CdSe QDs in a poly viologen matrix with a native ligand of HS single bond(CH₂) single bondCOOH (n = 1, 2, 5, 7, 10, or 15). The acceptor moieties cannot be PET-active because they are not in direct contact with QDs, unlike isolated

viologen molecules. Very fast PET was seen when QDs were coated with mercapto carboxylic acid ligands with methylene groups varying from 1 to 7 dispersed in a polyviologen matrix. PET rates were substantially greater than those for PDDA and QDs. Compared to QDs with short ligands, the PET rate of longer-chain QDs ($n = 12-15$) was much lower. According to the donor and acceptor's energy level positions and ligand length, an interesting case of electron transfer has been published. The study looked at CdSe and CdTe QD assemblies that were produced in a liquid state by electrostatic relations among surface ligands' external polar groups. The interparticle distance, QD band alignment, and the direction of the applied electric field all have great effects on the PL quenching of CdTe QDs, which pointed out that the nonradiative relaxation pathway was introduced due to electron transfer. By simultaneously flipping the surface charges of naturally negatively charged CdTe and positively charged CdSe QDs, the researchers were able to show that PL quenching due to charge transfer could be avoided. This charge flipping is necessary because the electric field between the particles can no longer affect the CdTe QDs, thereby distinguishing quenching due to energy transfer from quenching affected by charge transfer. In core/shell QDs, shell thickness often becomes a determining factor for electron transfer rates. Recently, a system of CdSe/CdS QDs of variable shell thickness was studied by Dworak et al., in the presence of viologen as the electron acceptor. In the absence of viologen, their transient absorption spectra exhibited no variation in the bleach recovery rate as a function of shell thickness. However, in the case of adding viologen, it proved that the bleach recovery rate significantly decreased with the rise in shell thickness. This result thus indicates that the thicker the shell, the more the electron transfer to the viologen acceptor is hindered, reducing the efficiency of charge transfer. The variation of electron transfer rates with shell thickness underlines the structural and materials considerations involved in the design of QD-based systems for optoelectronic applications. Such systems can take advantage of interparticle interaction engineering, band alignment, and surface charge modification to optimize performance in energy harvesting and sensing, among other nanotechnological applications.

Nowadays, one of the most important alternative technologies for the energy transition to green energy is the solar cell. Solar cells stand today as one of the major contributors to green energy globally. Of the many different solar technologies under development, QDSCs are emerging as one of the most exciting approaches due to their exceptional

optical and electronic properties. Among the first studies on the perspectives of QDSCs were Robel et al., in whose work the basics of further development in this area were laid. In their work, Robel et al. used bifunctional linker molecules HOOC-R-SH (where R could be C1, C2, or C15) and successfully attached ≈ 3 nm CdSe QDs onto dispersed TiO_2 nanoparticles. These linker molecules were important in providing the chemical bridge that enabled strong binding of CdSe QDs onto the surface of TiO_2 , hence allowing efficient electronic coupling of QDs with the semiconductor substrate. This attachment is important in enabling effective electron injection from the photoexcited QDs into the conduction band of TiO_2 , a quintessential operation of QDSCs. Their new approach emphasized the optimization of the QD interface. The researchers, by using strong and stable interconnections with bifunctional linkers, were able to ensure that improved charge transfer was ensured, minimizing recombination losses that are critical for the enhancement of QDSC efficiency. In addition to advances in CdSe QDs, several advances in PbS-based solar cells are also impressive. Recently, surface modification of PbS QDs has emerged as an effective way to enhance the photovoltaic properties of PbS QDs. The approaches adopted for the optimization of the electronic properties of PbS QDs involve ligand exchange and surface passivation that enhance the stability, charge transportability, and light absorption properties. Such modifications reduce the amount of surface defects often acting as recombination centers and hence enhance the efficiency of PbS-based QDSCs.¹²¹ The power conversion efficiency of the cells made using solely PbS QDs treated with TBAI was 6%. However, the power conversion efficiency increased by about 35% (8.2%) when PbS-EDT was used in place of the uppermost QD layers. Band offsets existing between two layers of differently surface-capped PbS QDs have been used to improve the performance of PbS QDSC. These band offsets served a vital function in this device architecture: one, they allowed only a very few charge carriers to migrate, and two, while electrons were stopped from transportation to the anode, it allowed better extraction of holes. This strategic control of the charge carrier dynamics reduced recombination losses, thereby improving charge separation and boosting the overall device efficiency. Ehrler et al. further investigate the influence of QD surface trap states on QDSC performance. The investigated system was PbSe and PbS QD depletion heterojunction solar cells. The trap states arise from defects or unpassivated dangling bonds on the QD surface and have been known to act as recombination centers for the photogenerated

carriers. Such states have a strong adverse impact on the efficiency of QDSCs by lowering the lifetime and mobility of charge carriers. Ehrler et al. reported that in their study, surface trap states dominated device performance and that different materials had different effects on device performance. Experimentally, it was shown that PbSe-based devices yielded a threefold higher PCE of about 3% than PbS-based devices.¹²² This was ascribed to the lower trap state density in PbSe QDs than in PbS QDs and the more effective passivation strategy employed for PbSe surfaces. The study analyzed PbSe and PbS-based depletion heterojunction solar cells, finding PbSe-based devices had a threefold higher power conversion efficiency of around 3%.

PET efficiency is influenced by surface ligands, surface traps, energy band alignment, and the distance between the QD and quencher. The dispersed, isolated QDs have no electronic coupling between individual QDs. Charge carriers are confined within individual QDs and limited carrier mobility due to isolation results in less PET. Recent studies by G. Rana. et. al. examined the effect of Cu(I) doping on the PET from aqueous CdS QDs to methyl viologen (MV^{2+}). Due to hole entrapment by the dopant ion, Cu(I) doping breaks electron-hole correlation, which results in a much higher effectiveness of PL quenching by MV^{2+} in doped QDs than in undoped ones, according to the study.¹²³ Faster electron transport for the doped QDs was validated by ultrafast transient absorption measurements.

In assembled QDs, inter-QD electronic coupling enables charge transport across the assembly. PET efficiency increases when excitons or free carriers diffuse to the QD-quencher interface. In large assemblies, collective effects provide improved charge separation. In QD-assembled films (such as CdS or PbS on TiO_2) electrons transfer efficiently from the QD CB to the TiO_2 CB, facilitating photocatalytic processes.¹²⁴

1.7 Applications

QDs are finding applications in various advanced technologies, including LEDs, solar cells, and PeLEDs, because of their outstanding optoelectronic properties. The excellent color purity from the narrow emission bands of QDs makes their colors highly accurate and very suitable for displays and lighting applications. Moreover, QDs can exhibit high PLQY, which means that QDs can re-emit an exceptionally high proportion of their

absorbed light as visible photons, due to which QDs become efficient and highly functional for optoelectronic devices. Perovskite-based solar cells, on the other hand, have attracted lots of recent interest in power conversion efficiency regarded as remarkable, together with scalable methods of fabrication. QDs, while bringing in complementary attributes related to the advance of technology on solar cells. With their adjustable bandgap, controlled with high fineness by the size and composition of the QDs, it enables QDs to have huge potential as light-absorbing materials. This tunability could potentially enable QDs to become effective absorbers in specific regions of the solar spectrum while providing good overlap with sunlight to maximize captured energy. Their wide absorption spectra also allow QDs to absorb light in a wide range of wavelengths. This capability, to further improve solar cell efficiency, enables devices to harvest larger portions of the sun's energy. To date, incorporating QDs into solar cells has empowered researchers to design multi-junction or tandem devices in which QDs are employed for high-energy photon absorption and other materials are utilized toward the capture of low-energy photons. This can achieve a huge improvement in energy conversion efficiency synergistically and therefore will pave the way to next-generation solar technologies. In PeLEDs, QDs allow for adequate charge carrier injection and well-balanced recombination-introducing high brightness and stability. Their ability to integrate well with perovskite material has led to the development of novel device architectures that combine their strengths. This opens the way toward high-performance devices from displays to efficient light sources.

The tunable bandgap, high PLQY, and wide absorption spectrum of QD materials make them a keystone in the next wave of optoelectronic development. Their incorporation in solar cells and PeLEDs represents a promising route to more efficient, durable, and cost-effective renewable energy and lighting solutions. It is generally accepted that PSCs fall into one of two types: p-i-n-i or n-i-p-i. The electron transport layer (ETL) and perovskites layer (HTL) enhance the transport and charge extraction capacities in both configurations. The HTL is in contact with either fluorene-doped tin oxide (FTO) or indium tin oxide (ITO), whereas the HTL is in contact with a counter electrode like Au, Ag, Cu, etc. An external load is linked to these electrodes. The figure shows the structure of a model of a solar cell. The transport layers HTL or ETL collect electron and hole carriers produced by the perovskite absorption layer upon irradiation.

Therefore, a key factor in determining PSC performance is the deployment of an appropriate charge transport layer. HTLs like 2,20,7,70-terakis-(N, N-dimethoxyphenylamino)-9,90-spirobifluorene (spiro-MeOTAD) and polystyrene sulfonate (PEDOT:PSS) are commonly used, as are a variety of ETLs like TiO_2 , SnO_2 , and ZnO . (Figure 1.16).

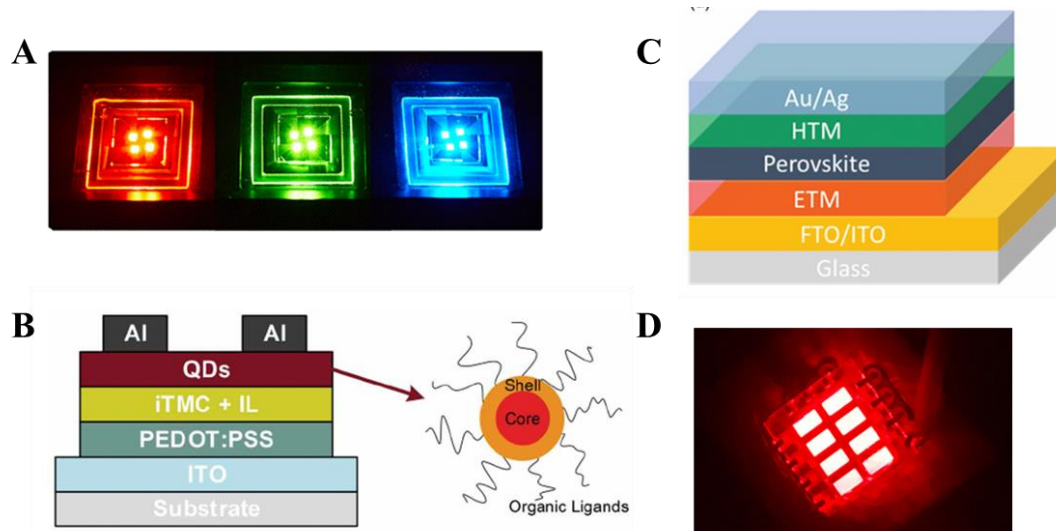


Figure 1.16 (A, B) QD-based LEDs and solar cells, (B, D) Perovskite-based solar cells and LEDs. Reported from (A) Jang and Jang et al.¹²⁵ (B) Sukharevskaya et al.¹²⁶ (C) Cui et al.¹²⁷ (D) Yang et al.¹²⁸

The lower empty molecular orbital of the ETL should be lower than CBM and the higher occupied molecular orbital should be higher than VBM for an energetically stable PSC. The most basic and important component for high-efficiency PSC, aside from the charge transporting layers, is the crystal quality. A reduction in carrier lifetime and mobility can result from shallow or deep charge traps caused by imperfections in perovskite thin films or single crystals. The stability of perovskite layers and their inherent crystal characteristics are also greatly impacted by several variables, including heat, light, oxygen, and moisture. The single-junction PSC power conversion efficiency is 26.5%, and the perovskite/Si multi-junction PSC power conversion efficiency is 29.5%, despite these limitations.¹²⁹

1.8 Research motivation and objectives

Luminescent semiconductor nanoparticles, such as chalcogenide QDs and PNCs, have shown great promise as materials for optoelectronic applications of the future. Their exceptional qualities, which make them appropriate for a variety of cutting-edge technologies, include excellent luminescence QYs, adjustable emission wavelengths of light, solution processability, and superior photostability. While the behavior and properties of individual nanocrystals are by now relatively well understood, their controlled assembly into functional structures containing nanoparticles remains a big challenge. This challenge, when responded to, may open up new opportunities both in device fabrication and performance enhancement.

This thesis focuses on three key aspects of PNC assemblies and electron transfer to provide insight into how to design and optimize PNC-based systems:

In Chapter 3, The formation and properties of PNC assemblies both in solution and as a film are discussed. Their interactions with a variety of electron acceptors are analyzed to understand the basic principles underlying charge transfer kinetics within the assemblies. In particular, the influence of the dense packing of the PNCs on the rates and efficiencies of electron transfers is studied. The results of this work will give an overview of the design for advanced perovskite-based optoelectronic devices.

In Chapter 4, Herein, a new approach is developed to achieve well-dispersed assemblies of CdSe/CdS QDs by using molecular cross-linkers. The precision in this assembly methodology allows for detailed investigation into the photoinduced electron transfer processes and gives insights into the crucial relationship between structural organization in QDs and electron transfer efficiency. This chapter develops guiding principles in designing QD assemblies with properties tailored for specific optoelectronic applications by linking assembly structure to charge transport properties.

In Chapter 5, a bio-inspired method is presented for assembling water-soluble QDs into mesoscopic structures using trypsin, a proteolytic enzyme. This assembly technique enhances the proximity between QDs and electron acceptor molecules, leading to a notable improvement in electron transfer efficiency. Such collective behavior is absent in isolated QDs, highlighting the significance of mesoscopic assembly design in boosting functional performance.

These focused studies aim at establishing the basic design principles of the controlled formation of nanocrystal assemblies and at elucidating how assembly architectures influence electron transfer processes. This work contributes to an improved understanding and expanded practical use of nanocrystals in next-generation optoelectronic systems by addressing these basic questions. The insights gained will enable the development of new technologies, closing the gap between nanoscale materials and functional device applications.

References

- (1) Sobhanan, J.; Rival, J. V.; Anas, A.; Sidharth Shibu, E.; Takano, Y.; Biju, V. Luminescent Quantum Dots: Synthesis, Optical Properties, Bioimaging and Toxicity. *Adv. Drug Deliv. Rev.* **2023**, *197*, 114830. <https://doi.org/10.1016/j.addr.2023.114830>.
- (2) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor Nanocrystals as Fluorescent Biological Labels. *Science (80-.)*. **1998**, *281* (5385), 2013–2016. <https://doi.org/10.1126/science.281.5385.2013>.
- (3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706–8715. <https://doi.org/10.1021/ja00072a025>.
- (4) Mo, D.; Hu, L.; Zeng, G.; Chen, G.; Wan, J.; Yu, Z.; Huang, Z.; He, K.; Zhang, C.; Cheng, M. Cadmium-Containing Quantum Dots: Properties, Applications, and Toxicity. *Appl. Microbiol. Biotechnol.* **2017**, *101* (7), 2713–2733. <https://doi.org/10.1007/s00253-017-8140-9>.
- (5) Vasudevan, D.; Gaddam, R. R.; Trinchì, A.; Cole, I. Core–Shell Quantum Dots: Properties and Applications. *J. Alloys Compd.* **2015**, *636*, 395–404. <https://doi.org/10.1016/j.jallcom.2015.02.102>.
- (6) Ratnesh, R. K.; Mehata, M. S. Synthesis and Optical Properties of Core-Multi-Shell CdSe/CdS/ZnS Quantum Dots: Surface Modifications. *Opt. Mater. (Amst)*. **2017**, *64*, 250–256. <https://doi.org/10.1016/j.optmat.2016.11.043>.
- (7) Katz, E. A. Perovskite: Name Puzzle and German-Russian Odyssey of Discovery. *Helv. Chim. Acta* **2020**, *103* (6). <https://doi.org/10.1002/hlca.202000061>.
- (8) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10), 2869–2885. <https://doi.org/10.1039/c9cs00848a>.
- (9) File:///D:/Users/BijuLabo-Dell1/Downloads/1-s2.0-S1364032115007807-main.pdf;file:///D:/Users/BijuLabo-Dell1/Downloads/1-s2.0-S1364032115007807-main.pdf. Recent Advances in Lead-Free;file:///D:/Users/BijuLabo-Dell1/Downloads/1-S2.0-S1364032115007807-Main.Pdf Halide Perovskites: From Synthesis to Applications. *J. Mater. Chem. C* **2024**, *12* (28), 10267–10329. <https://doi.org/10.1039/D4TC01556H>.
- (10) Surana, K.; Mehra, R. M.; Bhattacharya, B.; Rhee, H.-W.; Polu, A. R.; Singh, P. K. A Comprehensive Study of Chalcogenide Quantum Dot Sensitized Solar Cells with a New Solar Cell Exceeding 1 V Output. *Renew. Sustain. Energy Rev.* **2015**, *52*, 1083–1092. <https://doi.org/10.1016/j.rser.2015.07.133>.
- (11) Sahu, A.; Kumar, D. Core-Shell Quantum Dots: A Review on Classification, Materials, Application, and Theoretical Modeling. *J. Alloys Compd.* **2022**, *924*, 166508. <https://doi.org/10.1016/j.jallcom.2022.166508>.
- (12) Todescato, F.; Fortunati, I.; Minotto, A.; Signorini, R.; Jasieniak, J.; Bozio, R. Engineering of Semiconductor Nanocrystals for Light Emitting Applications. *Materials (Basel)*. **2016**, *9* (8), 672. <https://doi.org/10.3390/ma9080672>.
- (13) Kleinert, H.; Chervyakov, A.; Hamprecht, B. Perturbation Theory for Particle in a Box. *Phys. Lett. A* **1999**, *260* (3–4), 182–189. [https://doi.org/10.1016/S0375-9601\(99\)00541-1](https://doi.org/10.1016/S0375-9601(99)00541-1).
- (14) Brus, L. E. Electron–Electron and Electron–Hole Interactions in Small

- Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80* (9), 4403–4409. <https://doi.org/10.1063/1.447218>.
- (15) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706–8715. <https://doi.org/10.1021/ja00072a025>.
 - (16) Efros, A. L.; Efros, A. L. Interband Light Absorption in Semiconductor Spheres. *Sov. Phys. Semicond.* **1982**, *16* (7), 772–775. [https://doi.org/10.1016/0038-0136\(82\)90072-5](https://doi.org/10.1016/0038-0136(82)90072-5).
 - (17) Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* (80-.). **1996**, *271* (5251), 933–937. <https://doi.org/10.1126/science.271.5251.933>.
 - (18) Peng, Z. A.; Peng, X. Formation of High-Quality CdTe, CdSe, and CdS Nanocrystals Using CdO as Precursor. *J. Am. Chem. Soc.* **2001**, *123* (1), 183–184. <https://doi.org/10.1021/ja003633m>.
 - (19) Protesescu, L.; Yakunin, S.; I. Bodnarchuk, M.; Krieg, F.; Caputo, R.; H. Hendon, C.; Xi Yang, R.; Walsh, A.; V. Kovalenko, M. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
 - (20) Becker, M. A.; Vaxenburg, R.; Nedelcu, G.; Serce, P. C.; Shabaev, A.; Mehl, M. J.; Michopoulos, J. G.; Lambrakos, S. G.; Bernstein, N.; Lyons, J. L.; Stöferle, T.; Mahrt, R. F.; Kovalenko, M. V.; Norris, D. J.; Rainò, G.; Efros, A. L. Bright Triplet Excitons in Cesium Lead Halide Perovskites. *Nature* **2018**, *553* (7687), 189–193. <https://doi.org/10.1038/nature25147>.
 - (21) Zhang, F.; Zhong, H.; Chen, C.; Wu, X.; Hu, X.; Huang, H.; Han, J.; Zou, B.; Dong, Y. Brightly Luminescent and Color-Tunable Colloidal CH₃NH₃PbX₃ (X = Br, I, Cl) Quantum Dots: Potential Alternatives for Display Technology. *ACS Nano* **2015**, *9* (4), 4533–4542. <https://doi.org/10.1021/acs.nano.5b01154>.
 - (22) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. *Science* (80-.). **2017**, *358* (6364), 745–750. <https://doi.org/10.1126/science.aam7093>.
 - (23) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10), 2869–2885. <https://doi.org/10.1039/c9cs00848a>.
 - (24) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, *119* (5), 3296–3348. <https://doi.org/10.1021/acs.chemrev.8b00644>.
 - (25) Schulz, P. Interface Design for Metal Halide Perovskite Solar Cells. *ACS Energy Lett.* **2018**, *3* (6), 1287–1293. <https://doi.org/10.1021/acsenergylett.8b00404>.
 - (26) Lignos, I.; Stavrakis, S.; Nedelcu, G.; Protesescu, L.; DeMello, A. J.; Kovalenko, M. V. Synthesis of Cesium Lead Halide Perovskite Nanocrystals in a Droplet-Based Microfluidic Platform: Fast Parametric Space Mapping. *Nano Lett.* **2016**, *16* (3), 1869–1877. <https://doi.org/10.1021/acs.nanolett.5b04981>.
 - (27) Udayabhaskararao, T.; Kazes, M.; Houben, L.; Lin, H.; Oron, D. Nucleation, Growth, and Structural Transformations of Perovskite Nanocrystals. *Chem. Mater.* **2017**, *29* (3), 1302–1308. <https://doi.org/10.1021/acs.chemmater.6b04841>.

- (28) Litvin, A. P.; Zhang, X.; Berwick, K.; Fedorov, A. V.; Zheng, W.; Baranov, A. V. Carbon-Based Interlayers in Perovskite Solar Cells. *Renew. Sustain. Energy Rev.* **2020**, *124* (September 2019), 109774. <https://doi.org/10.1016/j.rser.2020.109774>.
- (29) Gil-Escrig, L.; Dreessen, C.; Palazon, F.; Hawash, Z.; Moons, E.; Albrecht, S.; Sessolo, M.; Bolink, H. J. Efficient Wide-Bandgap Mixed-Cation and Mixed-Halide Perovskite Solar Cells by Vacuum Deposition. *ACS Energy Lett.* **2021**, *6* (2), 827–836. <https://doi.org/10.1021/acsenenergylett.0c02445>.
- (30) Li, Y.; Wu, F.; Han, M.; Li, Z.; Zhu, L.; Li, Z. Merocyanine with Hole-Transporting Ability and Efficient Defect Passivation Effect for Perovskite Solar Cells. *ACS Energy Lett.* **2021**, *6* (3), 869–876. <https://doi.org/10.1021/acsenenergylett.1c00124>.
- (31) Miyata, A.; Mitoglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J. Direct Measurement of the Exciton Binding Energy and Effective Masses for Charge Carriers in Organic–Inorganic Tri-Halide Perovskites. *Nat. Phys.* **2015**, *11* (7), 582–587. <https://doi.org/10.1038/nphys3357>.
- (32) K. R., P.; Acharya, D.; Jain, P.; Gahlot, K.; Yadav, A.; Camellini, A.; Zavelani-Rossi, M.; Cerullo, G.; Narayana, C.; Narasimhan, S.; Viswanatha, R. Harvesting Delayed Fluorescence in Perovskite Nanocrystals Using Spin-Forbidden Mn d States. *ACS Energy Lett.* **2020**, *5* (2), 353–359. <https://doi.org/10.1021/acsenenergylett.9b02399>.
- (33) Zhai, Y.; Wang, K.; Zhang, F.; Xiao, C.; Rose, A. H.; Zhu, K.; Beard, M. C. Individual Electron and Hole Mobilities in Lead-Halide Perovskites Revealed by Noncontact Methods. *ACS Energy Lett.* **2020**, *5* (1), 47–55. <https://doi.org/10.1021/acsenenergylett.9b02310>.
- (34) Qiao, T.; Son, D. H. Synthesis and Properties of Strongly Quantum-Confined Cesium Lead Halide Perovskite Nanocrystals. *Acc. Chem. Res.* **2021**, *54* (6), 1399–1408. <https://doi.org/10.1021/acs.accounts.0c00706>.
- (35) Bhatia, H.; Steele, J. A.; Martin, C.; Keshavarz, M.; Solis-Fernandez, G.; Yuan, H.; Fleury, G.; Huang, H.; Dovgaliuk, I.; Chernyshov, D.; Hendrix, J.; Roeflaers, M. B. J.; Hofkens, J.; Debroye, E. Single-Step Synthesis of Dual Phase Bright Blue-Green Emitting Lead Halide Perovskite Nanocrystal Thin Films. *Chem. Mater.* **2019**, *31* (17), 6824–6832. <https://doi.org/10.1021/acs.chemmater.9b01277>.
- (36) Amendola, V.; Meneghetti, M. Laser Ablation Synthesis in Solution and Size Manipulation of Noble Metal Nanoparticles. *Phys. Chem. Chem. Phys.* **2009**, *11* (20), 3805. <https://doi.org/10.1039/b900654k>.
- (37) Hulteen, J. C.; Treichel, D. A.; Smith, M. T.; Duval, M. L.; Jensen, T. R.; Van Duyne, R. P. Nanosphere Lithography: Size-Tunable Silver Nanoparticle and Surface Cluster Arrays. *J. Phys. Chem. B* **1999**, *103* (19), 3854–3863. <https://doi.org/10.1021/jp9904771>.
- (38) Liversidge, G. G.; Cundy, K. C. Particle Size Reduction for Improvement of Oral Bioavailability of Hydrophobic Drugs: I. Absolute Oral Bioavailability of Nanocrystalline Danazol in Beagle Dogs. *Int. J. Pharm.* **1995**, *125* (1), 91–97. [https://doi.org/10.1016/0378-5173\(95\)00122-Y](https://doi.org/10.1016/0378-5173(95)00122-Y).
- (39) Merisko-Liversidge, E.; Liversidge, G. G.; Cooper, E. R. Nanosizing: A Formulation Approach for Poorly-Water-Soluble Compounds. *Eur. J. Pharm. Sci.* **2003**, *18* (2), 113–120. [https://doi.org/10.1016/S0928-0987\(02\)00251-8](https://doi.org/10.1016/S0928-0987(02)00251-8).
- (40) Chrissafis, K.; Bikiaris, D. Can Nanoparticles Really Enhance Thermal Stability

- of Polymers? Part I: An Overview on Thermal Decomposition of Addition Polymers. *Thermochim. Acta* **2011**, 523 (1–2), 1–24. <https://doi.org/10.1016/j.tca.2011.06.010>.
- (41) Valizadeh, A.; Mikaeili, H.; Samiei, M.; Farkhani, S. M.; Zarghami, N.; Kouhi, M.; Akbarzadeh, A.; Davaran, S. Quantum Dots: Synthesis, Bioapplications, and Toxicity. *Nanoscale Res. Lett.* **2012**, 7 (1), 480. <https://doi.org/10.1186/1556-276X-7-480>.
 - (42) Meena, M.; Zehra, A.; Swapnil, P.; Harish; Marwal, A.; Yadav, G.; Sonigra, P. Endophytic Nanotechnology: An Approach to Study Scope and Potential Applications. *Front. Chem.* **2021**, 9 (May), 1–40. <https://doi.org/10.3389/fchem.2021.613343>.
 - (43) Qu, L.; Peng, Z. A.; Peng, X. Alternative Routes toward High Quality CdSe Nanocrystals. *Nano Lett.* **2001**, 1 (6), 333–337. <https://doi.org/10.1021/nl0155532>.
 - (44) Yu, W. W.; Peng, X. Formation of High-Quality CdS and Other II-VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chemie Int. Ed.* **2002**, 41 (13), 2368–2371. [https://doi.org/10.1002/1521-3773\(20020703\)41:13<2368::AID-ANIE2368>3.0.CO;2-G](https://doi.org/10.1002/1521-3773(20020703)41:13<2368::AID-ANIE2368>3.0.CO;2-G).
 - (45) Bullen, C. R.; Mulvaney, P. Nucleation and Growth Kinetics of CdSe Nanocrystals in Octadecene. *Nano Lett.* **2004**, 4 (12), 2303–2307. <https://doi.org/10.1021/nl0496724>.
 - (46) Abe, S.; Capek, R. K.; De Geyter, B.; Hens, Z. Reaction Chemistry/Nanocrystal Property Relations in the Hot Injection Synthesis, the Role of the Solute Solubility. *ACS Nano* **2013**, 7 (2), 943–949. <https://doi.org/10.1021/nn3059168>.
 - (47) Deng, Z.; Cao, L.; Tang, F.; Zou, B. A New Route to Zinc-Blende CdSe Nanocrystals: Mechanism and Synthesis. *J. Phys. Chem. B* **2005**, 109 (35), 16671–16675. <https://doi.org/10.1021/jp052484x>.
 - (48) Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, 15 (21), 1844–1849. <https://doi.org/10.1002/adma.200305395>.
 - (49) Acharya, K. P.; Khon, E.; O'Connor, T.; Nemitz, I.; Klinkova, A.; Khnayzer, R. S.; Anzenbacher, P.; Zamkov, M. Correction to Heteroepitaxial Growth of Colloidal Nanocrystals onto Substrate Films via Hot-Injection Routes. *ACS Nano* **2011**, 5 (11), 9299–9299. <https://doi.org/10.1021/nn204019r>.
 - (50) Henglein, A. Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. *Chem. Rev.* **1989**, 89 (8), 1861–1873. <https://doi.org/10.1021/cr00098a010>.
 - (51) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. Photochemistry of Colloidal Semiconductors. 20. Surface Modification and Stability of Strong Luminescing CdS Particles. *J. Am. Chem. Soc.* **1987**, 109 (19), 5649–5655. <https://doi.org/10.1021/ja00253a015>.
 - (52) Youn, H. C.; Baral, S.; Fendler, J. H. Dihexadecyl Phosphate, Vesicle-Stabilized and in Situ Generated Mixed Cadmium Sulfide and Zinc Sulfide Semiconductor Particles: Preparation and Utilization for Photosensitized Charge Separation and Hydrogen Generation. *J. Phys. Chem.* **1988**, 92 (22), 6320–6327. <https://doi.org/10.1021/j100333a029>.

- (53) Hoener, C. F.; Allan, K. A.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. Demonstration of a Shell-Core Structure in Layered Cadmium Selenide-Zinc Selenide Small Particles by x-Ray Photoelectron and Auger Spectroscopies. *J. Phys. Chem.* **1992**, *96* (9), 3812–3817. <https://doi.org/10.1021/j100188a045>.
- (54) Honma, I.; Sano, T.; Komiyama, H. Surface-Enhanced Raman Scattering (SERS) for Semiconductor Microcrystallites Observed in Silver-Cadmium Sulfide Hybrid Particles. *J. Phys. Chem.* **1993**, *97* (25), 6692–6695. <https://doi.org/10.1021/j100127a020>.
- (55) Zhou, H. S.; Honma, I.; Komiyama, H.; Haus, J. W. Controlled Synthesis and Quantum-Size Effect in Gold-Coated Nanoparticles. *Phys. Rev. B* **1994**, *50* (16), 12052–12056. <https://doi.org/10.1103/PhysRevB.50.12052>.
- (56) Ghosh Chaudhuri, R.; Paria, S. Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. *Chem. Rev.* **2012**, *112* (4), 2373–2433. <https://doi.org/10.1021/cr100449n>.
- (57) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. Hybrid Electronic Properties between the Molecular and Solid State Limits: Lead Sulfide and Silver Halide Crystallites. *J. Chem. Phys.* **1985**, *83* (3), 1406–1410. <https://doi.org/10.1063/1.449407>.
- (58) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. Nucleation and Growth of CdSe on ZnS Quantum Crystallite Seeds, and Vice Versa, in Inverse Micelle Media. *J. Am. Chem. Soc.* **1990**, *112* (4), 1327–1332. <https://doi.org/10.1021/ja00160a005>.
- (59) Manser, J. S.; Christians, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116* (21), 12956–13008. <https://doi.org/10.1021/acs.chemrev.6b00136>.
- (60) Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A. Electronic Structures of Lead Iodide Based Low-Dimensional Crystals. *Phys. Rev. B* **2003**, *67* (15), 155405. <https://doi.org/10.1103/PhysRevB.67.155405>.
- (61) Even, J.; Pedesseau, L.; Jancu, J.-M.; Katan, C. Importance of Spin–Orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* **2013**, *4* (17), 2999–3005. <https://doi.org/10.1021/jz401532q>.
- (62) Even, J.; Pedesseau, L.; Katan, C. Analysis of Multivalley and Multibandgap Absorption and Enhancement of Free Carriers Related to Exciton Screening in Hybrid Perovskites. *J. Phys. Chem. C* **2014**, *118* (22), 11566–11572. <https://doi.org/10.1021/jp503337a>.
- (63) Jang, D. M.; Park, K.; Kim, D. H.; Park, J.; Shojaei, F.; Kang, H. S.; Ahn, J.-P.; Lee, J. W.; Song, J. K. Reversible Halide Exchange Reaction of Organometal Trihalide Perovskite Colloidal Nanocrystals for Full-Range Band Gap Tuning. *Nano Lett.* **2015**, *15* (8), 5191–5199. <https://doi.org/10.1021/acs.nanolett.5b01430>.
- (64) Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberger, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single-Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science* (80-.). **2019**, *363* (6431), 1068–1072. <https://doi.org/10.1126/science.aau7392>.
- (65) Amat, A.; Mosconi, E.; Ronca, E.; Quarti, C.; Umari, P.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. Cation-Induced Band-Gap Tuning in Organohalide

- Perovskites: Interplay of Spin–Orbit Coupling and Octahedra Tilting. *Nano Lett.* **2014**, *14* (6), 3608–3616. <https://doi.org/10.1021/nl5012992>.
- (66) Stoumpos, C. C.; Kanatzidis, M. G. The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791–2802. <https://doi.org/10.1021/acs.accounts.5b00229>.
- (67) Im, J.; Stoumpos, C. C.; Jin, H.; Freeman, A. J.; Kanatzidis, M. G. Antagonism between Spin–Orbit Coupling and Steric Effects Causes Anomalous Band Gap Evolution in the Perovskite Photovoltaic Materials $\text{CH}_3\text{NH}_3\text{Sn}_{1-x}\text{Pb}_x\text{I}_3$. *J. Phys. Chem. Lett.* **2015**, *6* (17), 3503–3509. <https://doi.org/10.1021/acs.jpcllett.5b01738>.
- (68) Even, J.; Pedesseau, L.; Jancu, J.; Katan, C. DFT and $k \cdot p$ Modelling of the Phase Transitions of Lead and Tin Halide Perovskites for Photovoltaic Cells. *Phys. status solidi – Rapid Res. Lett.* **2014**, *8* (1), 31–35. <https://doi.org/10.1002/pssr.201308183>.
- (69) Lee, S.-W.; Kim, S.; Bae, S.; Cho, K.; Chung, T.; Mundt, L. E.; Lee, S.; Park, S.; Park, H.; Schubert, M. C.; Glunz, S. W.; Ko, Y.; Jun, Y.; Kang, Y.; Lee, H.-S.; Kim, D. UV Degradation and Recovery of Perovskite Solar Cells. *Sci. Rep.* **2016**, *6* (1), 38150. <https://doi.org/10.1038/srep38150>.
- (70) Deng, Y.; Peng, E.; Shao, Y.; Xiao, Z.; Dong, Q.; Huang, J. Scalable Fabrication of Efficient Organolead Trihalide Perovskite Solar Cells with Doctor-Bladed Active Layers. *Energy Environ. Sci.* **2015**, *8* (5), 1544–1550. <https://doi.org/10.1039/C4EE03907F>.
- (71) Milot, R. L.; Eperon, G. E.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Temperature-Dependent Charge-Carrier Dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Thin Films. *Adv. Funct. Mater.* **2015**, *25* (39), 6218–6227. <https://doi.org/10.1002/adfm.201502340>.
- (72) Whitfield, P. S.; Herron, N.; Guise, W. E.; Page, K.; Cheng, Y. Q.; Milas, I.; Crawford, M. K. Structures, Phase Transitions and Tricritical Behavior of the Hybrid Perovskite Methyl Ammonium Lead Iodide. *Sci. Rep.* **2016**, *6* (1), 35685. <https://doi.org/10.1038/srep35685>.
- (73) Wang, Y.; Lü, X.; Yang, W.; Wen, T.; Yang, L.; Ren, X.; Wang, L.; Lin, Z.; Zhao, Y. Pressure-Induced Phase Transformation, Reversible Amorphization, and Anomalous Visible Light Response in Organolead Bromide Perovskite. *J. Am. Chem. Soc.* **2015**, *137* (34), 11144–11149. <https://doi.org/10.1021/jacs.5b06346>.
- (74) Jaffe, A.; Lin, Y.; Beavers, C. M.; Voss, J.; Mao, W. L.; Karunadasa, H. I. High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybrid Perovskites and Pressure Effects on Their Electronic and Optical Properties. *ACS Cent. Sci.* **2016**, *2* (4), 201–209. <https://doi.org/10.1021/acscentsci.6b00055>.
- (75) 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. *J. Am. Chem. Soc.* **2015**, *137* (51), 16008–16011. <https://doi.org/10.1021/jacs.5b11199>.
- (76) Levchuk, I.; Osvet, A.; Tang, X.; Brandl, M.; Perea, J. D.; Hoegl, F.; Matt, G. J.; Hock, R.; Batentschuk, M.; Brabec, C. J. Brightly Luminescent and Color-Tunable Formamidinium Lead Halide Perovskite FAPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) Colloidal Nanocrystals. *Nano Lett.* **2017**, *17* (5), 2765–2770. <https://doi.org/10.1021/acs.nanolett.6b04781>.

