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PEROVSKITE-BASED NANOHYBRIDS: SYNTHESIS AND PHOTOPHYSICS

Alejandro Cortés Villena

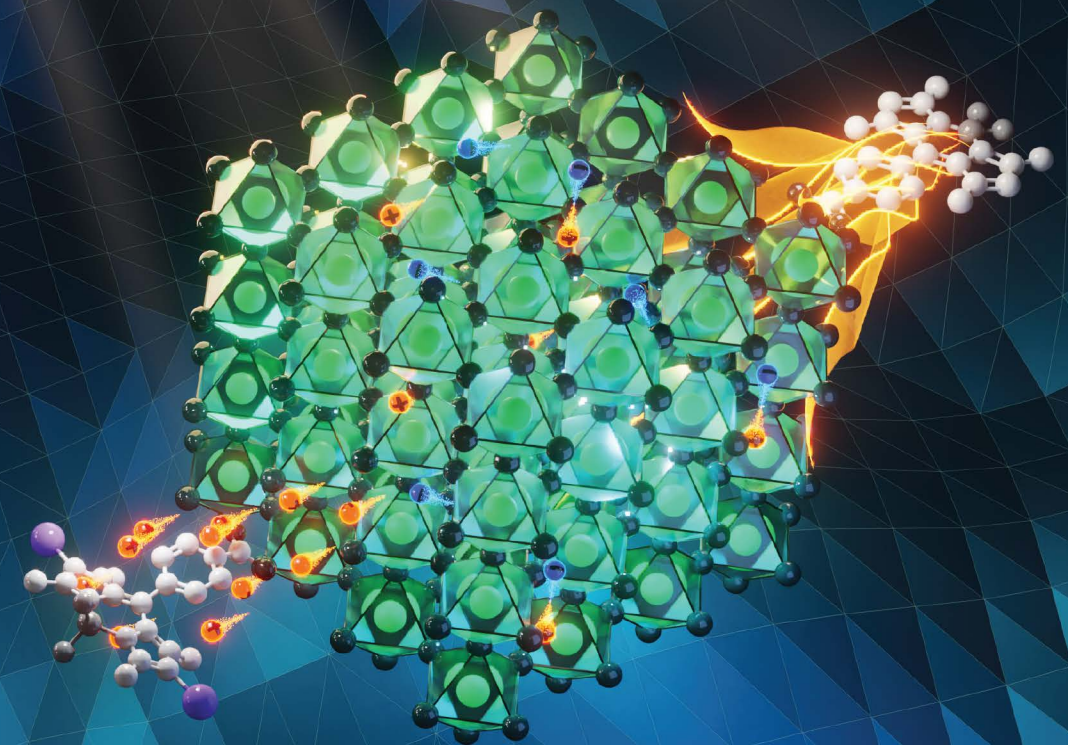
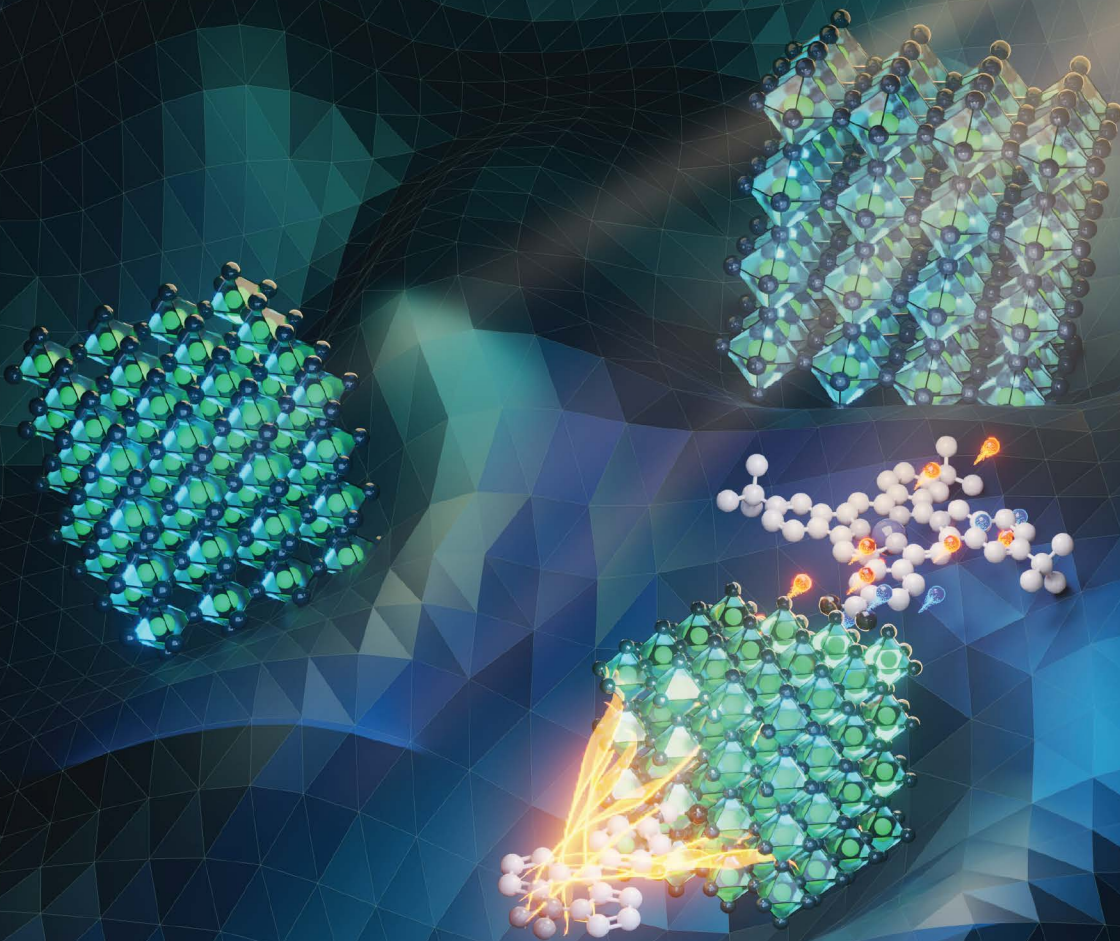
Ph.D. Thesis

Alejandro Cortés Villena

2024

Supervisors:
Dra. Raquel E. Galian
Prof. Dra. Julia Pérez Prieto

VNIVERSITAT DE VALÈNCIA





VNIVERSITAT DE VALÈNCIA

Instituto de Ciencia Molecular
Departamento de Química Orgánica

Doctorado en Química Sostenible

Ph.D. Dissertation

Perovskite-Based Nanohybrids: Synthesis and Photophysics

Ph.D. Candidate

Alejandro Cortés Villena

Supervisors:

Prof. Julia Pérez Prieto

Dra. Raquel E. Galian

Octubre, 2024

La Prof. Julia Pérez Prieto, Catedrática de Química Orgánica de la Universitat de València y la Dra. Raquel E. Galian, Investigadora de la Universitat de València.

CERTIFICAN:

Que la presente Tesis Doctoral, titulada: ***Perovskite-Based Nanohybrids: Synthesis and Photophysics***, se ha realizado bajo su dirección en el Instituto de Ciencia Molecular (ICMol) de la Universitat de València por el graduado en Química Alejandro Cortés Villena y autorizan su defensa para ser calificada como tesis doctoral internacional.

En Valencia, 10 de Octubre de 2024



Fdo. Prof. Julia Pérez Prieto

Directora



Fdo. Dra. Raquel E. Galian

Co-directora

*Nothing in life is to be feared, it is only to be understood. Now is the time to
understand more, so that we may fear less.*

Marie Curie

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Abstract

This thesis explores the light-harvesting ability of CsPbBr₃ NCs and the energy/charge transfer (ET/CT) mechanisms at the interface in perovskite-based nanohybrids functionalized with different organic dyes, such as a family of BODIPY and Zn-phthalocyanine. We systematically demonstrated how quantum confinement and surface chemistry effects of CsPbBr₃ nanocrystals (NCs) influence the singlet energy transfer efficiency from the NCs to surface-anchored 4-carboxyphenyl BODIPY dyes. The smallest NCs (ca. 6 nm) favored the Förster resonance energy transfer (FRET), while the largest NCs (ca. 12 nm) exhibited charge transfer (CT) as the dominant nonradiative pathway. By modifying the NC surface and using this BODIPY molecular rotor, we tracked the dye localization with no impact on the ET efficiency, highlighting the critical role of surface ligands. The incorporation of iodide substituents into the BODIPY (I2-BDP) core led to the efficient sensitization of the triplet excited state of the dye, achieving singlet oxygen generation via triplet energy transfer (TET). This nanohybrid (NC@I2-BDP) demonstrated potential application as singlet energy transfer photocatalysis for the oxidation of ascaridole. Additionally, we uncovered an unusual, concerted Dexter-type energy transfer (DET) mechanism in perovskite-phthalocyanine (NC@ZnPc) nanohybrids, where the NC surface chemistry controlled dye aggregation and extended ZnPc triplet state lifetimes, offering the potential for singlet oxygen-mediated photocatalytic applications. Then, novel linear and co-assemblies of upconversion nanoparticles (UCNPs) and CsPbX₃ (X: Br, I) NCs were successfully prepared, demonstrating near-infrared (NIR) light harvesting applications. The efficient lanthanide resonance energy transfer (LRET) mechanism under NIR excitation can be used in photovoltaic due to the broadening of the active absorption window. Lastly, we analyzed the relaxation pathways in biphenyl derivatives, focusing on push-pull systems with electron-donating amino groups and electron-accepting pyrimidine moieties. This study showed how molecular

structure and solvent environments significantly affect their optical and photophysical properties. Collectively, these findings advance the development of light-harvesting and photocatalytic nanosystems, opening new possibilities for solar energy conversion and sustainable chemical synthesis.

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Chapter 1.

Introduction

1.1 General overview

1.1.1. The power of solar energy

It is undeniable that energy demand will increase in the coming years due to several factors, such as population growth, economic development, technological advancements, and climate change mitigation efforts. Approximately 85 % of the rise in global electricity demand by 2026 is projected to originate from outside advanced economies, with significant contributions from China, India, and countries in Southeast Asia.¹ During the 20th century, fossil fuels, namely coal, oil, and natural gas, provided remarkable benefits to wealthy nations in the Western world for energy production. However, humanity now faces significant challenges due to the extensive exploitation of these resources.² In addition to the limited availability of fossil resources, their ongoing utilization results in the well-documented air pollution with particulate matter (PM), carbon oxides (CO_x), sulfur oxides (SO_x), nitrogen oxides (NO_x), and other pollutants,³ primarily affecting public health, environmental quality, biodiversity and social well-being, contributing to global warming and climate change.⁴ While the transition to renewable energy is a major focus of climate change mitigation efforts, it must be complemented by other strategies.⁵ Sufficient supplies of clean energy are intimately linked with global stability, economic prosperity, and quality of life. Finding energy sources to satisfy the world's growing demand is one of society's foremost challenges for the coming decades.⁶ Therefore, the pursuit of renewable energy alternatives, such as wind, hydroelectric, and especially **solar energy**, holds great promise as a solution to our energy needs.⁷

The amount of solar energy received from the sun on Earth's surface in just one hour is indeed more than enough to meet global energy demand for an entire year. To put it in perspective, to harvest 20 TW of power from the total solar energy reaching Earth's surface (which is approximately 120,000 TW), using solar cells with

moderate 10 % efficiency, we would need to cover about 0.16 % of Earth's land surface with solar panels. This, which at first glance seems surprising, represents the impressive magnitude of the solar resource. Nevertheless, one of the challenges lies in efficiently harnessing solar energy through the use of **light-harvesting materials**.⁸

1.1.2. Light-harvesting materials

Photosynthesis is undoubtedly the most well-known process for converting solar energy into chemical energy, wherein solar photons are first harvested in the peripheral antenna of photosynthetic systems, and subsequently, the excitation energy is transferred to the reaction center by multistep photoinduced energy transfer (ET) processes to produce chemical energy.⁹ At the heart of the reaction center, water is split into oxygen and hydrogen, which combined with carbon, dioxide produce organic molecules such as sugars.¹⁰ Inspired by this fascinating natural process, scientists have developed several strategies to design novel artificial light-harvesting materials that mimic such natural systems, aiming to efficiently capture and utilize light, such as dendrimers,¹¹ organogels,¹² porphyrin assemblies,¹³ biopolymer assemblies,¹⁴ organic-inorganic hybrid materials,¹⁵ and lastly, **inorganic semiconductor materials**.¹⁶

1.1.3. Inorganic semiconductor materials

In the realm of inorganic II-VI and III-V semiconductor materials, the semiconductor factories have profoundly influenced our lives. They constitute fundamental components such as every silicon-based diode and transistor, which share the common attribute of conductivity under bias conditions. Interestingly, they provide several advantages over traditional silicon, such as lower effective masses and higher mobilities, among them. Despite captivating advances in alternative materials, silicon-based materials will remain the preferred semiconductor for the electronics industry, in particular due to its abundance and low cost.¹⁷ The combination of both technologies is therefore of great technical and

economic interest and has actively been pursued for years. According to electrical conductivity and energy-band structure, materials are commonly classified into three main categories: metals, semiconductors, and insulators.¹⁸ In a solid, the combination of multiple atomic orbitals (AOs) clearly results in the formation of a lower energy valence band (VB) and a higher energy conduction band (CB), with a gap between them, commonly known as the band gap energy (E_g). Thus, these VB and CB consist of individual and discrete molecular orbitals (MOs), which are formed by the linear combination of atomic orbitals (LCAOs). Because of the subtle energy difference between these discrete MOs, they become quasi-continuous when many atoms form a solid. Consequently, the different behavior between metals, semiconductors and insulators can be understood in terms of the electron filling of the bands and the magnitude of the E_g , as illustrated in **Figure 1.1**.