- (77) 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* (8), 7943–7954. <https://doi.org/10.1021/acsnano.6b03863>.
- (78) Biju, V.; Itoh, T.; Ishikawa, M. Delivering Quantum Dots to Cells: Bioconjugated Quantum Dots for Targeted and Nonspecific Extracellular and Intracellular Imaging. *Chem. Soc. Rev.* **2010**, *39* (8), 3031. <https://doi.org/10.1039/b926512k>.
- (79) Hu, Y. Z.; Koch, S. W.; Peyghambarian, N. Strongly Confined Semiconductor Quantum Dots: Pair Excitations and Optical Properties. *J. Lumin.* **1996**, *70* (1–6), 185–202. [https://doi.org/10.1016/0022-2313\(96\)00054-3](https://doi.org/10.1016/0022-2313(96)00054-3).
- (80) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. The Quantum Mechanics of Larger Semiconductor Clusters (“Quantum Dots”). *Annu. Rev. Phys. Chem.* **1990**, *41* (1), 477–496. <https://doi.org/10.1146/annurev.pc.41.100190.002401>.
- (81) Bajorowicz, B.; Kobylański, M. P.; Gołębiewska, A.; Nadolna, J.; Zaleska-Medynska, A.; Malankowska, A. Quantum Dot-Decorated Semiconductor Micro- and Nanoparticles: A Review of Their Synthesis, Characterization and Application in Photocatalysis. *Adv. Colloid Interface Sci.* **2018**, *256*, 352–372. <https://doi.org/10.1016/j.cis.2018.02.003>.
- (82) Ma, Y.; Zhang, Y.; Yu, W. W. Near Infrared Emitting Quantum Dots: Synthesis, Luminescence Properties and Applications. *J. Mater. Chem. C* **2019**, *7* (44), 13662–13679. <https://doi.org/10.1039/C9TC04065J>.
- (83) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe and CdS Nanocrystals. *Chem. Mater.* **2004**, *16* (3), 560–560. <https://doi.org/10.1021/cm033007z>.
- (84) Rosenthal, S. J.; Chang, J. C.; Kovtun, O.; McBride, J. R.; Tomlinson, I. D. Biocompatible Quantum Dots for Biological Applications. *Chem. Biol.* **2011**, *18* (1), 10–24. <https://doi.org/10.1016/j.chembiol.2010.11.013>.
- (85) Ayele, D. W.; Su, W. N.; Chou, H. L.; Pan, C. J.; Hwang, B. J. Composition-Controlled Optical Properties of Colloidal CdSe Quantum Dots. *Appl. Surf. Sci.* **2014**, *322*, 177–184. <https://doi.org/10.1016/j.apsusc.2014.10.079>.
- (86) Maćkowski, S.; Karczewski, G.; Kossut, J.; Sęk, G.; Misiewicz, J.; Prechtel, G.; Heiss, W. Optical Properties of CdTe/ZnTe Quantum Dot Superlattices. *Phys. E Low-dimensional Syst. Nanostructures* **2002**, *12* (1–4), 503–506. [https://doi.org/10.1016/S1386-9477\(01\)00343-5](https://doi.org/10.1016/S1386-9477(01)00343-5).
- (87) Chen, X.; Lu, H.; Li, Z.; Zhai, Y.; Ndione, P. F.; Berry, J. J.; Zhu, K.; Yang, Y.; Beard, M. C. Impact of Layer Thickness on the Charge Carrier and Spin Coherence Lifetime in Two-Dimensional Layered Perovskite Single Crystals. *ACS Energy Lett.* **2018**, *3* (9), 2273–2279. <https://doi.org/10.1021/acsenrgylett.8b01315>.
- (88) Crothers, T. W.; Milot, R. L.; Patel, J. B.; Parrott, E. S.; Schlipf, J.; Müller-Buschbaum, P.; Johnston, M. B.; Herz, L. M. Photon Reabsorption Masks Intrinsic Bimolecular Charge-Carrier Recombination in CH₃NH₃PbI₃ Perovskite. *Nano Lett.* **2017**, *17* (9), 5782–5789. <https://doi.org/10.1021/acs.nanolett.7b02834>.
- (89) Yoon, J. H.; Lim, J.; Yoon, S. Controlled Assembly and Plasmonic Properties of Asymmetric Core–Satellite Nanoassemblies. *ACS Nano* **2012**, *6* (8), 7199–7208. <https://doi.org/10.1021/nn302264f>.
- (90) Zhang, Z.; Ghimire, S.; Okamoto, T.; Sachith, B. M.; Sobhanan, J.; Subrahmanyam, C.; Biju, V. Mechano-Optical Modulation of Excitons and Carrier Recombination

- in Self-Assembled Halide Perovskite Quantum Dots. *ACS Nano* **2022**, *16* (1), 160–168. <https://doi.org/10.1021/acsnano.1c04944>.
- (91) Nair, V. C.; Muthu, C.; Rogach, A. L.; Kohara, R.; Biju, V. Channeling Exciton Migration into Electron Transfer in Formamidinium Lead Bromide Perovskite Nanocrystal/Fullerene Composites. *Angew. Chemie* **2017**, *129* (5), 1234–1238. <https://doi.org/10.1002/ange.201610070>.
 - (92) Peng, H.-L.; Callender, R. Mechanism for Fluorescence Quenching of Tryptophan by Oxamate and Pyruvate: Conjugation and Solvation-Induced Photoinduced Electron Transfer. *J. Phys. Chem. B* **2018**, *122* (25), 6483–6490. <https://doi.org/10.1021/acs.jpcc.8b02433>.
 - (93) Vauthey, E. Elucidating the Mechanism of Bimolecular Photoinduced Electron Transfer Reactions. *J. Phys. Chem. B* **2022**, *126* (4), 778–788. <https://doi.org/10.1021/acs.jpcc.1c10050>.
 - (94) Kumar, K.; Kurnikov, I. V.; Beratan, D. N.; Waldeck, D. H.; Zimmt, M. B. Use of Modern Electron Transfer Theories To Determine Electronic Coupling Matrix Elements in Intramolecular Systems. *J. Phys. Chem. A* **1998**, *102* (28), 5529–5541. <https://doi.org/10.1021/jp980113t>.
 - (95) Sachith, B. M.; Zhang, Z.; Subramanyam, P.; Subrahmanyam, C.; Furube, A.; Tamai, N.; Okamoto, T.; Misawa, H.; Biju, V. Photoinduced Interfacial Electron Transfer from Perovskite Quantum Dots to Molecular Acceptors for Solar Cells. *Nanoscale* **2023**, *15* (17). <https://doi.org/10.1039/d3nr01032e>.
 - (96) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10). <https://doi.org/10.1039/c9cs00848a>.
 - (97) Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X. G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C. J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Mora-Seró, I.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Pérez-Prieto, J.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roeffaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Müller-Buschbaum, P.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoyer, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>.
 - (98) Rhee, S.; An, K.; Kang, K. T. Recent Advances and Challenges in Halide Perovskite Crystals in Optoelectronic Devices from Solar Cells to Other Applications. *Crystals* **2021**, *11* (1), 1–28. <https://doi.org/10.3390/cryst11010039>.
 - (99) Jiménez-López, J.; Puscher, B. M. D.; Guldi, D. M.; Palomares, E. Improved Carrier Collection and Hot Electron Extraction across Perovskite, C60, and TiO₂ Interfaces. *J. Am. Chem. Soc.* **2020**, *142* (3), 1236–1246. <https://doi.org/10.1021/jacs.9b09182>.
 - (100) Jeon, I.; Ueno, H.; Seo, S.; Aitola, K.; Nishikubo, R.; Saeki, A.; Okada, H.; Boschloo, G.; Maruyama, S.; Matsuo, Y. Lithium-Ion Endohedral Fullerene (Li+@C60) Dopants in Stable Perovskite Solar Cells Induce Instant Doping and

- Anti-Oxidation. *Angew. Chemie - Int. Ed.* **2018**, 57 (17), 4607–4611. <https://doi.org/10.1002/anie.201800816>.
- (101) Schulz, P. Interface Design for Metal Halide Perovskite Solar Cells. *ACS Energy Lett.* **2018**, 3 (6), 1287–1293. <https://doi.org/10.1021/acsenenergylett.8b00404>.
- (102) Wang, H.; Rahaq, Y.; Kumar, V. A Composite Light-Harvesting Layer from Photoactive Polymer and Halide Perovskite for Planar Heterojunction Solar Cells. *Sci. Rep.* **2016**, 6 (1), 29567. <https://doi.org/10.1038/srep29567>.
- (103) Gerbert, D.; Tegeder, P. Molecular Ion Formation by Photoinduced Electron Transfer at the Tetracyanoquinodimethane/Au(111) Interface. *J. Phys. Chem. Lett.* **2017**, 8 (19), 4685–4690. <https://doi.org/10.1021/acs.jpcllett.7b01897>.
- (104) Jeong, H. W.; Zsigmond, T. S.; Samu, G. F.; Janáky, C. Sacrificial Agent Gone Rogue : Electron-Acceptor-Induced Degradation of CsPbBr₃ Photocathodes. *ACS Energy Lett.* **2022**, 7 (1), 417–424. <https://doi.org/10.1021/acsenenergylett.1c02130>.
- (105) Hsu, C.; Lin, C.; Huang, J.; Chu, C.; Wei, K.; Li, L. Layer-by-Layer Graphene/TCNQ Stacked Films as Conducting Anodes for Organic Solar Cells. *ACS Nano* **2012**, 6 (6), 5031–5039. <https://doi.org/10.1021/nn301721q>.
- (106) Wu, K.; Liang, G.; Shang, Q.; Ren, Y.; Kong, D.; Lian, T. Ultrafast Interfacial Electron and Hole Transfer from CsPbBr₃ Perovskite Quantum Dots. *J. Am. Chem. Soc.* **2015**, 137 (40), 12792–12795. <https://doi.org/10.1021/jacs.5b08520>.
- (107) Long, R.; Fang, W. H.; Prezhd, O. V. Strong Interaction at the Perovskite/TiO₂ Interface Facilitates Ultrafast Photoinduced Charge Separation: A Nonadiabatic Molecular Dynamics Study. *J. Phys. Chem. C* **2017**, 121 (7), 3797–3806. <https://doi.org/10.1021/acs.jpcc.6b12921>.
- (108) Yang, D.; Yang, R.; Wang, K.; Wu, C.; Zhu, X.; Feng, J.; Ren, X.; Fang, G.; Priya, S.; Liu, S. High Efficiency Planar-Type Perovskite Solar Cells with Negligible Hysteresis Using EDTA-Complexed SnO₂. *Nat. Commun.* **2018**, 9 (1), 3239. <https://doi.org/10.1038/s41467-018-05760-x>.
- (109) Kamat, P. V.; Pradhan, N.; Schanze, K.; Weiss, P. S.; Buriak, J.; Stang, P.; Odom, T. W.; Hartland, G. Challenges and Opportunities in Designing Perovskite Nanocrystal Heterostructures. *ACS Energy Lett.* **2020**, 5 (7), 2253–2255. <https://doi.org/10.1021/acsenenergylett.0c01216>.
- (110) Sachith, B. M.; Okamoto, T.; Ghimire, S.; Umeyama, T.; Takano, Y.; Imahori, H.; Biju, V. Long-Range Interfacial Charge Carrier Trapping in Halide Perovskite-C₆₀ and Halide Perovskite-TiO₂ Donor–Acceptor Films. *J. Phys. Chem. Lett.* **2021**, 12 (35), 8644–8651. <https://doi.org/10.1021/acs.jpcllett.1c01909>.
- (111) STILES, C. W. Proposed Suspension of Rules of Nomenclature in the Case of Bohadsch 1761. *Nature* **1936**, 138 (3483), 206–206. <https://doi.org/10.1038/138206c0>.
- (112) Pal, A.; Srivastava, S.; Gupta, R.; Sapra, S. Electron Transfer from CdSe–ZnS Core–Shell Quantum Dots to Cobalt(III) Complexes. *Phys. Chem. Chem. Phys.* **2013**, 15 (38), 15888. <https://doi.org/10.1039/c3cp51834e>.
- (113) Vokhmintcev, K. V.; Samokhvalov, P. S.; Nabiev, I. Charge Transfer and Separation in Photoexcited Quantum Dot-Based Systems. *Nano Today* **2016**, 11 (2), 189–211. <https://doi.org/10.1016/j.nantod.2016.04.005>.
- (114) Huang, J.; Huang, Z.; Yang, Y.; Zhu, H.; Lian, T. Multiple Exciton Dissociation in CdSe Quantum Dots by Ultrafast Electron Transfer to Adsorbed Methylene Blue. *J. Am. Chem. Soc.* **2010**, 132 (13), 4858–4864. <https://doi.org/10.1021/ja100106z>.

- (115) Boulesbaa, A.; Issac, A.; Stockwell, D.; Huang, Z.; Huang, J.; Guo, J.; Lian, T. Ultrafast Charge Separation at CdS Quantum Dot/Rhodamine B Molecule Interface. *J. Am. Chem. Soc.* **2007**, *129* (49), 15132–15133. <https://doi.org/10.1021/ja0773406>.
- (116) Jagadeeswari, S.; Asha Jhonsi, M.; Kathiravan, A.; Renganathan, R. Photoinduced Interaction between MPA Capped CdTe QDs and Certain Anthraquinone Dyes. *J. Lumin.* **2011**, *131* (4), 597–602. <https://doi.org/10.1016/j.jlumin.2010.10.037>.
- (117) Morris-Cohen, A. J.; Frederick, M. T.; Cass, L. C.; Weiss, E. A. Simultaneous Determination of the Adsorption Constant and the Photoinduced Electron Transfer Rate for a Cds Quantum Dot - Viologen Complex. *J. Am. Chem. Soc.* **2011**, *133* (26), 10146–10154. <https://doi.org/10.1021/ja2010237>.
- (118) Lou, Y.; Samia, A. C. S.; Cowen, J.; Banger, K.; Chen, X.; Lee, H.; Burda, C. Evaluation of the Photoinduced Electron Relaxation Dynamics of Cu_{1.8}S Quantum Dots. *Phys. Chem. Chem. Phys.* **2003**, *5* (6), 1091–1095. <https://doi.org/10.1039/b211104g>.
- (119) Bang, J. H.; Kamat, P. V. CdSe Quantum Dot–Fullerene Hybrid Nanocomposite for Solar Energy Conversion: Electron Transfer and Photoelectrochemistry. *ACS Nano* **2011**, *5* (12), 9421–9427. <https://doi.org/10.1021/nn204350w>.
- (120) Mammeri, F.; Ballarin, A.; Giraud, M.; Brusatin, G.; Ammar, S. Photoluminescent Properties of New Quantum Dot Nanoparticles/Carbon Nanotubes Hybrid Structures. *Colloids Surfaces A Physicochem. Eng. Asp.* **2013**, *439*, 138–144. <https://doi.org/10.1016/j.colsurfa.2013.03.026>.
- (121) 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. *Nat. Mater.* **2014**, *13* (8), 796–801. <https://doi.org/10.1038/nmat3984>.
- (122) Tabachnyk, M.; Ehrler, B.; Gélinas, S.; Böhm, M. L.; Walker, B. J.; Musselman, K. P.; Greenham, N. C.; Friend, R. H.; Rao, A. Resonant Energy Transfer of Triplet Excitons from Pentacene to PbSe Nanocrystals. *Nat. Mater.* **2014**, *13* (11), 1033–1038. <https://doi.org/10.1038/nmat4093>.
- (123) Rana, G.; Das, S.; Singha, P. K.; Ali, F.; Maji, R.; Datta, A. The Effect of Cu(I)-Doping on the Photoinduced Electron Transfer from Aqueous CdS Quantum Dots. *J. Chem. Phys.* **2024**, *161* (2). <https://doi.org/10.1063/5.0218548>.
- (124) Lee, J.-W.; Makuta, S.; Sukarasep, S.; Bo, J.; Suzuki, T.; Nakayama, T.; Suematsu, H.; Niihara, K.; Tachibana, Y. Electron Injection from a CdS Quantum Dot to a TiO₂ Conduction Band as an Efficiency Limiting Process: Comparison of QD Depositions between SILAR and Linker Assisted Attachment. *J. Photopolym. Sci. Technol.* **2016**, *29* (3), 357–362. <https://doi.org/10.2494/photopolymer.29.357>.
- (125) Jang, E.; Jang, H. Review: Quantum Dot Light-Emitting Diodes. *Chem. Rev.* **2023**, *123* (8), 4663–4692. <https://doi.org/10.1021/acs.chemrev.2c00695>.
- (126) Sukharevska, N.; Bederak, D.; Dirin, D.; Kovalenko, M.; Loi, M. A. Improved Reproducibility of PbS Colloidal Quantum Dots Solar Cells Using Atomic Layer–Deposited TiO₂. *Energy Technol.* **2020**, *8* (1), 1–9. <https://doi.org/10.1002/ente.201900887>.
- (127) Cui, X.; Chen, Y.; Zhang, M.; Harn, Y. W.; Qi, J.; Gao, L.; Wang, Z. L.; Huang, J.; Yang, Y.; Lin, Z. Tailoring Carrier Dynamics in Perovskite Solar Cells via Precise Dimension and Architecture Control and Interfacial Positioning of Plasmonic Nanoparticles. *Energy Environ. Sci.* **2020**, *13* (6), 1743–1752.

- <https://doi.org/10.1039/C9EE03937F>.
- (128) Yang, L.; Zhang, Y.; Ma, J.; Chen, P.; Yu, Y.; Shao, M. Pure Red Light-Emitting Diodes Based on Quantum Confined Quasi-Two-Dimensional Perovskites with Cospacer Cations. *ACS Energy Lett.* **2021**, *6* (7), 2386–2394. <https://doi.org/10.1021/acsenergylett.1c00752>.
- (129) Kim, D.; Jung, H. J.; Park, I. J.; Larson, B. W.; Dunfield, S. P.; Xiao, C.; Kim, J.; Tong, J.; Boonmongkolras, P.; Ji, S. G.; Zhang, F.; Pae, S. R.; Kim, M.; Kang, S. B.; Dravid, V.; Berry, J. J.; Kim, J. Y.; Zhu, K.; Kim, D. H.; Shin, B. Efficient, Stable Silicon Tandem Cells Enabled by Anion-Engineered Wide-Bandgap Perovskites. *Science* (80-.). **2020**, *368* (6487), 155–160. <https://doi.org/10.1126/science.aba3433>.

Chapter 2

Experimental

2.1. General

This chapter describes the synthesis and characterization processes of several QD derivatives and PNCs performed by using various experimental techniques aimed at the optimization of properties and functionalities of these nanomaterials. Detailed characterizations were performed to evaluate their structural, optical, and chemical properties. The synthesized organic compounds were characterized by advanced spectroscopy, such as proton nuclear magnetic resonance (^1H -NMR) and carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy. In addition, ESI-MS was used to confirm molecular weights and composition, further confirming the integrity of the synthesized materials.

PNCs were synthesized through two distinct methods. The employed strategies that can be used to synthesize nanocrystals include the ligand-assisted reprecipitation (LARP) technique and the hot injection strategy. The method of drop casting was employed to produce thin films to undertake further inspection of the deposition of the fabricated nanocrystals. To analyze the PNC's optical properties and the electron transfer kinetics, UV-visible (UV-vis) absorption spectroscopy and fluorescence spectroscopy were used. These methods provided additional essential insights into the materials' emission characteristics and absorption behavior. STEM which offered information about the dimensions of the surface morphology of the nanocrystals. The DLS measurement offered information about the measures of the size of the nanocrystals in solution. In the actual state of affairs of the PNCs, their lifetime was determined, utilizing the QuantaTaurus Tau (Q-Tau) apparatus designed for lifetime measurements. For the film state, the ultrafast dynamics of the materials were recorded using the picosecond laser or ps-laser technology. These experiments provided a clear understanding of the photophysical behavior of both the soluble as well as solid PNCs. In addition, the same spectroscopic techniques were applied to the study of CdSe/CdS QDs and their structures.

Indeed, I was able to create well-dispersed **ms-QD** assemblies through the use of trypsin. To comprehensively study the native PL characteristics of ms-QDs, I synthesized carboxylic acid-functionalized CdSe/CdS QD (QD-COOH) and monodisperse QDs (mono-QDs) for comparative analysis. UV visible (UV-vis) spectrophotometry was used to investigate the absorption spectra of the materials. The emission properties, as well as the electron transfer capabilities to acceptor molecules, were assessed using fluorescence spectroscopy to reveal the three distinctive categories of QDs. Additionally, the lifetimes of **ms-QD**, QD-COOH, and mono-QDs were also determined using the Quantaurus Tau (Q-Tau) system which is a highly advanced lifetimes measurement instrument meant for acquiring reliable PL decay profiles. Such a comparison afforded some insight into the excitonic dynamics and relaxation processes in these material systems and provided a greater understanding of how the assembly and functionalization affect the optical properties of QDs. The findings help the future applicability of **ms-QD** assemblies in higher-end optical and electronics applications.

2.2. Materials

The compounds utilized in this investigation are mentioned below, along with the suppliers and analytical grades.

Methylammonium bromide (MABr, >98%), lead dibromide (PbBr₂, >98%), and oleic acid (>85%) were provided from the Chemical Industry of Tokyo, Japan. Sigma-Aldrich of Japan supplied ethanol (EtOH, anhydrous, >98%), fullerene (C₆₀), TiO₂, 4-hydroxy benzaldehyde (>98%), and ethyl acetate (EtOAc, anhydrous, >98%), poly(ethylene glycol) methyl ether thiol (CH₃O(CH₂CH₂O)_nCH₂CH₂SH), 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DM-TMM). Hexadecyl amine (HAD, >95%), trypsin-5.3mmol/L EDTA, L(+)-Lysine monohydrochloride, dehydrated hexane (<99%), acetone, dimethyl sulfoxide (DMSO, >98%), dehydrated toluene (spectroscopic grade), dehydrated *N,N*-dimethyl formamide (DMF), acetonitrile, dodecanedioic acid, methanol (MeOH, >98%) were purchased from FUJIFILM Wako Pure Chemical Corporation, Japan. Thiol-poly(ethylene glycol)-carboxyl, 3500 Da, (HS-PEG3500-COOH) was obtained from Nanosoft of Biotechnology LLC, NC, the United States (USA).

2.3. Methods

2.3.1 Synthesis of MAPbBr₃ perovskite nanocrystals

The ligand-assisted reprecipitation (LARP) method¹ was followed to prepare MAPbBr₃ NCs. To begin the synthesis, dry DMF (1.0 mL) was used to mix methylammonium bromide (MABr, 28.0 mg, 0.250 mmol) and lead bromide (PbBr₂, 99.1 mg, 0.270 mmol). The prepared precursor mixer was utilized for the subsequent crystallization process. Similarly, deoxygenated toluene (50.0 mL) was added into a round-bottom container containing oleic acid (0.250 mmol) and hexadecylamine (46.0 mg, 0.191 mmol). This ligand solution was then deoxygenated by providing vigorous stirring under an inert atmosphere of argon for 15 minutes. Before the incorporation of the precursors, the individual mixture was warmed to a temperature of 80°C for the reaction. The precursor mixture was added to the ligand combination dropwise once the temperature reached 80°C. Successful preparation of MAPbBr₃ PNCs was evidenced by a color change of the solution from green to yellowish orange which shows that crystallization has taken place.

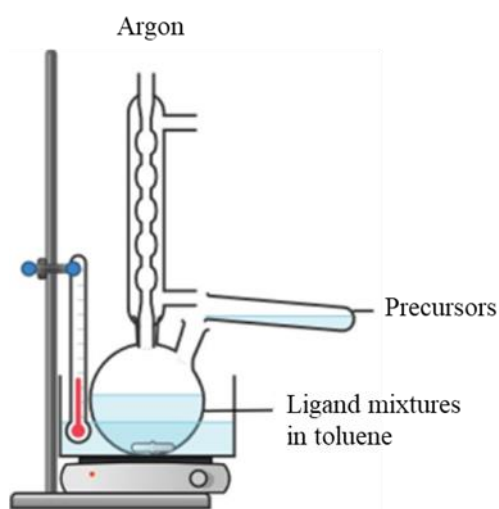


Figure 2.1 The synthesis method scheme of perovskite nanocrystals (PNCs).

Further, the formation of MAPbBr₃ PNCs was achieved through centrifugation at higher rpm. This collected residue was redispersed in toluene so that there was a probability of having a stable suspension of the nanocrystals in this solvent for characterization and use in other experiments. This method enabled obtaining MAPbBr₃ PNCs counteracted with good dispersiveness for studying their properties and their

possible applications in other fields. In the formation of FAPbBr₃ NCs, I use the same LARP technique.

2.3.2 Synthesis of FAPbBr₃ perovskite nanocrystals and their assemblies

Perovskite FAPbBr₃ NC assemblies were also prepared via a LARP method, which is well-known and commonly used for preparing perovskite nanomaterials. The synthesis started with the synthesis of a ligand mixture in which octyl ammonium bromide (0.12 mmol, 25.2 mg), oleic acid (0.6 mmol), and octadecene (4 mL) was introduced into a round-bottom flask. This mixture was then maintained under an anhydrous and inert argon atmosphere to minimize its contact with oxygen and stirred at 80°C for 30 minutes to ensure homogeneity and activation of ligands. At the same time, the predecessors had been produced via dissolving PbBr₂ (0.200 mmol, 73.4 mg) and FABr (0.200 mmol, 25.0 mg) to 400 μ L of DMF solution to get a homogeneous solution. When the ligand mixture attained stable conditions at 80°C, the precursor solution was gradually introduced into the ligand mixture while continuously stirring. Adding hexane and acetone in a 2:1 (v/v) ratio to the reaction combination resulted in the instantaneous development of yellowish crystals, which are attributed to the formation of the FAPbBr₃ PNCs.²⁻³ The mixture was then placed in a centrifuge for 5 minutes at a speed of 12,000 rpm to allow the deposition of the solid FAPbBr₃ NCs across the bottom of the vial while leaving the supernatant on the top. Then the residue was washed times with toluene two times at a higher speed, and then lower speed and collected the residue in toluene. This method produced highly reproducible FAPbBr₃ NC assemblies in terms of optical and structural characteristics required for optoelectronic and photophysical applications.

2.3.3 Synthesis of CsPbBr₃ perovskite nanocrystals

The protocol for the synthesis of CsPbBr₃ PNCs has been adopted by Protesescu et al. using a hot injection technique.⁴ Accordingly, 1.1 mmol (420 mg) of PbBr₂ was added to a three-necked flask with 10 mmol (3.2 mL) of oleic acid and 10 mmol (2.4 g) of hexadecyl amine, capped with 50 mL of 1-hexadecene, followed by heating it under vacuum at 120 °C for an hour until complete dissolution of the precursors. To prepare the cesium precursor solution, in a parallel three-necked flask, 0.15 mmol (30 mg) of cesium acetate, 1.2 mL of 1-hexadecene, and 0.5 mmol (180 μ L) of oleic acid were heated to

120 °C under vacuum for one hour. After the complete dissolution of both solutions, the lead bromide solution was heated to 170 °C, with flushing of the system by argon gas for 30 minutes. Then, the hot cesium acetate solution was rapidly injected into the PbBr₂ solution at this temperature within a couple of seconds, which initiated crystallization. To quench the reaction and save the product, it was cooled down in ice within one minute of the injection. The obtained CsPbBr₃ PNC colloid was centrifugated after the addition of 50 mL of toluene at 14,000 rpm for 30 min, discarding the supernatant to get rid of impurities and unreacted precursors. Precipitates containing nanocrystals were further suspended in toluene for further use or characterization.

2.3.4 Preparation of FAPbBr₃ perovskites nanocrystals assemblies in the presence of electron acceptors

Oleic acid (0.6 mmol) mixed with 4 mL of octadecene and octyl ammonium bromide (0.120 mmol, 25.2 mg), the combination was held under an argon environment for 15 min at 80 °C to form an active gas-free atmosphere. Lead bromide (0.200 mmol, 73.4 mg) was dissolved in 400 µL dimethylformamide (DMF) with the appropriate volume of formamidinium bromide (0.200 mmol, 25.0 mg) to form a precursor solution. When the mixture of ligands attained a steady state at 80 °C, the precursor solution was added to it slowly. During this stage, desired product formation was facilitated with the addition of a 5.0 µM quencher dissolved in a mixture of acetone and hexane to the reaction system with rapid addition. Centrifugation was used to collect the crystal at higher rpm for 15 min. The residue was then washed with care and kept in toluene for further experimental uses.

2.3.5 Preparation of FAPbBr₃ nanocrystal films

To prepare the FAPbBr₃ PNC films, I follow the drop-casting method.⁵ As shown in Figure 2.2, the solution of PNC was subjected to a glass coverslip and air-dried by itself at room temperature. To make uniform films, the FAPbBr₃ PNCs in toluene must be concentrated correctly. Drop-casting a FAPbBr₃ PNCs solution onto a glass cover slip and letting it dry at room temperature. In Chapter 3, such films were fabricated, and the PL lifetime decay profiles were measured. After making the PNC films, the quenchers were added separately, and the PL lifetime decays were recorded.⁶

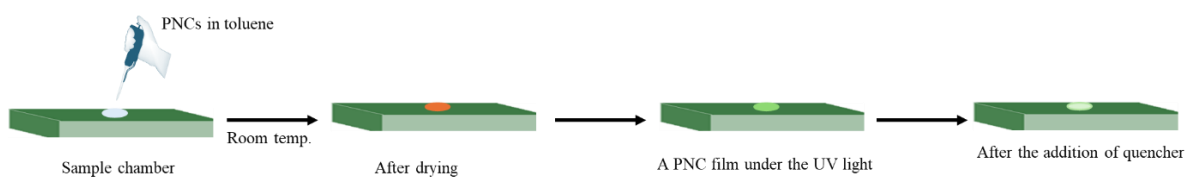
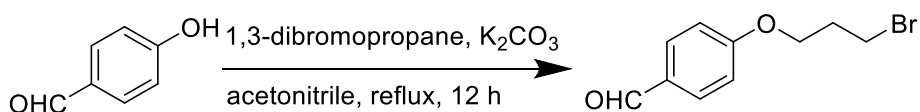


Figure 2.2 A system for producing thin films using a drop-casting process.

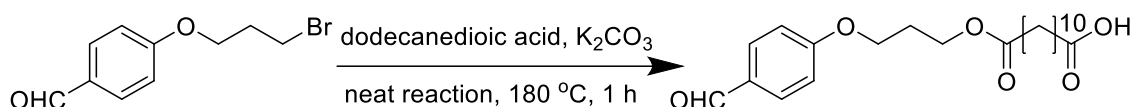
2.3.6 Synthesis of the C₆₀-RCOOH ligand

The C₆₀-RCOOH ligand was synthesized by the azomethine ylide cyclo-addition reaction.⁷⁻⁸ 1,3-dibromo propane (49.0 mmol, 10.0 g.), 4-hydroxybenzaldehyde (24.5 mmol, 2.99 g), and K₂CO₃ (49.0 mmol, 6.70 g) were mixed, and refluxed in acetonitrile (40.0 mL) for 12 h. After the reaction was over, the reaction solution was allowed to cool down to room temperature to stabilize it, preventing any thermal degradation of the product. The solution was filtered with care to remove all the undissolved solids and impurities after cooling. The filtered product would be subjected to reduced pressure, usually through the use of a vacuum apparatus, to aid its collection by removing the residual solvent. To verify this product's formation and identify any byproducts, thin-layer chromatography (TLC) was employed. The purification process involved using a brine solution and ethyl acetate. Finally, the product was isolated through column chromatography using silica (SiO₂). The isolated oily products were confirmed by the ¹H NMR. Yield 56 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.90 (s, 1H, -CHO), 7.84-7.87 (d, 2H, Ar-H), 7.01-7.04 (d, 2H, Ar-H), 4.20-4.23 (t, 3H, -CH₂Br), 3.61-3.64, (t, 3H, O-CH₂), 2.34-2.37 (m, 5H, -CH₂).

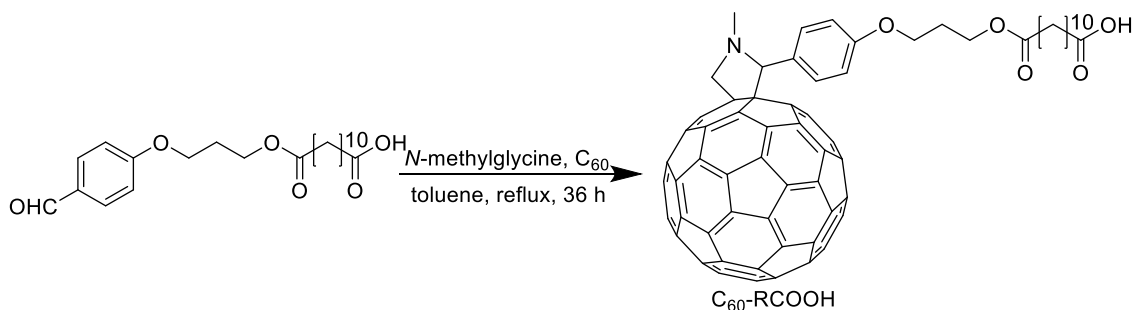


The mixture of K₂CO₃ (19.3 mmol, 2.67 g) and dodecanedioic acid (9.98 mmol, 2.30 g) was heated at 180 °C with continuous churning in an argon environment. When it started melting by releasing CO₂, 4-(3-bromopropoxy)-benzaldehyde (1.50 g, 6.10 mmol) was put gradually with continuous stirring. TLC was used to monitor the reaction to confirm the production of the product. Acidic water (HCl) and ethyl acetate were used to purify the product. Then, column chromatography (SiO₂) (5% methanol and 95% toluene mixture) was performed to collect the purified product. The obtained brownish solid was

confirmed using ^1H NMR and ^{13}C NMR. Yield 45%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.90 (s, 1H, -CHO), 7.84-7.85 (d, 2H, Ar-H), 7.0-7.01 (d, 2H, Ar-H), 4.27-4.30 (t, 3H, $-\text{OCH}_2$), 4.13-4.16 (t, 3H, $-\text{OCH}_2$), 2.30-2.38 (m, 5H, $-\text{COCH}_2$), 2.13-2.19 (m, 5H, $-\text{COCH}_2$), 1.27-1.65 (m, 16H). ^{13}C NMR (CDCl_3 , 400 MHz): δ 190.9, 179.3, 173.9, 163.9, 132.1, 130.0, 114.8, 64.8, 60.8, 34.3, 29.4, 28.5, 24.7. ESI-MS: calculated for $\text{C}_{22}\text{H}_{32}\text{O}_6$: 392.48 m/z , found: 392.22 m/z .



Toluene was used to dissolve 2-(12-(3-(4-formylphenoxy)propoxy)-12-oxododecanoic acid) (0.500 mmol, 196.0 mg) and N-methyl glycine (2.24 mmol, 200.0 mg). Separately, again toluene was employed to dissolve C_{60} (0.510 mmol, 360.0 mg). The solutions were then mixed and bubbled using argon gas. Then, Refluxed was done for 36, and check the TLC to confirm. By using column chromatography (SiO_2) with 5% methanol and 95% toluene, the verified product was obtained. The resulting product was verified using ^1H and ^{13}C NMR. Yield: 40%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.71 (s, 2H, Ar-H), 6.94-6.96 (d, 2H, Ar-H), 4.99-5.02 (d, 2H, $-\text{NH}_2$), 4.90 (s, 1H, $-\text{NH}$), 4.22-4.28 (m, 4H, $-\text{OCH}_2$), 4.02-4.05 (m, 4H, $-\text{OCH}_2$), 2.80 (s, 1H, $-\text{NCH}_3$), 2.33-2.38 (t, 3H, $-\text{COCH}_2$), 2.26-2.30 (t, 3H, $-\text{COCH}_2$), 1.27-1.65 (m, 16H). ^{13}C NMR (CDCl_3 , 400 MHz): δ 178.1, 173.9, 158.9, 156.3, 154.1, 153.7, 153.6, 147.4, 145.6, 142.3, 142.1, 141.6, 140.2, 136.6, 135.8, 129.0, 114.6, 83.3, 69.9, 69.0, 64.4, 64.1, 40.0, 34.3, 33.9, 29.4, 29.2, 25.0, 24.8. ESI-MS: calculated for $\text{C}_{84}\text{H}_{37}\text{NO}_5$: 1140.20 m/z , found: 1140.28 m/z .



2.3.7 Preparation of CdSe/CdS quantum dots functionalized with carboxylic acids

The synthesis of CdSe/CdS QDs followed the methodology described in the earlier work.^{9–11} To introduce the carboxylic acid functional group, QDs CdSe/CdS (10.0 mg) were added to chloroform (10.0 mL). The QD dispersion was then thoroughly mixed with poly(ethylene glycol)-methyl-ether thiol ($M_n > 2000$, 46.1 nmol) and thiol-poly(ethylene glycol)-carboxyl (HS-PEG3500COOH, 3500 Da, 11.4 nmol) that had been separately dissolved in chloroform. Later, the mixture was sonicated for three minutes before being placed in a heat shaker overnight at 25 °C. The process yielded a clear and transparent solution, indicating that the components dissolved completely. To initiate the precipitation, hexane was added to the solution gradually while stirring until the desired product separated from the mixture. The resultant precipitate was collected through centrifugation at a high speed of 10,000 g, where the solid material was concentrated at the bottom of the centrifuge tube. The supernatant was carefully decanted and discarded, containing unwanted soluble impurities. It was washed several times with hexane subsequently to remove further traces of impurities and/or unreacted materials, affording a higher purity of the final product. After being dried, a yellow-coloured solid was obtained, which was identified as QD-COOH. It symbolizes the carboxyl-functionalized QDs that might be used in subsequent applications or analyses regarding this study.

2.3.8 Preparation of assemblies of the mesoscopic quantum dot¹²

In the synthesis of ms-QD, 5.0 mg of QD-COOH was dispersed in ethanol (EtOH) and subjected to sonication until a uniform consistency was achieved. Carboxylic acid activation was initiated by the addition of 0.411 mmol of DMT-MM, followed shortly by the inclusion of 0.137 mmol of L-lysine. Further sonication and incubation occurred in a heat shaker at 40 °C (1000 rpm) for 12 hours. This is followed by separation by high-speed centrifugation, which efficiently concentrates the solid material at the bottom of the centrifuge tube. The solid was then washed thoroughly with water after centrifugation to remove any soluble impurities. The product obtained was then collected and freed from residual solvent under reduced pressure, usually with the assistance of a vacuum system, to ensure the solid was free of unwanted solvents. The dried solid was dissolved in 10 mM HEPES aqueous solution, which provides a constant pH value. Then, trypsin (1.0

mL, 0.5 wt%) had been added to this solution. Trypsin is an enzyme and thus could have been introduced to catalysed some sort of specific reaction. Then, the mixture was shaken at 40 °C and 1000 rpm for 12 hours to allow the reaction to take place and the enzyme to act on the solution. After the reaction was over, the precipitate was washed once more with water to remove residual reagents or byproducts. The washed product was then collected and dried again under reduced pressure to remove any remaining water or solvents. Finally, the yellow solid, ms-QD, was collected with a yield of 45.6 wt%. The as-obtained product was stored in water for further use in subsequent experiments, making sure that the product would be in an appropriate form when future analyses or applications required it.

2.3.9 Preparation of monomeric quantum dot

5.0 mg of **QD-COOH** was dispersed in EtOH and sonicated. Then, added DMT-MM (0.227 μmol) to the sample solution, and sonicated thoroughly. After that, L-lysine (0.103 μmol) was poured into the mixture solution, and mixed with sonication. The sample combination was subsequently kept at a hot shaker set to 1000 rpm and 40 °C for 12 hours. Following this period, a precipitate formed and was collected via centrifugation. The product was rinsed using water, and any leftover liquid was extracted using decreased force. The resulting yellow solid, called mono-QD, was then mixed using water and stored for later use.

2.4 Instrumentations

2.4.1 UV-vis spectroscopy technique

This spectroscopy refers to the method of measurement of the amount of electromagnetic radiation absorbed by a substance through different wavelengths and frequencies.¹³ It is used in finding the concentration of a substance, its photophysical properties, and chemical kinetics, among characteristics of particles. This is a technique based on the interaction of light with the material. The relationship between the wavelength of light and the energy of the radiation is fundamental to an understanding of the interaction of electromagnetic waves with matter. Light, like all other electromagnetic radiation, travels in waves with characteristics defined by wavelength distance between successive peaks or troughs of the wave. Wavelength is inversely related to the radiation energy. In

particular, as the wavelength of light decreases, the energy of the radiation increases, and vice versa: as the wavelength increases, the energy decreases. For a substance to absorb light, electrons must be excited to some excited energy state, and this requires energy of a certain magnitude. Different materials absorb light at different wavelengths because the energy required to excite electrons in different bonding sites in the substance varies. The electronic transition can be understood by the Frank-Condon principle, assuming that during the transition the positions or momenta of the nuclei are not changed. These transitions are normally referred to as vertical or Frank-Condon transitions. It follows that the Frank-Condon factor will determine the population of the excited state and thus the absorption intensity.

The normal state of molecules at room temperature is the ground vibrational state corresponding to the lowest vibrational energy level ($v = 0$). Thus, their absorption spectrum covers from the ground state ($v = 0$) to excited energy levels ($v' = 0, 1, 2, 3, \dots$). This originates the fine vibrational structure of an electronic absorption spectrum. The transition from $v = 0$ to $v' = 0$ is called the (0, 0) band, from $v = 0$ to $v' = 1$ is called the (0, 1) band, and from $v = 0$ to $v' = 2$ is the (0, 2) band. This represents the largest overlap of vibrational modes because of the vertical transition from the ground state at $v = 0$; hence, this point will have the maximum absorption value.

UV-Vis spectroscopy is based on the Beer-Lambert law, which gives a mathematical relationship between the absorption of light by a substance with the properties of the medium the light has to travel. According to this law, the amount of light absorbed by a substance is directly proportional to two key factors: the concentration of the absorbing molecules in the medium and the path length through which the light travels. It also says that the absorbance does not depend upon the incident light intensity—that it is determined solely by the substance involved in the medium but is independent of the incoming light intensity.

The Absorbance A of light that passes through a solution may be measured by employing a formula given as $A = \epsilon C l$, in this equation, A represents the absorbance of the solution, while ϵ is the molar absorption coefficient, a constant that is specific to the substance being analyzed and the wavelength of light used. C refers to the concentration of the absorbing species within the solution, and l is the path length, which is the distance the light travels through the solution. That means that, according to the Beer-Lambert law,

if one of two factors is bigger, the amount of light absorbed by the solution increases, making this law quite an important tool in the technique of using UV-Vis spectroscopy to ascertain the concentration of an analyte in a solution. In solution, the law assumes homogeneity and that the light is interacting with the absorbing species in a straightforward, linear manner.

The experimental setup for UV-Vis absorption spectroscopy is depicted in Figure 2.3. The source, in this kind of spectroscopy, covers a wide range from 190 nm to 1100 nm, using both a tungsten lamp and a deuterium lamp to provide the proper light for exciting the sample solution. If the sample is exposed to monochromatic light, part of the light is absorbed by the light-absorbing particles in the solution. The residual transmitted light passes through the sample and is detected by the spectrometer. A spectrometer is any device that measures the quantity of light passing through a sample, recorded as transmittance. Transmittance is defined as the fraction or percent of light that is transmitted through a sample compared to the total light that initially enters the sample.

Measurements by spectroscopy were done using either an Evolution 220 model from Thermo Fisher Scientific, USA, or a UV-1900i model from Shimadzu, Japan, both being quality instruments designed for UV-Vis absorption spectroscopy. These two spectrometers were designed to accurately and reliably measure the light absorption of a sample in both the UV and visible regions of the spectrum. Based on the transmittance data, absorption characteristics could be calculated, which form an important part in realizing the properties and behaviors that a material will exhibit under specified wavelengths.

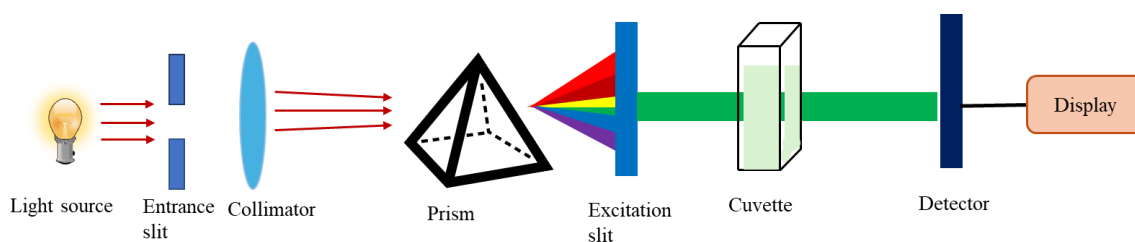


Figure 2.3 A diagram showing the optical arrangement and setup of the UV-Vis spectrometer.

2.4.2 Steady-state fluorescence spectroscopy

Fluorescence spectroscopy can be defined as a form of electromagnetic spectroscopy that is widely used for the characterization and analysis of substances based on fluorescence emitted. This technique is commonly adopted in several disciplines, including chemistry, biology, medical science, and forensic science since it allows one to gain detailed information about the molecular properties of a given substance. In essence, the process involves exciting the electrons of a sample by a continuous beam of light, raising them to excited or higher energy states. Fluorescence can be said to be the process where a substance, upon excitation, releases its energy in returning to its ground state through radiative processes. This light which is emitted as a result of this phenomenon is termed fluorescence. The transition to the ground state from this excited state may be considered several pathways and levels of energy that may further be elaborated with the help of a Jablonski diagram.¹⁴ A Jablonski diagram is the energy states of a molecule explaining different processes such as absorption, excitation, and emission of light. Figure 2.4 presents the Jablonski diagram for an explanation of these transitions and the phenomenon of fluorescence.

According to Boltzmann distribution theory, the ground state contains most molecules in their lowest vibrational state. A fluorophore is normally stimulated to a higher vibrational level, which occurs in 10^{-15} - 10^{-16} s. The excited electron releases its excitation energy. Non-radiative decay is the process that involves the loss of energy by a molecule without emitting a photon. This can be done through several mechanisms, such as internal conversion and vibrational relaxation. In vibrational relaxation, the molecule on excitation to higher energy status undergoes a loss of energy by cascading down through lower vibrational levels of the same electronic state. During this process, the excess energy is either dissipated as heat or distributed to the surrounding molecules, thereby leading to thermal energy dissipation within the system. This kind of relaxation happens within $\sim 10^{-14}$ - 10^{-12} s. The electron at the higher vibrational level can relax into the lower one with the same spin multiplicity by internal conversion within 10^{-12} seconds. Internal conversion increases when the vibrational levels of two electronic states overlap significantly. Intersystem crossing is a quantum mechanical process whereby a molecule moves between two different electronic states having different spin multiplicities. This

transition occurs from a vibrational level with the same energy in one electronic state to a different electronic state. This transition is referred to as spin forbidden due to the lack of spin angular momentum conservation, resulting in a substantially slower transition time ($\sim 10^{-8}$ s).

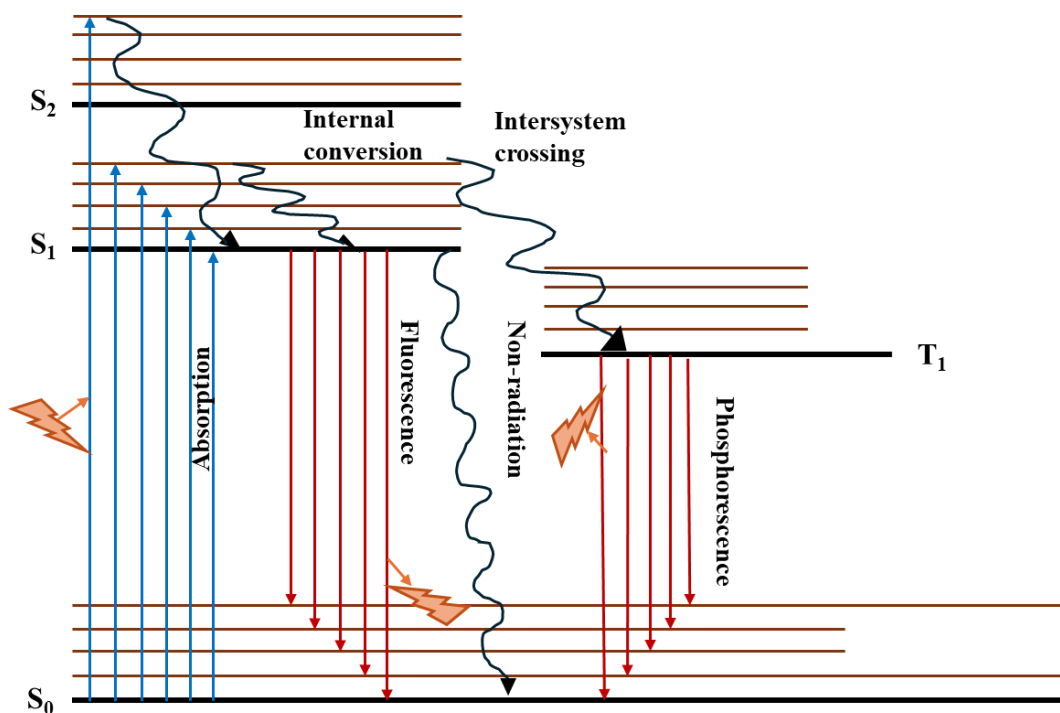


Figure 2.4 A simplified Jablonski diagram.

According to Kasha's rule, luminescence begins with the stimulated electronic level's most minimal vibrational state, resulting in a Stokes shift. Internal conversions and vibrational relaxations cause this energy loss.

The scheme of the fluorescence spectrometer is shown in Figure 2.5. An Xe-lamp is utilized as an exciting light source, providing continuous light that varies with wavelength from UV to NIR. The two slits located at the entry and exit of the monochromator manage the light's bandwidth and slit width, respectively. Following the irradiation of the sample, fluorescence is directed to the emission monochromator at 90° and eventually reaches the detector. In this research, I used a fluorescence spectrometer (RF-6000, Shimadzu, Japan) to see the optical properties of the samples.

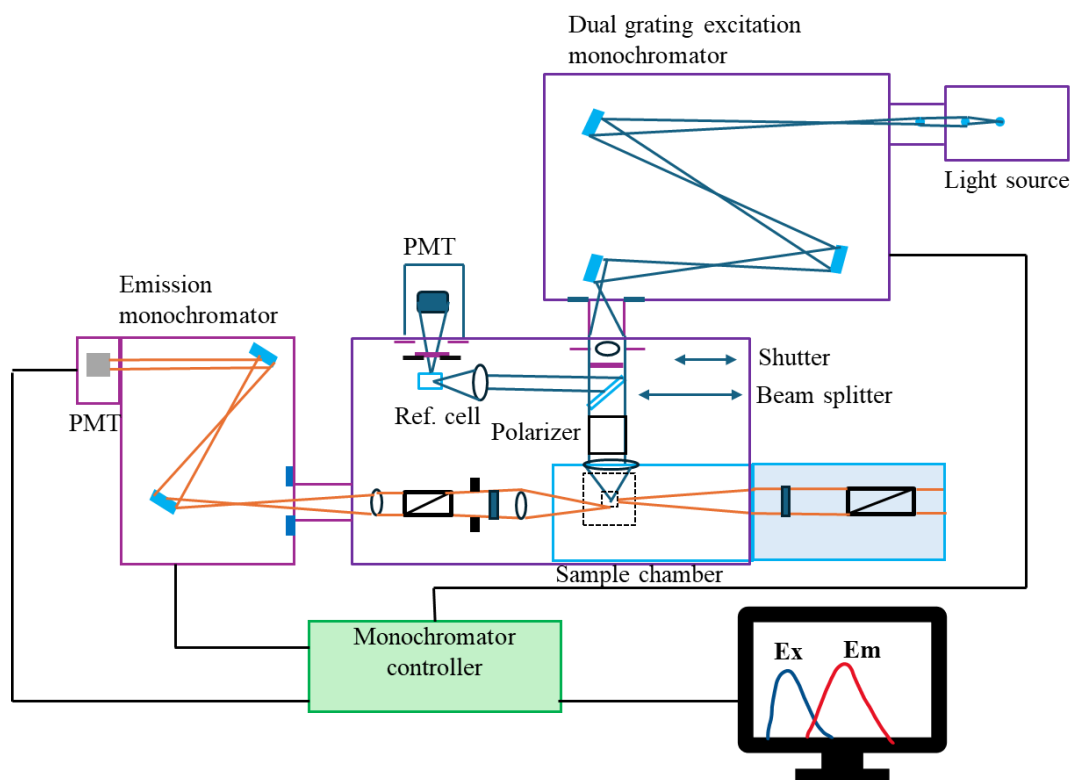


Figure 2.5 illustrates a steady-state fluorescence spectroscopy apparatus.

2.4.3 Nuclear magnetic resonance spectroscopy

NMR is one of the major instrumental analysis methods that are broadly used for the structural elucidation of organic compounds.¹⁵ Certain atomic nuclei possess this property known as spin, which makes them behave like small magnets. When these nuclei are brought near an external magnetic field, they either align with or against it with an angular frequency called *Larmor frequency*, which is linearly proportional to the provided magnetic field's strength. When a sample containing these nuclei is exposed to radiofrequency (RF) radiation, the nuclei absorb energy which can promote electrons or nuclei to higher energy states from lower ones. This absorption of radiofrequency radiation by nuclei is dependent on the magnetic field strength applied and the immediate chemical environment, which dictates the energy level of the nuclei. This state is known as the resonance energy state. Gradually the nuclei come back to their initial energy state after obtaining RF energy and releasing the absorbed energy. The NMR spectrometer detects and measures the released energy, resulting in a signal (Figure 2.6).

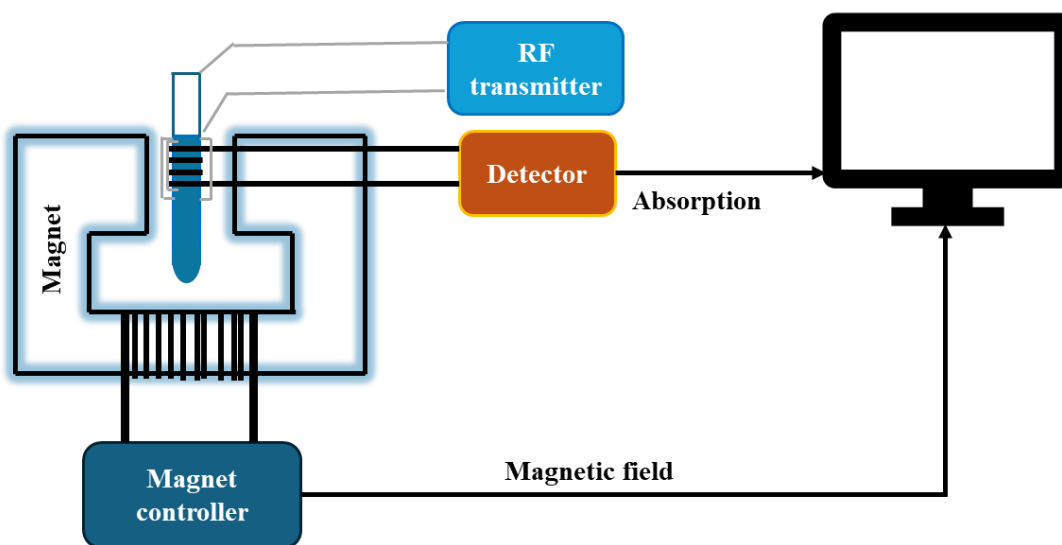


Figure 2.6 An illustration of the NMR spectroscopy process.

The nuclei of a sample face different magnetic environments when it is subjected to a strong magnetic field. Electrons "shield" nuclei from the external field, resulting in a slightly weaker magnetic field around them. These nuclei resonate with larger field strengths (downfield). The effective magnetic field is stronger in nuclei that are close to electronegative atoms or groups because they are "shielded." Modest field strengths (upfield) are resonant for these nuclei. The NMR spectrum shows peaks that represent the nuclei's resonance frequencies. Where such peaks are located and details about the chemical environment of each nucleus are represented by the chemical shift (measured in parts per million). In proton (^1H) NMR, a 0-ppm peak belongs to TMS (the reference), but a 7-8 ppm peak may relate to aromatic protons. Neighboring nuclei interact with one another's magnetic fields, resulting in several peaks in NMR signals. This is referred to as spin-spin coupling. A doublet (two peaks) is formed when a nucleus is with one of its neighbours. With two neighbors, it forms a triplet (three peaks). But so on for larger numbers of nearby nuclei. The coupling constant J is calculated as the distance between these split peaks (measured in Hz). It measures the strength of the interaction between the linked nuclei. In my experiments, the NMR spectra were measured using an Agilent Unity INOVA 400 MHz. This high-resolution instrument has been employed in data gathering to analyze proton and carbon-13 nuclear magnetic resonance signals with very small chemical shifts; hence, it is used to deduce minute details about the sample's

molecular structure. A schematic diagram showing the setup and instrumentation used in this setup is given in Figure 2.7.

2.4.4 Electrospray ionization mass spectroscopy

The technique works through the conversion of a sample, normally in solution, into charged particles other words, through electrospray ionization. The produced ions are then analyzed in a mass spectrometer based on their m/z value: the ratio of the mass of an ion to its charge. This gives information concerning the molecular weight and, therefore, the structure of compounds in the sample. Large biomolecules like proteins and nucleic acids, as well as the minor components in the complex mixture of small molecules, can be analyzed with high sensitivity and precision; therefore, wide applications have been found in ESI-MS. A sample, usually was liquid form, is taken into the ESI source via capillary. A thin spray of charged droplets is formed after applying a high voltage (1-5 kV) to the liquid. The high voltage causes a Taylor cone at the capillary tip, emitting charged droplets holding analyte molecules. These droplets hold the analyte molecules. As the charged droplets pass across the ESI location, the solvent evaporates, assisted by a nitrogen flow. The droplet experiences a coulombic explosion when the charge density is too high. As a result, splitting into smaller droplets and subsequently emitting gas-phase ions are formed. The gas-phase ions are then sent to the spectrometer, where they are separated using their mass-to-charge ratio (m/z). The molecular weight and structure of the analyte are revealed by the mass spectrum. ThermoFisher Scientific Ex-active was used for the mass analysis in this work.

2.4.5 Fourier-transform infrared spectroscopy

This instrument represents a very powerful and informative analytical technique, basically taking the input on the vibration modes of molecules to contribute to understanding the chemical structure of the material.¹⁶ The molecule absorbs the infrared radiation of a specific wavelength, which causes the excitation of molecules to a higher vibrational state. FT-IR provides a broad spectrum of infrared. To create an interferogram, light is split into two beams by a Michelson interferometer and then recombined. Chemical bonds influence the interferogram in the sample, and a computer converts it into an infrared spectrum using a mathematical Fourier transform. Then it provides

detailed information about the sample's structure. In this work, a JASCO FT/IR-6800 type A, spectrometer-high-performance Fourier-transform infrared spectrometer was used due to its excellent performance based on precision and reliability during molecular analysis was used. A diamond-enabled attenuated total reflectance sample holder, likewise manufactured by JASCO in Japan, was installed on the instrument. The ATR accessory is designed to allow direct sample analysis without complex preparation such as making a thin film or forming pellets. A diamond crystal, with high hardness and excellent infrared transmittance, improves quality and accuracy in the acquired infrared spectra and is particularly effective with a wide range of samples like liquids, solids, and powders. This setup enabled the observation of the detailed vibrational modes of the molecules and provided valuable structural insight into the compounds under study.

2.4.6 Scanning transmission electron microscopy

STEM is the higher order imaging process that combines substantial principles of SEM and TEM. It finds wide applications in the imaging of nanoparticles among other small-size particles due to its provision for high resolution with major structural details. In STEM, a beam of electrons is first produced by an emission electron gun and then passed through several electromagnetic lenses serving to condense the beam into a very fine probe - usually below 1 nm in diameter. The probe is subsequently scanned over the specimen in a raster scan fashion as schematically illustrated in Figure 2.7. The sample has to be thin enough for the electron beam to pass through during effective imaging. According to atomic structure and material composition, the electron beam will scatter differently while interacting with the sample. A detector containing these scattered electrons will therefore generate high-resolution images, with great detail in the composition and structural characteristics of the sample. STEM was performed on the shape and size studies of QDs and PNCs using an ultra-thin film observation system, Hitachi HD-2000 STEM at 200-kV accelerating voltage. Images of highly detailed particles can be attained by the electrons transmitted through the sample in the observation area. This is suitable for STEM, which does a very good job of detecting performance in the size of particles less than 100 nm in diameter.¹⁷ In preparing the sample, coated with carbon (Cu100P) grids were utilized by dropping a solution of the sample onto the grid carefully. These were allowed to dry under a vacuum overnight

before imaging. The image analysis will be done through ImageJ software by taking into consideration the mean size of the particles from the data observed in the images collected analyzing the images and calculating the particle's mean size.

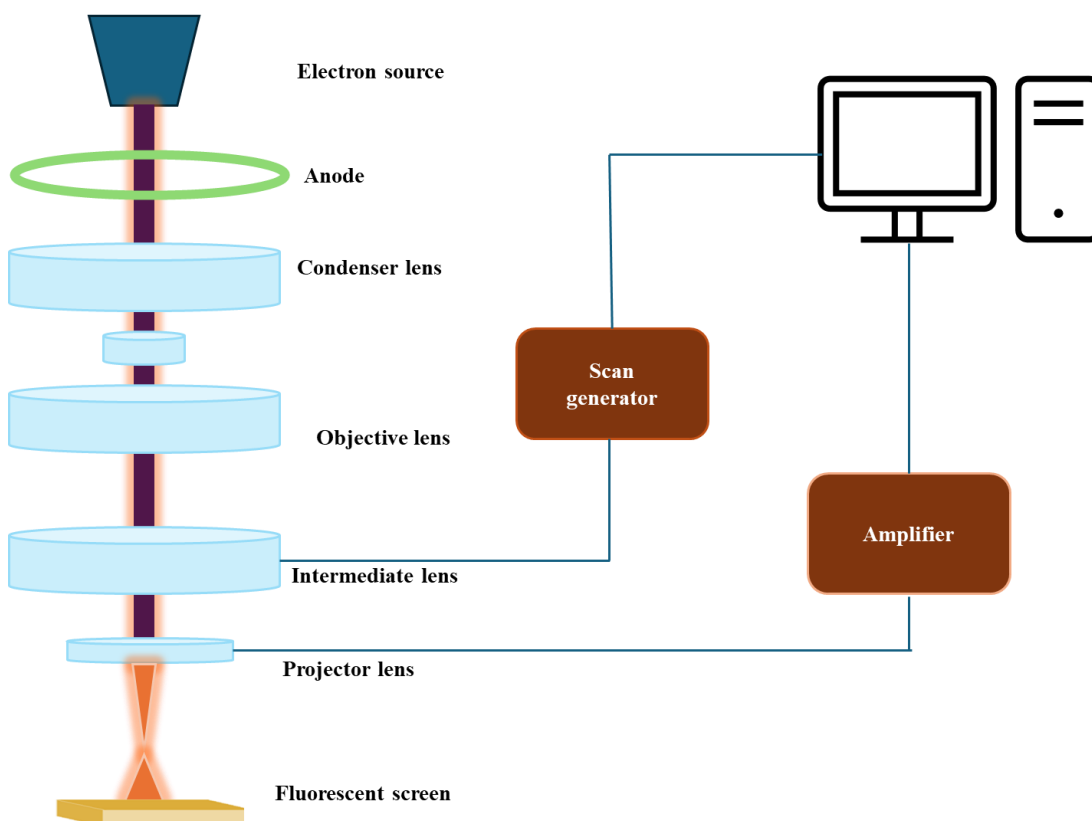


Figure 2.7 A diagram illustrating the schematic of the STEM setup.

2.4.7. Dynamic light scattering system

Samples in solution or a chemical in suspension can have their particle size measured using DLS. It measures the particles' sizes based on their Brownian motion in the solution. When particles are added to a solution, they move randomly due to their collisions with the solvent. The laser light source ejects a beam of light that is scattered after passing through the particles in the sample. To approximate the particle sizes, this method analyzes the light intensity dispersed by the particles. A beam of light will interact with a sample and then get scattered in various directions through the action of particles within it. The form, composition, and size of these particles are some of the variables that affect the amount of scattering and how it happens. By analyzing the intensity of the scattered light at different angles, the size of the particles can be inferred. The larger the particles,

the stronger the light scattering. Smaller particles scatter light differently and mostly produce weaker or differently distributed scattered light. This scattered light is quantified with sophisticated detectors and analysis software, delivering precise information about the particle size distribution in the sample. The method is one of the general ways to characterize nanoparticles and other fine-particulate materials, having wide applications in material science, chemistry, and biology. The oscillations in scattered light are studied to estimate the particles' diffusion coefficient. The diffusion coefficient may vary with particle size. The Stokes-Einstein equation is a simple mathematical relation to calculate the size of particles in a fluid by their characteristics of diffusion. In this study, the particle sizes of **ms-QD**, **QD-COOH**, **mono-QD**, and PNCs were investigated through this technique. The DLS data were analyzed using NanoSAQLA (Otsuka Electronics Co., Ltd., Japan) and accompanying software. Figure 2.8 shows the instrumental setup.

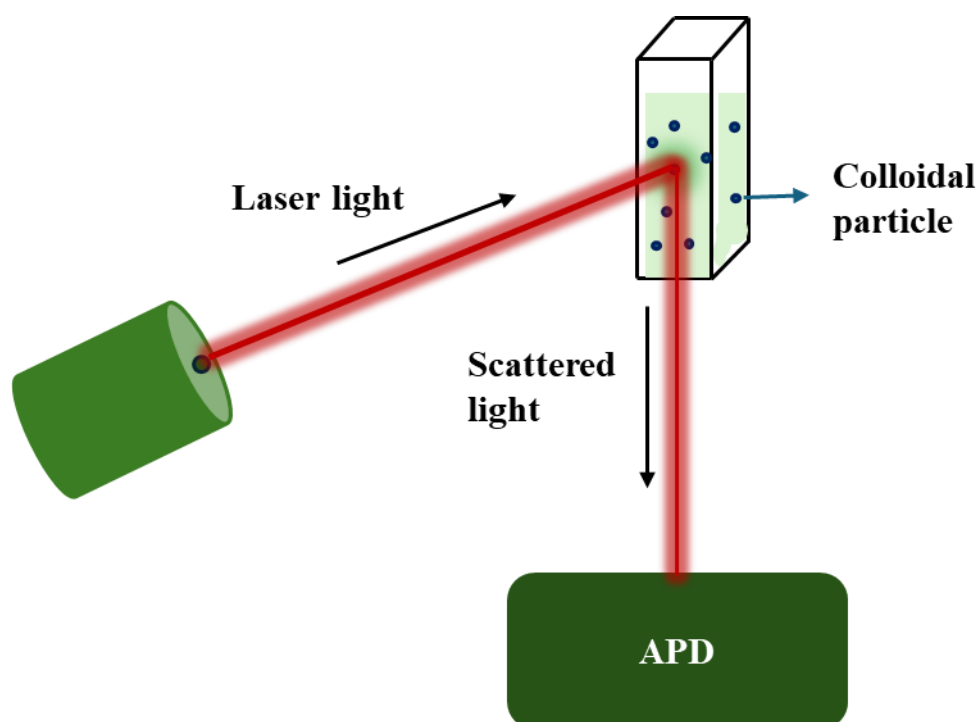


Figure 2.8 A scheme of dynamic light scattering (DLS) measurement.

2.4.8 Quantaurs Tau system

The Quantaurs Tau Technique is one of the most advanced time-resolved fluorescence measurement techniques that have so far been applied for the investigation of the fluorescence lifetime of molecules. This is important in studies on the interactions of

molecules, and dynamic processes within materials, and has great applications in environmental sensing. This process starts by illuminating a sample containing fluorescent molecules with a very short light pulse, normally emitted by a laser or an LED. The molecules, under the pulse of light, get excited as they shift electrons from the so-called ground state (S_0) to an upper energy state now defined as the excited singlet state, (S_1). From this excited state, the molecule has ways to return to the electronic ground state, either by emission (which corresponds to fluorescence) or without the emission of a photon through vibrational relaxation and internal conversion. Importantly, fluorescence does not occur in one transition, but over a length of time, often using an exponential decaying curve, where molecules relax back into the initial state. Fluorescence decay and the period are those which have commonly been regarded as the 'lifetime'; yet again, it decays by giving plenty of information concerning the surrounding milieu, such as its surroundings in interactions with other fluorescent entities or even nonfluorescent ones.

The analysis of fluorescence decay data is done by fitting the decay curve to a third-order equation, which assists in extracting essential parameters, such as lifetime and other dynamic features of the sample.

$$\tau_{avg} = A_1\tau_1 + A_2\tau_2 + A_3\tau_3 / (A_1 + A_2 + A_3)$$

In this equation, τ_{avg} is the average lifetime, A_i ($i = 1-3$) amplitude, and τ_i ($i = 1-3$) is the corresponding lifetime. It enables the study of the molecular environment and the kinetics of processes like energy transfer, conformational changes, or binding interactions in complex systems. The QuantaTaurus Tau technique finds broad applications in a wide circle of sciences, including biochemistry, physics, and material science, providing very precise time-sensitive means of studying the behavior of molecules and their interaction on very short timescales. I used this technique to measure the lifetime of QD, QD assemblies, and PNC assemblies in the solution phase.

2.4.9 A time-correlated single photon counting system

This is a highly sensitive approach for measuring the temporal behavior of weak optical signals with picosecond accuracy. This approach is very effective for fluorescent lifetime imaging, single-molecule detection, and quantum optics.¹⁸ This system works by precisely monitoring the time intervals between a sample's excitation and the detection of emitted photons. A pulsed laser source releases light pulses at a high repetition rate (usually in the MHz range). Each pulse stimulates the sample and causes it to produce photons. The emitted photons are then detected by very sensitive detectors, such as either a photomultiplier tube or an avalanche photodiode, where the detection of each photon produces an electric pulse. The time intervals between the excitation pulse serving as the START signal and the detection of the emitted photon as a STOP signal are measured by the TCSPC electronics. Resultant time intervals are then presented as a histogram graph in which the x-axis corresponds to time while the y-axis represents the number of detected photons. This histogram depicts the decay profile of the sample's fluorescence or other light-emitting processes. The histogram data is examined to obtain information such as fluorescence lifetimes, which can reveal details about the sample's molecular environment and dynamics.

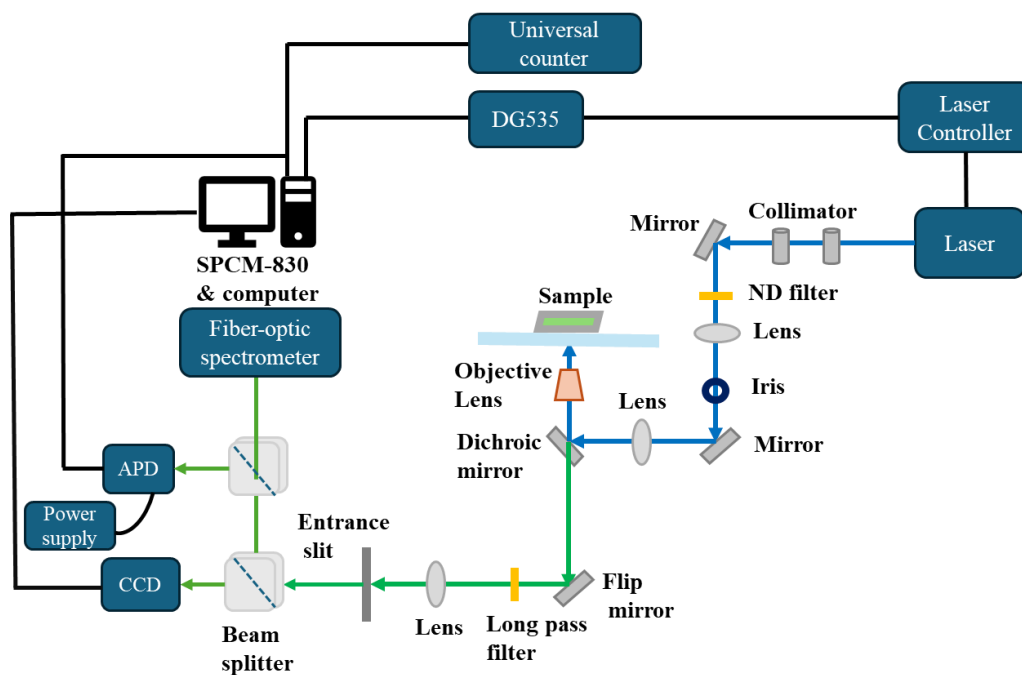


Figure 2.9 The diagram illustrating the optical arrangement and the TCSPC system. (CCD: Charge-Coupled Device, APD: Avalanche Photodiode).

To investigate fluorescence decays, the third-order equation was fitted,

$$\tau_{avg} = A_1\tau_1 + A_2\tau_2 + A_3\tau_3 / (A_1 + A_2 + A_3)$$

In this equation, τ_{avg} is the average lifetime, A_i ($i = 1-3$) amplitude, and τ_i ($i = 1-3$) is the corresponding lifetime.

In this work, time-correlated single-photon counting was performed with great precaution to measure the PL lifetimes of the PNC assemblies. A 405 nm picosecond laser system was used as the excitation source, from an advanced laser diode operating at 1 MHz with a pulse width below 50 ps for precise stimulation of the sample. Figure 2.10 depicts the complete optical configuration used during experiments. The figure shows the whole setup in detail of how it was arranged in the system. In the measurements, the sample material was mounted on the stage of an Olympus iX71 confocal microscope. This setup allowed accurate alignment and ensured the optimal interaction between the excitation light and the sample. The PL decay signals were detected by an avalanche photodiode (APD, Perkin Elmer, SPCM-AQRH-15), a very sensitive device with excellent timing resolution, capable of detecting single-photon events. The recorded photon events passed through a TCSPC module, model Becker & Hickl GmbH, SPC-M830, which thus calculated the time interval with the excitation pulses and emitted photons with very high precision. In this way, one can accurately reconstruct the PL decay profiles and investigate important insight into the photophysics and dynamic processes that occur inside such PNC assemblies. Advanced instrumentation combined with a well-conceived experimental design enabled high-quality data on the fluorescence lifetime to be obtained that contributed to an understanding of the material behavior.

References

- (1) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10). <https://doi.org/10.1039/c9cs00848a>.
- (2) Levchuk, I.; Osvet, A.; Tang, X.; Brandl, M.; Perea, J. D.; Hoegl, F.; Matt, G. J.; Hock, R.; Batentschuk, M.; Brabec, C. J. Brightly Luminescent and Color-Tunable Formamidinium Lead Halide Perovskite FAPbX₃ (X = Cl, Br, I) Colloidal Nanocrystals. *Nano Lett.* **2017**, *17* (5), 2765–2770. <https://doi.org/10.1021/acs.nanolett.6b04781>.
- (3) Nair, V. C.; Muthu, C.; Rogach, A. L.; Kohara, R.; Biju, V. Channeling Exciton Migration into Electron Transfer in Formamidinium Lead Bromide Perovskite Nanocrystal/Fullerene Composites. *Angew. Chemie* **2017**, *129* (5), 1234–1238. <https://doi.org/10.1002/ange.201610070>.
- (4) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
- (5) Zuo, C.; Scully, A. D.; Gao, M. Drop-Casting Method to Screen Ruddlesden-Popper Perovskite Formulations for Use in Solar Cells. *ACS Appl. Mater. Interfaces* **2021**, *13* (47), 56217–56225. <https://doi.org/10.1021/acsami.1c17475>.
- (6) Sachith, B. M.; Okamoto, T.; Ghimire, S.; Umeyama, T.; Takano, Y.; Imahori, H.; Biju, V. Long-Range Interfacial Charge Carrier Trapping in Halide Perovskite-C₆₀ and Halide Perovskite-TiO₂ Donor-Acceptor Films. *J. Phys. Chem. Lett.* **2021**, 8644–8651. <https://doi.org/10.1021/acs.jpclett.1c01909>.
- (7) Maggini, M.; Scorrano, G.; Prato, M. Addition of Azomethine Ylides to C₆₀: Synthesis, Characterization, and Functionalization of Fullerene Pyrrolidines. *J. Am. Chem. Soc.* **1993**, *115* (21), 9798–9799. <https://doi.org/10.1021/ja00074a056>.
- (8) Prato, M.; Maggini, M. Fulleropyrrolidines: A Family of Full-Fledged Fullerene Derivatives. *Acc. Chem. Res.* **1998**, *31* (9), 519–526. <https://doi.org/10.1021/ar970210p>.
- (9) Carbone, L.; Nobile, C.; De Giorgi, M.; Della Sala, F.; Morello, G.; Pompa, P.; Hytch, M.; Snoeck, E.; Fiore, A.; Franchini, I. R.; Nadasan, M.; Silvestre, A. F.; Chiodo, L.; Kudera, S.; Cingolani, R.; Krahne, R.; Manna, L. Synthesis and Micrometer-Scale Assembly of Colloidal CdSe/CdS Nanorods Prepared by a Seeded Growth Approach. *Nano Lett.* **2007**, *7* (10), 2942–2950. <https://doi.org/10.1021/nl0717661>.
- (10) Chen, O.; Zhao, J.; Chauhan, V. P.; Cui, J.; Wong, C.; Harris, D. K.; Wei, H.; Han, H. S.; Fukumura, D.; Jain, R. K.; Bawendi, M. G. Compact High-Quality CdSe-CdS Core-Shell Nanocrystals with Narrow Emission Linewidths and Suppressed Blinking. *Nat. Mater.* **2013**, *12* (5), 445–451. <https://doi.org/10.1038/nmat3539>.

- (11) Boldt, K.; Kirkwood, N.; Beane, G. A.; Mulvaney, P. Synthesis of Highly Luminescent and Photo-Stable, Graded Shell CdSe/Cd XZn1-XS Nanoparticles by in Situ Alloying. *Chem. Mater.* **2013**, 25 (23), 4731–4738. <https://doi.org/10.1021/cm402645r>.
- (12) Akter, R.; Kirkwood, N.; Zaman, S.; Lu, B.; Wang, T.; Takakusagi, S.; Mulvaney, P.; Biju, V.; Takano, Y. Bio-Catalytic Nanoparticle Shaping for Preparing Mesoscopic Assemblies of Semiconductor Quantum Dots and Organic Molecules. *Nanoscale Horizons* **2024**, 9 (7), 1128–1136. <https://doi.org/10.1039/d4nh00134f>.
- (13) L.C. Passos, M.; M.F.S. Saraiva, M. L. Detection in UV-Visible Spectrophotometry: Detectors, Detection Systems, and Detection Strategies. *Meas. J. Int. Meas. Confed.* **2019**, 135, 896–904. <https://doi.org/10.1016/j.measurement.2018.12.045>.
- (14) Jabłoński, A. Über Den Mechanismus Der Photolumineszenz von Farbstoffphosphoren. *Zeitschrift für Phys.* **1935**, 94 (1–2), 38–46. <https://doi.org/10.1007/BF01330795>.
- (15) Tsuchiya, M.; Wakuda, T.; Maki, K.; Shiino, T.; Tanaka, H.; Saho, N.; Tsukamoto, H.; Kido, S.; Takeuchi, K.; Okada, M.; Kitaguchi, H. Development of Superconducting Split Magnets for NMR Spectrometer. *IEEE Trans. Appl. Supercond.* **2008**, 18 (2), 840–843. <https://doi.org/10.1109/TASC.2008.920683>.
- (16) Möllmann, K.-P.; Vollmer, M. Fourier Transform Infrared Spectroscopy in Physics Laboratory Courses. *Eur. J. Phys.* **2013**, 34 (6), S123–S137. <https://doi.org/10.1088/0143-0807/34/6/S123>.
- (17) Bals, J.; Epple, M. Deep Learning for Automated Size and Shape Analysis of Nanoparticles in Scanning Electron Microscopy. *RSC Adv.* **2023**, 13 (5), 2795–2802. <https://doi.org/10.1039/d2ra07812k>.
- (18) Lyons, A.; Zickus, V.; Álvarez-Mendoza, R.; Triggiani, D.; Tamma, V.; Westerberg, N.; Tassieri, M.; Faccio, D. Fluorescence Lifetime Hong-Ou-Mandel Sensing. *Nat. Commun.* **2023**, 14 (1), 8005. <https://doi.org/10.1038/s41467-023-43868-x>.

Chapter 3

Electron transfer from perovskite nanocrystal assemblies to quencher molecules in solutions and films

3.1 Abstract

The mechanism of electron transfer from PNC assemblies to quencher molecules has garnered significant attention due to its critical role in future optical electronics. Properties of high absorption coefficients, tunable bandgaps, and efficient generation of charge carriers make PNCs ideal candidates for these applications. However, the behavior of these nanocrystals in assemblies introduces some opportunities and challenges that directly affect electron transfer efficiency. Charge carrier tunneling is possible due to their proximity to individual nanoparticles in highly packed PNC assemblies. Increased mobility of carriers due to such a tunneling effect would increase the carrier diffusion length and carrier lifetime. Such characteristics are quite desirable for applications requiring efficient charge transport and extraction, as in photovoltaic devices or photocatalysis. The dense arrangement of nanocrystals furthermore provides a huge surface area interacting with quencher molecules and facilitating effective electron transfer at the interface. These interactions are key to enabling processes like energy harvesting and catalytic reactions. Despite these advantages, uncontrolled aggregates can affect carrier transport and suppress interfacial electron transfer. Therefore, control assembly formation is necessary for efficient electron transfer. The path to optimum interfacial electron transfer lies with controlled assembly. That means one should be able to control the spatial arrangement, packing density, and connectivity of the nanocrystals to balance carrier transport efficiency with interface accessibility.

This work, therefore, systematically investigates the controlled assembly formation of FAPbBr₃ PNCs and their interaction mechanisms with electron acceptor molecules in both solution and film states. However, classic perovskite nanocrystals (PNCs) have

always faced such challenges as undesired aggregations, which hinder efficient electron transfer and energy transfer processes. In the present study, I modified well-regulated assemblies of FAPbBr_3 PNCs using the ligand assistant reprecipitated method (LARP). The interaction with three kinds of electron acceptors, including fullerene (P-C_{60}), fullerene functionalized with carboxylic acid ($\text{C}_{60}\text{-RCOOH}$), 7,7,8,8-tetracyanoquinodimethane (TCNQ) had been studied with the help of detailed spectroscopic investigations. This research has also disclosed substantial electron transfer behavior differences in solution-state vs. film-state conditions. Nanocrystal assemblies were quenched by the electron acceptors through interactions in the solution state, while the co-aggregated assemblies formed when attaining a film state that resulted in the complete quenching phenomenon.

The understanding developed in this work from the structure of nanocrystal assembly to its optoelectronic functionality was enlightening. These findings have wide ramifications in the design of advanced materials and devices, especially next-generation solar cells, LED displays, and photocatalysis. This work opens new design principles based on controlled assembly formation and interaction mechanisms for innovations in high-performance optoelectronic systems and the development of multifunctional materials.

3.2 Introduction

Lead halide PNCs have been, one of the most intriguing classes of materials because of their exceptional photo-physical properties, which include high absorption coefficient, tunable and remarkable PL, robust PLQYs, and excellent charge transport.^{1–14} These unique features make PNCs highly suitable for a wide variety of advanced optical and electronic applications. Besides that, their flexibility in application also allowed them to find their place in vital technologies like solar cells, LEDs, lasers, photodetectors, and photocatalytic systems, which reshaped the face of modern optoelectronics.^{15–20} PNCs boast a particular advantage like quantum confinement effects that enhance their remarkable optical properties. This means that their very efficient light absorption and emission, besides their tunable bandgap, make them particularly suitable for some applications. Moreover, in PSCs, PCEs have been able to exceed 25%, positioning them among the most aggressive competitors for conventional silicon-based photovoltaics.^{21,22} These few accomplishments underline how important it is to understand and optimize the electron

transfer mechanisms intrinsic in perovskite-based systems. Despite their fascinating properties, the practical realization of PNCs still meets serious difficulties, especially concerning electron transfer processes. In conventional PNCs, surface ligand molecules used for the stabilization of nanocrystals often act as insulating barriers. These ligands prevent efficient charge transfer, hence limiting energy and electron transfer processes. The challenge lies in maintaining the delicate balance between the stabilization of nanocrystals and their effective interaction with electron acceptor molecules.²³ Recent studies have shown that the controlled assembly of PNCs is one of the promising ways to go beyond these limitations. Controlled assemblies can allow inter-nanocrystal coupling, thus improving charge transport properties and thereby improving photonic performance.²⁴ Such assemblies also allow for closer proximity between nanocrystals, allowing charge carrier tunneling and significantly extending carrier diffusion lengths and lifetimes.^{25,26} The case is different when the solid films or microcrystalline structures are formed, which adds extra complications. In contrast to PNCs, which show radiative recombination, delayed recombination processes may appear in solid films. Such a discrepancy can affect the efficiency of electron transfer mechanisms. Aggregation of PNCs within such assemblies aggravates the problem; uncontrolled clustering introduces defects and traps serving as charge recombination centers. In general, electron transfer is essentially the basic principle behind the functionality of the D-A system in the operation of dye-sensitized solar cells, among many other optoelectronic devices.²⁷ Their efficiency for PNC-based systems would depend on several parameters, such as the distance between the donor-acceptor, the nature of surface ligands, and the degree of nanocrystal aggregation. Li et al. reported interfacial electron transfer from perovskites to 1,8-naphthalimide electro-acceptors in colloidal systems.²⁸ They pointed out that amino-functionalized naphthalene imide acceptors modulate quenching efficiency, the proximity of D-A being imperative. Shah et al. again showed that bulky ligands such as oleic acid and oleylamine could act as an insulating layer and inhibit charge transfer.²⁹ They exchanged these with shorter-chain alternatives through post-synthesis ligand exchange and obtained enhanced electron transfer efficiency.