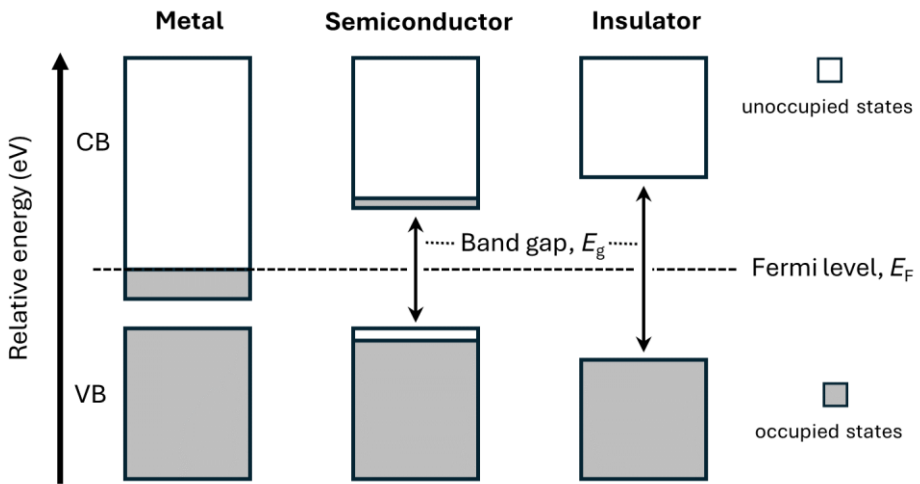


Figure 1.1. Band structure for metals, semiconductors and insulators.

In metals, electrical conductivity occurs when an electric field is applied or when photoexcitation takes place because the Fermi level (E_F), which represents the highest energy an electron can have at absolute zero (0 K), lies within an energy band. This band is partially filled and has an energy gap below the thermal energy at

room temperature ($E_g < 25$ meV), allowing electrons to easily move within the band. In semiconductors, electrons of VB do not freely move due to their nearly full occupancy and the presence of a band gap separating the VB and CB ($25 \text{ meV} < E_g < 3 \text{ eV}$). However, under application of either enough bias or photon energy ($h\nu \geq E_g$), electrons are promoted from the VB to the CB, thus resulting in electrical conductivity. In the case of insulators, the band gap is too large ($E_g > 3 \text{ eV}$) that electrical conduction is greatly suppressed.¹⁹

1.1.4. Quantum dots

Among these semiconductor materials, colloidal inorganic semiconductor nanocrystals, the so-called “**quantum dots (QDs)**”, have emerged as attractive nanomaterials due to their outstanding properties such as the high molar extinction coefficient (ca. $10^5 - 10^7 \text{ M}^{-1}\text{cm}^{-1}$), excellent photostability, ability to generate charge carriers after photoexcitation, and the size-, and shape-tunable optical and electronic properties.²⁰⁻²¹ In particular, the capacity to generate free charge carriers or excitons (bound electron-hole pairs by Coulombic interaction), when a photon interacts with the QD, allows them to be used for different purposes, depending on how efficient charges are extracted (photovoltaics), recombined again to emit a photon (lighting) and transferred to another specie (photocatalysis), as shown in **Figure 1.2**.



Figure 1.2. Representation of an exciton in a quantum dot framework after light interaction, and its potential application in the field of photovoltaics, lighting, and photocatalysis.

The origin of these tunable properties arises from the well-established concept of quantum mechanics, specifically the “particle in a box” model, and

stems from two important effects in nanoscience: the size,²² and dimensionality effects.²³ While the size is critical in determining the energy levels and *quantum-confinement* effects, the dimensionality affects the density of states (DOS) of the material. This quantum confinement occurs when at least, one of the nanocrystal's spatial dimensions is equal to or smaller than the characteristic length scale of excitons of the bulk semiconductor material, the so-called "Bohr exciton radius (a_0)", and results in the quantization of energy levels (from continuous bands to discrete energy levels),²⁴⁻²⁵ as depicted in **Figure 1.3a**. This a_0 represents the distance over which the electron and hole are bound together by Coulombic interaction and is characteristic of each material.²⁶

As the material dimension shifts from bulk-like (3D) down to quantum dot-like (0D), *quantum confinement* effects arise from 0 up to 3 dimensions, according to the size and shape of the material. While the "three dimensional" (3D) nanocrystal exhibits bulk-like properties, the "zero dimensional" (0D) nanocrystal shows the strongest *quantum confinement* effects because all dimensions (x, y, z) are spatially confined, hence the term "quantum dots".²⁷⁻²⁸

The number of allowed energy levels within a band per unit volume of a solid is given by the DOS. As shown in **Figure 1.3b**, the DOS varies substantially with dimensionality in Fermi's golden rule: in 3D semiconductors or bulk-like materials, it increases with the square root of excess energy above the band edge; in 2D semiconductors or nanoplatelets (NPLs), it increases stepwise with energy; in 1D semiconductors or nanorods (NRs), it exhibits Van Hove singularities and decreases with the square root of excess energy; in 0D semiconductors or QDs, it transforms into discrete, atomic-like energy levels.

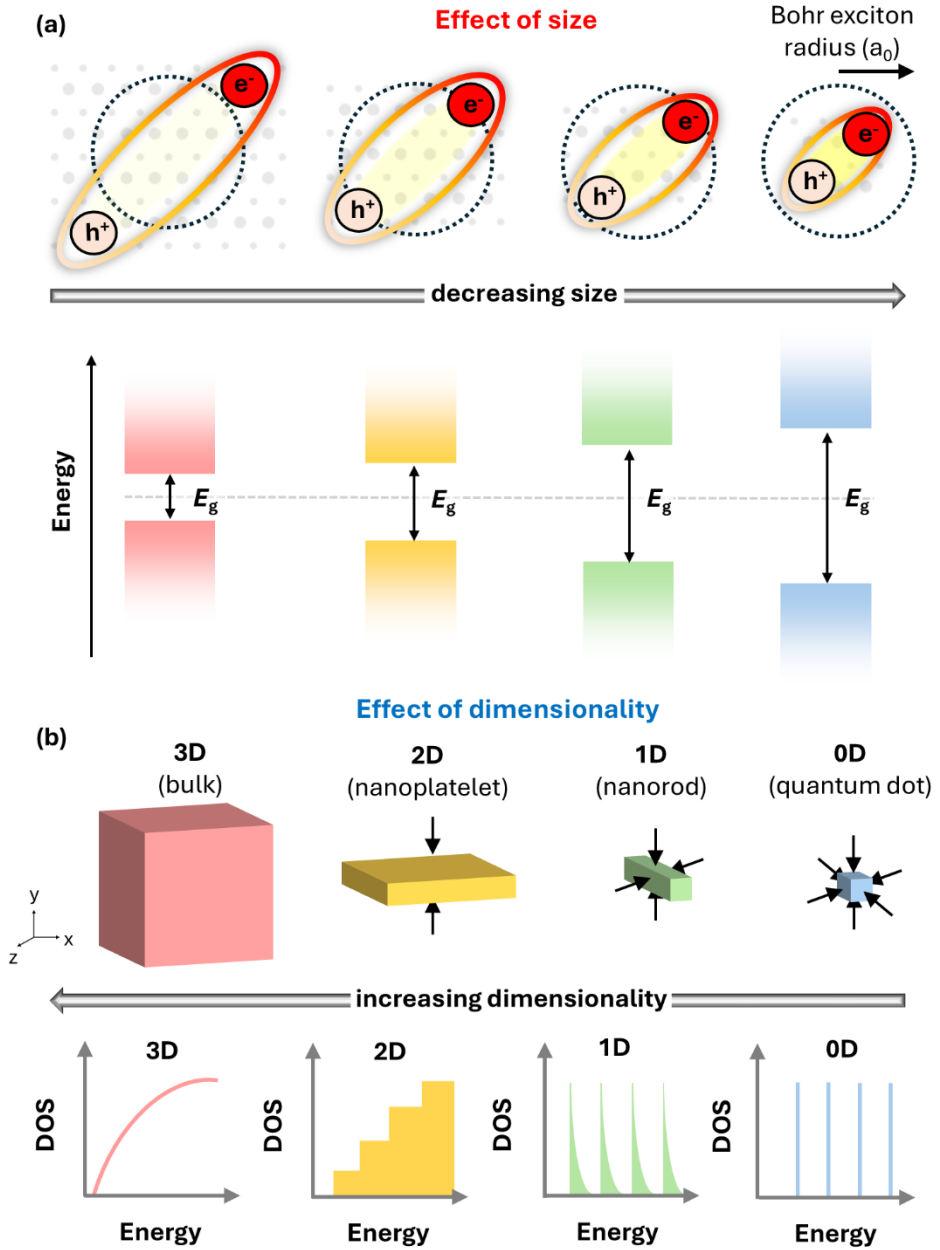


Figure 1.3. (a) Effect of material size on the quantum confinement. **(b)** Effect of material dimensionality on the DOS.

This quantization of energy levels is directly manifested in the absorption spectra of QDs, by the apparition of the first exciton band as the lowest-energy absorption feature, which unequivocally corresponds to the E_g , i.e., the energy difference between the VB and CB (**Figure 1.4a**).²⁹ As the nanocrystal size decreases from 6 to 2 nm and the E_g is increased, *quantum-confinement* effects start to influence the excitonic wavefunction (electron and hole wavefunctions) and the energy of the excitonic states of the nanomaterial, leading to a blueshift in the optical properties (absorption and emission), as shown in **Figure 1.4b**.³⁰ Note that as the nanocrystal size decreases, the electronic states near the band edge tend to resemble molecular states rather than bulk states. However, from a practical standpoint, the absorption spectra of QDs, NRs, and NPLs all deviate significantly from their respective DOS spectra in many cases due to the nonidealized shapes and heterogeneous size distribution, as well as the oversimplification of the realistic band structure of semiconductors and, for NR and NPLs, the neglect of electron–hole Coulomb interactions and their self-interactions.³¹

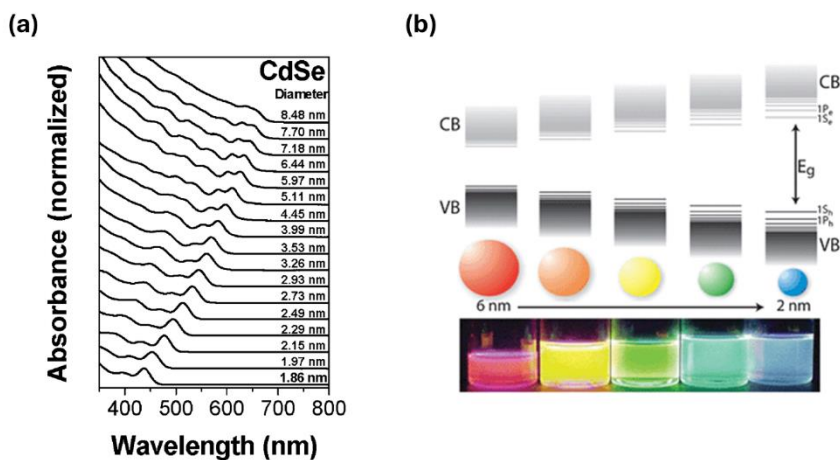


Figure 1.4. (a) Size-dependent absorption spectra of CdSe QDs. Adapted with permission from ref.²⁹ Copyright © 2011 American Chemical Society. (b) Schematic representation of the quantum-confinement effect on the energy levels. Reproduced with permission from ref.³⁰ Copyright © 2011 Royal Society of Chemistry.

From now on, we will only focus on QDs. Owing to the small size of these spherical nanocrystals, QDs exhibit a large surface-to-volume ratio compared to their bulk-like counterparts, i.e. a high percentage of atoms are at the surface, where their properties and derived applications are predominantly dictated by these atoms.³² Nonetheless, the atoms located at the surface of a QD are undercoordinated, unlike those found in the fully coordinated core, leading to the formation of the so-called “dangling bonds”. These dangling bonds in QDs frequently cause surface trap states below and above the CB and VB, respectively, thereby trapping photogenerated electrons/holes, which are responsible for the fast nonradiative losses. Even though, to address this issue, material chemists have designed protective organic ligand shells, such as long alkyl chain organic molecules, that are commonly used not only to colloiddally stabilize the QDs and prevent aggregation but also to efficiently passivate any undercoordinated atoms at the surface.³³ This passivation strategy places the energy levels of surface trap states within the valence and conduction bands, and consequently, enhances radiative emission efficiency. Thus, the surface termination of a QD is a critical factor in determining the overall properties of the nanocrystal. Other methods to stabilize QDs, such as using inorganic shells or polymers,³⁴⁻³⁵ exist, but these are beyond the scope of this dissertation. Additionally, the interaction between surface atoms and organic ligands plays a key role in the growth kinetics of QDs, influencing both their size and shape, which has previously been found to have a strong influence on the optical and electronic properties of the material. Thereby, this precise control of the optical and electronic properties holds promise for creating functional materials with novel properties.³³ Another notable aspect of QDs is that, due to the substantial mixing character of singlet and triplet states at room temperature,³⁶ QDs are widely known to have ill-defined spin quanta, which minimizes energy losses from singlet-to-triplet intersystem crossing (*isc*) processes generally observed in organic molecules and thus are perfect candidates to transfer either singlet or triplet excitons.³⁷ These energy differences are therefore rather

small (5–20 meV) compared to the singlet-triplet splitting in molecules (0.1–1 eV). This mixing is a consequence of various effects, including exchange interaction, spin-orbit coupling, and crystal field effects, whose detailed insights are beyond the scope of this thesis.³⁸ Having introduced the fundamentals of conventional semiconductors, we will now shift our focus to a relatively novel type of inorganic semiconductors, known as **metal-halide perovskites**.

1.1.5. Metal-halide perovskites

Apart from conventional semiconductors, metal-halide perovskites (MHPs) have emerged at the forefront of materials for the 21st Century, offering promising applications in diverse fields such as photovoltaics, light-emitting diodes (LEDs), and photocatalysis, among a great deal of more applications.³⁹ Although early research on MHPs began in the late 1800s,⁴⁰ with detailed structural characterization in the 1900s,⁴¹ and investigations into their potential applications in optical and electronic devices in the late 1990s,⁴² it was not until 2009 that MHPs demonstrated their use as visible-light sensitizers in solar cells, yielding a power conversion efficiency (PCE) of only 3.8 %.⁴³ Since then, MHPs have been in the spotlight, leading to a rapid and widespread increase in research and publications within the MHP community over the following years.⁴⁴⁻⁴⁵ Nowadays, the certified PCE of single-junction and perovskite/silicon tandem solar cells have reached 25.3 % and 33.7 %, respectively.⁴⁶⁻⁴⁷ This rapid advancement has demonstrated an order of magnitude higher rate of improvement compared to other photovoltaic technologies, highlighting the significant potential of MHPs in driving future advancements in solar energy.⁴⁸ There is a vast array of MHP structures based on the combination of both crystalline inorganic framework (3D, 2D, 1D, and 0D) and dimensionality (3D, low-dimensional 2D, 1D, and 0D).⁴⁹ Concerning the general stoichiometry (3D),⁵⁰ and the dimensionality (0D) used in this dissertation, MHP nanocrystals, hereafter NCs, typically crystallize with formula AMX_3 , being “A” a monovalent inorganic (Cs^+) or small organic ($CH_3NH_3^+$, $CH(NH_2)_2^+$) cation, “M” a

divalent (Pb^{2+}) cation and, “X” a halide (Cl^- , Br^- , I^-) anion or a mixture of them, as shown in **Figure 1.5a**. While the “M” cation is coordinated to six “X” anions in an octahedra configuration, the “A” cation is situated in a cavity formed by eight corner-sharing “ MX_6 ” octahedra, thus forming the long-range crystalline structure.