This work focuses on the solution and film state electron transfer properties of FAPbBr₃ PNC assemblies. In this study, three different electron acceptors are used: pristine fullerene (P-C₆₀), carboxylic acid-functionalized fullerene (C₆₀-RCOOH), and 7,7,8,8-

tetracyanoquinodimethane (TCNQ) to elucidate assembly-specific electron transfer mechanisms.^{30–33} Investigations into how controlled assembly formation can affect electron transfer efficiency were conducted via a combination of spectroscopic techniques which indicated large differences between solution-state quenching and film-state co-aggregation phenomena. Valuable guidelines for designing high-performance optoelectronic devices are given by insights from the present work. The work overcomes the challenges of uncontrolled aggregation and optimization of interactions, thereby opening further technological advances in solar energy harvesting, LED displays, and photocatalysis. Again, controlled PNC assembly formation forms a vital parameter to achieve efficient charge transfer, which will open a new frontier in the design of multifunctional materials and next-generation optoelectronic systems.

3.3 Results and Discussion

3.3.1 Synthesis and characterization of perovskites nanocrystals

Lead halide PNCs have developed into a game-changing class of materials in optoelectronics, owing to their exceptional photophysical and charge transport properties. Lead halide PNCs with different A-site cations (Cs^+ , MA^+ , and FA^+) were systematically investigated to understand their fundamental optoelectronic properties. The selection of these three cation systems was based on their complementary characteristics: CsPbBr_3 representing the all-inorganic system with excellent thermal stability, MAPbBr_3 offering established solution processability, and FAPbBr_3 demonstrating enhanced stability and superior optical properties.

CsPbBr_3 PNCs were synthesized using the hot injection method proposed by Protesescu et al., a well-established and reproducible technique.³⁴ By this technique, the precursors will be injected rapidly into the hot solvent to permit nanocrystal development with uniform particles. The details procedure was discussed in the experimental section. STEM imaging of CsPbBr_3 (Figure 3.1A) showed that nanocrystals in a cubic crystalline structure were prepared with an average edge length of about 10 nm. MAPbBr_3 and FAPbBr_3 were prepared using the LARP method.³⁵ This preparation method is highly preferred because of the simplicity involved, coupled with the possibility of obtaining nanocrystals that have consistent size distributions. Figure 3.1B and C represent the STEM images of such nanocrystals exhibiting regular cubic phase structures, with an

approximate edge length of about 10 nm, comparable in size to those of CsPbBr₃. The morphological and dimensional homogeneity again underlines the usefulness of the LARP technique in providing good-quality PNCs. Nanocrystal solutions were prepared at a concentration of 0.050 mg/mL in toluene to facilitate detailed structural characterization. The solutions were carefully deposited onto 100 μ M copper STEM grids where the nanocrystals self-assemble into ordered structures. This was done in careful preparation to ensure that imaging was done at high resolution, representing the actual morphology of the nanocrystals and, hence in-depth analysis of their structural attributes.

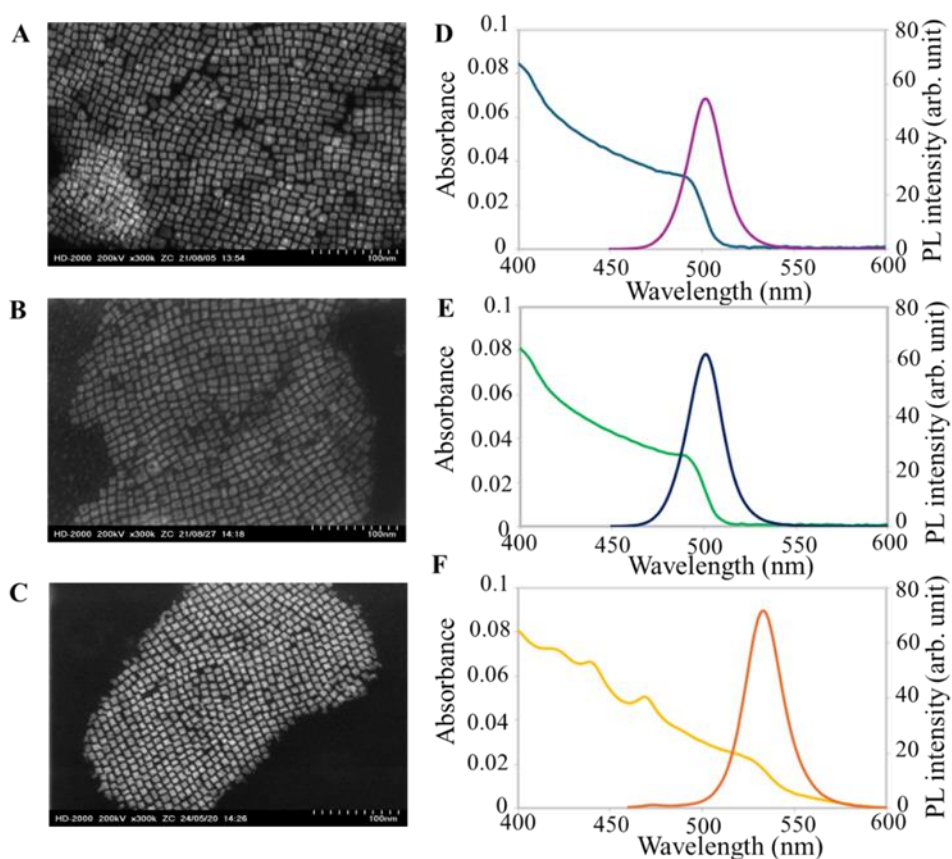


Figure 3.1 Characterization of various PNC. (A, B, C) STEM images of CsPbBr₃, MAPbBr₃, and FAPbBr₃ PNCs showing cubic phase morphology. (D, E, F) The absorption and spectrum of PL of PNCs distributed in toluene, (λ_{ex} = 400 nm).

The PL and absorption spectra of PNCs dissolved in toluene solution for Figures 3.1D, E, and F give crucial insight into their optoelectronic properties. It will be very important in understanding the nature of light absorption and emission in CsPbBr₃, MAPbBr₃, and

FAPbBr₃, giving further information on A-site cations responsible for their tuned optical properties. UV-vis absorption spectra indicate that all three PNCs have distinct excitonic peaks, reflecting their quantum-confined nature and high-quality crystalline structure. For CsPbBr₃, the excitonic absorption peak is located at 495 nm, reflecting its inherent electronic structure and relatively smaller size effect. The MAPbBr₃ has its excitonic peak at 500 nm, which is a little redshifted from the excitonic peak of CsPbBr₃. The position is expected, taking into account structural and electronic differences given by the MA⁺ cation. In FAPbBr₃, the excitonic peak lies at 530 nm; hence, the large red shift compared to the other two PNCs exists. This may be due to weaker quantum confinement effects as the nanocrystal size and morphology of FAPbBr₃ change. Such a red shift in FAPbBr₃ is remarkable because it is associated with variations in size, shape, and structural packing of the nanocrystals as induced by synthesis conditions.^{36–38} Indeed, the redshift implies larger nanocrystals that provide less quantum confinement, in good agreement with earlier findings. PL spectra of the three PNCs show their emission peaks, indicating excellent optical quality and high luminescence efficiency. In this case, the CsPbBr₃ emission peak appears at 502 nm, which coincides well with its absorption character, indicating very minimal Stokes shift and efficient radiative recombination. Regarding MAPbBr₃, the emission peak is located at 508 nm, slightly red-shifted concerning that of CsPbBr₃, in agreement with the absorption behavior. The emission peak for FAPbBr₃ is at 534 nm, further red-shifted compared to MAPbBr₃ and CsPbBr₃, in agreement with its excitonic absorption peak. The FWHM values of the PL spectra for the PNCs give a measure of the spectral purity and size distribution. In the case of, CsPbBr₃ and MAPbBr₃ PNCs have narrow FWHM values of 22 nm, indicating their highly uniform size distribution and high crystallinity. The FWHM for FAPbBr₃ is 23 nm, which is slightly broader but still in agreement with previous reports.³⁵ This slightly broader FWHM may be due to slight variations in size or morphology during the synthesis process. The red shift in FAPbBr₃, together with its narrow emission linewidth, underlines its possible application in near-infrared LEDs and photovoltaics requiring lower bandgap materials.

3.3.2 Photoluminescence quenching study in solution

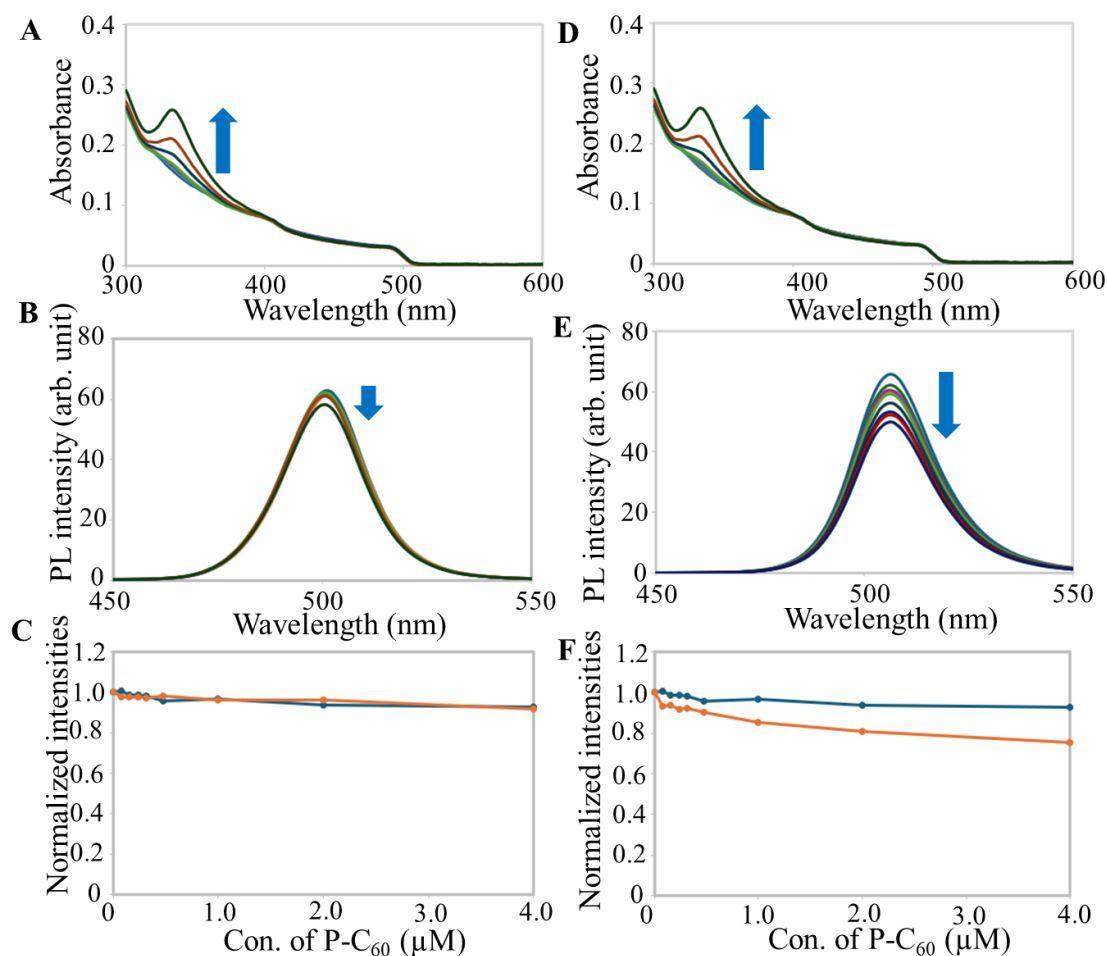


Figure 3.2 PL quenching study of PNCs in the solution phase. (A) Absorption spectra and (B) PL spectra ($\lambda_{\text{ex}} = 400$ nm) of CsPbBr₃ PNCs with various concentrations of P-C₆₀. (C) Concentration-dependent normalized absorbance (blue) at 400 nm and PL intensity (orange) at 502 nm. (D-F) Corresponding data was acquired with MAPbBr₃ and P-C₆₀.

To understand the electron transfer characteristics of the PNC, pristine fullerene (P-C₆₀) was chosen as the electron acceptor, given its high electron affinity and well-understood performance in the context of donor-acceptor systems.³⁹ In this work, P-C₆₀ serves as a benchmark acceptor molecule for charge transfer studies and provides a robust platform in the study of optoelectronic interactions with PNCs. For experiments, 0.050 mg/mL solution concentrations for both CsPbBr₃ and MAPbBr₃ PNCs were prepared in toluene. Baseline measurements of absorption and PL spectra were performed first,

without adding P-C₆₀, to establish reference data. The concentration of P-C₆₀ in toluene was increased step by step from 0.16 μ M up to 5.0 μ M; at each increase, the spectral changes were monitored. No significant change in the absorption spectrum, especially at 400 nm (Figures 3.2A and C), was observed for CsPbBr₃ upon adding P-C₆₀. That is, no spectral shift nor new absorptions were developed, thus indicating no ground-state donor-acceptor interactions.⁴⁰ Such a phenomenon implies minimum electronic coupling between the ground states of CsPbBr₃ and P-C₆₀, thus confirming similar literature reports. Similarly, PL intensities of the CsPbBr₃ solutions showed a negligible drop with increasing the concentration of P-C₆₀. Generally, in normal donor-acceptor systems, effective electron transfer often leads to fluorescence quenching because the excited electron can be delocalized over the entity of the acceptor molecule.^{41,42} Therefore, inefficient quenching indicates poor electron transfer.

For MAPbBr₃, the absorption spectra did not change in the entire P-C₆₀ concentration range (Figures 3.2D and F), indicating the same ground-state behavior as CsPbBr₃. The PL intensities of the MAPbBr₃ solutions also exhibited only a slight quenching (Figure 3.2E). This minimal quenching reflects the inefficiency of electron transfer in the MAPbBr₃-P-C₆₀ system, pointing to barriers to effective donor-acceptor interactions. The ineffective electron or energy transfer in both CsPbBr₃ and MAPbBr₃ systems could be explained. There was a physical barrier that existed due to the free ligands present in the solution—for example, oleic acid and oleylamine.⁴³ Free ligands surrounded the PNCs to prevent the acceptor molecules from coming closer to the donor molecules at an optimal distance required for efficient electron transfer. In other words, the strong binding of capping ligands on the PNC surface further confines the nanocrystals and restricts accessibility for donor-acceptor interactions. The process of electron transfer, in particular, requires such a proximity between the spatial donor and acceptor molecules and is impeded by the ligand shell and the concentration of free ligands in solution.^{44,45}

To overcome these limitations and improve electron transfer efficiency, another approach based on PNC assemblies (FAPbBr₃) was developed. This drastically reduces the concentration of free ligands and allows donors and acceptors to get closer, while interaction sites are more accessible. The assemblies allow for a denser packing of PNCs, enabling more efficient charge transfer mechanisms. The alternative approach will not only overcome the excess ligand challenges but also provide a route for optimizing

electron transfer properties in PNCs. The data obtained so far forms a basis for further study in the controlled assembly formation process and its influence on electron transfer in advanced optoelectronic systems.

3.3.3 Characterization of the FAPbBr₃ nanocrystal assemblies

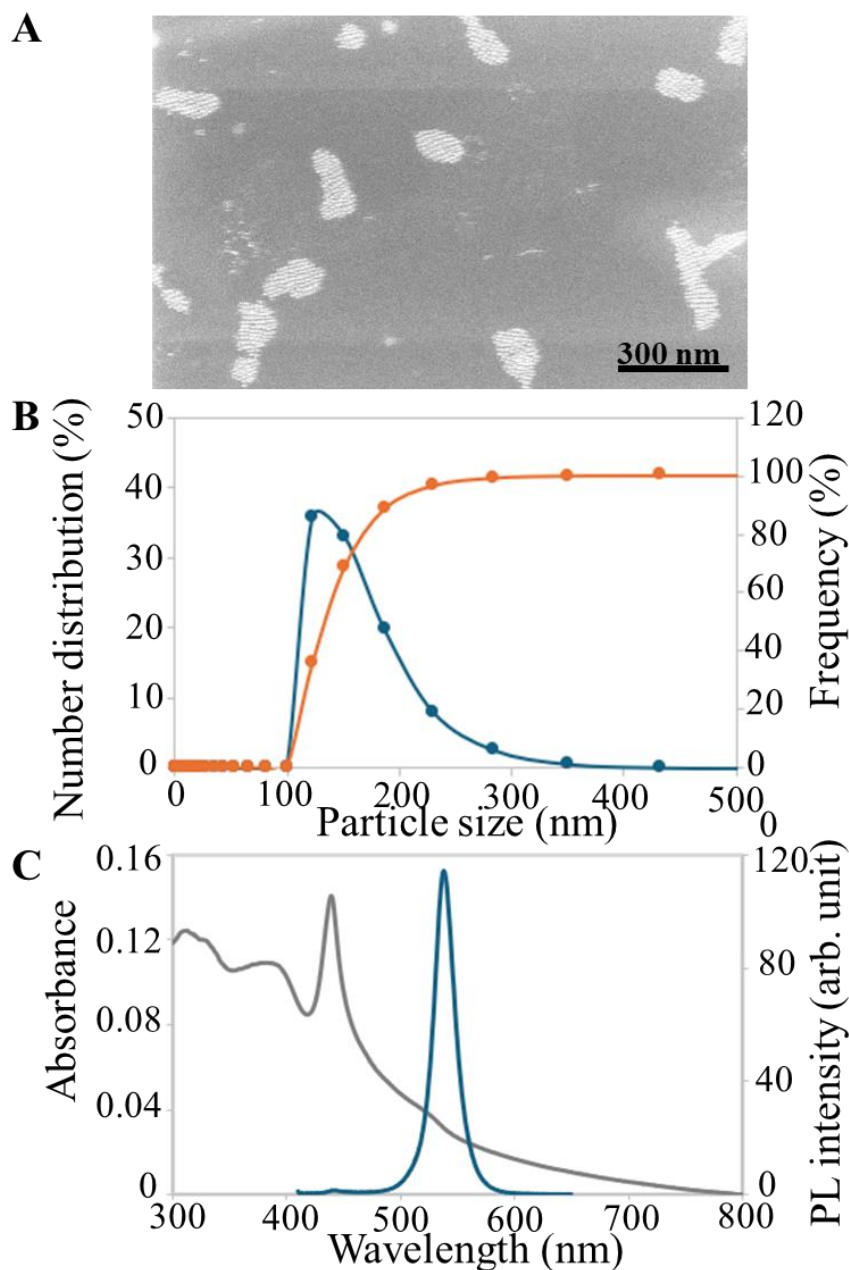


Figure 3.3 Characterization of the FAPbBr₃ PNCs assembly. (A) STEM image showing the morphology of the assembly. (B) DLS measurement shows the particle size distribution. (C) Absorption and PL spectra of the assembly in toluene.

The LARP method, which has been widely used for high-quality nanocrystal production, is the general preparation way for the FAPbBr₃ PNC assemblies. The modification of a specific purification protocol gave birth to the controlled assembly. As an example, crude FAPbBr₃ PNCs were centrifugally washed with toluene three times. Indeed, such meticulous purifications are capable of eliminating the extra amount of unreacted precursors with ligands to obtain only well-dispersed nano-assemblies containing uniform morphology and optical properties.

STEM was used to analyze the structural characteristics of the FAPbBr₃ PNC assemblies. From Figure 3.3A, it can be seen that the assemblies are well dispersed and the size of a single assembly falls in the range of 100-150 nm. The microscopy data suggest that, within the assemblies, the nanocrystals remain well-ordered; this is consistent with the hypothesis that controlled assembly formation has been achieved. Complementarily, DLS measurements were also performed to complement microscopy observations. Figure 3.3B displays DLS data that further support good dispersion of the PNC assemblies in toluene, reflected by a relatively low PDI of 0.147. This suggests a narrow size distribution for the assemblies. The size of the assemblies (160.0±42.5 nm) measured by DLS shows good agreement with the results of STEM and thus confirms the homogeneity and stability of the obtained assemblies. Figure 3.3C presents PL and absorption spectroscopy of the optical characteristics of PNC assemblies in FAPbBr₃. It has been seen in the absorption spectrum, with an excitonic peak at 440 nm consistent with earlier reports on FAPbBr₃ PNCs, a signature for the strong light-absorbing capacity of PNCs. The PL spectrum, which evidences the redshift of the emission peak from 535 nm for individual nanocrystals to 540 nm for assemblies, represents a key observation and thus indicates electronic coupling among the nanocrystals in assemblies. This type of coupling results from reduced interparticle spacing in assemblies, which allows increased interaction between electronic states of neighboring nanocrystals. The capping ligands, while ensuring the stabilization of the individual nanocrystals, affect the formation of the assemblies. Controlled washing during the synthesis reduces excess free ligands, which allows for closer packing of the nanocrystals in the assemblies. This, in turn, causes better electronic coupling that reflects in the optical spectra. Structural and optical characterizations indicate the successful synthesis of well-organized FAPbBr₃ PNC assemblies. In consequence, these assemblies display unique optoelectronic properties

because of the interplay of nanostructure with electronic interactions and, therefore, are promising candidates for advanced optoelectronic applications.

3.3.4 Photoluminescence quenching study for FAPbBr₃ PNCs assemblies in solutions

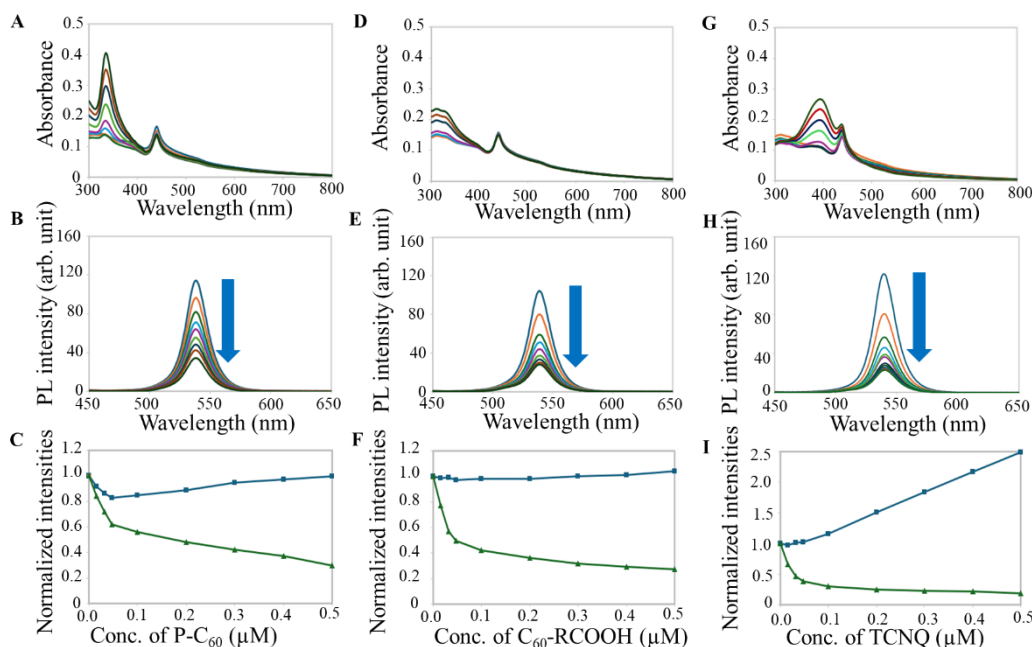


Figure 3.4 PL quenching study of FAPbBr₃ PNCs assembly in solution. (A) Absorption spectra and (B) PL spectra ($\lambda_{\text{ex}} = 400$ nm) with various concentrations of P-C₆₀. (C) Concentration-dependent normalized absorbance (blue) and PL intensity (green) at 540 nm. (D-F) and (G-I) Corresponding data acquired with C₆₀-R₂COOH and TCNQ, respectively.

In this regard, electron transfer properties of the FAPbBr₃ PNC assemblies were studied using three various electron acceptor molecules: pristine fullerene (P-C₆₀), COOH-functionalized fullerene (C₆₀-R₂COOH), and 7,7,8,8-tetracyanoquinodimethane (TCNQ). All three acceptors have been selected based on their distinct electronic properties. P-C₆₀ is a neutral molecule of exceptionally high electron affinity widely used in electron transfer studies. Fullerene was functionalized with carboxylic acid groups, including additional electronic and steric interactions due to COOH groups. TCNQ is a well-known strong electron acceptor, widely investigated for its redox activity due to its high electron affinity. The optical behaviors of the assembled FAPbBr₃ PNCs in the presence of P-C₆₀ were recorded by monitoring changes in absorption and photoluminescence spectra, respectively (Figures 3.4A, 3.4B, and 3.4C). The absorption at 400 nm decreases

progressively upon stepwise addition of P-C₆₀ in toluene at concentrations from 0.16 to 5.0 μ M to the PNC assembly solution, as shown in Figure 3.4C. Such a progressive reduction of absorption suggests ground-state donor-acceptor interactions between the PNCs and P-C₆₀ molecules through the interaction. Consistent spectral change supports a common interaction mechanism in the whole concentration range.

The behavior of the assembly in the presence of C₆₀-RCOOH was distinctly different, whereas the absorption spectra of the PNC assembly were hardly affected upon increasing the concentrations of C₆₀-RCOOH (Figure 3.4D), indicative of the absence of ground-state complex formation. Therefore, interaction of C₆₀-RCOOH with the PNC assembly is distinctly different from P-C₆₀, the PL intensity gradually decreased upon increasing the concentration of C₆₀-RCOOH (Figure 3.4E), indicating effective electron transfer. However, at higher concentrations, saturation behavior was observed for the system (Figure 3.4F). Such a phenomenon indicates the formation of a static donor-acceptor complex where most of the available interaction sites on the PNC assembly are occupied by C₆₀-RCOOH molecules and the electron transfer process has reached its limit. As observed for C₆₀-RCOOH, investigations into the interaction of TCNQ with FAPbBr₃ PNC assemblies revealed a weak ground-state interaction due to the absence of significant absorption spectral changes (Figure 3.4G). PL intensity was reduced with increasing concentration of TCNQ (Figure 3.4H, I), similar to the observations made in the case of interaction with C₆₀-RCOOH, thus indicating successful electron transfer from the PNC assembly to TCNQ.

These results strongly establish that efficient electron transfer occurred in all these experimental trials among FAPbBr₃ PNC assemblies with selected acceptor molecules. However, the mode of electron transfer was quite different because it is sensitive to the electronic properties of the selected acceptors. For instance, with the participation of P-C₆₀, obvious features of donor-acceptor interaction along with dynamic electron transfer have been evident in ground-state interaction. In the case of C₆₀-RCOOH, efficient electron transfer is observed; however, this gives way to a static donor-acceptor complex upon higher acceptor concentrations, due presumably to steric or surface interaction effects of the COOH group. TCNQ with its strong electron affinity, the efficient electron transfer process is observed; the latter process is only excited-state interactions.

The presented findings emphasize the need for tailoring donor-acceptor systems to optimize electron transfer properties in nanocrystal assemblies and provide valuable lessons in the design of advanced optoelectronic devices.

3.3.5 Photoluminescence lifetime measurements of FAPbBr₃ assemblies in solutions

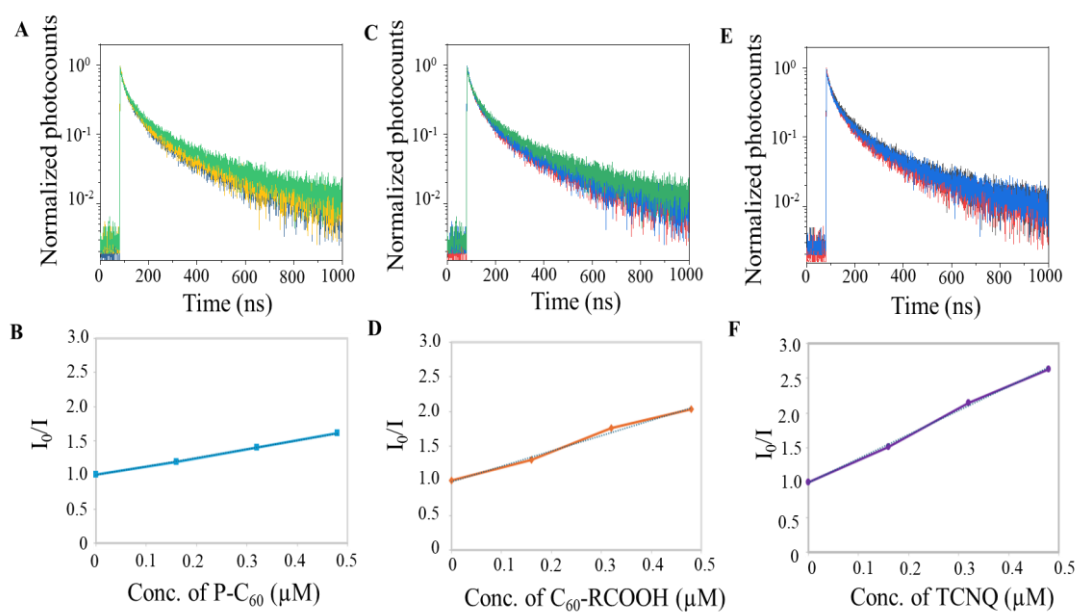


Figure 3.5 Time-resolved PL measurements in solution. (A) PL decay profiles of assembly with various concentrations of P-C₆₀. (B) Corresponding Stern-Volmer plot. (C-D) and (E-F) Corresponding data for C₆₀-RCOOH and TCNQ, respectively.

Lifetime measurements and Stern-Volmer analysis were performed to unfold the interaction mechanisms between the FAPbBr₃ PNC assemblies and selected electron acceptor molecules, P-C₆₀, C₆₀-RCOOH, and TCNQ. These experiments give critical insight into the quenching pathways and efficiency of electron transfer in the system. The PL lifetimes of FAPbBr₃ PNC assemblies were measured in the presence and absence of the acceptor molecules. In the absence of any acceptors, the PNC assembly exhibited a pretty long lifetime of 59.0 ns. The extended lifetime represents large assemblies, and this corresponds to a low probability of the non-radiative decay processes because of the spatial separation of the charge carriers in assemblies. The PL lifetime was slightly reduced by the addition of P-C₆₀ to 57.1 ns (Figure 3.5A). The small lifetime reduction indicates that the interaction between the PNC assembly and P-C₆₀ is mainly through a static quenching mechanism where the interaction is not dynamic but through the formation of

ground-state complexes. The PL decay profiles, upon the addition of C₆₀-RCOOH and TCNQ, exhibited negligible changes similar to P-C₆₀ (Figures 3.5C and 3.5E). This observation further reiterates that the interaction between the acceptor molecules and PNC assembly mainly involves static rather than dynamic processes.

To quantitatively analyze the quenching behavior, Stern-Volmer (SV) analysis was performed using the following equations:

$$I_0/I = \tau_0/\tau = 1 + K_{sv}[q] \quad (\text{eq. 1})$$

Where I_0 and I are the PL intensities of the NC assembly without or with acceptors, τ_0 , and τ are the average lifetimes of the NC assembly without, and with the acceptors, $[q]$ is the concentration of acceptor, and K_{sv} is the SV constant. The rate constant of quenching, K_q , is linearly related to K_{sv} , according to the equation (2),

$$K_{sv} = K_q \tau_0. \quad (\text{eq. 2})$$

The Stern-Volmer plots for P-C₆₀, C₆₀-RCOOH, and TCNQ with the NC assembly showed linear relationships (Figures 3.5B, D, and F), providing further evidence for static quenching mechanisms.^{28,46} The Stern-Volmer constant was calculated based on the slope of the Stern-Volmer plot and the values obtained are $1.32 \times 10^6 \text{ M}^{-1}$ for P-C₆₀, $2.28 \times 10^6 \text{ M}^{-1}$ for C₆₀-RCOOH, and $3.50 \times 10^6 \text{ M}^{-1}$ for TCNQ. Then, the quenching constant K_q was calculated from eq. 2. The corresponding observed quenching constants are $22.3 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for P-C₆₀, $41.5 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for C₆₀-RCOOH, and $60.1 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for TCNQ, indicating highly efficient quenching by all three acceptor molecules.⁴⁷

Negligible variation of lifetime values and linear Stern-Volmer plots indicate that the major interaction of the acceptors with the PNC assembly is through a static pathway, i.e., via ground-state complex formation rather than by dynamic collision processes. Quenching constants reveal that among the three acceptor molecules, TCNQ is the most efficient quencher followed by C₆₀-RCOOH and P-C₆₀. This trend is in good agreement with the known electron affinity of the acceptors, with TCNQ having the highest electron-accepting capability among them. The high quenching efficiency for all three kinds of acceptors underlines the potential of the FAPbBr₃ PNC assemblies in electron transfer systems, while it explores applications like solar cells, light-emitting diodes, and photodetectors. The static quenching mechanism indicates that further optimization of the donor-acceptor interface can lead to better device performance. The present comprehensive analysis gives evidence of the flexibility and efficiency of FAPbBr₃ PNC assemblies in facilitating

electron transfer processes, thus providing a solid basis for their application in advanced optoelectronic systems.

3.3.6 Photoluminescence lifetime measurement in the film state

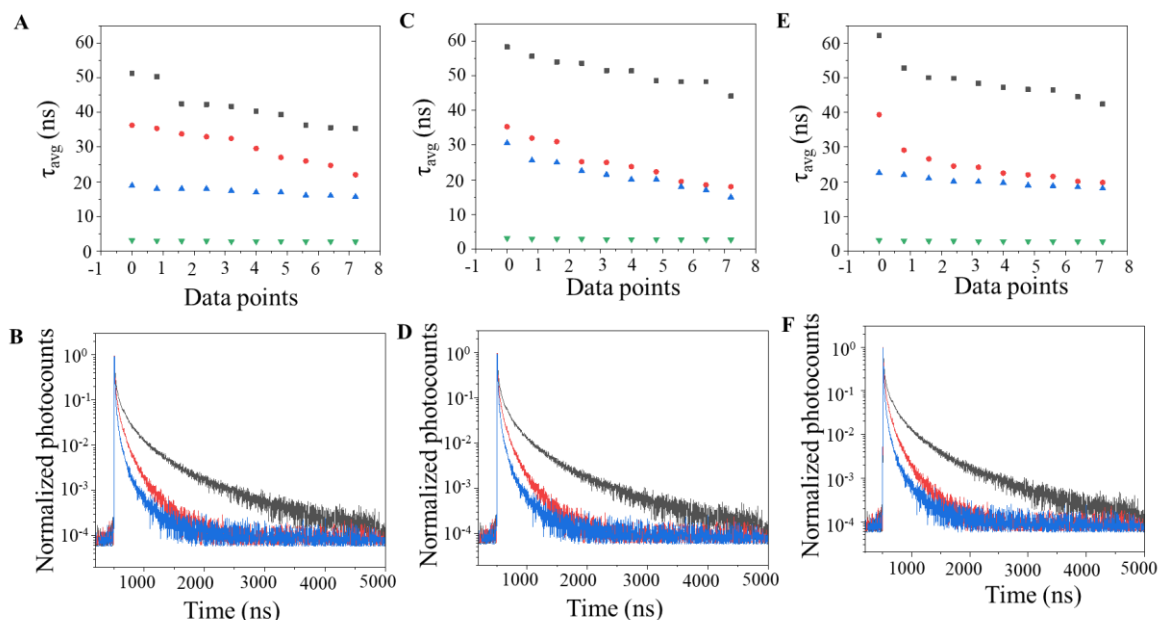


Figure 3.6 Time-resolved PL measurements in film state. (A) Average PL lifetimes and (B) PL decay profiles of FAPbBr₃ PNCs assembly (black), with P-C₆₀ (red), and co-aggregated with P-C₆₀ (blue). (C-D) and (E-F) Corresponding data for C₆₀-RCOOH and TCNQ, respectively.

The study of donor-acceptor interactions in the film state will look into the influence of aggregation and electron acceptors on the photophysical properties of FAPbBr₃ PNC assemblies. This experiment gives very valuable information on how electronic interactions present themselves in a solid-state configuration relevant to practical applications, such as optoelectronic devices. The PNC assemblies of FAPbBr₃ were prepared using a drop-casting method by evenly spreading onto the substrate in the form of a thin film. The film was dried and then PL lifetime measurements were carried out at different positions to check the homogeneity and reproducibility. Accordingly, the average PL lifetime of FAPbBr₃ PNCs in assembled thin-film form was much longer than that in the dispersed state, represented by black points in Figure 3.6A and green in Figure 3.6B, respectively. The longer lifetime in the assembled state may be associated with changes in excited-state dynamics in the course of aggregation. These changes can lead to a non-radiative

decay pathway that is diminished, hence stabilizing the excited state and enhancing the overall lifetime of the material.

To investigate the effects of added electron acceptors on the photophysical behavior of the assembly in the film state, the following experimental conditions were employed. A solution containing 5.0 μM P-C₆₀ was deposited on top of the preformed FAPbBr₃ PNC assembly film. This post-synthesis application resulted in a measurable decrease in the average PL lifetime of the assembly, red points in Figures 3.6A and 3.6B. This reduction in lifetime is indicative of successful donor-acceptor interactions where excited-state electrons from the PNC assemblies are transferred to the P-C₆₀ molecules, resulting in the quenching of the PL signal.

For the further investigation of the interaction mechanism, one co-aggregated sample was prepared by the LARP method, and during the synthesis process, 5.0 μM of P-C60 was added. Then, a film of this co-aggregated sample was prepared via the drop-casting method on a glass cover slip. Compared with the case after film addition, in this co-aggregated sample, the averaged PL lifetime has been more greatly reduced, as evidenced by the blue points in Figures 3.6A and 3.6B. These considerably reduced lifetime values and PL decay profiles signify the efficient quenching promoted by intimate donor-acceptor interactions during the co-aggregation process.

To compare the behavior of different electron acceptors, similar experiments were carried out using C₆₀-RCOOH and TCNQ as electron acceptors. Both C₆₀-RCOOH and TCNQ showed trends similar to that of P-C₆₀, where significant reductions in PL lifetimes and decay profiles were observed for both post-film addition and co-aggregated samples. These results thus not only prove that the quenching mechanism is not unique for P-C₆₀ but also represent a common feature in the effective donor-acceptor system-involving FAPbBr₃ PNC assemblies and suitable electron acceptors.

These findings underscore the crucial role of aggregation in modulating the excited-state dynamics, as evidenced by the longer lifetimes recorded for the PNC assembly films relative to that of the dispersed PNCs. The co-aggregation method tends to show better efficiency in donor-acceptor interactions compared to post-film addition, suggesting an optimized quenching process upon pre-synthesis incorporation of acceptors. Consistent results among P-C₆₀, C₆₀-RCOOH, and TCNQ attest to the robustness of the FAPbBr₃ PNC assembly in facilitating efficient donor-acceptor interactions in the film state. Most

of these findings are highly relevant in application to solar cells, photodetectors, and LEDs, where effective charge transfer and quenching mechanisms are highly vital for device performance. These findings collectively lead to the conclusion that the film-state studies unequivocally establish FAPbBr₃ PNC assemblies as versatile platforms of donor-acceptor interactions whose properties can be tuned by aggregation and choice of acceptor.

3.3.7 Charge transfer mechanisms in solutions and the films

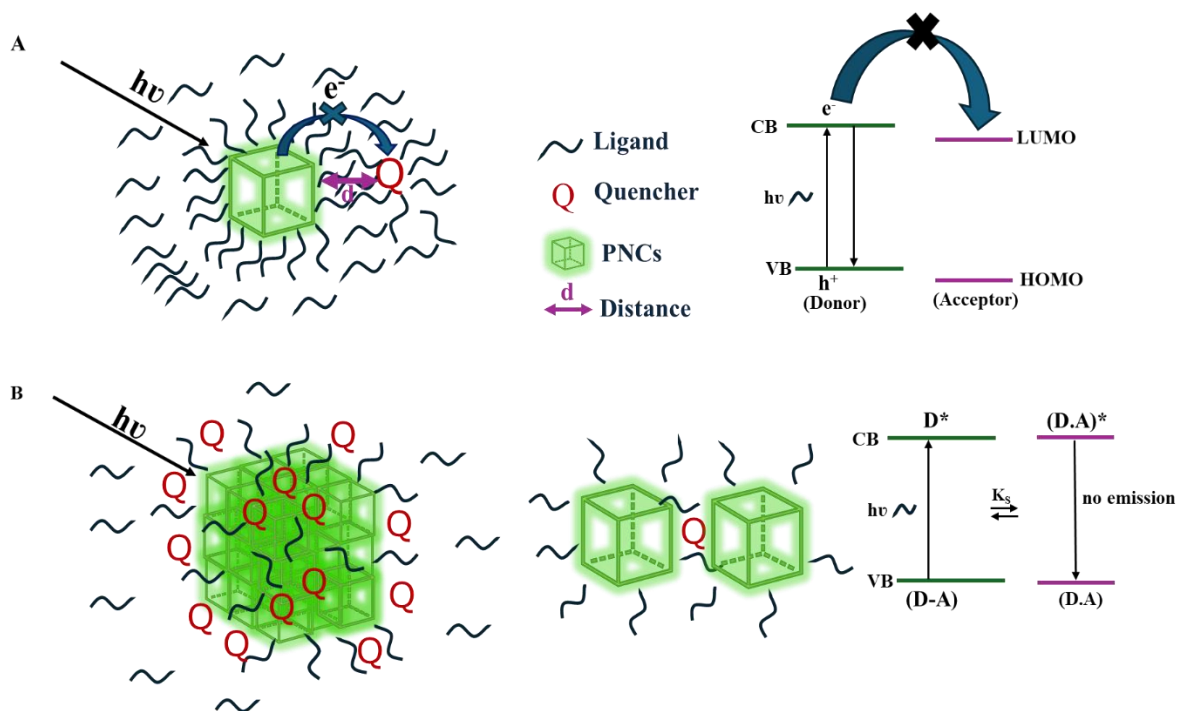


Figure 3.7 Schematic representation of the overall dynamics of charge carriers of perovskites in the solution phase. (A) FAPbBr₃ PNCs with a quencher, (B) FAPbBr₃ PNCs assembly with quenchers. (VB, valence band; CB, conduction band, HOMO, highest occupied molecular orbital; LUMO, lowest occupied molecular orbital).

Charge carrier dynamics were systematically studied in solution and film states of FAPbBr₃ PNC systems, with a focus on unraveling structural characteristics of donor-acceptor systems that would provide an understanding of the dynamics involved. These observations have given great insight into how aggregation and ligand interactions influence charge transfer and quenching mechanisms. Figure 3.7 (A) shows the most salient features of the differences in the solution phase properties of individual PNCs versus assemblies of PNCs. Individual FAPbBr₃ PNCs in solution are surface-passivated with a dense layer of free ligands along with surface-capping ligands like oleic acid and

oleylamine. These ligands are protective shells of nanocrystals that are colloidal and at the same time are preventing quencher molecules from approaching the surface of the PNC. This creates a physical barrier that prevents the quencher molecules from coming into proximity with the PNCs. The lack of proximity prevents any significant electron transfer/quenching, and the interaction between donor and acceptor is negligible in individual PNCs at the solution state. The structural arrangement in FAPbBr₃ PNC assemblies is vastly different. Though stabilized by surface ligands similar to individual PNCs, it is much loosely held. The looser ligand packing forms gaps and exposed sites on the aggregated nanocrystals, allowing quencher molecules to approach the surface of the assembly more easily. These accessible sites, as illustrated in Figure 3.7 (B), allow for possible donor-acceptor interactions via a static quenching pathway. This would involve the formation of a stable complex between the quencher molecules and the assemblies of PNC, thus allowing efficient charge transfer to result in observable quenching effects.

In contrast to the solution state, different dynamics in a film state should arise due to the change in the structural organization of nanocrystals and the role of aggregation. When acceptor molecules are not present, compact film formation in which nanocrystals agglomerate stabilizes excited states and is followed by increasing PL lifetime, as in FAPbBr₃ PNCs. This aggregation decreases the non-radiative pathways due to better confinement of the charge carriers in the film. Upon the addition of quencher molecules such as P-C₆₀, C₆₀-RCOOH, or TCNQ, the interactions in the film state are significantly increased as compared to the solution state. The aggregated structure of the film allows direct interaction of the acceptor molecules with the surface-exposed nanocrystals without the limitations imposed by free ligands in solution. These interactions result in a reduction in PL lifetimes, evidencing successful charge transfer between the donor-PNC assemblies and the respective acceptors.

Basically, in these systems, the structural properties of the donor-acceptor systems influence charge transfer efficiency. Ligands have a double role. They stabilize PNCs in solution but act also as barriers to donor-acceptor interactions. In assemblies, partial ligand removal or loosening provides better access for the quenchers. This stresses again that optimization of the ligand concentration and arrangement is crucial for effective charge transfer. Aggregation in assemblies inherently provides more available surface area for interaction with corresponding adequate stability. This structural configuration

bridges the solution-phase and film-state dynamics, hence positioning assemblies as the ideal intermediate systems to explore mechanistic issues revolving around donor-acceptors. The static pathway of quenching observed in the assemblies suggests that the interactions are stable involving the formation of donor-acceptor complexes. This pathway is especially favorable in applications that rely on consistent and effective charge transfer, such as in solar cells or photodetectors.

The results in Figure 3.7B emphasize the importance of structural features in determining the charge carrier dynamics in FAPbBr₃ PNC systems. It is the interplay of ligand arrangement, aggregation, and accessibility that defines the efficiency of donor-acceptor interactions in both solution and film states. These insights are opening up new avenues for modifying nanocrystal systems to optimize their performance in optoelectronic applications.

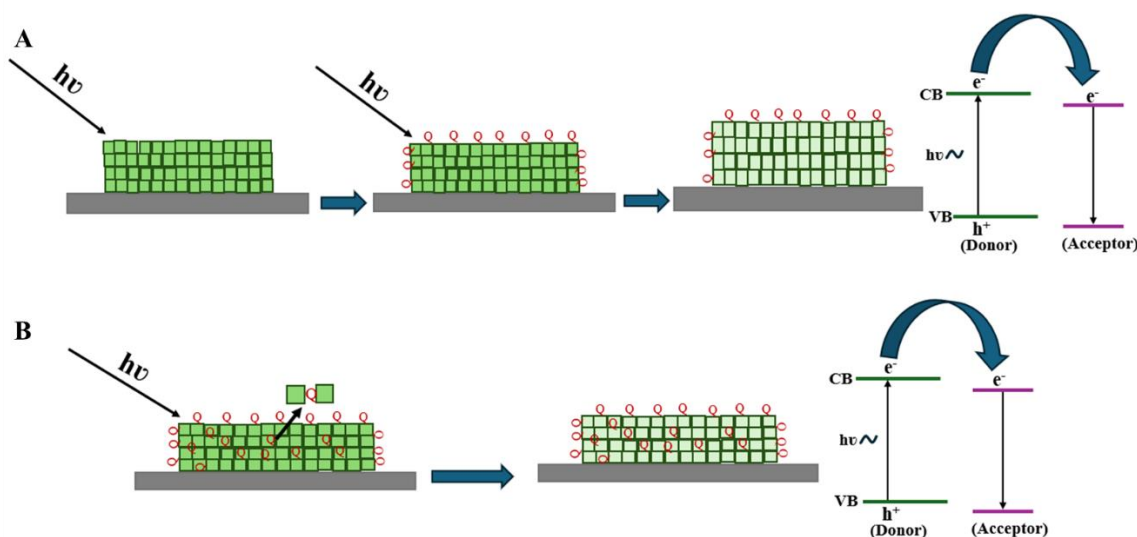


Figure 3.8 Schematic representation of the overall dynamics of charge carriers of perovskites in the film state. (A) FAPbBr₃ PNCs with a quencher. (B) Co-aggregated sample.

Charge transfer dynamics in the film state of FAPbBr₃ PNC systems are unique and highly efficient as compared to the solution phase. These differences, as depicted in Figure 3.8, have been due to the molecular arrangement and accessibility of quencher molecules to donor surfaces, outlining the crucial role of structural organization in optimizing electron transfer efficiency. While self-assembling into nano-aggregates in a thin film, the structural arrangement of FAPbBr₃ PNCs is such that it remains compact yet

accessible to charge transfer interactions. Quenchers came directly in contact with the surface of the nanocrystal when 5.0 μM of P-C₆₀ was added on top of the nanoaggregate layer. This interaction promotes efficient electron transfer from the donor nanocrystals to the acceptor molecules, as reflected in a measurable reduction of PL lifetimes. However, the quenching efficiency, though high, is not complete because the interaction remains confined to the surface dynamics level due to the presence of protective ligands and the compact nature of the aggregates. In the case of co-aggregated samples, quencher molecules, such as P-C₆₀, are introduced during the synthesis and thus become part of the assembly at the molecular level. This co-aggregation allows the quencher molecules to interact not only with the surface of the nanocrystals but also with their internal crystalline structure, thereby creating a more robust donor-acceptor interface. This increased interaction thus results in the complete quenching of PL lifetimes, as experimentally observed, showing the strong influence of structural integration on charge transfer efficiency.

Complete quenching for co-aggregated samples reflects very efficient donor-acceptor interaction, which is important for several applications in optoelectronic devices such as: Efficient charge transfer will ensure that maximum photogenerated carriers will be utilized to enhance the device's performance. Dynamic adjustment due to structural modification quenching properties allows tailored sensitivity and time response of photodetectors. Understanding the mechanisms of quenching, on the other hand, helps in minimizing none radiative path that enhances brilliance and efficiency in LEDs.

The charge transfer mechanism, in the case of FAPbBr₃ PNC systems in their film state, is highly dependent on molecular arrangement and quencher molecule accessibility. The incorporation of acceptor molecules in co-aggregated samples yields complete quenching by providing access to interaction with both the surface and internal crystal structure of nanocrystals. These results again highlight the crucial importance of structural control in designing and optimizing nanocrystal systems for advanced optoelectronic applications.

3.5 Conclusions

The electron transport properties of FAPbBr₃ PNCs, when organized into controlled assemblies, were thoroughly investigated by using steady-state and time-resolved spectroscopy. This study will show the superiority of FAPbBr₃ in comparison with other perovskite systems like CsPbBr₃ and MAPbBr₃ for advanced optoelectronic applications by systematically comparing the efficiency of electron transfer in FAPbBr₃. In both CsPbBr₃ and MAPbBr₃ PNC systems, the electron transfer efficiency was restricted; the major reason for this restriction was the presence of surface capping ligands. These ligands create an insulating barrier that prevents effective interaction between the donor nanocrystals and acceptor molecules. FAPbBr₃ PNCs showed superior optical properties and enhanced stability, rendering them an ideal candidate for assembly formation and electron transport studies. The reduced ligand density and better crystalline structures are unique advantages of FAPbBr₃, which accounts for higher electron transfer efficiency compared to other perovskites. Despite the challenge from the surface ligands, efficient electron transport in FAPbBr₃ PNCs was enabled via careful regulation of the assembly formation. Controlled purification and an assembly process led to a structure with greater accessibility to the sites of donor-acceptor interaction. Surface capping ligands loosely hold the nanocrystals in the assemblies, which thus allows the acceptor molecules to penetrate and interact with the donor moieties inside more effectively. The presented study was carried out using three different electron-acceptor molecules, namely P-C₆₀, C₆₀-RCOOH, and TCNQ. The electron-transfer mechanisms are strongly determined by the structural and electronic properties of both the donor assemblies and the acceptors. Accordingly, each of the acceptors presented different interaction dynamics with FAPbBr₃ assemblies, and in general, co-aggregated samples demonstrated remarkable quenching efficiencies. In the film state, the incorporation of the acceptor molecules during the assembling synthesis resulted in a co-aggregation phenomenon where the acceptors became part of the assembly of PNCs. This structural integration resulted in complete PL quenching, underlining the possibility of highly efficient electron transfer in a solid-state configuration. Through a systematic comparison between the solution and film states, the electron transfer mechanisms have been determined to be very dependent on the molecular arrangement and accessibility of the acceptor molecules to the donor surfaces. In the state of film, the compact and orderly

assembly structure can provide more robust interactions between donor-acceptor in comparison with the dispersed nanocrystals in the solution state. The work herein emphasizes the huge possibility of FAPbBr₃ PNC assemblies for providing fresh impetus toward the advancement of optoelectronic technologies. Regulated assembly and efficient electron transport Properties of FAPbBr₃ PNCs open avenues for high-performance solar cells with improved charge carrier dynamics. Complete PL quenching by co-aggregation suggests the possibility of optimization in light-emission efficiency and color purity in LEDs. The higher efficiency of electron transfer in FAPbBr₃ assemblies can thus be used to improve the photocatalytic system performance for various energy conversions and environmental remediation purposes.

This comprehensive study underlines the advantages of FAPbBr₃ PNC assemblies in achieving efficient electron transfer. By using the structural and electronic characteristics of FAPbBr₃, together with controlled assembly formation in this work, critical insights into the design and optimization of high-performance optoelectronic devices are provided. The results have opened a new vista toward the development of high-performance solar cells, LEDs, and photocatalytic systems, showing how PNC assemblies can dramatically change modern technology.

References

- (1) Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X. G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C. J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Mora-Seró, I.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Pérez-Prieto, J.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roelofs, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Müller-Buschbaum, P.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>.
- (2) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10), 2869–2885. <https://doi.org/10.1039/c9cs00848a>.
- (3) Zhai, Y.; Wang, K.; Zhang, F.; Xiao, C.; Rose, A. H.; Zhu, K.; Beard, M. C. Individual Electron and Hole Mobilities in Lead-Halide Perovskites Revealed by Noncontact Methods. *ACS Energy Lett.* **2020**, *5* (1), 47–55. <https://doi.org/10.1021/acsenenergylett.9b02310>.
- (4) Shahjahan, M. D.; Okamoto, T.; Chouhan, L.; Sachith, B. M.; Pradhan, N.; Misawa, H.; Biju, V. Halide Perovskite Single Crystals and Nanocrystal Films as Electron Donor-Acceptor Heterojunctions. *Angew. Chemie - Int. Ed.* **2023**, *62* (4). <https://doi.org/10.1002/anie.202215947>.
- (5) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M. Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. *Science* (80-.). **2015**, *347* (6221), 519–522. <https://doi.org/10.1126/science.aaa2725>.
- (6) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. *Science* (80-.). **2017**, *358* (6364), 745–750. <https://doi.org/10.1126/science.aam7093>.
- (7) Yin, W. J.; Shi, T.; Yan, Y. Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Adv. Mater.* **2014**, *26* (27), 4653–4658. <https://doi.org/10.1002/adma.201306281>.
- (8) Sum, T. C.; Mathews, N.; Xing, G.; Lim, S. S.; Chong, W. K.; Giovanni, D.; Dewi, H. A. Spectral Features and Charge Dynamics of Lead Halide Perovskites: Origins and Interpretations. *Acc. Chem. Res.* **2016**, *49* (2), 294–302. <https://doi.org/10.1021/acs.accounts.5b00433>.
- (9) Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P. Essentially

- Trap-Free CsPbBr₃ Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J. Am. Chem. Soc.* **2017**, *139* (19), 6566–6569. <https://doi.org/10.1021/jacs.7b02817>.
- (10) Sum, T. C.; Chen, S.; Xing, G.; Liu, X.; Wu, B. Energetics and Dynamics in Organic-Inorganic Halide Perovskite Photovoltaics and Light Emitters. *Nanotechnology* **2015**, *26* (34). <https://doi.org/10.1088/0957-4484/26/34/342001>.
 - (11) Tan, Z. K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9* (9), 687–692. <https://doi.org/10.1038/nnano.2014.149>.
 - (12) Xie, F. X.; Zhang, D.; Su, H.; Ren, X.; Wong, K. S.; Grätzel, M.; Choy, W. C. H. Perovskite Solar Cells with High Efficiency and Flexibility. *ACS Nano* **2015**, *9* (1), 639–646.
 - (13) Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Low-Temperature Solution-Processed Wavelength-Tunable Perovskites for Lasing. *Nat. Mater.* **2014**, *13* (5), 476–480. <https://doi.org/10.1038/nmat3911>.
 - (14) Gong, M.; Sakidja, R.; Goul, R.; Ewing, D.; Casper, M.; Stramel, A.; Elliot, A.; Wu, J. Z. High-Performance All-Inorganic CsPbCl₃ Perovskite Nanocrystal Photodetectors with Superior Stability. *ACS Nano* **2019**, *13* (2), 1772–1783. <https://doi.org/10.1021/acsnano.8b07850>.
 - (15) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Adv. Mater.* **2017**, *29* (5). <https://doi.org/10.1002/adma.201603885>.
 - (16) Burschka, J.; Pellet, N.; Moon, S. J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, *499* (7458), 316–319. <https://doi.org/10.1038/nature12340>.
 - (17) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. Il. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, *517* (7535), 476–480. <https://doi.org/10.1038/nature14133>.
 - (18) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. Il. High-Performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange. *Science* (80-.). **2015**, *348* (6240), 1234–1237. <https://doi.org/10.1126/science.aaa9272>.
 - (19) Nie, W.; Tsai, H.; Asadpour, R.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H. High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. **2015**, *347* (6221), 522–525.

- (20) Liu, S.; Biju, V. P.; Qi, Y.; Chen, W.; Liu, Z. Recent Progress in the Development of High-Efficiency Inverted Perovskite Solar Cells. *NPG Asia Mater.* **2023**, *15* (1). <https://doi.org/10.1038/s41427-023-00474-z>.
- (21) Singh, S. P.; Nagarjuna, P. Organometal Halide Perovskites as Useful Materials in Sensitized Solar Cells. *Dalt. Trans.* **2014**, *43* (14), 5247–5251. <https://doi.org/10.1039/c3dt53503g>.
- (22) Jeong, J.; Kim, M.; Seo, J.; Lu, H.; Ahlawat, P.; Mishra, A.; Yang, Y.; Hope, M. A.; Eickemeyer, F. T.; Kim, M.; Yoon, Y. J.; Choi, I. W.; Darwich, B. P.; Choi, S. J.; Jo, Y.; Lee, J. H.; Walker, B.; Zakeeruddin, S. M.; Emsley, L.; Rothlisberger, U.; Hagfeldt, A.; Kim, D. S.; Grätzel, M.; Kim, J. Y. Pseudo-Halide Anion Engineering for α -FAPbI₃ Perovskite Solar Cells. *Nature* **2021**, *592* (7854), 381–385. <https://doi.org/10.1038/s41586-021-03406-5>.
- (23) Ray, S.; Sahoo, M. R.; Mukherjee, S.; Perumal, A.; Nayak, S. K.; Bhaumik, S. Understanding the Charge Transfer Mechanism in CsPbBr₃ Nanocrystals and Nitrogen-Doped Carbon Quantum Dot Heterostructures: Effect of Nanocrystal Encapsulation. *RSC Adv.* **2023**, *13* (50), 35551–35561. <https://doi.org/10.1039/D3RA06307K>.
- (24) Marjit, K.; Ghosh, G.; Ghosh, S.; Ghosh, D.; Medda, A.; Patra, A. Electron Transfer Dynamics from CsPbBr₃ Nanocrystals to Au 144 Clusters. *ACS Phys. Chem. Au* **2023**, *3* (4), 348–357. <https://doi.org/10.1021/acspphyschemau.2c00070>.
- (25) Tian, C.; Wang, F.; Wang, Y.; Yang, Z.; Chen, X.; Mei, J.; Liu, H.; Zhao, D. Chemical Vapor Deposition Method Grown All-Inorganic Perovskite Microcrystals for Self-Powered Photodetectors. *ACS Appl. Mater. Interfaces* **2019**, *11* (17), 15804–15812. <https://doi.org/10.1021/acsami.9b03551>.
- (26) He, H.; Yu, Q.; Li, H.; Li, J.; Si, J.; Jin, Y.; Wang, N.; Wang, J.; He, J.; Wang, X.; Zhang, Y.; Ye, Z. Exciton Localization in Solution-Processed Organolead Trihalide Perovskites. *Nat. Commun.* **2016**, *7*, 1–7. <https://doi.org/10.1038/ncomms10896>.
- (27) Wu, S. H.; Lin, M. Y.; Chang, S. H.; Tu, W. C.; Chu, C. W.; Chang, Y. C. A Design Based on a Charge-Transfer Bilayer as an Electron Transport Layer for Improving the Performance and Stability in Planar Perovskite Solar Cells. *J. Phys. Chem. C* **2018**, *122* (1), 236–244. <https://doi.org/10.1021/acs.jpcc.7b11245>.
- (28) Li, M.; Valandro, S. R.; He, R.; Zhao, Y.; Yang, P.; Schanze, K. S. Charge-Transfer Dynamics between Cesium Lead Halide Perovskite Nanocrystals and Surface-Anchored Naphthalimide Acceptors. *J. Phys. Chem. C* **2021**, *125* (27), 14778–14785. <https://doi.org/10.1021/acs.jpcc.1c02622>.
- (29) Shah, S. A. B.; Ghimire, S.; Lesyuk, R.; Diamanti, M. V.; Lughi, V.; Klinker, C. Tailoring Charge Donor–Acceptor Interaction in CsPbBr₃ Perovskite Nanocrystals through Ligand Exchange. *Small Sci.* **2024**, *4* (5). <https://doi.org/10.1002/smssc.202300348>.
- (30) Jiménez-López, J.; Puscher, B. M. D.; Guldí, D. M.; Palomares, E. Improved

- Carrier Collection and Hot Electron Extraction across Perovskite, C60, and TiO₂ Interfaces. *J. Am. Chem. Soc.* **2020**, *142* (3), 1236–1246. <https://doi.org/10.1021/jacs.9b09182>.
- (31) Jeon, I.; Ueno, H.; Seo, S.; Aitola, K.; Nishikubo, R.; Saeki, A.; Okada, H.; Boschloo, G.; Maruyama, S.; Matsuo, Y. Lithium-Ion Endohedral Fullerene (Li⁺@C60) Dopants in Stable Perovskite Solar Cells Induce Instant Doping and Anti-Oxidation. *Angew. Chemie - Int. Ed.* **2018**, *57* (17), 4607–4611. <https://doi.org/10.1002/anie.201800816>.
 - (32) Wang, H.; Rahaq, Y.; Kumar, V. A Composite Light-Harvesting Layer from Photoactive Polymer and Halide Perovskite for Planar Heterojunction Solar Cells. *Sci. Rep.* **2016**, *6* (1), 29567. <https://doi.org/10.1038/srep29567>.
 - (33) Sachith, B. M.; Zhang, Z.; Subramanyam, P.; Subrahmanyam, C.; Furube, A.; Tamai, N.; Okamoto, T.; Misawa, H.; Biju, V. Photoinduced Interfacial Electron Transfer from Perovskite Quantum Dots to Molecular Acceptors for Solar Cells. *Nanoscale* **2023**, *15* (17). <https://doi.org/10.1039/d3nr01032e>.
 - (34) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
 - (35) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, *119* (5), 3296–3348. <https://doi.org/10.1021/acs.chemrev.8b00644>.
 - (36) Mannino, G.; Deretzis, I.; Smecca, E.; La Magna, A.; Alberti, A.; Ceratti, D.; Cahen, D. Temperature-Dependent Optical Band Gap in CsPbBr₃, MAPbBr₃, and FAPbBr₃ Single Crystals. *J. Phys. Chem. Lett.* **2020**, *11* (7), 2490–2496. <https://doi.org/10.1021/acs.jpclett.0c00295>.
 - (37) Wang, X.; Wang, Q.; Chai, Z.; Wu, W. The Thermal Stability of FAPbBr₃ nanocrystals from Temperature-Dependent Photoluminescence and First-Principles Calculations. *RSC Adv.* **2020**, *10* (72), 44373–44381. <https://doi.org/10.1039/d0ra07668f>.
 - (38) Polavarapu, L.; Nickel, B.; Feldmann, J.; Urban, A. S. Advances in Quantum-Confinement Perovskite Nanocrystals for Optoelectronics. *Adv. Energy Mater.* **2017**, *7* (16), 1–9. <https://doi.org/10.1002/aenm.201700267>.
 - (39) Liu, T.; Troisi, A. What Makes Fullerene Acceptors Special as Electron Acceptors in Organic Solar Cells and How to Replace Them. *Adv. Mater.* **2013**, *25* (7), 1038–1041. <https://doi.org/10.1002/adma.201203486>.
 - (40) Mahato, M. K.; Govind, C.; Karunakaran, V.; Nandy, S.; Sudakar, C.; Prasad, E. Enhanced Charge Transport and Excited-State Charge-Transfer Dynamics in a Colloidal Mixture of CdTe and Graphene Quantum Dots. *J. Phys. Chem. C* **2019**,

123 (33), 20512–20521. <https://doi.org/10.1021/acs.jpcc.9b02708>.

- (41) Shen, D.; Chen, W. C.; Lo, M. F.; Lee, C. S. Charge-Transfer Complexes and Their Applications in Optoelectronic Devices. *Mater. Today Energy* **2021**, *20*, 100644. <https://doi.org/10.1016/j.mtener.2021.100644>.
- (42) Oevering, H.; Paddon-row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. Long-Range Photoinduced Through-Bond Electron Transfer and Radiative Recombination via Rigid Nonconjugated Bridges: Distance and Solvent Dependence. *J. Am. Chem. Soc.* **1987**, *109* (11), 3258–3269. <https://doi.org/10.1021/ja00245a014>.
- (43) Sun, S.; Yuan, D.; Xu, Y.; Wang, A.; Deng, Z. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature. *ACS Nano* **2016**, *10* (3), 3648–3657. <https://doi.org/10.1021/acs.nano.5b08193>.
- (44) Zuliani, C.; Formaggio, F.; Scipionato, L.; Toniolo, C.; Antonello, S.; Maran, F. Insights into the Distance Dependence of Electron Transfer through Conformationally Constrained Peptides. *ChemElectroChem* **2020**, *7* (5), 1225–1237. <https://doi.org/10.1002/celec.202000088>.
- (45) Panuganti, S.; Besteiro, L. V.; Vasileiadou, E. S.; Hoffman, J. M.; Govorov, A. O.; Gray, S. K.; Kanatzidis, M. G.; Schaller, R. D. Distance Dependence of Förster Resonance Energy Transfer Rates in 2D Perovskite Quantum Wells via Control of Organic Spacer Length. *J. Am. Chem. Soc.* **2021**, *143* (11), 4244–4252. <https://doi.org/10.1021/jacs.0c12441>.
- (46) Devi, L. B.; Das, S. K.; Mandal, A. B. Impact of Surface Functionalization of AgNPs on Binding and Conformational Change of Hemoglobin (Hb) and Hemolytic Behavior. *J. Phys. Chem. C* **2014**, *118* (51), 29739–29749. <https://doi.org/10.1021/jp5075048>.
- (47) Lakowicz, J. R.; Weber, G. Quenching of Fluorescence by Oxygen. a Probe for Structural Fluctuations in Macromolecules. *Biochemistry* **1973**, *12* (21), 4161–4170. <https://doi.org/10.1021/bi00745a020>.

Chapter 4

Electron transfer from CdSe/CdS QD assemblies to the acceptor molecules

4.1 Abstract

Over the last two decades, semiconductor QDs have enjoyed active investigations, with striking size-dependent properties that exhibit versatility in processability with relevance to the development of optoelectronic applications. Optical and electronic unique features present an array of great usability possibilities for nanomaterials of the class for basic application research that involves solar cells, LEDs, and photodetectors. One of the most striking properties of QDs is their strong fluorescence, which provides excellent response and reproducibility, especially in developing high-performance solar cells and QD-based LEDs. On the other hand, apart from many pros, some serious disadvantages prevent QDs from practical realization. The agglomeration of QDs, nonspecific binding of QDs, and the presence of excess ligands might seriously restrict their efficiency. Therefore, the research area for overcoming these issues and obtaining stable and well-dispersed QD assemblies is very important. This study overcomes the limitations of QDs by focusing on the stabilization of QDs against undesired aggregations. In this respect, well-dispersed assemblies of CdSe/CdS QDs were successfully prepared by using 1,6-hexanedithiol (HDT) as a cross-linking agent. These newly synthesized QD assemblies are called **QD@HDT** and showed enhanced stability and dispersion. STEM images indeed showed the cross-linking of QDs into assemblies with sizes comparable to the dimensions of a single QD. Further evidence for assembly formation came from DLS measurements, where the assemblies showed a narrow distribution in size.

In photosystems, electron transport is critical for charge separation as well as light harvesting. The electron-transfer properties of **QD@HDT** assemblies have been investigated in detail in this chapter. This work will investigate the interaction of electron

transfer among the isolated QDs, **QD@HDT** assemblies, and three types of quencher molecules: pristine fullerene (P-C₆₀), COOH-functionalized fullerene (C₆₀-RCOOH), and 7,7,8,8-tetracyanoquinodimethane (TCNQ). To one's surprise, **QD@HDT** assemblies exhibited higher interactions of electron transfer with those quencher molecules compared with that of the isolated QDs, indicating a better performance induced by their cross-linked assembly.

PL decay measurements of the TRPL and Stern-Volmer plots were therefore performed to gain a deeper understanding of these interactions. Such analysis has unveiled detailed quenching mechanisms concerning whether the quenching observed is of a static, dynamic, or both types. These S-V plots and PL lifetime data are in good agreement and further confirm that there are close interactions between **QD@HDT** assemblies and quencher molecules, hence corroborating how efficient the assemblies are in facilitating electron transfer.

This research underlines the potential of cross-linked QD assemblies to advance the field of optoelectronics. The present study, while improving the understanding of electron transfer mechanisms in QD assemblies, thus paves the way for the rational design and application of these nanoscale structures in advanced optoelectronic devices. These results not only overcome intrinsic problems usually associated with QDs' stability but also open new perspectives for their use in next-generation applications.

4.2 Introduction

One of the well-known core-shell nanostructures is CdSe/CdS QDs, comprising a cadmium selenide core coated with a protective shell of cadmium sulfide.¹⁻⁵ This unique structure makes these QDs exceptionally versatile and hence highly adaptable in an array of applications, including photonics, optoelectronics, and bioimaging.⁶⁻¹¹ The light emission of such nanostructures is thoroughly dominated by the CdSe core, considering that it expresses a direct band gap.¹² Importantly, the bandgap of CdSe can be well tuned with the core size, so that the emitting wavelength covering the visible and near-infrared region can be controlled.^{13,14} While the CdS shell plays an important role in enhancing the performances of QDs. The large bandgap of CdS confines the charge carriers within CdSe because of the quantum confinement effect due to the wide bandgap of CdS.^{15,16}

Thus, the shell of CdS passivates surface imperfections of the core CdSe and increases its PLQY along with the overall stability of the structure. This confinement also greatly facilitates the accurate tunability of the emission wavelength, attained by fine-tuning the shell thickness of CdS and the core size of CdSe.

Among other important factors, surface ligands are crucial in defining QDs regarding stability and functionality. The ligands influence the size, shape, optical properties, stability, and solubility of QDs and hence their performances in intended applications.¹⁷ While long-chain ligands provided excellent colloidal stability, they acted as insulating barriers to charge transfer in electrical devices. To overcome this inefficiency, methodologies involving ligand exchange techniques have been adopted in which insulating ligands are replaced by shorter ones that can conduct better. In most cases, this procedure results in a loss of colloidal stability for QDs, promoting aggregation, which may limit their applicability.

In optoelectronic devices, like LEDs, QDs are very important because of their ability to provide pure and saturated colors thanks to their intense and narrow emission spectra.^{11,18,19} In solar cells, QDs can broaden the absorption spectrum and enhance efficiency through mechanisms such as multiple exciton generation. Although many applications exploit properties of isolated QDs, a large number rely on QD films and self-assemblies. In isolated QDs, charge carriers are confined within individual QDs, with limited electronic coupling and restricted carrier mobility. This isolation hinders efficient electron transfer. In contrast, interdot interactions in QD assemblies become a critical factor that determines the collective optoelectronic properties of the material. These interactions have a great influence on the charge transport and overall performance of the assemblies.

Accordingly, in this work, I prepared well-dispersed assemblies using 1,6-hexanedithiol (HDT) as a cross-linking agent with highly controllable assembly stability, established in the STEM and DLS studies. The assembled QDs revealed rich dynamic effects due to electron transfers occurring within the timescale of nanoseconds. The detailed electron transfer dynamic studies were monitored by a selection of spectroscopy techniques. In particular, I studied the electron transfer behavior between isolated QDs, QD assemblies, and three quencher molecules: pristine fullerene (P-C₆₀), COOH-functionalized fullerene (C₆₀-RCOOH), and 7,7,8,8-tetracyanoquinodimethane (TCNQ).

This work describes how these different interdot interactions modulate the electron transfer process by comparing the corresponding electron transfer kinetics. These findings further support the higher degree of electron transfer interaction in assemblies compared to that of isolated QDs, which therefore points out the important role of interdot coupling in enabling higher performance in optoelectronic devices. Further evidence of the nature of the operating interactions was gained in time-resolved spectroscopic techniques, such as either static or dynamic quenching.

This comprehensive investigation advances our understanding of small QD assemblies and their optoelectronic properties. The findings reported in this study have pointed the way for critical bottlenecks, like uncontrolled aggregation or inefficient charge transfer when creating next-generation devices such as light-emitting displays, solar cells, and sensors of nanometric dimension. These studies will thus show, under real conditions, the great capabilities that could be provided with QD assembly.

4.3. Results and discussion

4.3.1 Preparation of quantum dot assemblies

For the preparation of the functionalized QD solution, 2.0 μL of CdSe/CdS solution was added to 1.6 mL of toluene to yield a mixture containing about 0.02 mg (0.03 picomoles) of QDs. Subsequently, the preparation of 1,6-hexane dithiol stock in toluene was made for further modification. The additions of the HDT solution to the QD solution were gradually done starting from 1:1 (v/v) up to higher ratios. After each addition, the solution was well mixed to achieve homogenous dispersion and sonicated for 3 minutes to facilitate the interaction between QDs and HDT. This procedure was repeated to a final ratio of 1:8 (v/v). At each step, the solution was mixed and then sonicated for consistency.

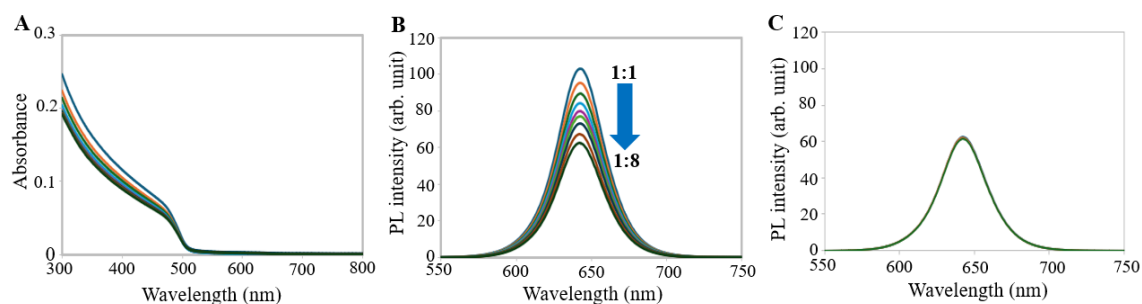


Figure 4.1 (A) Absorption spectra of P-QD in the absence and presence of HDT from 1:1 to 1:8 (v/v) ratio, (B) PL spectra (λ_{ex} , 405 nm) of P-QD in the absence and presence of

HDT from 1:1 to 1:8 (v/v) ratio, (C) Time-dependent PL spectra of P-QD with HDT (1:8) ratio.

Absorbance and PL spectra were measured after each addition as a means to track changes in the optical properties of the QD solution. The absorbance spectrum showed a progressive decrease with increased HDT content in the QD solution (Figure 4.1A), which might be due to the variation of particle size or the interaction at the surface that the HDT molecules caused. Analogously, PL intensity at 645 nm progressively decreased upon successive addition of HDT, as shown in Figure 4.1B.

To maintain a specific size distribution and avoid over-modification, the reaction was purposefully halted after the 1:8 (v/v) ratio of HDT had been reached. Then let this solution keep stationary for about 2h to get some idea of **QD@HDT** assemblies' stabilities. No further changes in PL intensity were observed during this time, indicating that the assemblies formed at the 1:8 ratio were stable and well-distributed. STEM and DLS measurements were done to validate the formation and structural integrity of **QD@HDT** assemblies. These results were compared with data from isolated QDs to confirm successful functionalization and ensure uniformity in the assembly process.

4.3.2 Characterization of the quantum dot assemblies

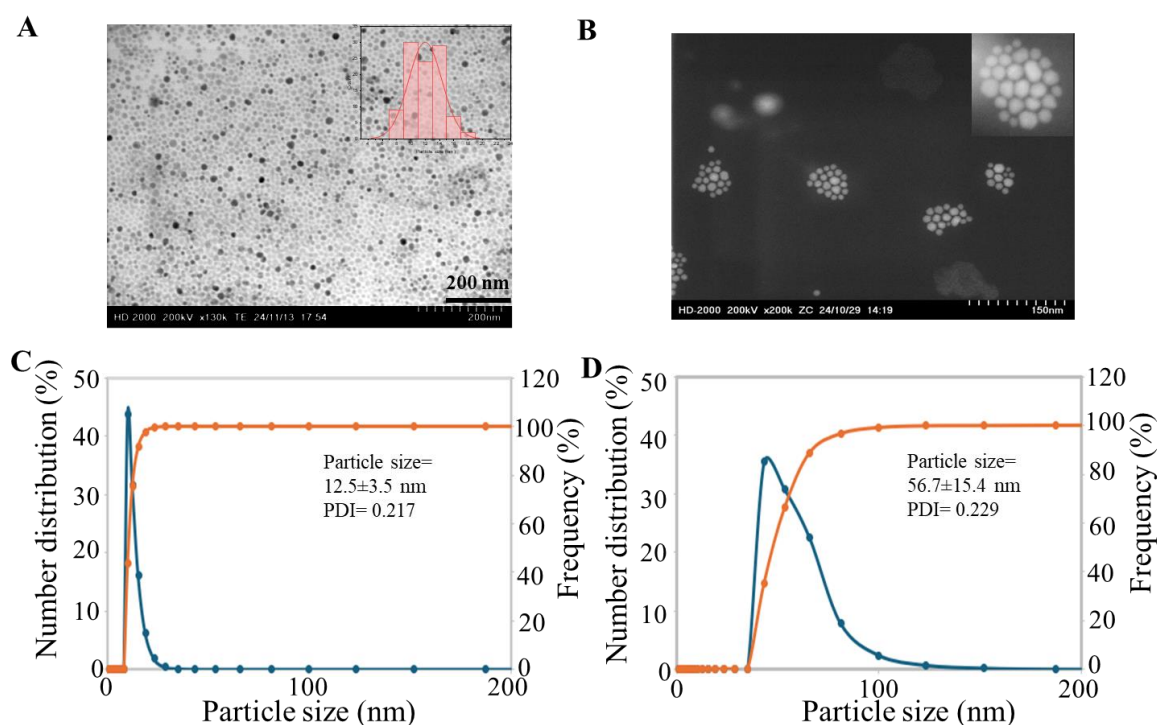


Figure 4.2 Characterization of the **QD@HDT** assembly. STEM images of (A) P-QD, (B) **QD@HDT** assembly. DLS profiles of (C) P- QD, (D) **QD@HDT** assembly.

The P-QD and QD assemblies (**QD@HDT**) were examined using STEM, and the DLS for confirmation of particle size and distribution. The STEM images of P-QD and **QD@HDT** assembly are shown in Figures (4.2A and B). The STEM photos show a homogeneous size distribution of P-QD and assembly. I used ImageJ software to analyze the STEM photos and determine their size distributions. The P-QD had a spherical shape and a size distribution of approximately 12 ± 2.3 nm (Figure 4.2A), while the **QD@HDT** assembly with several QDs measured 55.0 ± 15 nm. The STEM sample for P-QD in toluene was taken at a moderate concentration. In the case of **QD@HDT** assembly STEM sample, the synthesized sample was used, as discussed in the 4.3.1 section.

For the DLS measurement, 0.20 mg of P-QD sample was dissolved in 1.6 mL toluene and measured the sample. For **QD@HDT** assembly, the synthesized sample was measured, as discussed in the 4.3.1 section. The DLS data was prepared by the nanoSAQLA. The particle size for P-QD showed 12.5 ± 3.5 nm (Figure 4.2C) which supported the STEM. The PDI value (0.217) also confirmed the particles are well distributed in toluene. In the case of **QD@HDT** assembly, the DLS showed the size is 56.7 ± 15.4 nm (Figure 4.3D), which is a good agreement with STEM. The PDI value (0.299) confirmed well dispersion. This type of nanoaggregate has great potential in the field of optoelectronics.

To further explore the functional properties of the **QD@HDT** assemblies, the electron transfer dynamics were investigated using three types of quencher molecules: pristine C_{60} , carboxyl-functionalized (C_{60} -RCOOH), and 7,7,8,8-tetracyanoquinodimethane (TCNQ). The electron transfer kinetics of the pristine P-QDs with these quencher molecules were first studied as a reference. These results were then compared to the electron transfer behavior of the **QD@HDT** assemblies to understand the effect of HDT-induced functionalization on the charge transfer processes.