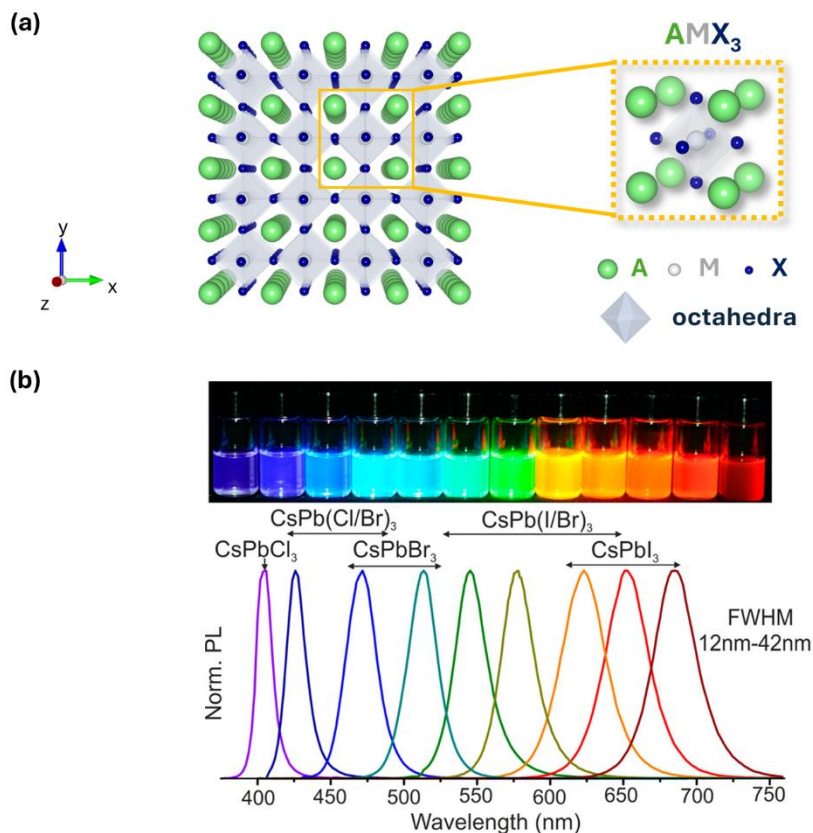


Figure 1.5. (a) Crystalline structure of the cubic AMX_3 perovskite. **(b)** Composition-tunable PL properties. Inset: digital photographs of perovskite dispersions under UV light. Adapted with permission from ref.⁵¹ Copyright © 2015 American Chemical Society.

Based on the composition of the “A” cation, MHPs can be classified into organic-inorganic MHPs and all-inorganic MHPs.⁵² The crystalline structure of an AMX_3 perovskite adopts a cubic lattice. Still, slight deviations from this cubic structure due to the influence of ionic sizes can result in different polymorphs such

as the orthorhombic structure. Here, the Goldsmith tolerance factor (t), which depends on the ionic radii of the “A”, “M” and “X” ions, plays a crucial role in determining the stability and distortion degree within the perovskite lattice.⁵³

This emerging class of materials demonstrates superior optical and electronic properties compared to the conventional semiconductor counterparts (QDs). They exhibit superior molar extinction coefficients (ca. $10^6 - 10^7 \text{ M}^{-1}\text{cm}^{-1}$), narrower PL bandwidths, and near-unity photoluminescence quantum yields (Φ_{PL}) without requiring rigorous passivation strategies such as inorganic shells. These materials offer tunable PL spanning from ultraviolet to near-infrared (NIR) wavelengths through fine-tuning either the halide composition or NC size. Coupled with their straightforward and cost-effective synthesis, these attributes make NCs very promising for applications in photovoltaics and LEDs.⁵⁴⁻⁵⁵ In particular, the ability to easily tune the absorption and PL properties based on composition is highly attractive compared to conventional QDs. This feature is illustrated in **Figure 1.5b**, where the composition of X in the CsPbX_3 NC ranges from pure Cl-based to pure I-based, thereby offering a wide and accessible spectral window.⁵¹ The remarkable level of compositional tunability in MHPs, which directly influences the bandgap E_g , stands out among semiconductors, making them especially intriguing for diverse applications including tandem photovoltaics,⁵⁶ where compositional band gap fine-tuning optimizes the solar light harvesting and therefore enhances the PCE.⁵⁷ This attractive property can rationally be elucidated through the electronic band structure of the perovskite material. For instance, in CsPbX_3 , the valence band results from the hybridization of Pb 6s orbitals and X np orbitals (where $n = 3, 4$, and 5 for Cl, Br, and I), while the conduction band is predominantly derived from Pb 6p orbitals with minimal contribution from X np orbitals. As a result, varying the X content directly controls the optical, electronic, and photophysical properties of CsPbX_3 NCs. Specifically, transitioning from Cl- to I-based NCs results in an upward shift of the valence band edge, also known as valence band maximum or VBM, reducing the E_g , and, consequently, shifting the optical properties towards

longer wavelengths. Furthermore, due to the high ionicity of bonding in MHPs (lattice formed by ions) and the antibonding character of both frontier orbitals (VBM and CBM), these materials are considered “defect tolerant” (see **Figure 1.6**), implying that defect states are mostly shallow in energy and thus do not significantly contribute to nonradiative losses.⁵⁸

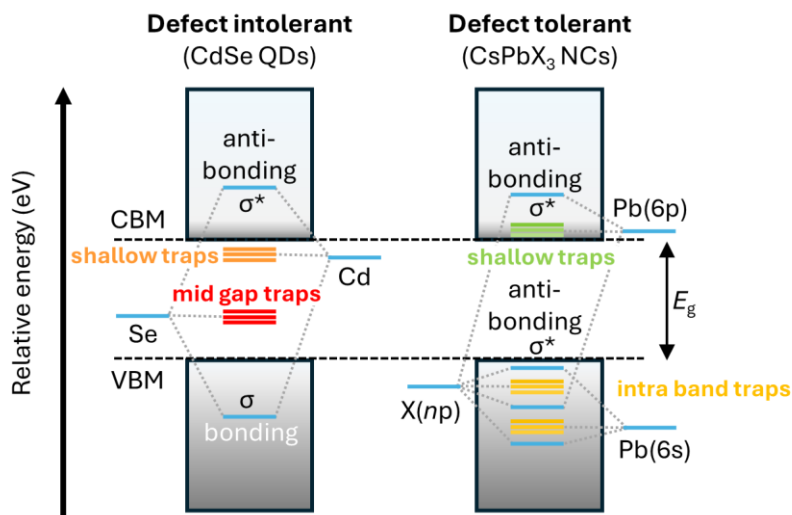


Figure 1.6. Comparison of the electronic band structure between conventional defect-intolerant semiconductors and defect-tolerant perovskites.

Interestingly, this electronic band structure causes defect energy levels to fall within the CB and VB, rather than lying within the band gap. By contrast, conventional defect-intolerant semiconductors, such as CdSe, have defect states within the band gap, either as shallow or mid gap states, due to the bonding-antibonding orbital formation, which severely affects the outcome properties.⁵⁸ Carrier mobility, diffusion length, and carrier lifetime are crucial parameters that define the electronic characteristics of optoelectronic devices. Using CsPbX₃ as a model, it has been observed that CsPbI₃ NCs exhibit the highest carrier mobility at $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, followed by CsPbBr₃ (ca. $2.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), and then CsPbCl₃. This

correlates strongly with their time-resolved PL properties, where CsPbI₃ NCs also demonstrate the longest lifetime, followed by CsPbBr₃, and lastly, CsPbCl₃ NCs.⁵⁹

Unlike conventional QDs, which possess high formation enthalpy and require extremely high reaction temperatures and inert conditions for synthesis,²⁰ CsPbX₃ NCs, on the other hand, can easily be prepared by simple mixing of the corresponding precursors even at room temperature under ambient conditions.⁶⁰ This stark contrast stems from the inherent ionic nature of the chemical bonds in MHPs already discussed compared to the covalent nature found in conventional QDs.⁶¹ Nevertheless, the ionic nature of MHPs has its own drawbacks, as it can make them susceptible to instability issues from external factors, such as moisture, oxygen, light, or heat.⁶² Moreover, maintaining colloidal and structural integrity following isolation and purification processes has consistently been a crucial challenge until today. The binding of the organic ligand shell is highly dynamic, leading to rapid desorption of these ligands after just a few centrifugation cycles and creating localized surface trap states.⁶³ Therefore, the scientific community is currently encouraged to devise novel strategies to address the limitations associated with the inherent instability of MHPs.⁴⁵ One of these solutions would be the use of a more stable ligand shell by using zwitterionic molecules,⁶⁴ addition of a mixture of PbBr₂-ligand to repair the surface,⁶⁵ quaternary ammonium organic ligand shell,⁶⁶ coating within an inorganic shell such as CdS,⁶⁷ encapsulation within a template such as PbSO₄,⁶⁸ among others strategies. Besides stabilizing agents, surface functionalization with photoactive organic molecules has always been a very attractive approach for increasing the sensitivity of attached photoactive organic molecules and tuning the overall photophysical and photochemical properties of conventional chalcogenide QDs.⁶⁹⁻⁷⁰

As it was discussed in the previous section, the ligand-surface interaction is key to understanding the chemical and physical properties of NCs since the size, shape, colloidal and structural stability, and band edge positions are also regulated

by surface organic ligands.^{69, 71} The classification of organic ligands attached to the semiconductor surface was introduced in 1995 to provide the Covalent Bond Classification (CBC) method to classify the type of bond between the ligand and metal in organometallic compounds.⁷² This classification can be divided into L-type, X-type, and Z-type, depending on a number of electrons involved in the bond, as depicted in **Figure 1.7**.⁷³ For L-type, ligands have an orbital filled with two electrons and thus act as electron donors (RNH_2) to the metal. For X-type, both ligands and metals have an electron (RCOO^-). For Z-type, ligands have an empty orbital and thus act as electron acceptors (CdCl_2) from the metal. The most common organic ligand pair is oleic acid (OA) / oleylamine (OAm), which belongs to the X-type classification upon deprotonation and protonation, respectively.⁷⁴

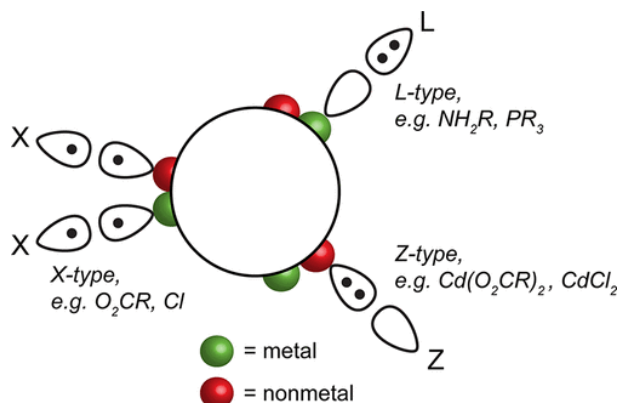


Figure 1.7. Schematic illustration of the ligand binding motifs according to the Covalent Bond Classification method. Reproduced with permissions from ref.⁷³ Copyright © 2018 American Chemical Society.

Our group pioneered in the preparation of colloidal hybrid $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystals in early 2014 using a "nontemplate" approach, also known as the reverse microemulsion technique, employing alkylammonium bromide and oleic acid as organic ligands.⁷⁵ Despite the low Φ_{PL} (20 %) it was used as an emissive layer in the first electroluminescent device based on MHP, with a luminance 10 times higher than the device prepared with the bulk perovskite. Since then, numerous

works and synthetic methods have been implemented, successfully improving their optical properties and colloidal stability.⁷⁶ The most significant advancement in the colloidal synthesis of well-defined, all-inorganic CsPbX₃ nanocrystals, which allows for precise control over size, size distribution, and thermodynamic stability of colloids, is the “hot-injection” method developed in 2015. This synthetic procedure yielded highly monodisperse colloidal CsPbX₃ NCs with extremely high Φ_{PL} , along with size- and composition-tunability optical properties.⁵¹ In addition, *quantum-confinement* effects similar to those previously observed in chalcogenide QDs were also observed using this methodology.

It is noteworthy that this hot-injection strategy was adopted for all synthesis of NCs in this dissertation due to the better control of shape, size, and stability compared to the ligand-assisted reprecipitation (LARP) strategy prepared at room temperature.⁷⁷

The combination of perovskite nanocrystals with photoactive organic molecules, to yield **perovskite-based nanohybrids**, can be custom-designed to induce energy or charge transfer processes, harnessing the synergistic effects of both systems for targeted applications.