4.3.3 Photoluminescence quenching study of quantum dot with C₆₀ in solutions

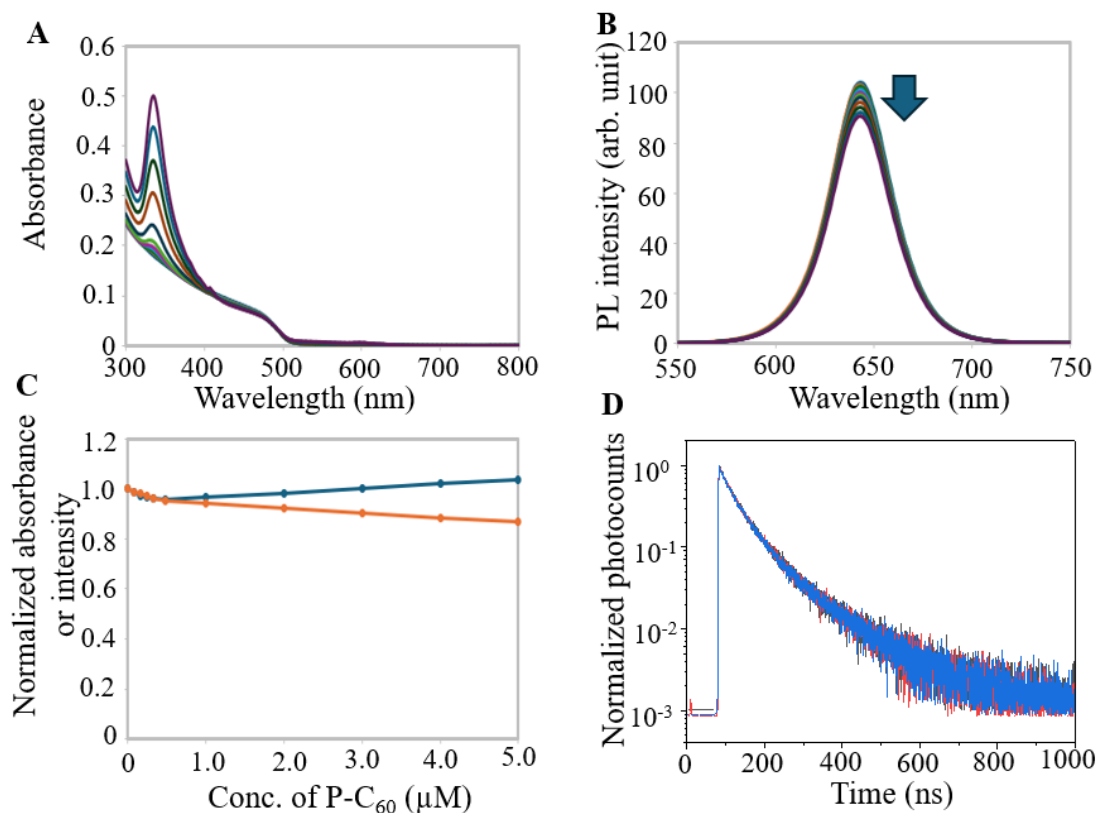


Figure 4.3 PL quenching study for P-QD in toluene. (A) Absorption, and (B) PL spectra of P-QD ($\lambda_{\text{ex}} = 405$ nm) with various concentrations of P-C₆₀, (C) Concentration-dependent image of normalized absorbance (blue) at 405 nm of Figure 4.3A, PL intensity (orange) at 645 nm of Figure 4.3B, (D) PL decay profile of pristine QD ($\lambda_{\text{ex}} = 405$ nm) with various concentrations of P-C₆₀.

To investigate the dynamics of electron transfer in the P-QD solution, pristine fullerene (P-C₆₀) was used as an electron acceptor. The D-A system was systematically investigated by using steady-state PL spectroscopy. Figure 4.3 shows the absorption and PL spectra of the P-QD solution in the absence and presence of P-C₆₀ with their normalized plots and PL decay profiles, respectively. First, the absorption and PL quenching of the P-QD solution were studied by titrating it with a P-C₆₀ solution prepared in toluene. Thus, absorption at 405 nm increased with an increase in the concentration of P-C₆₀ from 0.08 μM to 5.0 μM (Figure 4.3A). This confirms that the present behavior follows the Beer-Lambert Law, showing the proportionality of absorbance versus the concentration of P-C₆₀.²⁰

In contrast, the PL intensity of the P-QD solution decreased upon the addition of P-C₆₀, though the reduction was not significant, indicating that the electron transfer efficiency was very limited. As shown in Figure 4.3C, the PL intensity at 645 nm only decreased by 20%, which means very few donor-acceptor interactions occurred in this system. This incomplete quenching suggests that only a small fraction of the P-C₆₀ molecules could interact effectively with the P-QD. To further investigate the interaction, PL decay profiles of the P-QD solution with different concentrations of P-C₆₀ were recorded using a Quantaurus Tau (Q-Tau) a fluorescence lifetime measurement system. The PL lifetimes of the P-QD solution were identical, 52.0 ns, regardless of the P-C₆₀ concentration, as presented in Figure 4.3D. This is further evidence of negligible electron transfer between P-QD and P-C₆₀ in the given conditions. Such an absence of significant quenching within both the steady-state PL intensity and PL lifetime measurements can be attributed to the presence of surface capping ligands and excess free ligands in the solution. These would have provided a steric hindrance, preventing the P-C₆₀ molecules from closely approaching the surface of the P-QDs to effect efficient electron transfer. The data suggest that while P-C₆₀ interacts with P-QDs to some extent, the interaction is limited and insufficient for significant electron transfer. This result highlights the importance of surface ligand optimization in improving donor-acceptor interactions and achieving more efficient charge transfer in such systems.

4.3.4 Photoluminescence quenching study of quantum dot assemblies with C₆₀

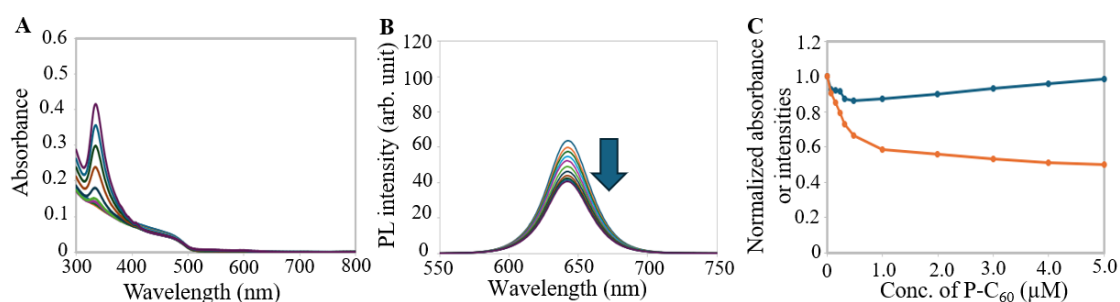


Figure 4.4 Quenching study for **QD@HDT** assembly. (A) Absorption, and (B) PL spectra of **QD@HDT** ($\lambda_{\text{ex}} = 405 \text{ nm}$) with various concentrations of P-C₆₀, (C) Concentration-dependent image of normalized absorbance (blue) at 405 nm of Figure 4.4A, PL intensity (orange) at 645 nm of Figure 4.4B.

To study the interaction and electron transfer kinetics between the **QD@HDT** assembly and P-C₆₀, a series of absorbance and PL measurements was conducted. The **QD@HDT** assembly solution was measured for its absorbance and PL in the absence of P-C₆₀. Then the gradual addition of P-C₆₀ in the range of 0.08-5.0 μ M to the assembly solution was done. The absorbance of the **QD@HDT** assembly showed a peculiar behavior, it first decreased at low concentrations of P-C₆₀ and then increased at higher concentrations of the latter (Figure 4.4A). Such an initial decrease could be explained by the aggregation effects associated with unwanted interactions between the **QD@HDT** assembly and P-C₆₀. The aggregates might partially obscure the optical path or result in modulation of the spectral properties of the assembly. With increased concentrations of P-C₆₀, this increase in absorbance could signal the presence of free P-C₆₀ molecules in solution contributing to the overall signal of absorbance. In contrast, Figure 4.4B depicts that the PL intensity of **QD@HDT** assembly monotonously decreased with increasing concentration of P-C₆₀. This decrease in PL intensity means the quenching occurred via D-A interactions between the **QD@HDT** assembly and P-C₆₀. A decrease in the rate of such a quenching process was observed at higher concentrations of P-C₆₀ due to either the saturation of available donor sites or limitations within the D-A complex formation. Figure 4.4C shows the variation of normalized absorbance and PL intensity with P-C₆₀ concentration. From the concentration-dependent quenching profile, one can observe that PL intensity decreases more drastically than absorbance, thus providing strong evidence for the hypothesis of effective donor-acceptor interactions. These interactions might take place both in the ground state and excited state, which initiate the electron transfer process, resulting in PL quenching.

Therefore, the structural and functional role of the cross-linker HDT could explain the enhanced efficiency in quenching for **QD@HDT** compared to that of pristine QDs. In this assembly, **QD@HDT**, HDT acts as a bridging molecule that places the QDs closer to each other and most importantly a more conducive environment to their interactions with acceptor molecules such as P-C₆₀. This specific structural arrangement would allow P-C₆₀ to effectively trap and form donor-acceptor complexes with **QD@HDT** and lead to electron transfer. These findings underline the crucial role played by controlled assembly in enhancing donor-acceptor interactions. The assembly mediated by HDT brings QDs closer but more importantly, provides a structurally organized platform

wherein electron transfer processes can occur with better efficiency. Present work provides fresh insights into the dynamics of electron transfer in QD assemblies and underlines the need to adopt strategic assembly designs while engineering the properties of nanomaterials for optoelectronic applications and beyond.

4.3.5 Time-resolved photoluminescent decay measurements of quantum dot assemblies with C₆₀

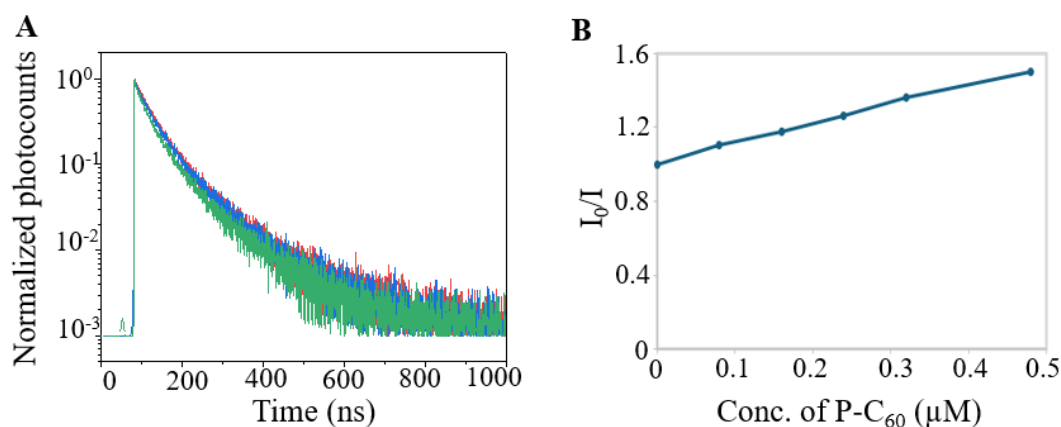


Figure 4.5 PL decay of (A) **QD@HDT** assembly without (blue) and with (green) of P-C₆₀ ($\lambda_{\text{ex}} = 405$ nm), (B) The Stern-Volmer (S-V) plot, (I_0 and I denoted the PL intensity of **QD@HDT** without and with P-C₆₀).

Time-resolved PL measurements of the **QD@HDT** assembly were made using a QuantaTaurus Tau (Q-Tau) system to gain deeper insight into the quenching mechanism. The first recording of the **QD@HDT** assembly was made without the addition of P-C₆₀, followed by that after the addition of 5.0 μM P-C₆₀. PL decay curves are presented in Figure 4.5A, in which the blue curve represents the **QD@HDT** assembly without P-C₆₀, and the green curve corresponds to the assembly with P-C₆₀ present. From these decay curves, it was obtained that the PL lifetime of **QD@HDT** assembly in the absence of P-C₆₀ was 53.2 ns, which decreased modestly to 48.5 ns upon the addition of P-C₆₀. This slight lifetime reduction further indicates that the quenching interaction between the **QD@HDT** assembly and P-C₆₀ involves a combination of mechanisms rather than dynamics. In the case of dynamic quenching, the lifetime usually shows a significant decrease upon increasing the concentration of the quencher.

To further investigate the nature of the quenching mechanism, a Stern-Volmer plot was constructed (Figure 4.5B) by plotting the PL quenching efficiency as a function of the P-C₆₀ concentration. The S-V plot was linear, indicating that the quenching mechanism was either static, dynamic, or a combination of the two. Linearity of the S-V plot and a moderate decrease in lifetime indicate the coexistence of both static and dynamic quenching mechanisms in the **QD@HDT**-P-C₆₀ system.

Static quenching corresponds to the formation of ground-state complexes between the fluorophore, **QD@HDT**, and the quencher, P-C₆₀. Static quenching decreases PL intensity without affecting the lifetime of uncompleted fluorophores.^{21,22} The other mode of quenching, called dynamic quenching, is related to collisional interaction in the excited state, which reduces the lifetime of PL. It follows that static quenching acts in the **QD@HDT** assembly since no changes in the PL lifetime of the isolated QDs were observed with the addition of P-C₆₀. The coexistence of the two modes of quenching is indicative of some unique structural properties of the **QD@HDT** assembly. The HDT cross-linker organizes QDs into assemblies while introducing diversity in binding sites and pathways due to the interaction of P-C₆₀. Dual-mode interaction probably occurs for the following reasons, ground-state donor-acceptor complexes form due to specific interactions promoted by the cross-linked structure. Dynamic Quenching corresponds to collisional interactions between P-C₆₀ and excited state QDs enabled by the accessibility of QD surfaces in the assembly. These findings are in good agreement with previously reported studies in the literature, which have documented the coexistence of static and dynamic quenching in QD systems. The dual-mode quenching behavior here points to a complicated interaction mechanism where the structural design of **QD@HDT** assembly plays a key role in the mediation of P-C₆₀ interactions.

Time-resolved PL measurements and analyses of the Stern-Volmer plot indicate that the quenching mechanism in the **QD@HDT** assembly-P-C₆₀ system involves both static and dynamic components. The interplay of the involved mechanisms underlines the importance of controlled structural assembly as a means to tailor QD systems toward enhanced donor-acceptor interactions with valuable insight into applications in the field of optoelectronics and nanomaterials design.

4.3.6 Photoluminescence quenching study of quantum dot with C₆₀-RCOOH

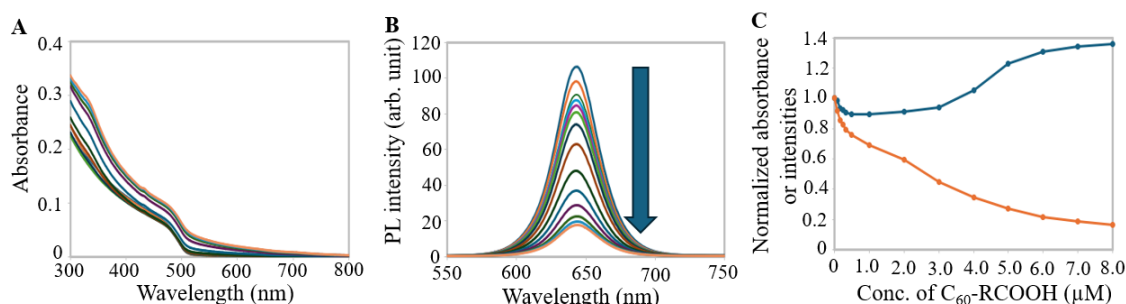


Figure 4.6 Absorption and PL spectra in toluene. (A) Absorption, and (B) PL spectra of pristine QD ($\lambda_{\text{ex}} = 405$ nm) with various concentrations of C₆₀-RCOOH, (C) Concentration-dependent image of normalized absorbance (blue) at 405 nm of Figure 4.6A, PL intensity (orange) at 645 nm of Figure 4.6B.

In previous studies, it has been shown that P-C₆₀ is unable to quench efficiently the PL emission of P-QDs, presumably because of the surface capping ligands and excess free ligands, which prevent effective interactions with P-C₆₀. Considering this limit and the interest in how surface functionalization could affect the efficiency of the quenching process, a carboxyl-functionalized fullerene derivative was synthesized, namely C₆₀-RCOOH. A synthesis of this derivative has been elaborated in Chapter 2 (Experimental Section). Several studies have demonstrated that functionalized fullerenes can serve as more effective electron acceptors in the donor-acceptor system compared to pristine C₆₀.^{23,24} Because the addition of electron-withdrawing functional groups (e.g., carboxyl, halogen, or cyano groups) to C₆₀ increases its electrophilicity. This modification lowers the LUMO energy level, making it easier to accept electrons from the donor in a donor-acceptor system. B. M. Illescas et. al. demonstrated that the pyrrolidino[3',4':1,2][60] fullerenes that are produced show cathodically altered reduction potentials of the C₆₀ framework when compared to the parent C₆₀. On the other hand, isoxazole fullerenes exhibit anodically shifted reduction waves for the fullerene core when compared to the parent C₆₀, suggesting that they are noticeably more potent acceptors than C₆₀.²³ Compared to pristine C₆₀, functionalized C₆₀ like PCBM (phenyl-C₆₁-butyric acid methyl ester), is more soluble in organic solvents.²⁵ In thin-film applications, this increases device performance and the creation of a uniform donor-acceptor blend. It is well-known

that functionalized fullerene is a good electron transport layer for optoelectronic devices.²⁶

A similar experiment was performed in the P-QD: P-C₆₀ D-A system. Figures 4.6A and 4.6B show the absorption and PL spectra of P-QD without and with C₆₀-RCOOH in toluene. The absorbance decreases at first and then increases as C₆₀-RCOOH is gradually added. PL intensity is reduced with the addition of C₆₀-RCOOH. Figure 4.6C illustrates the normalized concentration-dependent profiles of absorbance at 405 nm and PL intensity at 645 nm. The significant decrease in the PL intensity from Figure 4.6B suggests efficient electron transfer from photoactivated P-QD to C₆₀-RCOOH. These observations indicate that electron transfer is likely occurring in this system. The functionalized C₆₀-RCOOH appears to act as a stronger electron acceptor compared to pristine C₆₀, which is consistent with previous reports in the literature.^{23,24} For example, K. Virki et al. reported efficient electron transfer from CdSe/ZnS QDs to a COOH-functionalized fullerene hybrid, further supporting the observed results.²⁷ The improved quenching effect of C₆₀-RCOOH might be attributed to the specific surface interactions provided by the carboxyl groups. It is thought that these groups allow the binding or approach of C₆₀-RCOOH to the surface of QD in a much more effective manner, increasing its efficiency of electron transfer. This can be due to hydrogen bonding or other favorable interactions of the carboxyl group with the surface ligands of the QDs that create a more favorable environment for the charge transfer.

4.3.7 Time-resolved photoluminescence decay measurements of quantum dot with C₆₀-RCOOH

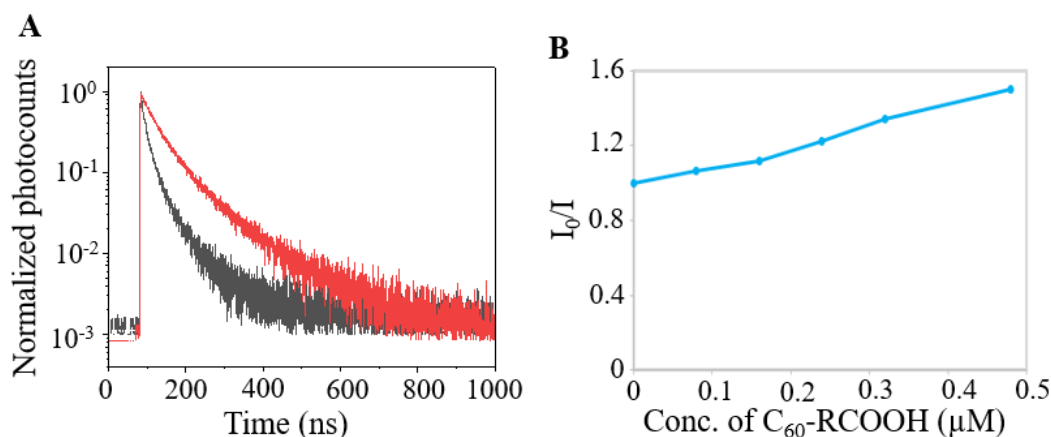


Figure 4.7 PL decay of (A) P-QD in the absence (red) and presence (black) of C₆₀-RCOOH QD (λ_{ex} = 405 nm), (B) The Stern-Volmer (S-V) plot, (I_0 and I denoted the PL intensity of P-QD without and with C₆₀-RCOOH).

I performed time-resolved PL measurements to obtain a better understanding of the quenching mechanism between P-QD and the functionalized fullerene C₆₀-RCOOH. These observations reveal critical information regarding excited state dynamics and the nature of the quenching process. Figure 4.7A presents the time-resolved PL decay curves for P-QD in the absence and presence of C₆₀-RCOOH. The data reveal significant changes in the PL lifetime. In the absence of C₆₀-RCOOH, P-QD exhibits a lifetime of 59.1 ns. Upon the addition of C₆₀-RCOOH (8.0 μ M), the lifetime decreases to 23.2 ns. This substantial reduction in lifetime (by approximately 61%) strongly indicates a dynamic quenching process. In dynamic quenching, the quencher molecule (C₆₀-RCOOH) interacts with the fluorophore (P-QD) during its excited state lifetime, providing an additional non-radiative pathway for de-excitation. This interaction effectively shortens the time the fluorophore spends in the excited state, resulting in a decreased lifetime. To further elucidate the quenching mechanism, I constructed a Stern-Volmer (S-V) plot, shown in Figure 4.7B. The initial fluorescence intensity to quenched fluorescence intensity ratio (I_0/I) as a function of quencher concentration is shown in the S-V curve. Here, I find that the concentration of C₆₀-RCOOH and I_0/I have a linear relationship. The linearity of the S-V plot is consistent with both dynamic and static quenching processes. However, when considered in conjunction with the significant decrease in lifetime, it strongly supports a predominantly dynamic quenching mechanism. The enhanced quenching efficiency of C₆₀-RCOOH compared to pristine C₆₀ (as observed in section 4.3.3) can be attributed to several factors, including surface interactions, which lead to more efficient electron transfer.

These results demonstrate that the functionalization of C₆₀ with a carboxyl group significantly enhances its ability to quench P-QD fluorescence through a dynamic mechanism. This finding has important implications for the design of QD-based systems for applications such as light-harvesting, sensing, and optoelectronic devices, where efficient electron transfer is crucial.

4.3.8 Photoluminescence quenching study of quantum dot assemblies with C₆₀-RCOOH

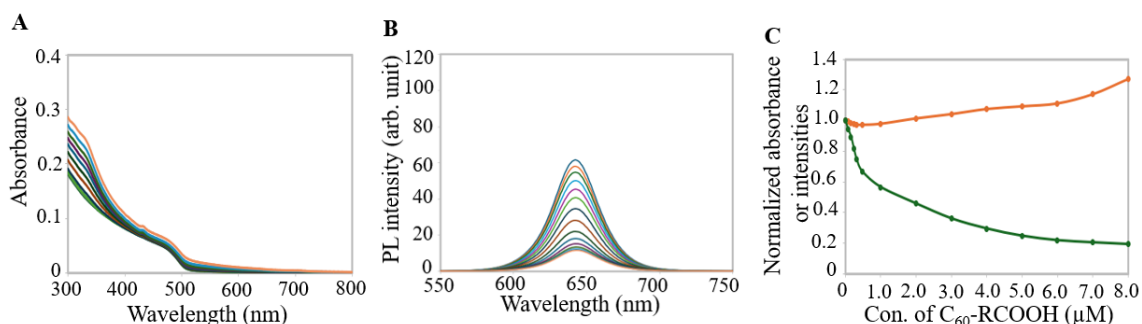


Figure 4.8 Quenching study for **QD@HDT** assembly with C₆₀-RCOOH. (A) Absorption and (B) PL spectra of **QD@HDT** ($\lambda_{\text{ex}} = 405$ nm) assembly with various concentrations of C₆₀-RCOOH, (C) Concentration-dependent image of normalized absorbance (orange) at 405 nm of Figure 4.8A, PL intensity (green) at 645 nm of Figure 4.8B.

The functionalized C₆₀-RCOOH ligand was also used as a quencher in the **QD@HDT** assembly to investigate how it affected the quenching process. The absorption spectra of the QD@HDT assembly at increasing C₆₀-RCOOH concentrations are shown in Figure 4.8A. As the concentration of the C₆₀-RCOOH ligand increases, I observe a corresponding increase in absorbance. This trend suggests that the C₆₀-RCOOH ligand is effectively interacting with the **QD@HDT** assembly. Concurrently, Figure 4.8B presents the PL spectra of the **QD@HDT** assembly under the same conditions. In contrast to the absorption spectra, the PL intensity exhibits a significant decrease with increasing C₆₀-RCOOH concentration. This dramatic quenching effect indicates an interaction between the QD@HDT assembly and the functionalized fullerene, which is anticipated to facilitate efficient electron transport. Figure 4.8C provides a quantitative analysis of the concentration-dependent quenching process. The graph depicts the normalized absorbance at 405 nm (orange) and PL intensity at 645 nm (green) as a function of C₆₀-RCOOH concentration. The PL intensity shows a dramatic decrease, reaching a quenching efficiency of approximately 80% at the highest C₆₀-RCOOH concentration. This substantial reduction in PL intensity, coupled with the relatively minor changes in absorbance, strongly suggests that electron transfer is occurring efficiently between the **QD@HDT** assembly and the C₆₀-RCOOH quencher. The enhanced quenching effect observed with C₆₀-RCOOH compared to pristine C₆₀ can be attributed to that the

functional group could facilitate stronger binding or closer proximity to the QD surface, thereby enhancing the efficiency of electron transfer. These findings show that, in comparison to the pristine C_{60} , the functionalized C_{60} -RCOOH functions as a more efficient quencher for the QD@HDT assembly. The notable PL quenching observed suggests that the C_{60} -RCOOH ligand creates efficient pathways for electron transfer, which could be advantageous for various optoelectronic applications.

4.3.9 Time-resolved photoluminescence decay measurements of quantum dot assemblies with C_{60} -RCOOH

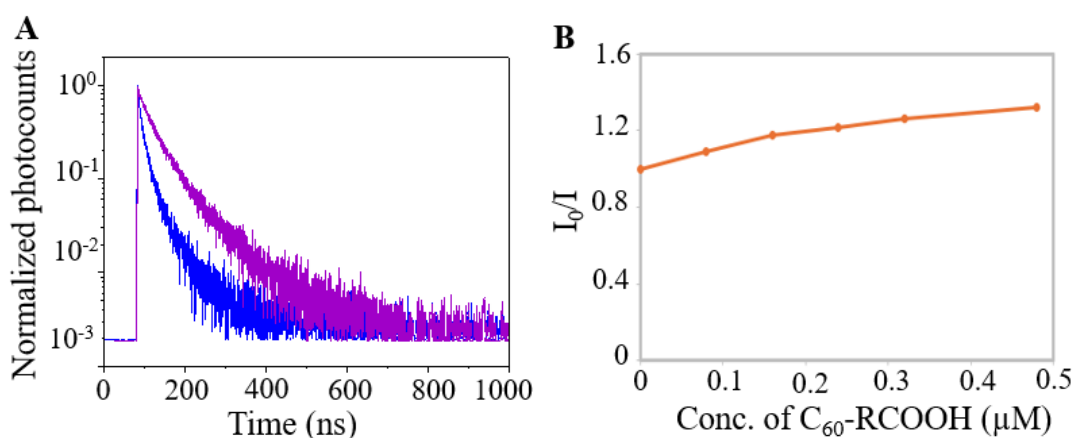


Figure 4.9 PL decay of (A) QD@HDT assembly in the absence (violet) and presence (blue) of C_{60} -RCOOH ($\lambda_{ex}=405$ nm), (B) The Stern-Volmer (S-V) plot, (I_0 and I denoted the PL intensity of QD@HDT without and with C_{60} -RCOOH).

I used time-resolved PL measurements to further comprehend the quenching mechanism of the QD@HDT assembly with C_{60} -RCOOH. Figure 4.9A presents the time-resolved PL decay curves for the QD@HDT assembly in the absence (violet) and presence (blue) of C_{60} -RCOOH. The results reveal significant changes in the fluorescence lifetime of the assembly upon interaction with the quencher molecule. In the absence of C_{60} -RCOOH, the QD@HDT assembly exhibits a lifetime of 52.8 ns. This relatively long lifetime is indicative of the stable excited state of the assembly, which is a desirable characteristic for potential applications in optoelectronic devices. However, upon the addition of C_{60} -RCOOH, I observe a dramatic decrease in the lifetime to 15.2 ns. This substantial reduction in lifetime, by approximately 71%, strongly suggests a dynamic quenching process is taking place. Dynamic quenching occurs when the quencher

molecule (in this case, C₆₀-RCOOH) interacts with the fluorophore (**QD@HDT** assembly) during its excited state lifetime. This interaction provides an additional non-radiative pathway for deexcitation, effectively shortening the time the assembly spends in the excited state. The significant decrease in lifetime observed here indicates that C₆₀-RCOOH is efficiently interacting with the excited **QD@HDT** assembly, likely through an electron transfer mechanism. To further elucidate the quenching mechanism, I constructed a S-V plot, shown in Figure 4.9B. Here, I find that the concentration of C₆₀-RCOOH and I₀/I have a linear relationship. This linearity, combined with the significant decrease in lifetime, provides strong evidence for a predominantly dynamic quenching mechanism.

The enhanced quenching efficiency of C₆₀-RCOOH in the **QD@HDT** assembly compared to the pristine QDs (as observed in previous sections) can be attributed to several factors. First, the cross-linked structure of the **QD@HDT** assembly may facilitate more efficient interactions with the quencher molecules. Second, the carboxyl functionalization of C₆₀ likely improves its solubility and compatibility with the assembly, leading to more effective quenching. These results demonstrate that the C₆₀-RCOOH ligand is dynamically coupled to the surface of the **QD@HDT** assembly, leading to efficient electron transfer.

4.3.10 Photoluminescence quenching study of quantum dot with 7,7,8,8-tetracyanoquinodimethane

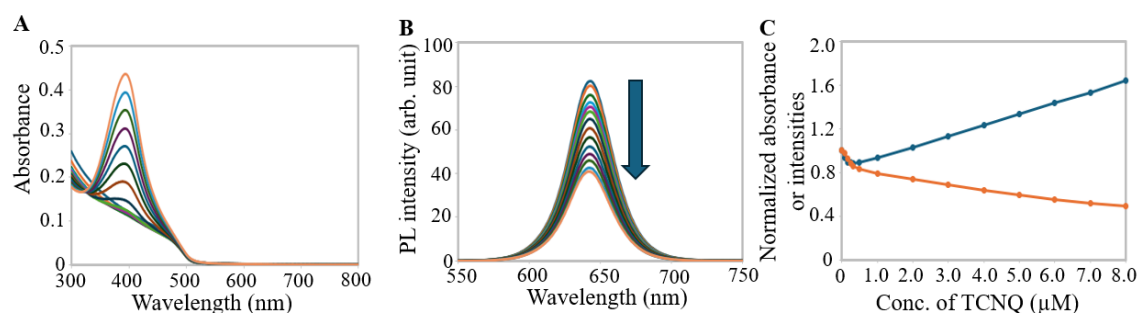


Figure 4.10 Quenching study for P-QD with TCNQ in toluene. (A) Absorption, and (B) PL spectra of pristine QD ($\lambda_{\text{ex}} = 405$ nm) with various concentrations of P-C₆₀, (C) Concentration-dependent image of normalized absorbance (blue) at 450 nm of Figure 4.10A, PL intensity (orange) at 645 nm of Figure 4.10B.

To confirm electron transfer, I used a standard acceptor TCNQ (7,7,8,8-tetracyanoquinodimethane) which is renowned for its strong electron-accepting properties, primarily due to its electron-withdrawing cyano groups (-CN) attached to the quinodimethane core. This structural feature significantly enhances the molecule's ability to accept electrons, making it an ideal candidate for studying electron transfer processes in QD systems.²⁸ The addition of TCNQ to pristine P-QDs resulted in interesting spectroscopic changes.

Initially, the absorbance of P-QDs decreased with TCNQ from 0.08 to 0.48 μM in toluene but increased from 1.0 to 8.0 μM at higher concentrations. This dual behavior suggests a complex interaction between TCNQ and the QDs, possibly involving surface interactions and aggregation effects. PL studies revealed significant quenching of P-QD emission upon TCNQ addition. The concentration-dependent quenching effect, as shown in Figure 4.10C, indicates an efficient interaction between TCNQ and the excited state of the QDs. This observation is consistent with the expected electron-accepting nature of TCNQ, suggesting the generation of a charge-transfer complex or rapid charge transfer from the photoexcited QDs to TCNQ.

4.3.11 Time-resolved photoluminescence measurements of quantum dot with 7,7,8,8-tetracyanoquinodimethane

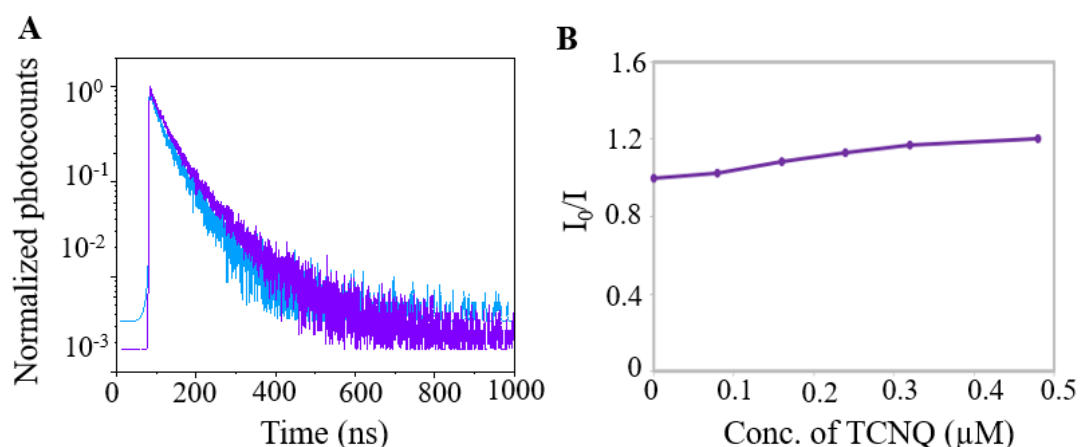


Figure 4.11 PL decay of (A) P-QD in the absence (violet) and presence (blue) of TCNQ ($\lambda_{\text{ex}} = 405 \text{ nm}$), (B) The Stern-Volmer (S-V) plot, (I_0 and I denoted the PL intensity of P-QD without and with TCNQ).

Time-resolved PL measurements were measured to investigate further the quenching mechanism of the P-QDs in the presence of an electron acceptor TCNQ. With the addition of TCNQ, the PL lifetime decreased from 58.5 ns to 53.7 ns for P-QDs. Although this is not spectacular, the lifetime reduction is well pronounced to show both static and dynamic quenching mechanisms. Static quenching corresponds to the formation of a non-emissive ground-state complex between P-QDs and TCNQ. Dynamic quenching is related to diffusion-controlled interactions which quench excited-state P-QDs via electron transfer. Decreasing PL lifetime evidences the presence of both mechanisms in the quenching process, with higher relevance of dynamic interactions. For quantification of these interactions, a Stern-Volmer analysis was performed. Figure 4.11B presents a linear Stern-Volmer plot, confirming the linear dependency of the quenching efficiency from the concentration of TCNQ toward a combined process in ground-state complex formation and a diffusion-limited quenching process, as already determined for this type of interaction. In such a well-defined interaction model, the TCNQ molecules could interact effectively with the P-QDs via static and dynamic pathways. The modest lifetime reduction together with the linearity of the Stern-Volmer plot underlines the complex interplay of these quenching mechanisms. The ground-state complex formation underlines specific affinity between the P-QD surface and TCNQ molecules, possibly mediated by the surface ligands or electronic properties of the QDs. On the other hand, the diffusion-controlled quenching underlines the role of collisional encounters driving electron transfer during the excited state.

These results view the general landscape of quenching dynamics and inform about interaction mechanisms in QD-based donor-acceptor systems. Such knowledge will be important in the optimization of these systems regarding their application in optoelectronics, sensing, and energy conversion, all of which require controlled quenching and effective electron transfer.

4.3.12 Photoluminescence quenching study of quantum dot assemblies with 7,7,8,8-tetracyanoquinodimethane

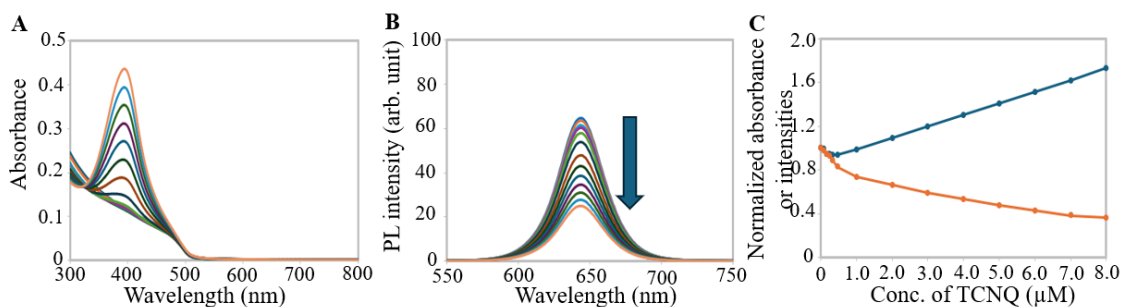


Figure 4.12 Quenching study for **QD@HDT** assembly with TCNQ. (A) Absorption, and (B) PL spectra of **QD@HDT** ($\lambda_{\text{ex}} = 405 \text{ nm}$) assembly with various concentrations of TCNQ, (C) Concentration-dependent figure of normalized absorbance (blue) at 405 nm of Figure 4.12A, PL intensity (orange) at 645 nm of Figure 4.12B.

To see electron transfer in the case of **QD@HDT assembly** to TCNQ, first absorption, and PL spectra were measured without using TCNQ in toluene. Then, TCNQ was gradually added to the assembly solution from 0.08 to 8.0 μM and measured. Like P-QD with TCNQ, absorption at 450 nm from 0.08 to 0.48 μM decreased and from 1.0 to 8.0 μM increased Figure (4.12A, C), suggesting complex interaction. On the other hand, the PL intensity of **QD@HDT** assembly was sharply decreased with increasing concentration of TCNQ in toluene. It indicates efficient electron transfer from photoexcited **QD@HDT** assembly to TCNQ. Figure 4.12C illustrates the concentration-dependent quenching effect, which suggests an effective interaction between TCNQ and the **QD@HDT**'s excited state.

At the maximum TCNQ concentration, the PL intensity dramatically drops and reaches a quenching efficiency of about 80%. In contrast, the PL intensity was reduced by almost 55% in the case of P-C₆₀. It demonstrates that **QD@HDT** with TCNQ has a higher quenching efficiency than P-QD. In other words, the impacts of TCNQ's interaction with **QD@HDT** assemblies were more noticeable than those of P-QDs. This enhanced quenching efficiency could be attributed to the altered surface chemistry and electronic structure of the QDs in the assembly, potentially providing more favorable pathways for electron transfer to TCNQ.

4.3.13 Time-resolved photoluminescence measurement quantum dot assemblies with 7,7,8,8-tetracyanoquinodimethane

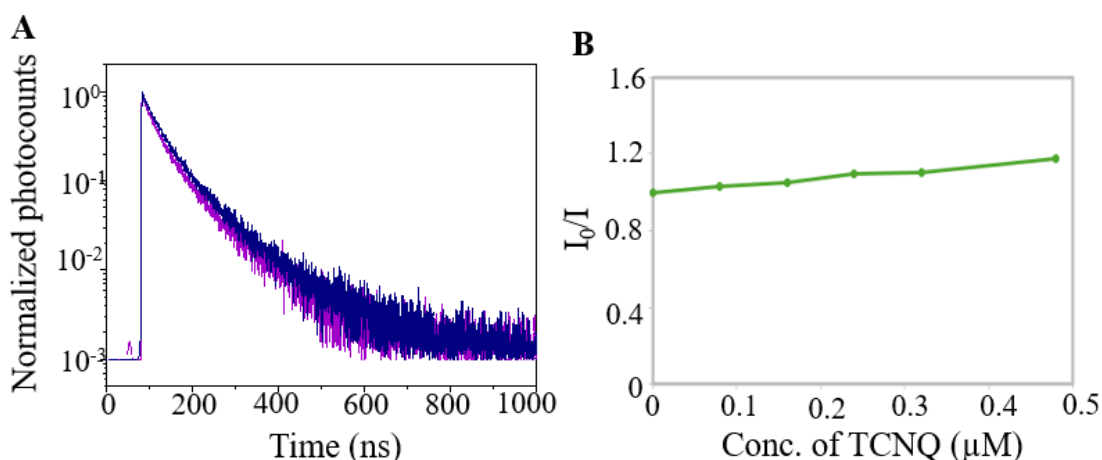


Figure 4.13 PL decay of (A) **QD@HDT** assembly without (blue) and with (indigo) of TCNQ ($\lambda_{\text{ex}} = 405 \text{ nm}$), (B) The Stern-Volmer (S-V) plot, (I_0 and I denoted the PL intensity of **QD@HDT** without and with TCNQ).

To check the lifetime and interaction between **QD@HDT** and TCNQ, a time-resolved PL measurement was also performed (Figure 4.13A). The PL lifetime of the assembly without using TCNQ was 53.7 ns. After the addition of TCNQ (8.0 μM), the lifetime did not change significantly, 48.6 ns. While this change is modest, it is more significant than observed with pristine QDs. The linear S-V plot (Figure 4.13B) again suggests a combination of static and dynamic quenching mechanisms. The enhanced quenching in assemblies could be due to the increased accessibility of TCNQ to the QD surface. The interaction of TCNQ with both pristine QDs and **QD@HDT** assemblies demonstrates the complex nature of electron transfer in these systems. The observed quenching effects are more pronounced in assemblies, suggesting that the structural organization of QDs plays a crucial role in facilitating electron transfer processes.

The combination of static and dynamic quenching mechanisms indicates that TCNQ interacts with QDs both through ground-state complex formation and diffusion-controlled processes. This dual mechanism could be advantageous for applications requiring efficient and versatile electron transfer, such as in photocatalysis or optoelectronic devices. The enhanced quenching efficiency in **QD@HDT** assemblies compared to pristine QDs highlights the potential of engineered QD structures in improving electron

transfer processes. This finding opens up possibilities for designing more efficient light-harvesting and charge-separation systems by tailoring the assembly architecture and surface chemistry of QDs.

In conclusion, the study of TCNQ interactions with QDs and their assemblies provides valuable insights into the factors governing electron transfer in these systems. The observed differences between pristine QDs and assemblies underscore the importance of nanostructure engineering in optimizing electron transfer processes.

4.4 Conclusions

Herein, I have successfully fabricated a QD assembly, named **QD@HDT**, by using 1,6-hexane dithiol (HDT) as a molecular linker for controlled assembly. STEM and DLS analyses were used in this work to confirm the structural integrity and the formation of **QD@HDT** assembly. STEM imaging revealed well-defined assemblies, while DLS measurements underlined the uniform particle size and effective dispersion in solution, proving the reproducibility and robustness of the assembly process. The charge transfer dynamics of the **QD@HDT** assembly were further investigated with various electron acceptors, including (P-C₆₀), C₆₀-RCOOH, and TCNQ. The results indicated various contact types based on the properties of the quenchers. When interacting with P-C₆₀ and TCNQ, the **QD@HDT** assembly used both static and dynamic quenching. Static quenching arose from ground-state complex formation, while dynamic quenching involved diffusion-controlled interactions leading to the transfer of electrons in the state of excitation. In contrast, the interaction of C₆₀-RCOOH was mostly dynamic, probably due to the functionalized carboxyl groups, which favored efficient diffusion and interaction with QDs in the excited state. The higher quenching efficiency for **QD@HDT** assemblies compared to pristine QDs testifies to the important role of HDT as a linker. HDT contributed not only to the structural organization of QDs but also provided the environment that favored donor-acceptor interactions, thus promoting electron transfer. In such a way, the double functionality of HDT acting both as a structural and electronic mediator point to its potential in the design of QD-based systems with preselected properties.

The work presented gives enough insight into the design and functionalization of QD assemblies. The dynamics of charge transfer described, along with the function of linker molecules, open new pathways for the advancement of QD-based materials in such applications as optoelectronics, photovoltaics, and sensors. The results show that the strategic design of assemblies can greatly influence the dynamics and efficiency of interactions in QD-based donor-acceptor systems and thus point to a very promising direction for future studies in QD assembly and related areas.

References

- (1) Shibu, E. S.; Hamada, M.; Nakanishi, S.; Wakida, S.; Biju, V. Photoluminescence of CdSe and CdSe/ZnS Quantum Dots: Modifications for Making the Invisible Visible at Ensemble and Single-Molecule Levels. *Coord. Chem. Rev.* **2014**, 263–264 (1), 2–12. <https://doi.org/10.1016/j.ccr.2013.10.014>.
- (2) Abbasi, S.; Molaei, M.; Karimipour, M. CdSe and CdSe/CdS Core–Shell QDs: New Approach for Synthesis, Investigating Optical Properties and Application in Pollutant Degradation. *Luminescence* **2017**, 32 (7), 1137–1144. <https://doi.org/10.1002/bio.3300>.
- (3) Cirillo, M.; Aubert, T.; Gomes, R.; Van Deun, R.; Emplit, P.; Biermann, A.; Lange, H.; Thomsen, C.; Brainis, E.; Hens, Z. “Flash” Synthesis of CdSe/CdS Core–Shell Quantum Dots. *Chem. Mater.* **2014**, 26 (2), 1154–1160. <https://doi.org/10.1021/cm403518a>.
- (4) Qian, H.; Li, L.; Ren, J. One-Step and Rapid Synthesis of High Quality Alloyed Quantum Dots (CdSe–CdS) in Aqueous Phase by Microwave Irradiation with Controllable Temperature. *Mater. Res. Bull.* **2005**, 40 (10), 1726–1736. <https://doi.org/10.1016/j.materresbull.2005.05.022>.
- (5) Hamood, R.; Abd El-sadek, M. S.; Gadalla, A. Facile Synthesis, Structural, Electrical and Dielectric Properties of CdSe/CdS Core-Shell Quantum Dots. *Vacuum* **2018**, 157 (August), 291–298. <https://doi.org/10.1016/j.vacuum.2018.08.050>.
- (6) Sobhanan, J.; Rival, J. V.; Anas, A.; Sidharth Shibu, E.; Takano, Y.; Biju, V. Luminescent Quantum Dots: Synthesis, Optical Properties, Bioimaging and Toxicity. *Adv. Drug Deliv. Rev.* **2023**, 197, 114830. <https://doi.org/10.1016/j.addr.2023.114830>.
- (7) Zhao, L.; Hu, L.; Fang, X. Growth and Device Application of CdSe Nanostructures. *Adv. Funct. Mater.* **2012**, 22 (8), 1551–1566. <https://doi.org/10.1002/adfm.201103088>.
- (8) Cotta, M. A. Quantum Dots and Their Applications: What Lies Ahead? *ACS Appl. Nano Mater.* **2020**, 3 (6), 4920–4924. <https://doi.org/10.1021/acsanm.0c01386>.
- (9) Surana, K.; Salisu, I. T.; Mehra, R. M.; Bhattacharya, B. A Simple Synthesis Route of Low Temperature CdSe–CdS Core-Shell Quantum Dots and Its Application in Solar Cell. *Opt. Mater. (Amst.)* **2018**, 82 (May), 135–140. <https://doi.org/10.1016/j.optmat.2018.05.060>.
- (10) Han, K.; Yoon, S.; Chung, W. J. CdS and CdSe Quantum Dot-Embedded Silicate Glasses for <sc>LED</Sc> Color Converter. *Int. J. Appl. Glas. Sci.* **2015**, 6 (2), 103–108. <https://doi.org/10.1111/ijag.12115>.
- (11) Zhang, F.; Wang, S.; Wang, L.; Lin, Q.; Shen, H.; Cao, W.; Yang, C.; Wang, H.; Yu, L.; Du, Z.; Xue, J.; Li, L. S. Super Color Purity Green Quantum Dot Light-Emitting Diodes Fabricated by Using CdSe/CdS Nanoplatelets. *Nanoscale* **2016**, 8 (24), 12182–12188. <https://doi.org/10.1039/C6NR02922A>.

- (12) Yuan, L.-D.; Deng, H.-X.; Li, S.-S.; Wei, S.-H.; Luo, J.-W. Unified Theory of Direct or Indirect Band-Gap Nature of Conventional Semiconductors. *Phys. Rev. B* **2018**, *98* (24), 245203. <https://doi.org/10.1103/PhysRevB.98.245203>.
- (13) Ghosh, Y.; Mangum, B. D.; Casson, J. L.; Williams, D. J.; Htoon, H.; Hollingsworth, J. A. New Insights into the Complexities of Shell Growth and the Strong Influence of Particle Volume in Nonblinking “Giant” Core/Shell Nanocrystal Quantum Dots. *J. Am. Chem. Soc.* **2012**, *134* (23), 9634–9643. <https://doi.org/10.1021/ja212032q>.
- (14) Pan, Z.; Zhang, H.; Cheng, K.; Hou, Y.; Hua, J.; Zhong, X. Highly Efficient Inverted Type-I CdS/CdSe Core/Shell Structure QD-Sensitized Solar Cells. *ACS Nano* **2012**, *6* (5), 3982–3991. <https://doi.org/10.1021/nn300278z>.
- (15) Zhang, L.; Lv, B.; Yang, H.; Xu, R.; Wang, X.; Xiao, M.; Cui, Y.; Zhang, J. Quantum-Confined Stark Effect in the Ensemble of Phase-Pure CdSe/CdS Quantum Dots. *Nanoscale* **2019**, *11* (26), 12619–12625. <https://doi.org/10.1039/C9NR03061A>.
- (16) Mathew, S.; Saran, A. D.; Singh Bhardwaj, B.; Ani Joseph, S.; Radhakrishnan, P.; Nampoory, V. P. N.; Vallabhan, C. P. G.; Bellare, J. R. Size Dependent Optical Properties of the CdSe-CdS Core-Shell Quantum Dots in the Strong Confinement Regime. *J. Appl. Phys.* **2012**, *111* (7). <https://doi.org/10.1063/1.3702430>.
- (17) Kuznetsova, V. A.; Mates-Torres, E.; Prochukhan, N.; Marcastel, M.; Purcell-Milton, F.; O’Brien, J.; Vishneratina, A. K.; Martinez-Carmona, M.; Gromova, Y.; Garcia-Melchor, M.; Gun’ko, Y. K. Effect of Chiral Ligand Concentration and Binding Mode on Chiroptical Activity of CdSe/CdS Quantum Dots. *ACS Nano* **2019**, *13* (11), 13560–13572. <https://doi.org/10.1021/acsnano.9b07513>.
- (18) Steckel, J. S.; Snee, P.; Coe-Sullivan, S.; Zimmer, J. P.; Halpert, J. E.; Anikeeva, P.; Kim, L.; Bulovic, V.; Bawendi, M. G. Color-Saturated Green-Emitting QD-LEDs. *Angew. Chemie Int. Ed.* **2006**, *45* (35), 5796–5799. <https://doi.org/10.1002/anie.200600317>.
- (19) Su, W.; Yuan, F. QD-LEDs: High Efficiency and Long-Term Stability toward Practical Applications. *Matter* **2022**, *5* (8), 2464–2466. <https://doi.org/10.1016/j.matt.2022.06.017>.
- (20) Swinehart, D. F. The Beer-Lambert Law. *J. Chem. Educ.* **1962**, *39* (7), 333–335. <https://doi.org/10.1021/ed039p333>.
- (21) Tanwar, A. S.; Parui, R.; Garai, R.; Chanu, M. A.; Iyer, P. K. Dual “Static and Dynamic” Fluorescence Quenching Mechanisms Based Detection of TNT via a Cationic Conjugated Polymer. *ACS Meas. Sci. Au* **2022**, *2* (1), 23–30. <https://doi.org/10.1021/acsmesuresciau.1c00023>.
- (22) Kohlmann, T.; Naumann, R.; Kerzig, C.; Goetz, M. Combined Static and Dynamic Quenching in Micellar Systems—Closed-Form Integrated Rate Laws Verified Using a Versatile Probe. *Phys. Chem. Chem. Phys.* **2017**, *19* (13), 8735–8741. <https://doi.org/10.1039/C6CP08491E>.

- (23) Illescas, B. M.; Martín, N. [60]Fullerene Adducts with Improved Electron Acceptor Properties. *J. Org. Chem.* **2000**, 65 (19), 5986–5995. <https://doi.org/10.1021/jo0003753>.
- (24) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. Photoinduced Intramolecular Electron Transfer in a Bridged C60 (Acceptor)—Aniline (Donor) System. Photophysical Properties of the First “Active” Fullerene Diad. *J. Am. Chem. Soc.* **1995**, 117 (14), 4093–4099. <https://doi.org/10.1021/ja00119a025>.
- (25) Yang, D.; Yang, R.; Wang, K.; Wu, C.; Zhu, X.; Feng, J.; Ren, X.; Fang, G.; Priya, S.; Liu, S. High Efficiency Planar-Type Perovskite Solar Cells with Negligible Hysteresis Using EDTA-Complexed SnO₂. *Nat. Commun.* **2018**, 9 (1), 3239. <https://doi.org/10.1038/s41467-018-05760-x>.
- (26) Jia, L.; Chen, M.; Yang, S. Functionalization of Fullerene Materials toward Applications in Perovskite Solar Cells. *Mater. Chem. Front.* **2020**, 4 (8), 2256–2282. <https://doi.org/10.1039/D0QM00295J>.
- (27) Virkki, K.; Demir, S.; Lemmetyinen, H.; Tkachenko, N. V. Photoinduced Electron Transfer in CdSe/ZnS Quantum Dot–Fullerene Hybrids. *J. Phys. Chem. C* **2015**, 119 (31), 17561–17572. <https://doi.org/10.1021/acs.jpcc.5b04251>.
- (28) Sachith, B. M.; Zhang, Z.; Subramanyam, P.; Subrahmanyam, C.; Furube, A.; Tamai, N.; Okamoto, T.; Misawa, H.; Biju, V. Photoinduced Interfacial Electron Transfer from Perovskite Quantum Dots to Molecular Acceptors for Solar Cells. *Nanoscale* **2023**, 15 (17), 7695–7702. <https://doi.org/10.1039/d3nr01032e>.

Chapter 5

Electron transfer from mesoscopic assemblies of semiconductor quantum dots

5.1. Abstract

With unique semiconductor photonic and electronic properties, quantum dots have emerged as one of the most important materials in modern technology. Because of their outstanding tunability, size-dependent optical behavior, and quantum confinement effects, QDs are a necessary ingredient for applications that include light-emitting diodes, all the way to photovoltaics and bioimaging. While single, isolated QDs have been the subject of intense studies, the development of efficient synthesis and dispersion methods for mesoscopic QD assemblies has remained a bottleneck toward the full realization of their potential. Moving from single QDs to structured assemblies introduces collective properties and interdot interactions that further significantly enhance the electron transfer efficiency and optoelectronic performance of QDs. This chapter introduces a new, simple way to prepare shaped nanoparticles by using a biocatalyst-based process; I term it the biocatalytic nanoparticle shaping method (BNS). This novel process enables the synthesis of well-dispersed mesoscopic QD assemblies with good control of size and morphology and allows a wide range of advanced studies and applications to take advantage of their electron transfer capabilities. In the BNS method, QDs first aggregate into large clusters ($>1\ \mu\text{m}$) with the help of oligo-L-lysine as a linker. The initial aggregation phase lays a framework for the eventual assembly at the mesoscopic scale. The action of trypsin, a highly specific and efficient proteolytic enzyme, cleaves the amide bonds within the oligo-L-lysine linkers. This represents an enzymatic breakup of the large aggregates into controlled, well-dispersed mesoscopic particles with a limited size distribution, averaging about 84 nm in hydrodynamic diameter. The resulting mesoscopic QD assemblies, **ms-QDs**, retain excellent colloidal stability and exhibit uniform structural properties. The

transformation from micron-scale aggregates to nanoscale assemblies is precisely controlled, with great reproducibility and scalability of the process.

Accordingly, the photophysical properties of the **ms-QDs** were carefully investigated and showed that, while retaining the intrinsic quantum mechanical features of the single QDs, new attributes emerged as a consequence of their collective organization. Spectroscopic analyses confirmed the preservation of photoluminescence and enhancement of charge mobility due to reduced interparticle distance in the assemblies. Critically, the **ms-QDs** showed robust electron transfer capabilities, a highly sought-after feature in applications related to solar energy harvesting, photocatalysis, and optoelectronics. The assembly structure favored closer contact between QDs and electron acceptor molecules, significantly improving electron transfer efficiency. This is a kind of collective behavior that does not exist in isolated QDs, further emphasizing the importance of mesoscopic assembly design in enhancing functional performance.

The electron transfer properties of the **ms-QDs** were explored by a variety of spectroscopic methods, including steady-state and time-resolved PL measurements. Electron transfer to suitable electron acceptors, such as TCNQ, was found to occur rapidly and efficiently from the QD assemblies. This efficiency is due to the unique mesoscopic structure that decreases insulating barriers typical for surface ligands while retaining stability and dispersion.

Electron transfer enabled by **ms-QDs** is highly efficient and opens great perspectives for their application in next-generation solar energy-converting devices. The effective charge separation and transport will contribute significantly to the enhancing performance of photovoltaic systems and other energy conversion devices based on such assemblies. Moreover, due to their structural versatility and scalable syntheses, they represent ideal candidates in the investigation of molecular-based mesoscopic particles for various optoelectronic applications. While these are important findings, the BNS method represents a paradigm-shifting approach toward fabricating well-dispersed mesoscopic QD assemblies with tailored properties. This integration of enzymatic precision into nanoscale engineering allows the generation of particles with optimized photophysical properties and superior electron transfer capabilities. Developments in this chapter support the potential of **ms-QDs** as superior platforms for solar energy harvesting to advance the design of molecular-based systems offering superior optoelectronic

performance. This study lays the groundwork for future research into transfer of electrons techniques in structured QD assemblies, as well as new insights on their significance in next-generation materials for energy and electronics.

5.2. Introduction

Recent advances in QDs have transformed their use in bioimaging, sensors, solar energy harvesting, and even quantum computing.¹⁻⁷ These nanomaterials, lauded for their size-dependent optical absorption, possess exceptional properties when reduced to dimensions comparable to the exciton Bohr radius.⁸⁻¹⁰ It is this quantum confinement effect that has opened Pandora's box of unique electrical and photonic behaviors at the heart of modern applications. The colloidal QDs, being solution-processable and thus easily integrated into various systems, have driven wide research.^{11,12} Their ease of synthesis, added to tunable size dispersion, makes them so valuable in optoelectronics and bioimaging. Therefore, from that perspective, with the transformative potentials of QDs, the invention received the 2023 Nobel Prize for its amazing effect on the technology and perspective that science will develop for future industries.^{13,14} However, to realize the whole possibility of QDs, researchers have put increasing emphasis on the intermolecular interaction of QD assemblies since electronic and optical property tailoring enabled by these kinds of interactions largely enable advanced applications.

While single QDs have extraordinary properties, the controlled assemblies introduce collective phenomena and interdot coupling. In this way, such assemblies allow tunable optical and electronic properties using interdot spacing and geometry.^{15,16} These features have catalyzed breakthroughs in designing high-efficiency solar cells¹⁷, photocatalysts¹⁸, molecular computing blocks¹⁹, and high-density data storage devices²⁰.

Recent work by Tahara et al. has pointed out the great possibilities that QD assemblies can offer after showing impressive up-conversion properties in substrate-supported QD structures.²¹ This indeed marks a potent avenue toward making state-of-the-art optoelectronic materials. Yet, preparation methodology for stable and well-dispersed QD assemblies is scarce, and the current methodologies lack scalability or control over reaction conditions in most cases.²²⁻²⁵

In particular, the attempts toward the preparation of QD assemblies include ion-mediated techniques and cross-linker methods. For example, Koole et al. used organic

linkers like 1,6-hexanedithiol (HDT) to fabricate molecular-like assemblies of CdTe QDs, showing that linker concentration affected the aggregate size.²⁴ Liu et al. recently developed a quick ion-mediated strategy to prepare hydrophilic and aggregate-free QD assemblies.²⁶ However, the synthesis of soluble, well-dispersed mesoscopic QD assemblies comprising a significant amount of QDs is still rarely reported.^{27–29}

The attempt to hybridize different approaches has also been developed, such as the work of Grzyb et al. who developed self-assembled antennas based on CdTe QDs combined with phycocyanin or phycobilisomes. These indeed evidenced energy transfer over distances larger than the Förster radius, which underlines the potential of QD assemblies for energy applications.¹⁵ However, most of them require either perfect control of the reaction or scaffolds to avoid undesirable large-scale aggregations, and thus call for versatile universal fabrication strategies.

In this thesis, I presented an enzyme-based methodology for the generation of functional mesoscopic QD particles, denoted as biocatalytic nanoparticle shaping, with controlled size and dispersibility. Enzymatic reactions usually enjoy popularity in their diversity, specificity, and even selectivity for a variety of chemical transformations. In particular, this new method utilizes an enzyme called trypsin-protease that cleaves an amide bond near an L-arginine or L-lysine residue to disassemble large-scale QD aggregations into homogeneous mesoscopic size and dispersed distributions.^{30–32, 33}

The process starts with QDs functionalized with carboxylic acid groups, which are interconnected via oligo-L-lysine chains to form aggregates larger than 1 μm .³⁴ Then, trypsin is added to cleave the oligo-L-lysine linkers, producing **ms-QDs** with a hydrodynamic size of about 84 nm. This enzymatic method is straightforward and scalable, thus providing a controlled pathway for the preparation of well-dispersed mesoscopic QD assemblies suitable for various applications.

The **ms-QDs** synthesized by the BNS method possess remarkable electron transfer properties that are very important for applications in solar energy conversion and optoelectronics. These assemblies combine the advantages of collective behavior with the intrinsic properties of individual QDs, thus creating a platform for efficient charge separation and transport. In addition, spectroscopic studies indicated that the strong luminescence of **ms-QDs** emanated from the constituent QDs in supporting efficient electron transfer due to their optimally developed architecture, which has minimized

insulating barriers and ensured increased donor-acceptor contacts. This mesoscopic structure can serve for long-range electron transport and hence has the potential to act in energy conversion devices, like solar cells and photocatalysts. The unique properties of **ms-QDs** go beyond energy applications.^{35–37} High specific surface area, combined with exceptional optical and electronic characteristics, makes them valuable in catalysis, drug delivery, and molecular computation.^{38–41} A biocatalytic approach can create well-dispersed functional mesoscopic particles, which opens new dimensions in designing materials with tailored properties.

The BNS method represents a great leap in QD assembly fabrication. Enzymatic processes used in this approach allow the production of mesoscopic QD assemblies in a versatile, scalable, and efficient way while significantly improving electron transfer. These results provide important insight into the basic principles of QD assembly and open exciting perspectives for further applications in next-generation optoelectronic devices, solar energy harvesting, and beyond. The presented work points to the possibility that QD assemblies will change the face of technologies relying on efficient charge transport and energy conversion, therefore it gives a background for further development in this field.

5.3. Results and discussion

5.3.1 Mesoscopic quantum dots assembly formation using a bioinspired method

In this work, a novel method was developed to prepare **ms-QDs** by taking advantage of the enzymatic cleavage action of trypsin on oligo-L-lysine chains bridging QDs. It successfully decomposes large QD aggregates into smaller, well-dispersed particles in water and hence opens up a facile route for the preparation of mesoscopic assemblies that can potentially be applied to optoelectronic and energy devices.

The functionalization of colloidal CdSe/CdS QDs with thiol-PEG introduced the carboxylic acid functional groups, yielding a structure of **QD-COOH**. To further link **QD-COOH** particles into large aggregates, they were treated with an amide-condensation reaction. The reaction involved DMT-MM (4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride) as a coupling agent and an excess of L-lysine (400 wt%) to ensure extensive cross-linking between QD particles (Figure 5.1A). Thus, this resulted in microscale aggregates wherein the particle size was well above 1000 nm.

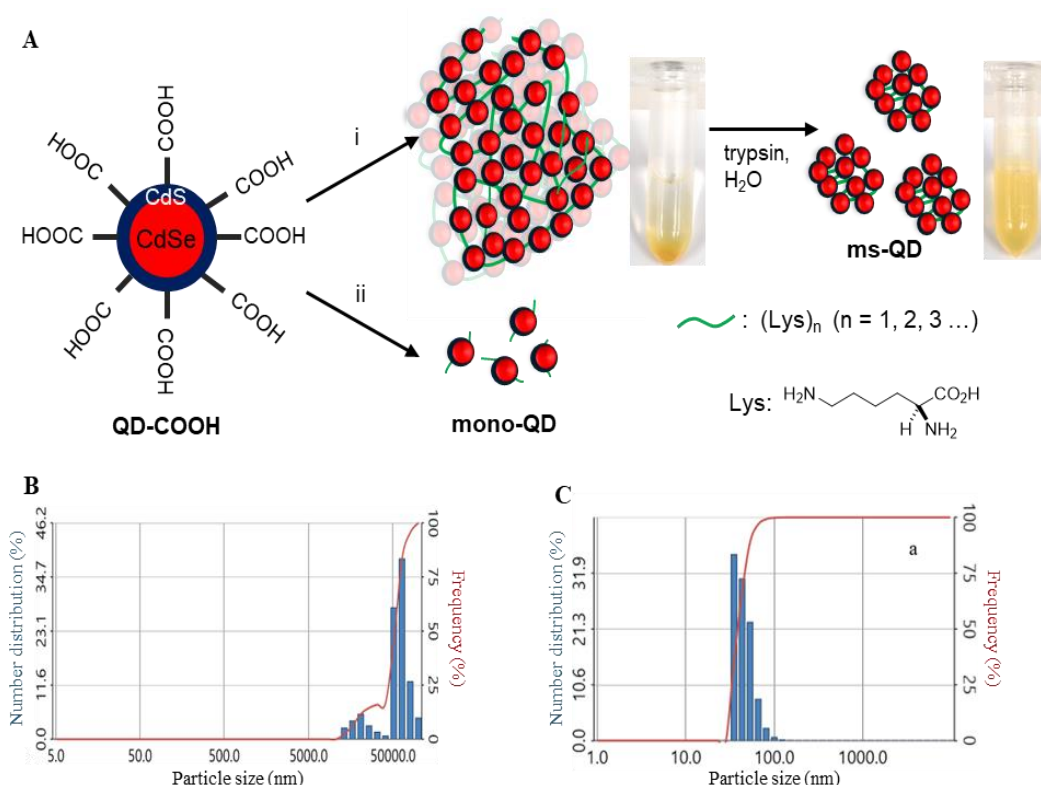


Figure 5.1 (A) A synthetic scheme to make **ms-QD** by the BNS method and **mono-QD**, as a reference compound. (i) 400 w% (to **QD-COOH**) L-lysine, DMT-MM, 40 °C, 12 h, in water; (ii) 0.30 w% (to **QD-COOH**) L-lysine, DMT-MM, 40 °C, 12 h, in water. The corresponding dispersions are shown in the inset photos. The DLS profiles of (B) **ms-QD** aggregates before adding trypsin, and (C) **ms-QD** dispersed in 10 mM HEPES aq.

The large aggregates were accordingly formed, evidenced quantitatively through the DLS measurements of such microscale precipitates, Figure 5.1B shows this. These would constitute an interim stage in these syntheses when they become precursors in forming mesoscopic assemblies. This will be done to reduce these large aggregates to well-dispersed mesoscopic particles by using trypsin. Finally, an acid-washed trypsin-type protease enzyme, which cuts in the vicinity of lysine and arginine at amide bond, was introduced to the precipitate at a temperature of 40 °C and incubated overnight for 12 hours. Accordingly, this digestion reaction cleaves the oligo-L-lysine linkers, leading to well-micro-sized QD products with considerable diminution in size compared to their initial aggregates. As shown in Figure 5.1C, **ms-QDs** have excellent dispersion in water which demonstrates that this enzymatic cleavage approach has been completed.

For direct comparison and to provide further insight, a reference compound known as mono-QD was prepared. Synthesis of **mono-QD** was proceeded by a procedure similar to **ms-QD**. In this work, QD-COOH was reacted with L-lysine and DMT-MM at 40 °C for 12 h to form a single QD-lysine assembly without enzymatic cleavage. After the reaction, unreacted L-lysine was washed off thoroughly with water, and **mono-QD** assemblies were collected.

This work illustrated the flexibility of the enzymatic cleavage approach and thus compared **ms-QDs** with **mono-QDs** to provide important insight into the structural and functional differences brought about by their distinct assembly processes. Characteristics of the resulting **ms-QDs** were quite promising for applications that need well-dispersed functionalized mesoscopic particles, including superior electron transfer capabilities. This enzymatic assembly and cleaving method represents a scalable and efficient pathway toward the synthesis of mesoscopic QD structures and opens new avenues to their integration into advanced optoelectronic systems and energy devices.

5.3.2 Size distribution of the assembled particles

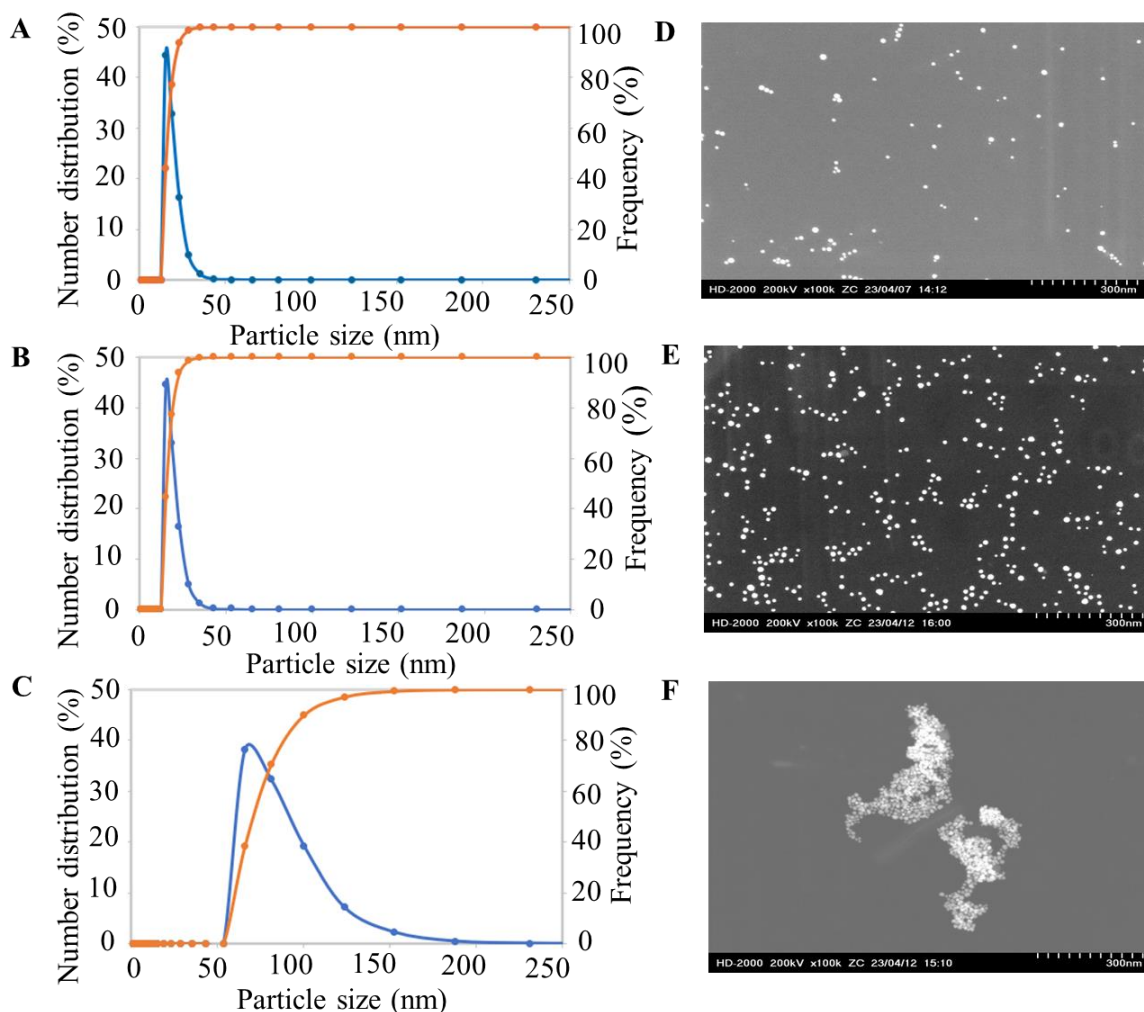


Figure 5.2 The DLS profiles of (A) **QD-COOH**, (B) **mono-QD**, and (C) **ms-QD** in 10 mM HEPES aq., and the STEM images of (D) **QD-COOH**, (E) **mono-QD**, and (F) **ms-QD**.

The hydrodynamic dimension, size distribution, and morphological properties of the QDs and their assemblies were investigated in detail by employing DLS and STEM analytical techniques, respectively. Such analytical techniques offer a deep insight into the hydrodynamic dimensions, size distribution, and morphological properties of the QD samples in question. Figure 5.2A illustrates that the DLS result of **QD-COOH** particles gave a mean hydrodynamic diameter of 8.6 ± 4.8 nm, while for **ms-QD** particles, a large mean hydrodynamic diameter is shown at 84.4 ± 22.1 nm in Figure 5.2C. The increased size certainly indicated the transformation of **mono-QDs** to **ms-QDs** assemblies through

the enzymatic cleavage and self-assembly process. Importantly, both **QD-COOH** and **ms-QD** samples showed small PDI (<0.2), indicating that the particles were well-dispersed in aqueous solutions with a restricted and uniform size distribution. Indeed, such well-dispersed and water-soluble nanoparticles with controlled size and shape have been a big challenge in the synthesis of nanomaterials. On the other hand, the successful preparation of **ms-QDs** in the current work underlines the efficacy of the enzymatic cleavage and assembly approach.

For comparison and a better understanding of the formation and necessity of mesoscopic assemblies, **mono-QD** particles were also prepared. DLS analysis of **mono-QDs** (Figure 5.2B) gave a mean hydrodynamic diameter of 22.6 ± 4.0 nm, representing an intermediate size between the smaller **QD-COOH** and the larger **ms-QD** particles. This confirmed that **ms-QDs** uniquely represent mesoscopic assemblies rather than simple aggregates or monomeric particles. Further confirmation of structural differences among the **QD-COOH**, **mono-QD**, and **ms-QD** particles was obtained from STEM analysis. **QD-COOH** and **mono-QD** samples showed discrete, monomeric QDs, Figures 5.2D-5.2F, while **ms-QD** samples demonstrated a characteristic structure of cross-linked aggregates organized in several layers. The newly formed unique multilayer arrangement is self-assembled into spherical **ms-QDs** in aqueous solutions, resulting in stable mesoparticles with well-defined morphologies.

It was considered that partial enzymatic cleavage of the amide bonds within the oligo-lysine chains was responsible for the formation of **ms-QDs**. The partial enzymatic reaction occurred, allowing cross-linking that, in turn, enabled the formation of spherical mesoscopic particles. This represents a feasible and effective route to obtain mesoscopic assemblies with controlled size and morphology, expanding the possibilities for synthesizing advanced nanomaterials. On the contrary, other studies, like one conducted by Chen et al., tried to form carbon-dot-based aggregates by regulating the addition of concentrated fatty acids.⁴¹ While that was a good attempt, the uniformity and dispersion achieved in the study point out the excellence of the enzymatic route toward QD assembly. Due to the multilayer and highly dispersed spherical structure, **ms-QDs** hold a privileged position in optoelectronics, catalysis, and energy harvesting. This overview of the size, distribution, and structural organization of QDs underscores the transformative power of

enzymatic cleavage in nanomaterial synthesis and points toward mesoscopic assemblies as a key to unlock further advances in quantum dot applications.

5.3.3 Optical properties of the assembled particles

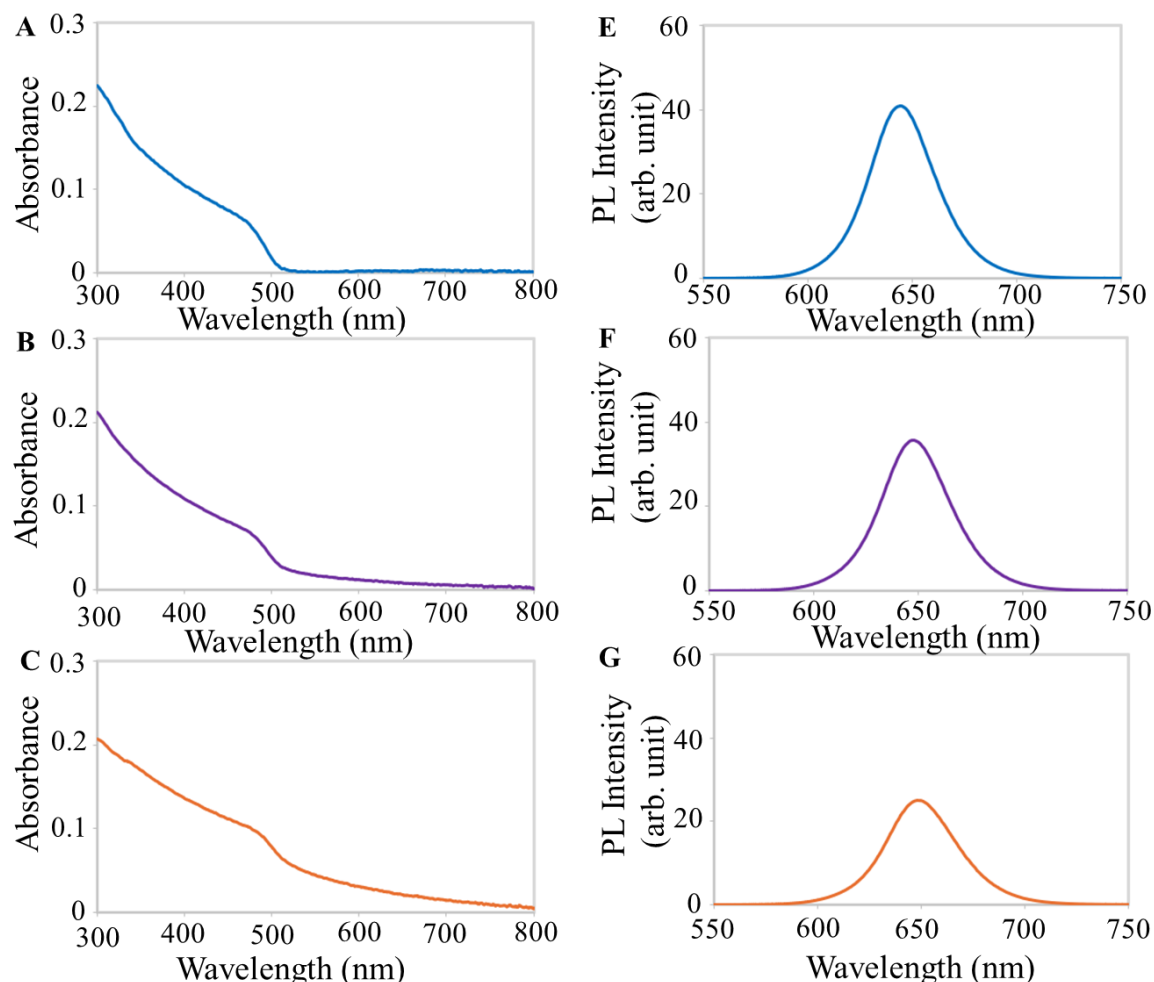


Figure 5.3 Absorption spectra of (A) **QD-COOH**, (B) **mono-QD**, and (C) **ms-QD**, and PL spectra (λ_{ex} : 405 nm) of (D) **QD-COOH**, (E) **mono-QD**, and (F) **ms-QD** in 10 mM HEPES aq. The absorbance at the excitation wavelengths was set to be identical (0.20) for all samples.

To study the optical properties of the QD samples, some analyses were performed using UV-vis absorption spectroscopy and steady-state fluorescence spectrometry. **ms-QD**, **mono-QD**, and **QD-COOH** each were dissolved in a 10 mM aqueous HEPES buffer for uniformity and consistency in measurement. The absorption and PL spectra were recorded to assess their optical behavior and to gain insights into the unique properties of

the mesoscopic QD assemblies (**ms-QDs**) compared to their monomeric counterparts. Absorption spectra of **QD-COOH**, **mono-QD**, and **ms-QD** revealed that these samples efficiently absorbed light in the ultraviolet to approximately 600 nm range of wavelength (Figures 5.3A, 5.3B, and 5.3C). Such a broad absorption may be indicative of semiconductor characteristics and may show promise in light-harvesting applications of CdSe/CdS QDs. However, this was a distinguishing point for **ms-QD**. The **ms-QD** sample exhibited distinct light-scattering signals beyond 600 nm due to its relatively larger particle size, which was absent in the spectra of **QD-COOH** and **mono-QD**. This scattering, as a result of the mesoscopic nature of **ms-QDs**, is because of their larger dimensions, which effectively alter the interactions with light using serious forward and backward scattering.⁴³ Such optical properties can be utilized in applications requiring strong light-matter interactions, like photovoltaics or photocatalysis. PL spectra were recorded upon photoexcitation at 405 nm to investigate the emission characteristics of the samples. Indeed, all three samples revealed distinct emission peaks located. **QD-COOH** showed a sharp emission peak at 645 nm, **mono-QD** also exhibited an emission peak at 645 nm, and **ms-QD** displayed a slightly redshifted emission peak at 650 nm (Figures 5.3D, 5.3E, and 5.3F). Specifically, this red shift in the **ms-QD** emission peak is attributed to some unique features of the mesoscopic arrangement in these assemblies. More precisely, internal emission reabsorption within the assembly can account for the red-shifted and slightly reduced emission intensity of **ms-QD**.⁴⁴ Such a phenomenon arises from interactions between closely packed QDs and the resulting energy exchange within the mesoscopic structure.