1.1.6. Perovskite-based nanohybrids

Developing strategies for the efficient use of solar energy into renewable energy is a challenging and highly active area of research today.⁷⁸ In particular, merging perovskite nanocrystals with photoactive organic dyes has been proposed as a strategy to capture photons across a wide range of the UV-vis-NIR region and store them in the form of chemical bonds.⁷⁹ Therefore, it is extremely important to precisely understand the size-, shape-, composition-, and surrounding-environment-dependent exciton dynamics to fully maximize the efficiency and performance of these systems.⁷⁸

First, upon photoexcitation of the NC an electron-hole exciton pair is created, and these charges can be transfer to acceptor or donor molecules that are strongly bound to the nanocrystal surface, depending on the excitation energy and the energy alignment between the VB and CB of the NC and the HOMO-LUMO of the molecules. As shown in **Figure 1.8**, a wide range of nanohybrids have been prepared: such as perovskite-rhodamine B (NC@RhB),⁸⁰ perovskite-zincphthalocyanine (NC@ZnPc), perovskite-triisopropylsilylethynyl pentacene (NC@TIPS-Pc),⁸¹ perovskite-pyrene (NC@Py),⁸² perovskite-borondipyrromethene (NC@I2-BDP),⁸³ perovskite-benzoquinone (NC@BQ),⁸⁴ perovskite-phenothiazine (NC@PTZ),⁸⁴ among many others, each exhibiting interesting and completely different interfacial properties, which will be explored in detail later in the next sections. The presence of a carboxylate group (X-type ligand) in the organic dye is fundamental to ensure the NC surface binding due to their interaction with surface atoms when deprotonated by replacing surface Br anions or native oleate ligands.⁸⁵

Due to the ability of nanocrystals to transfer either singlet or triplet excitons, as previously discussed for QDs, these materials have shown potential as promising sensitizers in various light-harvesting and energy conversion applications. There are several cases using NCs as efficient singlets⁷⁹ and, in particular, many more as triplet sensitizers because of the bright triplet nature of the lowest-energy state, as will be discussed in *Chapters 4* and *5*.⁸⁶ The lowest-energy bright triplet character in NCs is attributed to the interplay of both (i) the inversion symmetry breaking of the crystal structure owing to the structural distortion, the so-called “Rashba effect”;⁸⁷ and (ii) the larger contribution of the electron-hole exchange interaction mostly for strongly confined systems.⁸⁸ Thus, according to their theoretical model, the Rashba effect will be more prominent under the weak quantum-confinement effect. As a consequence of this Rashba effect, the energetic order between the singlet and triplet states is inverted, leading to a unique fine structure featuring a lowest-energy bright triplet state in NCs. The large oscillator strength of the bright triplet state in NCs, compared to conventional

chalcogenide QDs, accelerates the radiative recombination of band edge excitons in just a few nanoseconds.³¹

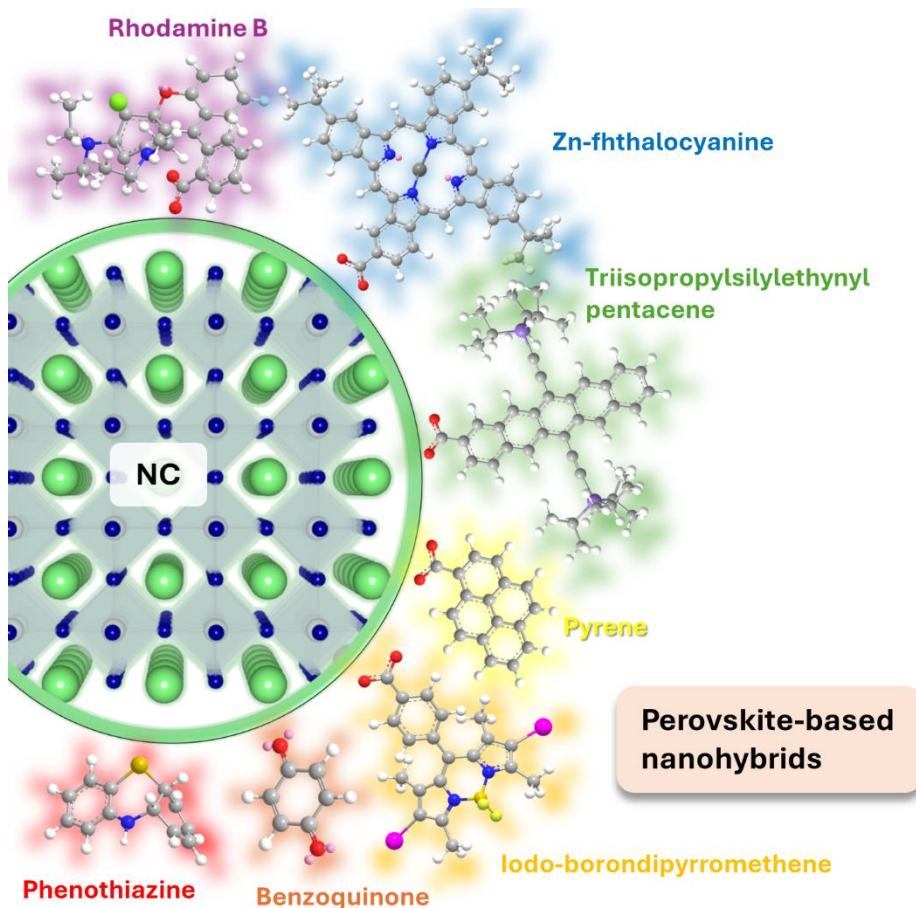


Figure 1.8. Perovskite-based nanohybrids with surface-anchored organic molecules.

Traditionally, the generation of surface-anchored singlet excited-state molecules has been leveraged to funnel the excitation energy in light-harvesting assemblies.⁸⁹ This singlet energy transfer is also especially interesting from the point of view of the singlet fission in solar cells,⁹⁰ by which a sensitized singlet excited state of a molecule produces two triplet states.⁹¹ On the other hand, the formation of long-lived triplet excited states are particularly attractive for room-

temperature phosphorescence, photocatalysis, and photon upconversion, by which two sensitized triplet excited states are able to produce a high-energy singlet excited state through triplet-triplet annihilation upconversion (TTA-UC).^{86, 92} Thus, one can devise appropriate energy levels to properly modulate the excited-state properties and maximize the photon-harvesting efficiency through these nanohybrids. Besides energy transfer events, NCs can also engage in charge transfer processes with corresponding donors or acceptors.⁹³ Because of these charge transfer properties, these materials allow them to be used for solar cells,⁹⁴ and photoredox catalysis applications.⁹⁵ Accounting for all of these phenomena, it is essential to fully understand how energy/charge transfer processes occur at the NC-organic interface and thus the corresponding **interfacial mechanism**.

1.1.7. Mechanisms of energy/charge transfer

According to energy transfer processes between NCs and organic dyes in which the NC acts as an energy donor, several considerations must be met. The most important one is that the energy gap of the organic dye (acceptor) should be similar or lower than the band gap energy of the NC (donor) to ensure thermodynamic feasibility of the process. In detail, the transfer of singlet excitons via singlet energy transfer (SET) can proceed via two widely-known nonradiative mechanisms (**Figure 1.9a**), either Förster resonance energy transfer (FRET) or dipole-dipole coupling,⁹⁶ and Dexter energy transfer (DET) or electron exchange,⁹⁷ or via a radiative mechanism such as emission-reabsorption (ERA) or trivial energy transfer mechanism,⁹⁸ which is not covered in this thesis.

On the one hand, the formalism for the FRET mechanism, expressed in terms of the energy transfer rate constant (k_{FRET}), is described as follows:

$$k_{FRET} = \frac{\Phi_D \kappa^2}{\tau_D} \frac{9000(\ln(10))J(\varepsilon_m)}{128\pi^5 N n^4} \frac{1}{r_{DA}^6} \quad (1.1)$$

where Φ_D is the PL quantum yield of the donor (pristine NC), κ^2 is the orientation factor between the two dipoles, τ_D is the lifetime of the pristine NC, $J(\varepsilon_m)$ is the

spectral overlap integral between the donor emission and acceptor absorption, n is the refractive index of the solvent and r_{DA} is the distance between the donor and acceptor. Because it is a dipole-dipole coupling mechanism, the FRET process depends heavily on the orientation of these two dipoles (κ^2), the PL quantum yield (Φ_D) and lifetime of the donor (τ_D), the extent of spectral overlap ($J(\varepsilon_m)$) and the donor-acceptor distance (r_{DA}). This mechanism only proceeds in the transfer of singlet excitons because it requires the conservation of spin states, whereas the transfer of triplet excitons is otherwise a spin-forbidden transition by spin selection rules.

On the other hand, the formalism for the DET mechanism is outlined below:

$$k_{DET} = K e^{-2r_{DA}/r_0} J \quad (1.2)$$

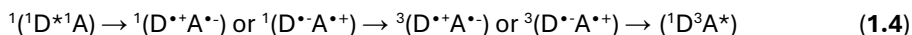
where K is the orbital (wavefunction) interaction and r_0 is the van der Waals radii of the donor and acceptor. The DET mechanism involves the concerted electron and hole transfer processes from the donor to the acceptor, facilitated by orbital overlap. This mechanism is, however, applicable to the transfer of both singlet and triplet excitons due to the insensitivity of spin conservation.

Both energy transfer rate constants depend differently on the donor-acceptor distance; FRET and DET follow r_{DA}^{-6} and $e^{-r_{DA}}$ dependences, respectively. Hence, while FRET operates over larger distances (up to 10 –12 nm), DET is limited only to shorter distances (up to 1 – 2 nm). This is because the DET mechanism relies on orbital overlap and thus close interaction between the donor and acceptor is required to enable efficient exchange interactions. Consequently, DET is highly effective at transferring triplet excitons, which cannot be transferred through FRET due to spin selection rules. On top of that, only FRET accounts for the molar extinction coefficient of the acceptor (ε_m) in the J value calculation, requiring FRET significant spectral overlap and making DET less influenced by the spectral properties.

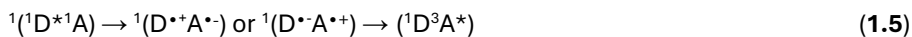
By contrast, to address triplet energy transfer (TET) efficiently, the singlet of the acceptor should be higher in energy than that of the donor to avoid competitive processes. In this respect, TET can take place through two mechanisms (**Figure 1.9b**), either direct Dexter energy transfer (DET),⁹⁷ or charge transfer-mediated triplet energy transfer (CT-TET).⁹⁹ While the first mechanism involves the simultaneous (concerted) electron and hole charge transfer steps between the donor and acceptor systems to yield triplet excited state in the molecular acceptor,¹⁰⁰ where the spin is conserved between the initial and final states:



The second one is mediated by a stepwise charge transfer process, where the recombination of the charge-separated state leads to the formation of the triplet excited state by two different pathways.^{37, 101} For instance, in molecular donor-acceptor systems, triplet excited states can generally be generated through a charge transfer intermediate by either radical pair-intersystem crossing (RP-ISC):¹⁰²



or spin-orbit coupling-mediated mechanisms (SOCT-ISC):¹⁰³



However, in the case of QDs or confined NCs systems, where strong spin-orbit coupling is present,¹⁰⁴ it is still in a relatively nascent stage, and sometimes, it remains uncertain whether the spin states can be effectively managed and selected.

Here, the triplet energy transfer rate constant for the direct Dexter process relies on the following formalism:⁹⁷

$$k_{TET} = \frac{2\pi}{\hbar} \rho_{DA} |V|^2 = \frac{2\pi}{\hbar} \rho_{DA} |\langle \psi_f | \frac{e^2}{\tilde{r}_{12}} | \psi_i \rangle|^2 \quad (1.6)$$

where $\hbar$ is the reduced Planck constant, ρ_{DA} is the joint density of states, $|V|^2$ is the squared matrix element of the perturbation between the initial ψ_i and final ψ_f

states, and $\frac{e^2}{r_{12}}$ is the two-electron operator. In this particular case, V is dominated by the exchange integrals, whose description in terms of the single-particle representation (HOMO and LUMO for highest-occupied molecular orbital and lowest-unoccupied molecular orbital, respectively), is as follows:¹⁰⁵

$$V \propto \langle \psi_{HO}^D | \psi_{HO}^A \rangle | \langle \psi_{LU}^A | \psi_{LU}^D \rangle \quad (1.7)$$

For the CT-TET mechanism, which involves sequential electron and hole transfer, it should be described in terms of electron transfer theory instead (**Figure 1.9c**); the nonadiabatic Marcus charge-transfer formalism, particularly when the donor-acceptor electronic coupling is weak:¹⁰⁶⁻¹⁰⁷

$$k_{CT} = \frac{2\pi}{\hbar} |V|^2 \frac{1}{\sqrt{4\pi k_B T}} e^{(-\frac{(\lambda + \Delta G_0)^2}{4\pi k_B T})} \quad (1.8)$$

where k_B is the Boltzmann constant, T is the temperature, λ is the reorganization energy owing to the electron-nuclear coupling (negligible effect in nonpolar solvents),¹⁰⁸ and ΔG_0 is the energy difference between the final and initial states (also known as the driving force). The λ includes two components: the inner-sphere contribution (λ_i) from the nuclear displacement of the reactants and products, as well as the outer-sphere contribution (λ_o) from the solvent dielectric response, which is given by:

$$\lambda = \lambda_i + \lambda_o \quad (1.9)$$

It is noteworthy that QDs typically contribute negligibly to λ_i because of the weak electron-phonon coupling in QDs and therefore λ_i come mostly from acceptor molecules.¹⁰⁶ The solvent molecules contribute to the charge transfer reorganization energy λ_o through the orientation polarization, which can be estimated by employing the dielectric continuum model:¹⁰⁷

$$\lambda_o = \frac{e^2}{4\mu\epsilon_0} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{d_D} + \frac{1}{d_A} - \frac{1}{r_{DA}} \right) \quad (1.10)$$

where ε_0 , ε_{op} and ε_s are the vacuum permittivity, solvent optical and static dielectric constants, respectively; d_D and d_A are the diameters of the donor and acceptor cavities, respectively.

Here, the V for an electron (eT) and hole (hT) transfer process would be:

$$V_{eT} \propto \langle \psi_{LU}^A | \psi_{LU}^D \rangle \quad (1.11)$$

$$V_{hT} \propto \langle \psi_{HO}^D | \psi_{HO}^A \rangle \quad (1.12)$$

This sequential mechanism dominates over the concerted one since the coupling matrix element for single-electron transfer is typically larger than that of the two-electron concerted transfer. Additionally, the rate constant for both types of mechanisms exhibits distinct dependences on the carrier wavefunctions, allowing comparison with the trend in the probability density of some of the charges on the surfaces, either electron ($|\psi_e^S|^2$) or hole ($|\psi_h^S|^2$), with distance.¹⁰⁵

In the case of a strong coupling regime, the charge transfer rate might enter in the adiabatic regime.¹⁰⁹ Yet, this is not discussed here, as the nanocrystals synthesized in this thesis are in a weak quantum-confinement regime.