The red-shifted emission and reduced intensity in **ms-QD** point toward an enhanced energy transfer process within this assembly, promising the advancement of optical materials. The structural arrangement in **ms-QD** assemblies has allowed efficient electron/ hole transfer or energy transfer processes, which is particularly attractive in applications such as solar energy harvesting and light-emitting devices. For instance, Liu and co-workers, by using similar optical properties, prepared highly efficient luminescent solar concentrators by using red-emissive carbon dots.⁴⁵ The capability of **ms-QD** to show reabsorption and energy redistribution processes further improves the potential of this material as a candidate for luminescent solar concentrators, photovoltaic systems, or light-harvesting devices.

UV-vis and PL spectroscopic investigations point out the peculiar optical properties of **ms-QD** concerning both **mono-QD** and **QD-COOH**. The broad UV-visible light absorption, the light-scattering effect due to mesoscopic structure, and the red-shifted emission all point out the advanced optical behavior of **ms-QDs**. Such features open up new avenues in designing novel optical materials with improved light manipulation and energy transfer capabilities, which can be tailored for next-generation optoelectronic applications in solar cells, light concentrators, and photodetectors.

5.3.4 Photoluminescence quenching study for mesoscopic quantum dots with 7,7,8,8-tetracyanoquinodimethane

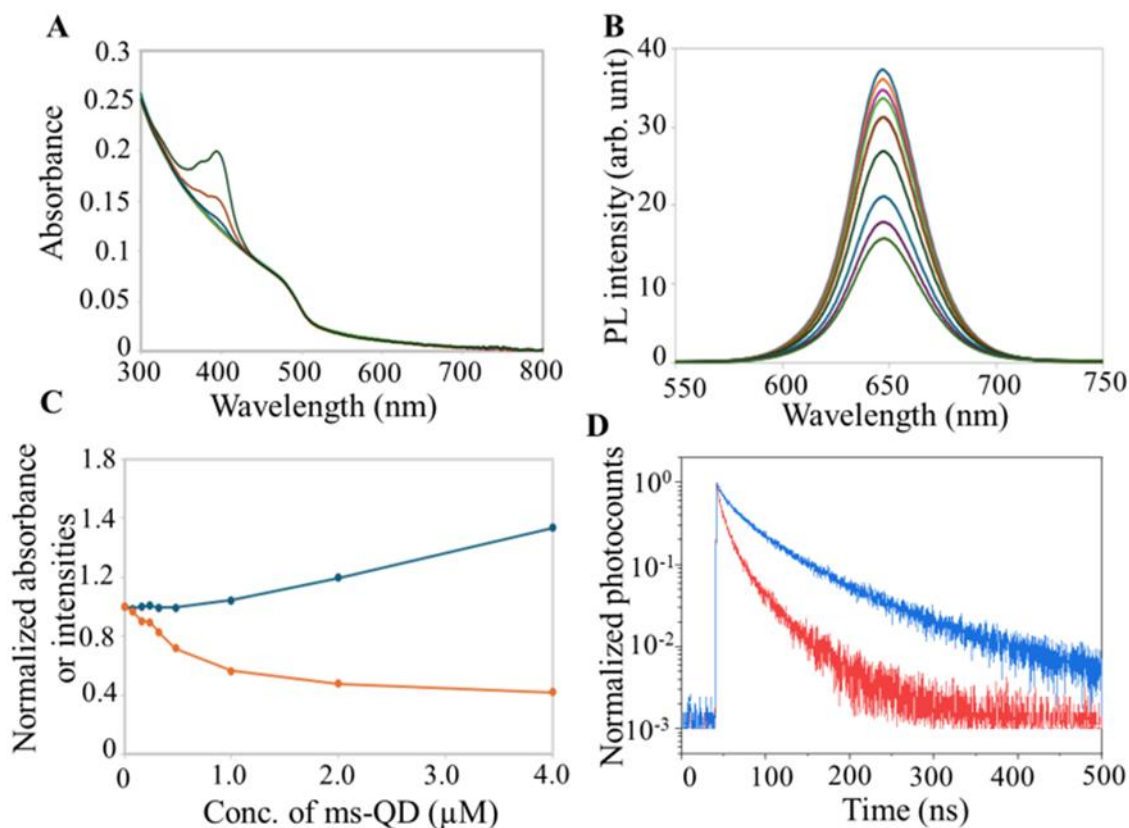


Figure 5.4 Quenching study for **ms-QD** with TCNQ in toluene. (A) Absorption, and (B) PL spectra of pristine QD ($\lambda_{\text{ex}} = 450$ nm) with various concentrations of TCNQ, (C) Concentration-dependent image of normalized absorbance (blue) at 450 nm of Figure 5.4A, PL intensity (orange) at 650 nm of Figure 5.4B, (D) PL decay profile without (blue) or with (red) **mono-QD** ($\lambda_{\text{ex}} = 405$ nm).

The **ms-QD** showed distinct differences in absorption, emission properties, and particle size compared to its monomeric counterpart, **mono-QD**.⁴⁶ To further explore these unique characteristics, a detailed study of electron transfer was conducted using 7,7,8,8-tetracyanoquinodimethane as the electron acceptor. Absorption and PL spectra of **ms-QDs** have been measured both in the absence and in the presence of TCNQ in toluene. For monitoring optical property variations of **ms-QDs**, a stepwise addition of TCNQ in the range of 0.08 μM to 4.0 μM has been employed. The initial absorption peak of **ms-QD** at 450 nm did not change much upon the addition of TCNQ. However, upon increasing the concentration of TCNQ, a huge enhancement of absorption at 450 nm in Figure 5.4A indicated the interaction of TCNQ molecules with the assemblies of **ms-QD** that changed their electronic environment. The significant quenching of the PL intensity of **ms-QD**, with increasing concentration of TCNQ, can be seen in Figure 5.4B. The PL intensity decay indicated that an electron transfer process, driven by proximity and electronic compatibility, was occurring between **ms-QDs** and TCNQ. From the normalized plot of absorption and PL changes in Figure 5.4C, it can be seen that the extent of PL quenching was far beyond the reduction of absorption, which constitutes a strong indication of electronic interaction for PL quenching rather than any light absorption or scattering effects. TRPL data was used further to determine the dynamics of electron transfer. The fluorescence lifetime for **ms-QD** in the absence of TCNQ measured 44.2 ns, showing the relatively long-lived excited state of the big assembly Figure 5.4D. In the presence of 4.0 μM TCNQ, its lifetime drastically dropped to 9.53 ns, providing compelling evidence for dynamic quenching. This enormous decrease in lifetime confirms electron transfer where excited-state electrons from **ms-QD** were transferred to TCNQ. Based on this result, it is suggested that strong dynamic interaction between **ms-QD** and TCNQ should be caused by a unique structure and electronic property of the mesoscopic assembly. For comparison, *mono-QD* containing TCNQ was studied concerning its PET performance.

5.3.5 Photoluminescence quenching study for mono-QD with 7,7,8,8-tetracyanoquinodimethane

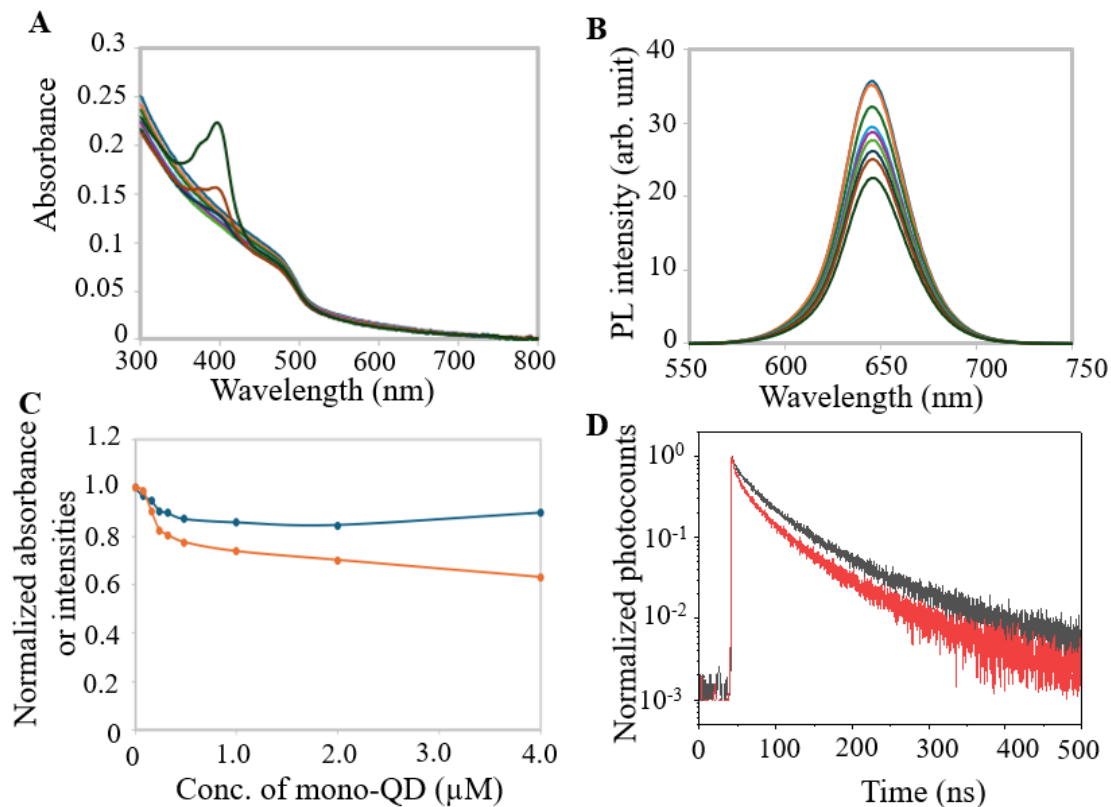


Figure 5.5 Quenching study for **mono-QD** with TCNQ in toluene. (A) Absorption, and (B) PL spectra of pristine QD ($\lambda_{\text{ex}} = 450$ nm) with various concentrations of TCNQ, (C) Concentration-dependent image of normalized absorbance (blue) at 450 nm of Figure 5.5A, PL intensity (orange) at 645 nm of Figure 5.5B, (D) PL decay profile without (black) or with (red) mono-QD ($\lambda_{\text{ex}} = 405$ nm).

The electron dynamics of electron transfer in QD systems were further realized by **mono-QD** with the electron acceptor, TCNQ. The present comparative study is carried out to indicate different behaviors of **ms-QDs** and **mono-QDs** within electron transfer processes, allowing more insight into how structural differences in one may affect its electronic behavior. The optical properties of **mono-QD** were studied by absorption and PL spectroscopy upon a stepwise addition of TCNQ in toluene. Figure 5.5A presents the absorption spectra of **mono-QD** in the absence and presence of TCNQ. Unlike **ms-QD**, the addition of TCNQ hardly changed the absorption spectra of **mono-QD**, indicative of

weaker interaction and less significant perturbation of the **mono-QD** electronic states. Figure 5.5B displays that the PL spectra decrease gradually in intensity with increasing TCNQ concentration owing to a quenching effect, indicating PET between **mono-QD** and TCNQ. However, in comparison with **ms-QD**, the extent of quenching in **mono-QD** is considerably less pronounced. Figures 5.4C and 5.5C represent the normalized comparison, which shows that **mono-QD** exhibits lower quenching efficiency than **ms-QD**. Such findings emphasize the important role of multilayered assembly architecture in **ms-QD** to provide increased donor-acceptor interactions and promote more efficient electron transfer pathways. To gain further insight into the nature of PL quenching, TRPL measurements were carried out. The fluorescence lifetime of **mono-QD** in the absence of TCNQ is 41.6 ns shown in Figure 5.5D. The addition of TCNQ did not show much variation in the lifetime of **mono-QD** (35.6 ns), proving a static type of quenching mechanism. Unlike the dynamic quenching observed in **ms-QDs**, the interaction in **mono-QDs** involves mainly the ground-state complex formation and hence TCNQ interacts dynamically with the excited states of QDs. Accordingly, static quenching in **mono-QD** implies negligible electronic interaction between **mono-QD** and TCNQ. This behavior contrasts sharply with the dynamic quenching mechanism in **ms-QD**, whereby efficient electron transfer is evidenced through the significant lifetime reduction. The distinct mode of PET operation between **mono-QD** and **ms-QD** is reflected in their structural and assembly features.

Therefore, the multilayered and mesoscopic assembly in **ms-QD** provides the conditions needed for a high number of sites of donor-acceptor contacts with optimized interface environments for electron transfer not present in its monomeric structure, **mono-QD**. While a highly effective process of electron transfer is reflected through the pronounced PL quenching for **ms-QD**, the lowest level of quenching reflects limited interactions in **mono-QD**. The **ms-QD** dynamic quenching mechanism, in which the lifetime reduction is significant, underlines a very effective electron transfer capability. In contrast, static quenching in **mono-QD** involves little lifetime change, and thus the interaction between electron transfers is weak or less effective. This poor static quenching is an indicator that **mono-QDs** are poorly suitable for various applications requiring highly effective charge transfer, such as photovoltaics or advanced sensing systems. As

opposed to that, strongly enhanced dynamics of PET underline the position of **ms-QDs** for performance high-performance optoelectronic devices.

The huge influence of the architecture in the assembly on electron transfer efficiency is enlightened by comparing the PET behavior between **mono-QD** and **ms-QD**. While **mono-QD** exhibits static quenching and weaker interactions with TCNQ, dynamic quenching of **ms-QD** with efficient electron transfer affirms it for the next-generation optoelectronic and energy-harvesting applications. This will shed light on how design considerations toward structured assemblies can aim at the optimization of electron transfer processes in the QD systems.

5.3.6 S-V plot for mesoscopic quantum dots and monomeric quantum dots

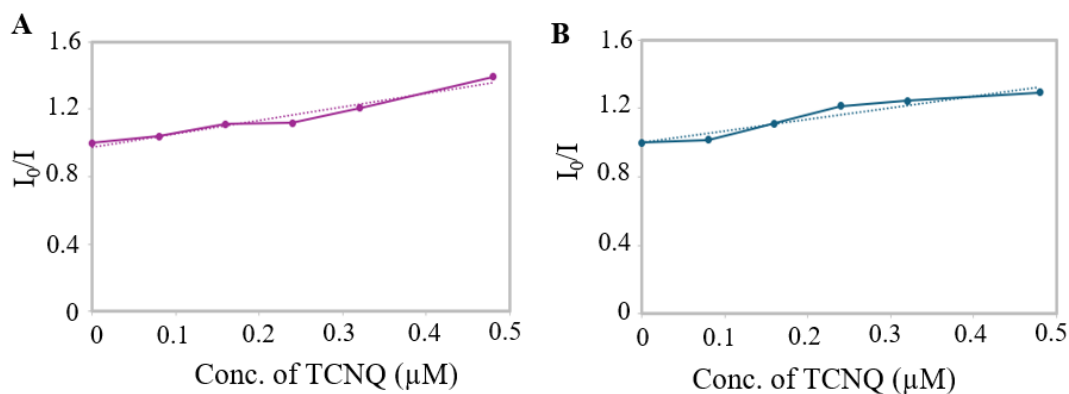


Figure 5.6 Stern-Volmer Plot of, (A) **ms-QD**, (B) **mono-QD** with TCNQ.

The Stern-Volmer plots for TCNQ with **ms-QD** and **mono-QD** showed linear relationships (Figures 5.6A & 5.6B), providing evidence of the mechanism of quenching. The Stern-Volmer plot gives a powerful means to analyze the efficiency of the PET processes between QDs and electron acceptors. I will be able to make a quantitative evaluation of the extent of quenching and the kinetics of the electron transfer process by estimating the Stern-Volmer constant. In this work, the K_{SV} value was extracted from the slope of the S-V plot, which is a plot of the ratio of the PL intensity (I_0/I) as a function of the concentration of the electron acceptor (Q), where I_0 is the PL intensity in the absence of the quencher and I is the intensity after the addition of the quencher. The Stern-Volmer constant for P-C₆₀ was estimated to be $0.863 \times 10^6 \text{ M}^{-1}$. This relatively high value reflects the efficient electron transfer interaction between the QDs and the P-C₆₀ acceptor

molecule. The Stern-Volmer constant for **ms-QD** was $0.678 \times 10^6 \text{ M}^{-1}$, showing strong quenching efficiency, though a little lower than that of P-C₆₀. That is to say, **ms-QD** also has a high propensity to interact with the electron acceptor; however, it exhibits somewhat reduced quenching efficiency compared with the pristine fullerene, P-C₆₀, probably due to its larger size or structural complexity relative to single QDs.

K_q also yields insight into the efficiency of quenching. It is representative of the speed at which the process between QDs and the electron acceptor occurs, or how fast PET occurs in short. The values were derived from Stern-Volmer constants and the lifetime of the QDs, indicating an in-depth process of electron transfer. The quenching rate constant of **ms-QD** was observed to be $19.5 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$. This high value reflects the fact that electron transfer in **ms-QD** occurs extremely efficiently. In the mesoscopic assembly, the presence of several donor-acceptor contact sites likely facilitates rapid electron transfer, leading to faster quenching of the PL. This efficient quenching is a signature of the well-structured, layered assembly architecture in **ms-QD**, wherein the electron transfer would be more effective due to enhanced interparticle interactions. The quenching rate constant for mono-QD was $16.2 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$, which, though high, is lower than that of **ms-QD**. This indicates that the electron transfer in mono-QDs is less efficient, probably due to the absence of structured assembly and reduced availability of donor-acceptor interactions. The monomeric nature of **mono-QD** results in less effective electron transfer, as reflected by the lower value of the quenching rate constant compared with **ms-QD**.

The large discrepancy between the Stern-Volmer constants and quenching rate constants between **ms-QD** and **mono-QD** points out the great enhancement of assembly architecture on the electron transfer processes. The extremely efficient quenching in the **ms-QDs** could be indicative of their application in systems requiring fast and efficient electron transfer, such as in solar energy harvesting, photocatalysis, and other optoelectronic devices. The higher quenching efficiency of **ms-QDs** would thus suggest that the mesoscopic structure confers a distinct advantage compared to single monomeric QDs, probably due to enhanced interparticle interactions and more pathways for electron transfer. This further brings into focus the importance of the assembly and organization of nanoparticles in optimizing electron transfer dynamics, probably a key consideration in the design of new materials for energy conversion and sensor applications.

5.4. Conclusions

While especially nanoparticle assembly and shaping in mesoscopic QD structures have great potential for several technological applications, the fascinating field remains barely explored. Even though some methods have already been suggested in the literature for preparing mesoscopic QD assemblies, the search is still open for an appropriate general versatile method by which well-dispersed and uniform particles can be fabricated of controlled size. In this work, I developed and successfully demonstrated a novel biocatalytic methodology, the so-called Biocatalyst Nanoparticle Shaping approach, using oligo-L-lysine and QDs to produce mesoscopic-sized particles with well-defined properties. Uniqueness in this method indeed lies in the simplicity of this approach and that mesoscopic assemblies of QDs are formed with very narrow size distribution and excellent dispersion in aqueous solutions.

The BNS approach produced mesoscopic QD assemblies with an average size of about 84 nm, which is favorable for achieving superior optical and electric properties. These showed excellent PL and electron transfer properties, which gives indications that **ms-QDs** serve as very effective materials for future optical devices. With improved features, particularly efficient electron transfer processes, **ms-QDs** are now recognized as promising candidates for use in solar power harvesting, and in the photodetectors.

One of the main advantages of the BNS approach involves control of the size and dispersion of mesoscopic particles—a very critical factor in the performance of optoelectronic materials. The method's versatility enables exact tweaking of particle size and, as a result, optical and electrical properties of QD assemblies. Moreover, being a biocatalytic process, the BNS approach enables nanoparticle processing in a green and selective way, a green alternative to the more traditional approaches involving toxic reagents or drastic conditions.

Looking ahead, the BNS method holds immense promise for furthering the synthesis of mesoscopically unique materials with unprecedented blends of optical, chemical, and mechanical properties together with electronic ones. Abilities to fabricate colloidal QD assemblies that are monodisperse in size, have tuned interparticle coupling, and possess improved optoelectronic attributes will broaden the scope of new applications in several key technology sectors. The BNS method can be further refined into mass production for

the assemblies in applications at an industrial scale. Similarly, this approach may also be extended to other kinds of nanoparticles or other materials from QD.

This will likely be achieved by the integration of the BNS technique with the solution processing methods to fabricate highly functional mesoscale materials that could easily be adapted into different device architectures. The investigation of the interactions of these materials with their environment, such as the behavior of such materials in thin films and/or layered structures, will contribute to a better understanding of how to exploit unique properties of the mesoscopic QDs for use in advanced optoelectronic applications. Next-generation materials for photovoltaic devices, advanced sensors, and several other emerging technologies could therefore be developed.

The approach of the BNS thus offers, in this respect, not only a new route toward the preparation of the mesoscopic assemblies of QD but also a bright perspective on the further development of nanoparticle-based materials. It will provide ways to manipulate properties and structures on the mesoscale with great potential in the high-performance functionality of optoelectronics and energy conversion applications.

References

- (1) 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* (6555). <https://doi.org/10.1126/science.aaz8541>.
- (2) Wang, Y.; Hu, R.; Lin, G.; Roy, I.; Yong, K. T. Functionalized Quantum Dots for Biosensing and Bioimaging and Concerns on Toxicity. *ACS Appl. Mater. Interfaces* **2013**, *5* (8), 2786–2799. <https://doi.org/10.1021/am302030a>.
- (3) Sobhanan, J.; Rival, J. V.; Anas, A.; Sidharth Shibu, E.; Takano, Y.; Biju, V. Luminescent Quantum Dots: Synthesis, Optical Properties, Bioimaging and Toxicity. *Adv. Drug Deliv. Rev.* **2023**, *197*, 114830. <https://doi.org/10.1016/j.addr.2023.114830>.
- (4) Carey, G. H.; Abdelhady, A. L.; Ning, Z.; Thon, S. M.; Bakr, O. M.; Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Chem. Rev.* **2015**, *115* (23), 12732–12763. <https://doi.org/10.1021/acs.chemrev.5b00063>.
- (5) Lv, Z.; Wang, Y.; Chen, J.; Wang, J.; Zhou, Y.; Han, S. T. Semiconductor Quantum Dots for Memories and Neuromorphic Computing Systems. *Chem. Rev.* **2020**, *120* (9), 3941–4006. <https://doi.org/10.1021/acs.chemrev.9b00730>.
- (6) Frasco, M. F.; Chaniotakis, N. Semiconductor Quantum Dots in Chemical Sensors and Biosensors. *Sensors* **2009**, *9* (9), 7266–7286. <https://doi.org/10.3390/s90907266>.
- (7) Ueno, T.; Nagano, T. Fluorescent Probes for Sensing and Imaging. *Nat. Methods* **2011**, *8* (8), 642–645. <https://doi.org/10.1038/nmeth.1663>.
- (8) Ekimov, A. I.; Efros, A. L.; Onushchenko, A. A. Quantum Size Effect in Semiconductor Microcrystals. *Solid State Commun.* **1985**, *56* (11), 921–924. [https://doi.org/10.1016/S0038-1098\(85\)80025-9](https://doi.org/10.1016/S0038-1098(85)80025-9).
- (9) Wang, Y.; Herron, N. Nanometer-Sized Semiconductor Clusters: Materials Synthesis, Quantum Size Effects, and Photophysical Properties. *J. Phys. Chem.* **1991**, *95* (2), 525–532. <https://doi.org/10.1021/j100155a009>.
- (10) Takagahara, T.; Takeda, K. Theory of the Quantum Confinement Effect on Excitons in Quantum Dots of Indirect-Gap Materials. *Phys. Rev. B* **1992**, *46* (23), 15578–15581. <https://doi.org/10.1103/PhysRevB.46.15578>.
- (11) Litvin, A. P.; Martynenko, I. V.; Purcell-Milton, F.; Baranov, A. V.; Fedorov, A. V.; Gun'Ko, Y. K. Colloidal Quantum Dots for Optoelectronics. *J. Mater. Chem. A* **2017**, *5* (26), 13252–13275. <https://doi.org/10.1039/c7ta02076g>.
- (12) Zhou, J.; Yang, Y.; Zhang, C. Y. Toward Biocompatible Semiconductor Quantum Dots: From Biosynthesis and Bioconjugation to Biomedical Application. *Chem. Rev.* **2015**, *115* (21), 11669–11717. <https://doi.org/10.1021/acs.chemrev.5b00049>.
- (13) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706–8715. <https://doi.org/10.1021/ja00072a025>.

- (14) Brus, L. E. Electron-Electron and Electron-Hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80* (9), 4403–4409. <https://doi.org/10.1063/1.447218>.
- (15) Grzyb, J.; Walczewska-Szewc, K.; Sławski, J.; Trojnar, M. Quantum Dot Clusters as Self-Assembled Antennae with Phycocyanine and Phycobilisomes as Energy Acceptors. *Phys. Chem. Chem. Phys.* **2021**, *23* (42), 24505–24517. <https://doi.org/10.1039/d1cp03347f>.
- (16) Mayilo, S.; Hilhorst, J.; Susha, A. S.; Höhl, C.; Franzi, T.; Klar, T. A.; Rogach, A. L.; Feldmann, J. Energy Transfer in Solution-Based Clusters of CdTe Nanocrystals Electrostatically Bound by Calcium Ions. *J. Phys. Chem. C* **2008**, *112* (37), 14589–14594. <https://doi.org/10.1021/jp803503g>.
- (17) Lv, H.; Wang, C.; Li, G.; Burke, R.; Krauss, T. D.; Gao, Y.; Eisenberg, R. Semiconductor Quantum Dot-Sensitized Rainbow Photocathode for Effective Photoelectrochemical Hydrogen Generation. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (43), 11297–11302. <https://doi.org/10.1073/pnas.1712325114>.
- (18) Kodaimati, M. S.; Lian, S.; Schatz, G. C.; Weiss, E. A. Energy Transfer-Enhanced Photocatalytic Reduction of Protons within Quantum Dot Light-Harvesting–Catalyst Assemblies. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (33), 8290–8295. <https://doi.org/10.1073/pnas.1805625115>.
- (19) Das, B. C.; Batabyal, S. K.; Pal, A. J. A Bit per Particle: Electrostatic Assembly of CdSe Quantum Dots as Memory Elements. *Adv. Mater.* **2007**, *19* (23), 4172–4176. <https://doi.org/10.1002/adma.200700309>.
- (20) He, X.; Li, Z.; Chen, M.; Ma, N. DNA-Programmed Dynamic Assembly of Quantum Dots for Molecular Computation. *Angew. Chemie - Int. Ed.* **2014**, *53* (52), 14447–14450. <https://doi.org/10.1002/anie.201408479>.
- (21) Tahara, H.; Sakamoto, M.; Teranishi, T.; Kanemitsu, Y. Coherent Electronic Coupling in Quantum Dot Solids Induces Cooperative Enhancement of Nonlinear Optoelectronic Responses. *Nat. Nanotechnol.* **2024**. <https://doi.org/10.1038/s41565-024-01601-9>.
- (22) Xu, X.; Stöttinger, S.; Battagliarin, G.; Hinze, G.; Mugnaioli, E.; Li, C.; Müllen, K.; Basché, T. Assembly and Separation of Semiconductor Quantum Dot Dimers and Trimers. *J. Am. Chem. Soc.* **2011**, *133* (45), 18062–18065. <https://doi.org/10.1021/ja2077284>.
- (23) Liu, J.; Yang, X.; Wang, K.; He, X.; Wang, Q.; Huang, J.; Liu, Y. Aggregation Control of Quantum Dots through Ion-Mediated Hydrogen Bonding Shielding. *ACS Nano* **2012**, *6* (6), 4973–4983. <https://doi.org/10.1021/nn300517k>.
- (24) Koole, R.; Liljeroth, P.; De Mello Donegá, C.; Vanmaekelbergh, D.; Meijerink, A. Electronic Coupling and Exciton Energy Transfer in CdTe Quantum-Dot Molecules. *J. Am. Chem. Soc.* **2006**, *128* (32), 10436–10441. <https://doi.org/10.1021/ja061608w>.

- (25) Schreiber, R.; Do, J.; Roller, E.-M.; Zhang, T.; Schüller, V. J.; Nickels, P. C.; Feldmann, J.; Liedl, T. Hierarchical Assembly of Metal Nanoparticles, Quantum Dots and Organic Dyes Using DNA Origami Scaffolds. *Nat. Nanotechnol.* **2014**, 9 (1), 74–78. <https://doi.org/10.1038/nnano.2013.253>.
- (26) Liu, J.; Yang, X.; Wang, K.; He, X.; Wang, Q.; Huang, J.; Liu, Y. Aggregation Control of Quantum Dots through Ion-Mediated Hydrogen Bonding Shielding. *ACS Nano* **2012**, 6 (6), 4973–4983. <https://doi.org/10.1021/nn300517k>.
- (27) Chen, D. X.; Sun, Y. L.; Zhang, Y.; Cui, J. Y.; Shen, F. Z.; Yang, Y. W. Supramolecular Self-Assembly and Photophysical Properties of Pillar[5]Arene-Stabilized CdTe Quantum Dots Mediated by Viologens. *RSC Adv.* **2013**, 3 (17), 5765–5768. <https://doi.org/10.1039/c3ra40436f>.
- (28) Liu, J.; Enomoto, K.; Takeda, K.; Inoue, D.; Pu, Y. J. Simple Cubic Self-Assembly of PbS Quantum Dots by Finely Controlled Ligand Removal through Gel Permeation Chromatography. *Chem. Sci.* **2021**, 12 (30), 10354–10361. <https://doi.org/10.1039/d1sc02096j>.
- (29) Yamauchi, M.; Masuo, S. Self-Assembly of Semiconductor Quantum Dots Using Organic Templates. *Chem. - A Eur. J.* **2020**, 26 (32), 7176–7184. <https://doi.org/10.1002/chem.201905807>.
- (30) Huber, R.; Bode, W. Structural Basis of the Activation and Action of Trypsin. *Acc. Chem. Res.* **1978**, 11 (3), 114–122. <https://doi.org/10.1021/ar50123a006>.
- (31) Ozawa, K.; Laskowski, M. The Reactive Site of Trypsin Inhibitors. *J. Biol. Chem.* **1966**, 241 (17), 3955–3961. [https://doi.org/10.1016/s0021-9258\(18\)99798-x](https://doi.org/10.1016/s0021-9258(18)99798-x).
- (32) Olsen, J. V.; Ong, S.-E.; Mann, M. Trypsin Cleaves Exclusively C-Terminal to Arginine and Lysine Residues. *Mol. Cell. Proteomics* **2004**, 3 (6), 608–614. <https://doi.org/10.1074/mcp.T400003-MCP200>.
- (33) Deng, W.; Chen, P.; Hu, P.; He, Z.; Zhang, M.; Yuan, X.; Huang, K. Enzymatic Reaction Modulated Synthesis of Quantum Dots for Visual Detection of Cholinesterase Activity and Inhibitor. *Sensors Actuators, B Chem.* **2019**, 292 (February), 180–186. <https://doi.org/10.1016/j.snb.2019.04.136>.
- (34) Akter, R.; Kirkwood, N.; Zaman, S.; Lu, B.; Wang, T.; Takakusagi, S.; Mulvaney, P.; Biju, V.; Takano, Y. Bio-Catalytic Nanoparticle Shaping for Preparing Mesoscopic Assemblies of Semiconductor Quantum Dots and Organic Molecules. *Nanoscale Horizons* **2024**, 9 (7), 1128–1136. <https://doi.org/10.1039/d4nh00134f>.
- (35) Nakatsuji, N. Mesoscopic Science, Where Materials Become Life and Life Inspires Materials. A Great Opportunity to Push Back the Frontiers of Life, Materials, and Biomaterials Sciences. *Biomater. Sci.* **2013**, 1 (1), 9–10. <https://doi.org/10.1039/c2bm90001g>.
- (36) Zelevinsky, V.; Volya, A. Nuclear Structure, Random Interactions and Mesoscopic Physics. *Phys. Rep.* **2004**, 391 (3–6), 311–352. <https://doi.org/10.1016/j.physrep.2003.10.008>.

- (37) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* (80-.). **2011**, 334 (6056), 629–634. <https://doi.org/10.1126/science.1209688>.
- (38) Takakura, Y.; Takahashi, Y. Strategies for Persistent Retention of Macromolecules and Nanoparticles in the Blood Circulation. *J. Control. Release* **2022**, 350 (May), 486–493. <https://doi.org/10.1016/j.jconrel.2022.05.063>.
- (39) Chen, K.; Jin, W.; Zhang, Y.; Yang, T.; Reiss, P.; Zhong, Q.; Bach, U.; Li, Q.; Wang, Y.; Zhang, H.; Bao, Q.; Liu, Y. High Efficiency Mesoscopic Solar Cells Using CsPbI₃ Perovskite Quantum Dots Enabled by Chemical Interface Engineering. *J. Am. Chem. Soc.* **2020**, 142 (8), 3775–3783. <https://doi.org/10.1021/jacs.9b10700>.
- (40) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, 2 (1), 591. <https://doi.org/10.1038/srep00591>.
- (41) Chen, T. H.; Tseng, W. L. Self-Assembly of Monodisperse Carbon Dots into High-Brightness Nanoaggregates for Cellular Uptake Imaging and Iron(III) Sensing. *Anal. Chem.* **2017**, 89 (21), 11348–11356. <https://doi.org/10.1021/acs.analchem.7b02193>.

General Conclusions

In this thesis, the interfacial electron transport processes in CdSe/CdS quantum dots and perovskite nanocrystal assemblies were thoroughly examined. Several electron acceptor molecules, including pristine fullerene (P-C₆₀), COOH-functionalized fullerene (C₆₀-RCOOH), and 7,7,8,8-tetracyanoquinodimethane (TCNQ), have been used to investigate electron transfer processes. I used a combination of steady-state and time-resolved fluorescence spectroscopic techniques to thoroughly examine the electron transfer.

For comparison, two popular perovskite systems were selected: MAPbBr₃ and CsPbBr₃. Both systems showed poor electron transfer efficiency in the solution phase owing to the presence of surface ligands such as oleic acid and oleyamine. These ligands, while protecting the nanocrystals in solution, act as insulating barriers to charge-carrier movement. As a result, the overall charge transfer efficiency was drastically reduced. FAPbBr₃ nanocrystals showing superior stability, phenomenal optical properties, and high photoluminescence quantum yield stood out as an ideal candidate for the study of electron transport and controlled assembly formation. Resistance to environmental degradation was observed in FAPbBr₃, thus allowing more reliable and consistent performance in electron transfer studies. A controlled assembly strategy for FAPbBr₃ nanocrystals was adopted to overcome the challenges arising from insulating surface ligands. This approach afforded some peculiar assembly architectures for efficient electron transport, as the donor-acceptor contact sites became more accessible. The interactions of three different acceptor molecules, P-C₆₀, C₆₀-RCOOH, and TCNQ were explored in different pathways. Compared to isolated nanocrystals, the assemblies showed a higher efficiency of electron transfer. These findings emphasize how structural organization has a strong impact on the dynamics of electron transfer and identify the advantages offered by well-structured assemblies concerning efficient charge transport.

I further observed an impressive feature, which was co-aggregation in the film state between the FAPbBr₃ PNCs and acceptor molecules. Co-aggregation resulted in the total quenching of the photoluminescence. For confirmation, the results were verified using TCSPC system. Systematic investigations of the donor and acceptor in the solution and film states indicated distinct electron transport pathways within these two different

milieus. In the solution state, electron transfer is dictated mainly by interactions within the diffusion limit. The film state and the co-aggregation state introduce additional mechanisms, such as enhanced electronic coupling and aggregation-induced quenching. The design and optimization of solid-state optoelectronic devices, in which film morphologies frequently play a crucial role in device performance, can benefit greatly from these findings.

In parallel, efforts have been directed toward the preparation of well-dispersed CdSe/CdS QD assemblies using a molecular crosslinker, 1,6-hexanedithiol (HDT). The formation of the assembly (QDs@HDT) was verified by STEM imaging and DLS measurements. These techniques showed that a uniform dispersion of QD assemblies, which is quite stable and appropriate for studies on photoinduced electron transfer processes, could be successfully realized. Three quencher molecules-P-C₆₀, C₆₀-RCOOH, and TCNQ, were used to study the electron transfer properties of QD assemblies using spectroscopic techniques. Indeed, a very high electron transfer efficiency has been determined with these QD assemblies, mainly because of their unique architecture, which allows closer proximity and stronger interactions of the QDs with the acceptor molecule.

The major innovation in this work was the development of a biocatalyst-based method for preparing mesoscopic-sized QD assemblies using a biocatalytic nanoparticle-shaping approach. It was developed using oligo-lysine to create well-dispersed assemblies with a hydrodynamic size of ~84 nm. These mesoscopic assemblies exhibited excellent optical and electrical properties, which make them highly attractive for advanced optoelectronic applications. Such interactions of mesoscopic QD ensembles with TCNQ represent very effective electron transfer and further confirm the great prospects of their application as novel-generation materials in optoelectronics. All the above substantially advance the design, synthesis, and nanoscale structuring with pre-engineered functionality for new applications in light-harvesting systems, sensors, and other optoelectronic devices.

This thesis systematically investigated the interfacial electron transfer processes of perovskite and QD assemblies to provide basic insights into the factors that control their performance. This work contributes to a deeper understanding of the underlying mechanism of interfacial electron transfer, including the role of surface ligands, architecture of the assembly, and acceptor molecules.

The results of this work provide strong driving forces for the development of light-emitting devices, photovoltaics, and sensors. Controlled assembly strategies allow innovative ways to realize well-dispersed nanoscale and mesoscopic structures with superior optoelectronic properties. The work done is a groundwork for further exploration and optimization of materials for the next generation of optoelectronic devices. It views the electron transfer dynamics of nanoscale assemblies as among the most valuable contributions this dissertation offers because it offers an explanation with which practical application is expected in advanced optoelectronic technology.

Achievements

Published article

Bio-catalytic nanoparticle shaping for preparing mesoscopic assemblies of semiconductor quantum dots and organic molecules. *Nanoscale Horizons*, Vol. 9, Issue-7, page:1128-01136, (2024), **Rumana Akter**, Nicholas Kirkwood, Samantha Zaman, Bang Lu, Tinci Wang, Satoru Takakusagi, Paul Mulvaney, Vasudevanpillai Biju, and Yuta Takano

Presented Conferences

(1) **Rumana Akter**, Yuta Takano, Vasudevanpillai Biju, Interfacial electron transfer from MAPbBr₃ nanocrystals to a ligand engineered C₆₀-acceptor; Chemical Society of Japan, Hokkaido branch, Winter meeting presentation, Hokkaido University, Japan, (January 24-25, 2023). (Oral)

(2) **Rumana Akter**, Palyam Subramanyam, Takuya Okamoto, Tianci Wang, Yuta Takano, Vasudevanpillai Biju, An investigation of halide perovskite-based electron donor-acceptor systems with C₆₀-RCOOH ligand for solar energy harvesting; The 9th Hokkaido University Cross-Departmental symposium, Hokkaido University, Sapporo, Japan, (October 11, 2023). (Poster) (**Awarded**)

(3) **Rumana Akter**, Palyam Subramanyam, Takuya Okamoto, Tianci Wang, Yuta Takano, Vasudevanpillai Biju, A fullerene-based ligand for halide perovskite surface capping and photoinduced electron transport layer formation; Annual meeting of The Japanese Photochemistry Association (JPA), International Conference Center Hiroshima, Hiroshima, Japan, (September 5-7, 2023). (Poster)

(4) **Rumana Akter**, Yuta Takano, Nicholas Kirkwood, Paul Mulvaney, Vasudevanpillai Biju, Development of photo-functional mesoscopic quantum dot assemblies; The 24th RIES-HOKUDAI International Symposium, Suzuki Akira Hall, Hokkaido University, Sapporo, Japan, (December 6-7, 2023). (Poster)

(5) **Rumana Akter**, Palyam Subramanyam, Takuya Okamoto, Tianci Wang, Yuta Takano, Vasudevanpillai Biju, An investigation of halide perovskite-based electron donor-acceptor systems with C₆₀-RCOOH ligand for solar energy harvesting; Integrated

Science for a Sustainable Society 14th ISAJ Annual Symposium, CRIS building conference hall, Hokkaido University, Japan, (November 10, **2023**). (Poster)

(6) **Rumana Akter**, Yuta Takano, Nicholas Kirkwood, Paul Mulvaney, Vasudevanpillai Biju, Photo-induced electron transfer from isolated MAPbBr₃ nanocrystals and their self-assembled films to C₆₀-based ligands; The 23rd RIES-HOKUDAI International Symposium, Suzuki Akira Hall, Hokkaido University, Sapporo, Japan, (December 5-6, **2022**). (Poster)

(7) **Rumana Akter**, Yuta Takano, Nicholas Kirkwood, Paul Mulvaney, Vasudevanpillai Biju, Developing mesoscopic semiconductor quantum dot assemblies formed by an enzymatic nanoparticle shaping; International Priority Graduate Programs (IPGP), Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan (March 13, **2024**). (Poster)

(8) **Rumana Akter**, Palyam Subramanyam, Takuya Okamoto, Tianci Wang, Yuta Takano, Vasudevanpillai Biju, Photoinduced electron transfer from perovskites nanocrystals to acceptor molecules, Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan, (March 10, **2023**). (Poster)