In the nonadiabatic Marcus model, it is assumed that the hole remains unchanged when the electron is transferred from the NC to the molecular acceptor. This model traditionally predicted very well the increase in the charge transfer rate constant in donor-acceptor molecules as the driving force increases in the normal Marcus regime, wherein $-\Delta G_0 < \lambda$.¹¹⁰ Nevertheless, the rate constant reaches a maximum when $-\Delta G_0 = \lambda$, and decreases when $-\Delta G_0 > \lambda$ in the inverted Marcus regime. In the case of QDs, the lack of an inverted region in QD-organic complexes stems from another mechanism, the so-called “Auger-assisted mechanism”, where the large driving force is used to excite the charge of the opposite sign inside the band, effectively circumventing the unfavorable Franck-Condon overlap in the inverted Marcus region.¹¹¹ This mechanism is especially common in quantum-

confined materials because the quantum and dielectric confinement effects significantly enhance the Coulomb coupling between charges.¹¹⁰

As a matter of fact, by changing the QD-organic distance using thickness-varying organic linkers or inorganic shells and thus the electronic coupling, the charge transfer rate constant (electron transfer: charge separation, hole transfer: charge recombination) decays exponentially with donor-acceptor distance, as previously observed in CdSe/ZnS type I core/shell QD-anthraquinone (AQ) complexes.¹¹²

The efficiency of all of these processes (energy and charge transfer) depends substantially on the number of dye molecules attached to the NC surface, which significantly depends on the size and shape of NCs.⁶⁹ The greater the number of organic dyes directly attached to the NC surface, the more efficient the energy/charge transfer process, resulting in higher measurement sensitivity.¹¹³ Another attractive way to increase the sensitivity in NC-NC systems is by using directed assemblies,¹¹⁴ which bring the two entities close together by a reduction in interfacial energy, thereby facilitating the excited-state interactions. However, the challenges in the linear assembly of NCs primarily stem from the absence of any directional interactions.¹¹⁵ The use of directing agents such as lead sulfate molecular clusters are therefore a promising alternative to achieve long 1D NC chains,¹¹⁶ as will be discussed in *Chapter 6*.

Sometimes, several of the above-mentioned pathways work cooperatively.¹¹⁷ Hence, determining the exact mechanism of sensitization, whether energy and/or charge transfer, entails careful studies and the use of advanced **pulsed laser techniques** of transient species (molecular singlets/triplets, and cation/anion radicals), such as time-resolved photoluminescence (TRPL) and transient absorption (TA) spectroscopy.

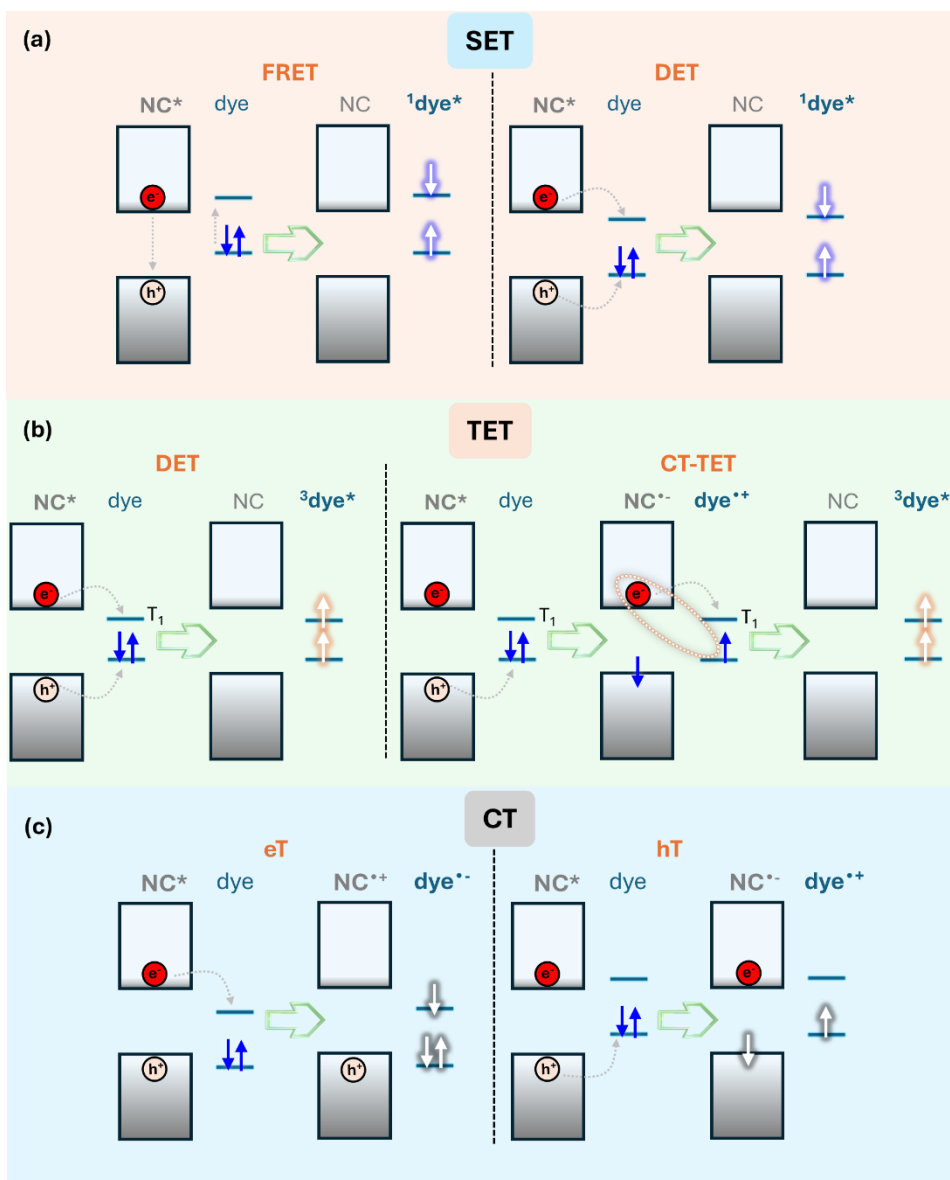


Figure 1.9. Interfacial mechanisms for **(a)** singlet energy transfer (SET), **(b)** triplet energy transfer, and **(c)** charge transfer for NC-dye interfaces.

However, this is frequently a difficult task due to the overlapping spectroscopic signatures of these species. Therefore, Global analysis, which

considers the whole spectrum, is needed to deconvolute the respective species and accurately identify and quantify their individual contributions. This approach allows for a more comprehensive understanding of the underlying mechanisms and interactions.

1.1.8. Pulsed laser techniques

The use of pulsed laser techniques as a tool for probing excited-state interactions between NCs and photoactive organic dyes is an effective way to understand the dynamic interactions of exciton states not only with photoactive organic molecules but also with the surrounding environment, which includes organic shells, solvent molecules, surface trap states, and other nearby NCs.¹¹⁸ The most commonly time-resolved techniques used, and the ones employed here, are time-resolved photoluminescence (TRPL),¹¹⁹ and transient absorption (TA) spectroscopies,¹²⁰ which are employed for all chapters and for *Chapters 4* and *5*, respectively. While TRPL provides valuable information regarding emissive excited states, TA probes the spectral and temporal evolution features with subpicosecond time resolution of the species that exist in both ground and excited states, such as charge carriers, hot state relaxations, exciton and trap states in NCs,¹²¹ but also new photoproduct species generated in the acceptor molecule after excitation and charge transfer processes, such as cation/anion radicals, etc., exhibit their own absorption fingerprints. The combination of both techniques is highly beneficial as they provide complementary information to have a broader picture of the excited-state properties; TRPL detects only emissive species, whereas TA can detect both emissive and non-emissive species. It is noteworthy to emphasize the importance of using monodisperse samples for TRPL and TA measurements to prevent the blurring of the dynamic processes caused by sample inhomogeneities.¹¹⁸

When recording time-resolved measurements, changes in PL lifetimes and TA dynamics give clues about the events occurring in the excited state. For instance, if energy or charge transfer is taking place from the NC to acceptor molecules, the

NC PL lifetime would decrease. This is because this interfacial process competes with the intrinsic radiative pathway, creating a new nonradiative pathway and offering an indirect method to monitor the interfacial interaction.

After a photon interacts with the NC, there exist several processes over a wide range of time scales that can be summarized as follows (**Figure 1.10a**): (1) generation of free charge carriers or excitons through light absorption, (2) intraband cooling or relaxation of electronically hot charge carriers/exciton states to their respective band edges, (3) exciton dissociation either by transferring one of the charge carriers to molecular acceptors or by trapping at surface dark trap states, (4) exciton recombination by either radiative or nonradiative pathways. All of these processes are strongly dependent on the composition, size, shape, density of defects in the NCs, and photon fluence.¹²¹

Because of the above-band gap energy excitation, higher-lying excited states are initially reached below the resolution limit of conventional fs-TA instruments, typically within a few femtoseconds (**Figure 1.10b**). Subsequently, relaxation of these electronically hot states can proceed via different ways such as carrier-phonon coupling, multiple phonon emission and Auger heating effect,¹²² to name a few, and also surface ligands have been found to play a significant role in the strength of the electron-phonon coupling.¹²³⁻¹²⁴ These relaxation pathways control key processes such as optical gain, hot carrier extraction and multiple exciton generation.¹²⁵ For instance, hot charge carrier relaxation channels represent a major energy loss mechanism in solar cells.¹²⁶ This intraband cooling takes place in the subpicosecond domain unless higher excitation fluences are used.¹²⁷ This effect is widely known as hot-phonon bottleneck effect, and it is explained by the increased competition for a finite number of available phonon modes, which results in the continuous emission and reabsorption of hot phonons by carriers that coexist in the same nanocrystal.¹²⁸ Therefore, extraction of these hot carriers/excitons is a promising route to boost the PCE in perovskite solar cells.¹²⁹

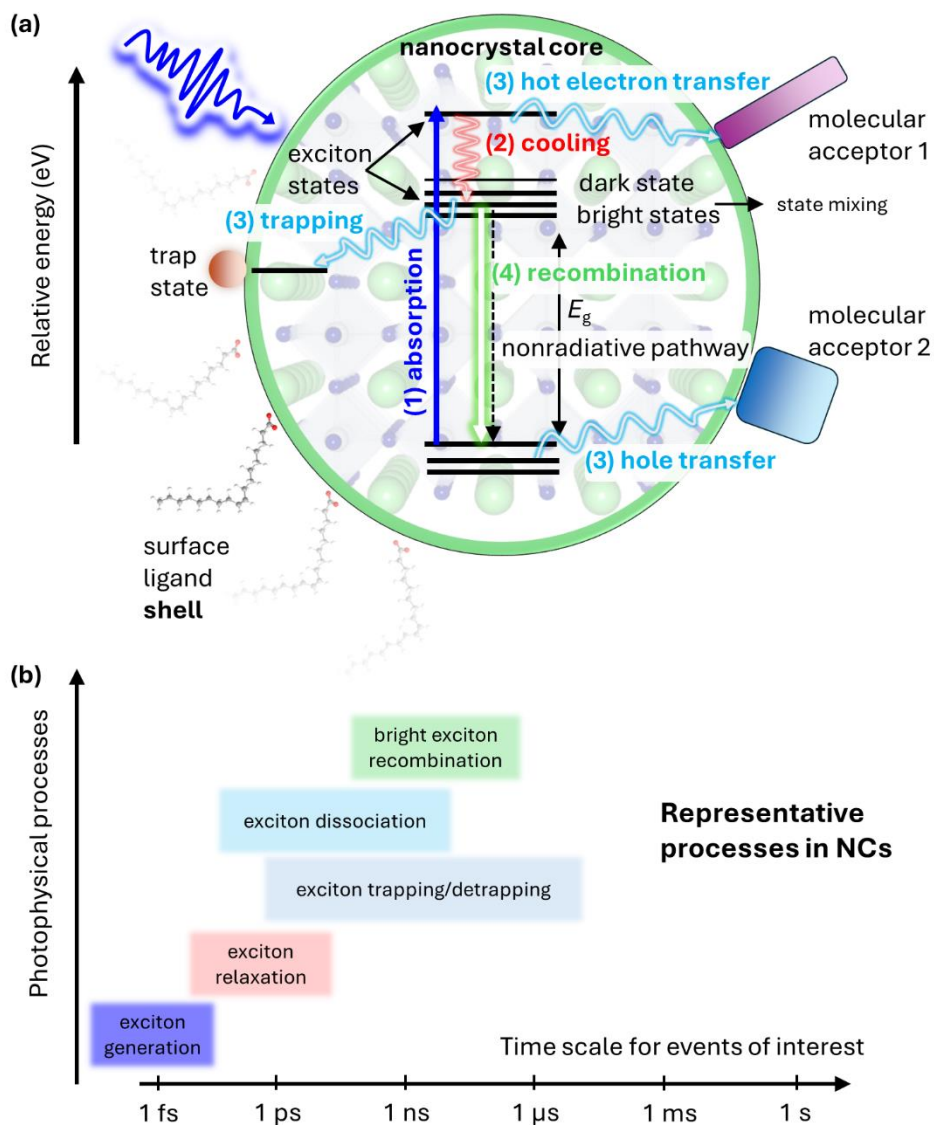


Figure 1.10. (a) Main photophysical processes occurring in NCs. (b) The characteristic time scale of the photophysical processes observed in (a).

Charge trapping processes by surface states are very common in small-sized NCs due to the large surface-to-volume ratio compared to larger counterparts, as it was previously discussed in the 1.1.4 section,¹³⁰⁻¹³¹ so that one of these charge

carriers can be trapped before or after it cools down to the band edge. Depending on the energy level of this trap state, there are two types: shallow- and deep-trap states. In the former, the trap energy is within the VB/CB or near the band edge of the NC ($\Delta E \leq k_B T$) and only affects the efficient movement of charge carriers whereas, in the latter, the trap state is located within the band gap ($\Delta E \geq k_B T$), also called as mid gap traps, and can hinder charge carrier mobility and recombination processes, thereby dramatically impacting the overall performance of optoelectronic devices.¹³² The trapping of one of these charge carriers can occur on a very fast time scale, typically in the range of picoseconds to nanoseconds, while detrapping processes, by releasing the carrier back to the VB/CB, likely occur over longer time scales ranging from nanoseconds to microseconds. Finally, the electron-hole recombination from the band edge, which determines the light-emitting properties of NCs, can proceed via radiatively or nonradiatively. In most of the QDs and NCs, it is usual to find complex PL decays (multiexponential decays), which are attributed to mixing of multiple emissive states (quite close in energy),¹³³ associated with direct electron-hole recombination and trap-assisted recombination states.¹³⁴ At room temperature, the NC PL lifetime is about 1 – 75 ns (depending on the halide composition),⁵¹ manifesting the bright character of the perovskite electronic structure.¹³⁵

1.1.9. Potential applications of perovskite materials

Metal-halide perovskite materials offer excellent prospects for their **application** in a wide variety of light energy conversion technologies. The vast majority of applications of perovskite-based materials (either in the form of nanocrystals, another type of dimensionality or as bulk materials) are related mainly to optoelectronics.¹³⁶ This is basically attributed to their inherent characteristics previously commented such as (1) facile, low-cost synthesis and processability in solution, (2) easy combination with other classes of solution-processable materials, (3) huge molar extinction coefficient, (4) easy tunability of

the optical properties from ultraviolet to NIR wavelengths by either halide composition, size or shape, (5) low nonradiative recombination rates, (6) efficient charge separation and transport, among others, which have had enormous impact on the development and performance of various optoelectronic devices, including solar cells,¹³⁷ photodetectors,¹³⁸ displays and lighting,¹³⁹ lasers,¹⁴⁰ and also for photocatalysis applications.¹⁴¹ Herein, we will solely focus on solar cells and photocatalysis applications, as they are relevant to the context of light-harvesting materials.

As the unique optical and electronic properties of perovskites became more widely recognized, they started being used as active layers in organic-inorganic light-emitting diodes (OLEDs),¹⁴² and as semiconducting channels in thin film field-effect transistors (TFTs).¹⁴³ Since the first report of MHPs as visible-light sensitizers in perovskite-based solar cells (PSCs) in 2009,⁴³ the number of PSCs has substantially increased in a very short period.¹⁴⁴ The striking performance of bulk-type PSCs nowadays has brought these materials to the forefront of cutting-edge optoelectronics research, rivaling the commercialized silicon technology. Despite the ongoing advancements, the vulnerability of MHPs to external stressors, such as those commented previously, due to their inherent ionic nature, still limits the practical manufacturing and commercialization.¹⁴⁵⁻¹⁴⁶ In addition, control over the crystallization becomes more demanding as the manufacturing scales up to few square centimeters or even larger sizes.

Parallel to this progress, a growing number of studies are beginning to shift focus from bulk-type perovskite materials (3D) to nanocrystals (0D) and thus opening up the possibility of harnessing *quantum-confinement* and surface-chemistry effects.⁵⁶ In the form of NCs, the ligand shell creates a protective barrier against the external environment and thus improves the stability. Harnessing the absorption features of CsPbI₃ NCs, the first report of perovskite nanocrystals-based solar cells (PNCSCs) was reported in 2016, where demonstrated significant

competitiveness against polycrystalline thin-film counterparts, with a PCE of 10.77 %, a high open-circuit voltage (V_{OC}) of 1.23 V and excellent air stability (**Figure 1.11a-c**).¹⁴⁷ However, the short-circuit current density (J_{sc}) was limited by transport, as organic ligands reduce the interfacial carrier transfer between neighboring NCs, which is detrimental to efficient solar cells. In the following years, rapid progress in the field afforded PCE of 13.4 % by a post-synthetic treatment with AX [where A = formamidinium (FA^+), methylammonium (MA^+), or cesium (Cs^+) and X = I^- or Br^-], which greatly improved the electronic coupling between NCs and enhanced the carrier mobility.¹⁴⁸ To date, mixed-cation $Cs_{1-x}FA_xPbI_3$ NCs are more desirable than pure $CsPbI_3$ and $FAPbI_3$ QDs in terms of stability and charge transport properties. The hero $Cs_{0.5}FA_{0.5}PbI_3$ PNCSC achieved a certified record PCE of 16.6 % with negligible hysteresis.¹⁴⁹ This compositional control of PNCSCs enables precise modification of their optical and electronic properties, thereby facilitating band gap tunability for tandem solar cells.¹⁵⁰

Besides perovskite materials as active layers, charge transport materials are also pivotal in determining charge dynamics, photovoltaic performance and device stability. These layers facilitate interfacial charge transfers to their respective electrodes.¹⁵¹ Although the energy alignment at the perovskite interface with both electron-transporting (ETMs) and hole-transporting materials (HTMs) are indispensable for high values of PCEs, we will solely consider the organic compounds investigated in *Chapter 8* as potential HTMs for PSCs. It has been shown that HTMs also serve as protective barriers, shielding the perovskite film from the surrounding environment and mitigating degradation in humid conditions.¹⁵² The conventional Spiro-MeTAD HTM exhibits remarkable PCE in PSCs due to the high film quality and matched energy levels. Yet, they are quite constrained by the high material costs, low carrier mobility and poor stability issues.¹⁵³

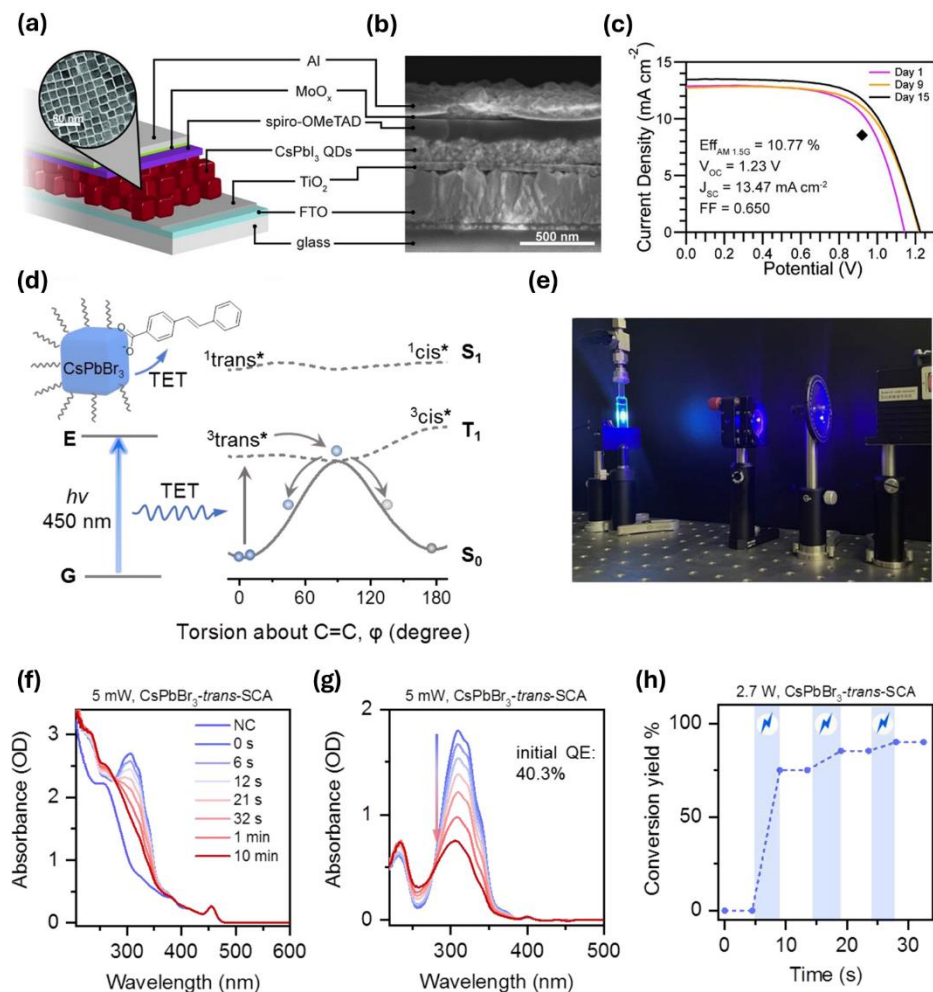


Figure 1.11. (a) Schematic illustration (with TEM image of NCs). (b) SEM cross-section of the CsPbI₃ solar cell. (c) Current density-voltage curves of a device measured in air over the course of 15 days on the right. Adapted from ref.¹⁴⁷ Copyright © 2016 American Association for the Advancement of Science. (d) Potential energy surfaces of stilbene along the torsional angle about the C=C bond and sensitization of triplets by visible-excited NCs. (e) Setup for the photochemical reactions driven by a 450 nm CW laser. (f) Time-dependent absorption spectra of a hexane dispersion of CsPbBr₃ NC-*trans*-SCA complexes under 5 mW 450 nm illumination. (g) The corresponding difference absorption spectra with the free NC absorption subtracted. (h) Light-modulated conversion yields under 2.7 W 450 nm

illumination. The blue shaded areas correspond to the light-on. Reproduced from ref.¹⁵⁴
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Consequently, efforts to seek new alternatives to HTMs are actively ongoing. HTMs based on donor-acceptor systems represent a highly promising approach for developing novel dopant-free HTMs, thanks to their easily tuned energy levels and huge dipolar moment in the excited state.¹⁵⁵⁻¹⁵⁶ A potential candidate is presented in *Chapter 8*, where the structure-property relationship is analyzed in the excited state. Understanding this relationship plays a key role in the charge extraction and transport for developing efficient PSCs.

The understanding of the photophysical behavior of NCs in solar cells, in terms of light absorption and charge separation/exciton transduction, has inspired the community of the field to use them for light-driven chemical reactions. To this end, NCs are employed as heterogeneous photocatalysts within a wide range of high-impact processes, including hydrogen production,¹⁵⁷ CO₂ reduction,¹⁵⁸ polymerizations,¹⁵⁹ organic degradations,¹⁶⁰ and the organic transformation of raw materials into value-added chemicals.¹⁶¹

Comparatively speaking, NCs offers better opportunities than traditional semiconductor oxides (TiO₂, ZnO, etc.) and metal chalcogenides (CdS, CdSe, etc.), because of the easy preparation and ability to tune their band gap by halide composition (Cl, Br, I or a mixture of them).¹⁶² In this context, the relative positions of the CB or VB of the nanocrystals compared to those of the substrate are crucial for driving the redox reaction forward.⁸⁴ However, the stability of NCs remains a major concern owing to two major limitations: (1) chemical instability in polar environments and (2) vulnerability of the surface to undergo transformation with chemical species present in solution. For instance, in aerobic conditions, NCs are known to generate superoxide anion radical (O₂^{•-}) due to the favorable reduction thermodynamics. This highly reactive species can attack the organic ligands of the NC, thereby affecting the stability and functionality of the NCs.¹⁶³ Efforts are also

being made toward realizing NCs which are intrinsically stabilized against exposure to polar solvents. One potential solution is surface modification with polymers,¹⁶⁴ or inorganic shells,¹⁶⁵ which serve as protective barriers, thereby enhancing both the photocatalytic performance and stability of the nanocrystals in polar conditions.

In particular, energy-transfer photocatalysis offers a gentler approach to photocatalysis, helping to avoid corrosion caused by charges and intermediates species.¹⁵⁴ In this regard, triplet sensitization represents a potential pathway for perovskite photocatalysts. For instance, when driving organic transformations using triplet excited states, it is more advantageous to conduct these reactions in nonpolar solvents like toluene, rather than in polar solvents.¹⁶⁶ In a recent study, they reported efficient visible-light isomerization of trans-to-cis interconversion of stilbenecarboxylic acid assisted by TET using CsPbBr₃ NCs (**Figure 1.11d-h**) under anaerobic conditions using a 450 nm CW laser.¹⁵⁴ The change of the absorption in the <350 nm region and the invariance of the NC absorption peak at 455 nm indicate that the NCs are indeed driving photochemical transformations without self-degradation. Notably, the conversion yield increases only under illumination but not under dark, giving rise to a final yield of 90.1 %.

With all, to fully unlock the potential of perovskites for solar-to-chemical energy conversion, more research on enhancing the long-term stability of perovskite nanocrystals and maximizing the interfacial processes is urgently needed, which represents a major technical hurdle.

1.2 Motivation and aim of the dissertation

Nature has been an inspiration for different research fields in the way in which light interacts with matter. Understanding how this occurs in nanoscale systems is therefore of vital importance to developing new and efficient light-

harvesting systems, which can further be exploited in the field of both photovoltaics and photocatalysis.

Hence, the aim of the present dissertation is the preparation of **new light-harvesting materials** based on perovskite nanocrystals, which, as mentioned in the introduction section, possess excellent light absorption capabilities and easy modulation of their optical and electronic properties. The study of the **excited state interactions** between the nanocrystal and molecular energy and/or charge acceptors by a battery of spectroscopic tools provides a deeper understanding of the energy dynamics in these **perovskite-based nanohybrids** and can thus be used appropriately for its **potential application**.

The objectives achieved in each chapter are outlined below:

- **Chapter 3:** demonstration of how quantum-confinement and surface chemistry effects dictate the energy transfer efficiency from CsPbBr₃ NCs to surface-anchored carboxyphenyl BODIPY dyes.
- **Chapter 4:** demonstration of how iodine substitution on the BODIPY core dramatically impact the photosensitization mechanism of two CsPbBr₃@BODIPY nanohybrids, with the concomitant use of the CsPbBr₃@I₂-BDP nanohybrid as proof-of-concept for triplet energy transfer photocatalysis.
- **Chapter 5:** in-depth analysis of the photosensitization mechanism of ZnPc dyes in CsPbBr₃@ZnPc nanohybrids and the effect of the disaggregation phenomena of ZnPc upon surface anchoring.
- **Chapter 6:** preparation of CsPbX₃-NaYF₄:Yb³⁺,Tm³⁺ and CsPbX₃-NaYF₄:Yb³⁺,Tm³⁺/NaYF₄ perovskite-upconversion coassemblies using PbSO₄ molecular clusters as directing agents along with the investigation of the NIR harvesting properties and lanthanide resonance energy transfer from the NaYF₄:Yb³⁺,Tm³⁺ to CsPbX₃.

- **Chapter 7:** thorough inspection of the fluorosolvatochromism properties of two biphenyl derivative push-pull systems in a wide range of solvents, and the effect of the donor substituents on the emissive properties.

Chapter 2.

Characterization Techniques

In this chapter, the common characterization techniques for studying the nanomaterials and organic dyes thorough this thesis shall be described in detail. Overall, these techniques can be classified into three main categories: spectroscopy, microscopy and electrochemistry techniques. Spectroscopy techniques provide information on electronic, vibrational, and molecular properties. Microscopy techniques offer detailed insights into the morphology and structure at the nanoscale. Electrochemistry offers information regarding the redox properties of nanomaterials and organic dyes in order to understand the flux of energy/electrons. Together, these techniques enable a complete understanding of the nanomaterials and organic dyes, providing critical insights into their properties and behavior.

2.1 Spectroscopy techniques

2.1.1. Steady-state absorption spectroscopy

Ultraviolet-visible-infrared (UV-Vis-NIR) absorption spectroscopy was used to analyze the optical transitions in the ground state and determine the optical band gap energy of semiconductor NCs by the Tauc plot method.¹⁶⁷ This methodology is generally used for nanomaterials and is based on the relationship between the absorption coefficient of the material and the photon energy. The Tauc relationship is given by:

$$(\alpha' h\nu)^n = K(h\nu - E_g) \quad (2.1)$$

where α' is the absorption coefficient, h is the Planck's constant, ν is the frequency of the incident photon, K is an energy independent constant, E_g is the optical band gap energy, and n is a constant that depends on the nature of the electronic transition (direct or indirect) involved and can have values of $n = 2$ and $n = 1/2$ for direct and indirect band gap materials. From the intersection of the straight line

drawn along the linear portion in the lowest-energy side of the plot with the x-axis ($(\alpha h\nu)^n = 0$), the E_g can be derived.

The absorption spectra were recorded using a PerkinElmer double beam Lambda 1050+ spectrometer, equipped with a three-detector module (PMT, InGaAs, and PbS) and a detection range from 175 to 3300 nm. The data registration was done by the UV Winlab software. The films prepared in *Chapter 6* were measured by employing a 150 mm InGaAs integrating sphere. The UV-Vis spectra were usually recorded using quartz cuvettes of 1 cm optical pathlength at room temperature, whereas quartz cuvettes of 0.2 cm optical pathlength were also used for *Chapter 5*.

2.1.2. Steady-state photoluminescence spectroscopy

Steady-state photoluminescence (PL) spectroscopy was used to study the emission properties of excited states. In combination with the absorption spectrum, the singlet state energy of organic dyes can easily be estimated from the intersection point between these two normalized spectra. The PL spectra were recorded on an Edinburgh Instruments FLS100 spectrometer equipped with an ozone-free continuous xenon arc lamp (450 W) that covers a range of 230 nm to >1000 nm, a UV-Vis-PMT, and NIR-PMT to cover from 185 to 900 nm, and from 900 to 1700 nm, respectively. The data registration was done by the Fluoracle software. The PL spectra were registered using quartz cuvettes of 1 cm optical pathlength at room temperature. For measuring the films prepared in *Chapter 6*, a front-face sample holder was used for accurate sample positioning along the XY stage and removing direct reflection.

Photoluminescence/fluorescence quantum yield ($\Phi_{\text{PL}}/\Phi_{\text{FL}}$) was used to evaluate the photoluminescence/fluorescence efficiency of nanomaterials and organic dyes. The $\Phi_{\text{PL}}/\Phi_{\text{FL}}$ quantifies the ratio of the number of emitted photons to the number of absorbed photons, providing insight into the efficiency of the luminescence process and thus give valuable information about the density of defects in the crystal structure or on the surface of perovskite NCs. The absolute

$\Phi_{\text{PL}}/\Phi_{\text{Fl}}$ was registered using an integrating sphere system inside the FLS1000 photoluminescence spectrometer with a reflectance higher than 99 % in the range 400-1500 nm. Sample solutions with 0.1 OD at excitation wavelength were used to minimize reabsorption effects. For reference, the neat solvent with exactly the same volume was used. All spectra were recorded using 1 cm optical path length quartz cuvettes at room temperature.

$$\Phi_{\text{PL/Fl}} = \frac{\text{emitted photons}}{\text{absorbed photons}} \quad (2.2)$$

2.1.3. Time-resolved photoluminescence spectroscopy

Time-resolved photoluminescence (TRPL) spectroscopy was used to investigate the recombination dynamics of the exciton states in the process of emitting a photon to return back to the ground state in NCs and also for the fluorescence/phosphorescence decays of organic dyes/UCNPs. Information about the time-resolved properties together with the quantum yield efficiency can provide direct information about the kinetics of the radiative (k_r) and nonradiative pathways (k_{nr}). The PL/fluorescence lifetime was recorded on a FLS1000 photoluminescence spectrometer through the time-correlated single photon counting (TCSPC) technique whereas the phosphorescence lifetime of UCNPs was registered using the multichannel scaling (MCS) as photon counting method. In *Chapter 3, 4 and 5*, the PL lifetime of NCs and organic dyes was measured with a picosecond pulsed supercontinuum white light laser (SuperK, repetition rate: 1.86 MHz, 74 ps pulse width, NKT Photonics) and a microchannel plate (MCP-900, 25 ps detector response) detector in cooled housing with spectral range from 200 to 850 nm. The instrument response function (IRF) was about 150-200 ps, which depended on the excitation wavelength and band widths. In *Chapter 6*, the PL lifetime with selective excitation to NCs was measured with a 375 nm picosecond pulsed diode laser (EPL-375, repetition rate: 10 MHz, 75 ps pulse width, Edinburgh Instruments) and a PMT (PMT-980, 600 ps response detector) detector. The kinetics of co-assemblies dispersed in hexane and deposited on solid films exciting the UCNPs were recorded

with a 2 W CW 980 nm diode laser (PSU-III-LED, CNI Optoelectronics Technology Co. Ltd.) in a time range of 0-8000 ms with 8 ms of step. In *Chapter 7*, the PL lifetime of push-pull systems was measured with a 375 nm picosecond pulsed diode laser (EPL-375, repetition rate: 10 MHz, 75 ps pulse width, Edinburgh Instruments) and an MCP-900 detector. The IRF was approximately 110 ps. All spectra were recorded using 1 cm optical path length quartz cuvettes at room temperature, unless for *Chapter 5*, in which 0.2 cm optical path length were also used. The Fluoracle software was used to fit the multiexponential decays through either reconvolution or tail fitting. The average PL lifetime (τ_{av}) was calculated according to the following equation, where τ_i and α_i represent the lifetime and weight parameters of the i th exponential component, respectively.

$$\tau_{av} = \frac{\sum \alpha_i \cdot \tau_i^2}{\sum \alpha_i \cdot \tau_i} \quad (2.3)$$

2.1.4. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used to determine the structure and environment of molecules. In *Chapter 3*, *4* and *6*, the ^1H -NMR spectra of dyes, ligands, PbSO_4 clusters and solvents were obtained at room temperature in a Bruker DPX300 spectrometer with a 300 MHz Bruker magnet (7 T). Particularly, in *Chapter 3* and *4*, the ^1H (500 MHz) and ^{13}C (126 MHz) spectra of organic dyes were recorded with a Bruker instrument. Chemical shifts (δ) are reported in ppm relative to TMS ($\delta = 1\text{H} = 0.0$ ppm) and coupling constants (J) are given in Hertz (Hz). The chemical shift range for each spectrum was calibrated using the residual solvent signals as internal reference. Deuterated toluene (C_7D_8), deuterated DMSO (DMSO-d_6) and deuterated chloroform (CDCl_3) were used as solvents for NMR characterization for *Chapters 3*, *4* and *6*, respectively. ^1H -NMR was also used to calculate the chemical yield of the obtained products during photocatalytic reactions with CHCl_3 as the internal standard in *Chapter 4*.

2.1.5. Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy was used to determine the chemical composition of the nanomaterials and organic dyes by providing information about molecular vibrations of the chemical bonds through infrared (IR) absorptions. In *Chapter 3* and *4*, the FTIR spectra were collected in attenuated total reflectance (ATR) mode. This technique was employed to confirm the attachment of the dyes to the NC surface by monitoring the alteration of the anchoring group binding energy (cm^{-1}) directly attached to the NCs. The ATR-FTIR spectra were recorded on a Bruker alpha II FTIR spectrometer in the $400\text{-}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} at room temperature. Few drops of a concentrated dispersion/solution were added and the solvent was completely dried. In *Chapter 6*, the FTIR spectra were recorded by using an FTIR Thermo Nicolet Nexus spectrophotometer (with 64 scans and a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1}). The sample preparation consisted of mixing the solid with KBr to form a pellet.

2.2 Microscopy techniques

Transmission electron microscopy (TEM) was used to analyze the NC size, morphology, and homogeneity of colloidal synthesis. In *Chapters 3* and *4* the TEM images were taken by a HITACHI HT7800 microscope with a filament of LaB_6 operated at 100 keV and a CMOS EMSIS XAROSA digital camera of 20 Mpx . In *Chapters 5* and *6*, the TEM images were taken by a JEOL 1010 microscope with a tungsten filament operated at 100 keV and an AMT digital camera of 8 Mpx . Size analyses were done by using the ImageJ software.

2.3 Electrochemistry techniques

Cyclic voltammetry (CV) technique was used to determine the redox events under an applied bias, providing valuable insights into the band-edge and frontier

molecular orbitals (MOs) energetics of semiconductor NCs and organic dyes, respectively. Redox properties characterization was performed on an Autolab potentiostat (Autolab 128N potentiostat/galvanostat) using a three-electrode system. In *Chapter 3*, cyclic voltammetry (CV) experiments were carried out in 0.1 M tetrabutylammonium tetrafluorophosphate (TBAPF₆) solution in dried acetonitrile (ACN) and a mixture of ACN:toluene (1:4 v/v) for the C-BDP and NCs, respectively, by using a Pt working electrode, a Pt wire auxiliary electrode and Ag/AgCl as a reference electrode. Experiments were performed under air conditions with scan rates varying from 5 to 100 mV/s. In *Chapter 4*, the CV experiments were carried out in 0.13 M TBAPF₆ solution in a mixture of dried ACN:toluene (1:3 v/v) for both dyes and NCs, by using a glassy carbon working electrode, Pt wire counter electrode and Ag as pseudoreference electrode. Concentration of both dyes and NCs were 1.13 mM and ca. 0.1 μ M, respectively. Experiments were performed under air conditions with a scan rate of 200 mV/s. In *Chapter 7*, the CV experiments were carried out in 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) solution in dried acetonitrile (ACN) using Pt as a working electrode, Pt wire as an auxiliary electrode, and Ag/AgCl as a reference electrode. The concentration of the compounds was ca. 0.2 mM in dried ACN. Experiments were performed under air conditions with a scan rate of 100 mV/s. All measurements were performed at room temperature (298 ± 1 K) partially deaerating the electrolyte solution by bubbling nitrogen for 2 min. To evaluate the electrochemical energy gaps, potentials were referred to the Fc/Fc⁺ couple using 0.2-0.4 mM solutions of ferrocene in their respective matrix (supporting electrolyte and solvent/solvents mixture).

Chapter 3.

Quantum-Confinement Effects on the Singlet Sensitization Efficiency of a BODIPY-Based Molecular Rotor

3.1 Introduction

Control over the excited-state nature between colloidal metal-halide perovskite nanocrystals (NCs) and organic chromophore molecules is crucial to designing novel hybrid materials in numerous technological fields such as photovoltaics, optoelectronics, sensing and photocatalysis.⁷⁹ The ease of tuning the optical, electronic and photophysical properties of NCs through modulation of the composition, size and shape allows them to not only probe the sensitization mechanisms but also to optimize their performance in the above-mentioned applications.⁵²

The earliest sensitization processes in perovskite nanocrystal-organic dye nanohybrids predominantly rely on triplet energy transfer (TET), as evidenced by existing research.^{82, 154, 168-182} By contrast, the number of examples based on singlet energy transfer (SET) has been rapidly growing in recent times.^{80-81, 181, 183-195} In particular, the SET may occur through three widely known mechanisms, as previously commented in the introduction chapter: Förster resonance energy transfer (FRET) or Coulomb coupling, Dexter energy transfer (DET) or electronic exchange, and emission-reabsorption (ERA) or trivial mechanisms.¹⁹⁶ While the latter happens through the emission of a photon and its subsequent reabsorption (with no apparent change in lifetime parameters), the first two are often difficult to distinguish from one another. Nevertheless, they operate under different distance constraints and physical mechanisms. While FRET can proceed over long distances through a resonant dipole coupling mechanism, DET operates through a simultaneous electronic exchange mechanism, where there is orbital overlap between the donor and acceptor energy wavefunctions. Thus, not only a downhill in energy but also a favorable energy level alignment has to be considered.⁹⁷

Surface ligand shell controls the crystal size during nucleation and growth in nanocrystal synthesis, guarantees colloidal and structural stability and facilitates dispersibility in organic media,^{85, 197} and also plays a central role in dictating the sensitization mechanism in perovskite nanocrystal-organic dye nanohybrids since a dense capping ligand would either prevent the energy acceptor from approaching the nanocrystal surface or impact the binding mode and geometry of the acceptor.⁷⁹ This could have implications for redox photocatalysis, in which orbital overlap is required for charge transfer (CT) to occur, contributing to the overall photocatalyst performance.¹⁹⁸

Additionally, the choice of chemical moiety (anchoring group) linking the semiconductor NC donor and the organic acceptor, acutely affects the energy and charge transfer processes in hybrid assemblies.¹⁹⁹ It has been reported that TET from metal chalcogenide quantum dots (QDs), such as CdSe CDs to BODIPY dyes, can take place through charge recombination (CR) of the QD radical anion and BODIPY radical cation ($QD^{\bullet-}$ BODIPY $^{\bullet+}$) pair after selective photoexcitation of QDs.^{117, 200} It has also been found that the coupling and self-assembly procedures used to ensure close proximity between CdSe QDs and BODIPY dyes notably increased the FRET efficiency between them.²⁰¹⁻²⁰² Although BODIPY dyes have recently been used to increase the stability of NCs by surface defect passivation,²⁰³⁻²⁰⁴ sensitization studies between NCs and BODIPY dyes were still lacking.

It has been shown that the rate and efficiency of TET from NCs to pyrene acceptors are indeed intensively influenced by the size of NCs, being maximum for strongly confined NCs, where there is a higher probability to find the electron/hole wavefunction on the surface, thereby providing further evidence for the Dexter-type nature of this energy transfer (ET) mechanism.⁸² Alternatively, size-dependent FRET analysis from CdSe QDs to Nile Red dyes has also shown to largely impact the ET process. However, a higher FRET efficiency was found for larger-sized QDs presumably owing to enhanced electronic coupling and Coulombic interaction

whereas,¹¹³ in another work employing also CdSe QDs and squaraine molecules, ET rate constants drastically decreased as the QD donor size increased.²⁰⁵

Considering the different surface chemistry and shape of MHP NCs compared to chalcogenide QDs, where the X-type ligands like ammonium and carboxylate moieties are mainly used for surface passivation in NCs,^{39, 72} our attention turned towards investigating the interaction between NCs and carboxyphenyl BODIPY dyes. Particularly, quantum-confinement engineering of NCs to control the SET efficiency in NC@BODIPY nanohybrids has not been investigated yet.

In this chapter, we demonstrate systematically how quantum-confinement effects of NCs and also its surface chemistry remarkably affects the ET efficiency (Φ_{ET}) from NCs to surface-anchored BODIPY dye acceptors. This ET has been thoroughly investigated by using a combination of steady-state and time-resolved optical properties; the in-depth analysis clearly indicates a predominant FRET mechanism for the smaller-sized NCs, whereas a CT mechanism occurs for larger-sized NCs. Additionally, the use of a BODIPY-based molecular rotor allowed us to track the localization of the BODIPY acceptor depending on the surface chemistry. In fact, the anchoring of BODIPY dyes to the NC surface was evidenced by ¹H-NMR and FTIR spectroscopies.²⁰⁶

3.2. Experimental section

Methods

3.2.1. Synthesis of lead-halide perovskite nanocrystals

The three ensembles of colloidal CsPbBr₃ perovskite nanocrystals (NCs) were synthesized using a Schlenk line accordingly by a previously reported hot injection strategy with some modifications.⁵¹ First of all, a solution of cesium oleate

(Cs-oleate, 0.125 M in 1-ODE) was prepared by mixing cesium carbonate (Cs_2CO_3 , 407 mg, 1.24 mmol) and OA (1.25 mL, 3.53 mmol) in 1-octadecene (1-ODE, 20 mL) in a 50 mL three-neck round-bottom flask and the mixture was degassed under vacuum at 100 °C for 1 h. Afterwards, the mixture was heated up to 150 °C under N_2 atmosphere until all Cs_2CO_3 was completely dissolved obtaining a clear solution. This solution was kept for subsequent use. On the other hand, for the synthesis of NCs, lead bromide (PbBr_2 , 72 mg, 0.196 mmol) was loaded into a 50 mL three-neck round-bottom flask with 1-ODE (4.8 mL) and degassed under vacuum at 100 °C for 15 min. Then, the valve was changed to N_2 flow and after 3 min, previously degassed oleylamine (0.71 mL, 1.5 mmol) and oleic acid (0.53 mL, 1.5 mmol) were added through a purged syringe to form a colorless solution. After complete solubilization of the PbBr_2 , the reaction temperature was raised to 190 °C and Cs-oleate (0.6 mL, 0.075 mmol) was immediately injected through a purged syringe and, 5 sec later, the reaction was quenched through an ice/water bath and the NCs were subjected to isolation/purification.

Three ensembles of different nanocrystal sizes were isolated by a size-selective centrifugation strategy. The crude dispersion was first diluted with 5 mL of toluene and transferred to a 50 mL centrifuge tube to initiate the isolation process. The crude was first centrifuged at 2500 rpm for 10 min (15 °C) and the supernatant was transferred to another 50 mL centrifuge tube. The first solid was redispersed in 5 mL of toluene and left decanted overnight. The supernatant was carefully pipetted out and filtrated through a 0.2 μm membrane filter (NC-7.6) meanwhile the precipitated solid was redispersed in toluene (NC-11.9). Anhydrous methyl acetate (MeOAc) (8 mL) was added to the first supernatant to help the precipitation of smaller nanocrystals and was secondly centrifuged at 5000 rpm for 10 min (15 °C). This second solid was finally redispersed in toluene (NC-5.6).

3.2.2. Synthesis of 8-(4-carboxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

The 8-(4-carboxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (C-BDP) compound was synthesized by Dr. Daniel A. Caminos from the National University of Cordoba (Argentina), following the protocol established by Gruzdev et al.²⁰⁷ In brief, 4-formylbenzoic acid (5 mmol) and pyrrole (3.5 mL, 15 mmol) were mixed as reactant and solvent, respectively, using 0.1 M chlorohydric acid (HCl) acid as a catalyst under Ar atmosphere. A dipyrromethane derivative substituted with a 4-carboxyphenyl at the *meso* position was obtained (80 % yield). Then, this compound was isolated by extraction with a dichloromethane (DCM)/water (H₂O) mixture, and the organic phase was evaporated under vacuum and 60 °C to remove the pyrrole content, obtaining a viscous brown residue, which was then purified by column chromatography with ethyl acetate (EtOAc) with a 0-10 % acetone gradient (64 % yield). Later, the dipyrromethene compound was dissolved in toluene and oxidized with 2 equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.705 g, 12 mmol) for 4 h. Then, triethylamine (TEA, 3.5 mL, 47 mmol) was added, followed by an excess of cold boron trifluoride diethyl etherate (BF₃·OEt₂, 3.5 mL, 21 mol), leaving it to react for 12 h. The C-BDP dye was isolated by extraction with a DCM/H₂O mixture, then the organic phase was evaporated and purified in consecutive silica gel column chromatography with EtOAc:DCM 90:10 followed by EtOAc:acetone 0 – 70 %, and finally recrystallized from hexane to obtain about 420 mg of the final product (26 % overall yield).

3.2.3. Synthesis of 8-[4-(3-bromopropoxyphenyl)]-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

8-(4-(3-bromopropoxy)phenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Br-BDP) compound was also synthesized following the same protocol for C-BDP, although combined with a protocol established by Tao Gao et al., to have

the 4-(3-bromopropoxy)benzaldehyde compound.²⁰⁸ The 4-(3-bromopropoxy)benzaldehyde compound was obtained (80 % yield) from solid p-hydroxybenzaldehyde (10 mmol) and the transparent liquid 1,3-dibromopropane (20 mmol) with potassium carbonate (K_2CO_3 , 15 mmol) in *N,N*-dimethylformamide (DMF, 20 mL) for 24 h at room temperature. Then, the crude was extracted with 3x50 mL EtOAc and H_2O . The organic layer was dried with anhydrous sodium sulfate (Na_2SO_4), then filtered and evaporated to obtain a white viscous oil. This oil was purified by silica gel chromatography eluting with hexane:DCM 90:10 (100 mL); 70:30 (150 mL); 50:50 (400 mL); 30:70 (100 mL) gradients. The obtained 4-(3-bromopropoxy)benzaldehyde (8 mmol) was mixed with a pyrrole excess (80 mmol, 5.5 mL) and 0.1 M HCl under Ar atmosphere. After 12 h of reaction, the pyrrole excess was evaporated under vacuum and 60 °C. In this step, a *meso*-(3-bromopropoxyphenyl)dipyrromethane compound was obtained with a 41 % yield. Without purification, this crude was dissolved in DCM (20 mL), and DDQ (2.64 g, 12 mmol) was added and reacted for 1 h at room temperature. Then, TEA (7 mL, 100 mmol) was added, followed by an excess of cold $BF_3 \cdot OEt_2$ (9 mL, 54 mmol), leaving it to react for 12 h. The reaction crude was filtered by a silica gel pad to retain scrambling. Then, the final product was isolated by extraction with a DCM/ H_2O mixture, the resulting organic phase was evaporated and purified by silica gel column chromatography with hexane:DCM gradient 0 – 90 % and recrystallized from hexane to obtain 1.32 g (3.66 mmol) of green color crystals as the product (32 % overall yield).

Instrumentation

High-resolution transmission electron microscopy (HR-TEM) images were taken by a FEI TECNAI G2 F20 microscope operated at 200 keV, with a resolution of 0.24 nm and a CCD GATAN digital camera was used.

3.3. Results and discussion

3.3.1. Size-selective precipitation strategy for CsPbBr₃ nanocrystals

The colloidal synthesis of cubic CsPbBr₃ perovskite NCs was conducted following a widely-known hot-injection approach,⁵¹ wherein an aliquot of a previously prepared cesium precursor (Cs-oleate) was swiftly injected into a 190 °C mixture composed of lead and bromide salt precursors (PbBr₂), and organic capping ligands, specifically OA and OAm ligand pairs, dissolved in a noncoordinating solvent such as 1-ODE, under inert conditions. The reaction was cooled down after 5 sec, by immersing the round bottom flask into an ice/water bath and gradually turning a yellow-greenish color as it reached room temperature. Initial wide size distribution is commonplace for conventional nanocrystal synthesis due to the fast reaction kinetics (1 – 5 s) with inefficient separation of nucleation and growth events.²⁰⁹ Therefore, an isolation/purification approach is often needed to obtain high-quality monodisperse NCs from the crude mixture. Applying several centrifugation/redispersion steps, using anhydrous MeOAc and toluene as antisolvent and solvent, respectively, were necessary to isolate three different ensembles of NC sizes from the same synthesis batch.²¹⁰

Steady-state UV-vis absorption and PL spectroscopies measured the exciton absorption, bandgap energy and PL recombination of the isolated NCs ensembles (**Figure 3.1a,d,g**). The lowest-energy excitonic absorption peaks for NC-5.6, NC-7.6 and NC-11.9 were at 494, 504 and 512 nm, respectively. The ca. 20 nm blueshift of the exciton peak for the smaller NCs is consistent with quantum-confinement effects. It is worth noting that the smallest one falls within the weak quantum-confinement regime, since the Bohr exciton diameter for this class of nanocrystal is ca. 7 nm, and explains the well-resolved exciton peak for this ensemble.³⁹ The PL maxima showed the same trend (502, 510 and 520 nm) with

moderate Φ_{PL} for pristine NCs in the range 18 – 57 %, which are much higher than the prototypical CdSe QDs as a result of the defect-tolerance nature of the NCs.⁷³ The higher Φ_{PL} for the medium-sized NCs denotes that the complex interplay between ligand concentration and proper surface passivation of trap states without steric hindrance of organic ligands play a key role in determining the dynamics and optical properties of the NCs.²¹¹ While TEM (**Figure 3.1b,e,h**) and HR-TEM (**Figure 3.1c,f,i**) confirmed the size of NCs and corroborated the formation of crystalline domains with an interplanar distance of 0.42 nm corresponding to the crystal face (121),²¹² which is consistent with the orthorhombic crystalline phase of CsPbBr₃. Note that the different ensembles were termed as NC-x (x = size measured by TEM).

3.3.2. Analysis of excited-state interactions

Excited-state interactions were performed in light-harvesting assemblies comprised of NCs and BODIPY dyes. Particularly, we used 8-(4-carboxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (C-BDP) molecular rotor as the energy acceptor for the following reasons (**Figure 3.2a**): (1) the huge spectral overlap integral ($J = 1.1\text{--}1.6 \times 10^{15} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$) between NC PL and C-BDP absorption; (2) the relatively large molar extinction coefficient ($\epsilon = 2.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) of C-BDP in toluene; (3) the low C-BDP fluorescence quantum yield ($\Phi_{\text{F}} = 1 \%$), due to high degree of rotational freedom of the carboxylphenyl substituent at the *meso* position of BODIPY, thereby triggering nonradiative pathways, which are expected to increase through (i) ET from the NCs and (ii) organic ligand anchoring to the NC surface/encapsulation within the organic ligand shell; and (iii) the presence of a carboxylic acid group at the *meso* position (8-position) enabling the binding of the BODIPY to the NC surface. Interestingly, it has already been reported that the carboxylic acid group in the *meso* position plays a key role for efficient electron injection compared to the 2-position of the BODIPY core.²¹³

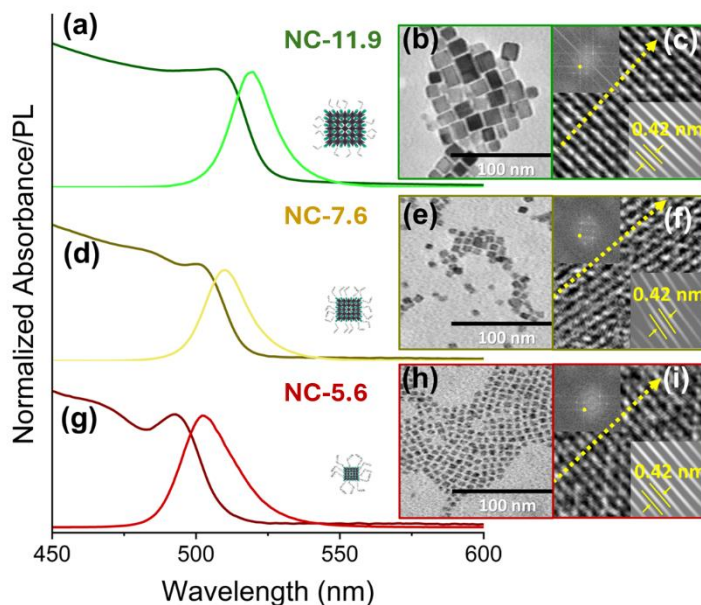


Figure 3.1. Normalized absorption and PL spectra (a,d,g) of NC-x (x = 5.6, 7.6, and 11.9 nm, respectively) registered under 420 nm excitation and their corresponding TEM (b,e,h) and HR-TEM (c,f,i) images of the three samples showing the NC morphology and the crystal plane (121) with a d-spacing of 0.42 nm. The fast-Fourier transform (FFT) of a selected nanocrystal is shown in the upper inset. The yellow dot indicates the (121) plane. The lower inset shows the region of the indicated plane (reference for *Pnma* space group orthorhombic CsPbBr₃ crystalline phase: COD 1 533 062). The scale bar for TEM images is 100 nm.

Titration experiments of a fixed concentration of NCs [22 nM] at increasing concentrations of C-BDP dye [0–5 μ M] in toluene were performed under inert conditions. Steady-state and time-resolved PL of the nanohybrid were recorded under selective excitation of the NCs at 420 nm, where C-BDP barely absorbs. **Figure 3.2b,c,d** shows the quenching of the steady-state and time-resolved PL properties of the NCs upon increasing C-BDP concentrations, concomitantly with the fluorescence enhancement associated with the C-BDP dye in the 500–580 nm range (not highlighted here). To account for the magnitude of this quenching, the NC PL deactivation was thoroughly analyzed by the Stern-Volmer (SV) relationship (3.1),

where the change of PL intensity (I) of the NCs in the presence of C-BDP, with respect to pristine NCs (I_0), was plotted as a function of the C-BDP concentration $[Q]$. A linear behavior was clearly observed for both NC-5.6 and NC-7.6 with Stern-Volmer quenching constants (K_{SV}) of 26.2 and 14.6 M⁻¹, respectively (**Figure 3.2e**), whereas NC-11.9 was best fitted to a modified SV equation (**3.2**); where α is the fraction of the initial PL accessible to the quencher and K_α is the Stern-Volmer quenching constant for this fraction (**Figure 3.2f**). Time-correlated single photon counting (TCSPC) was used to study the complex PL decays of NCs in the presence of C-BDP dyes. A similar approach was performed for the PL lifetime of NCs (**3.3**), where K_D is now the Stern-Volmer constant for dynamic quenching, which accounts for the collisional interaction during the NC lifetime with $K_D = k_q \tau_0$, being k_q and τ_0 the bimolecular quenching rate constant and PL lifetime of NCs in the absence of C-BDP, respectively (**Figure 3.2g**).

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (3.1)$$

$$\frac{I_0}{I_0 - I} = \frac{1}{\alpha} + \frac{1}{\alpha K_\alpha [Q]} \quad (3.2)$$

$$\frac{\tau_0}{\tau} = 1 + K_D [Q] \quad (3.3)$$

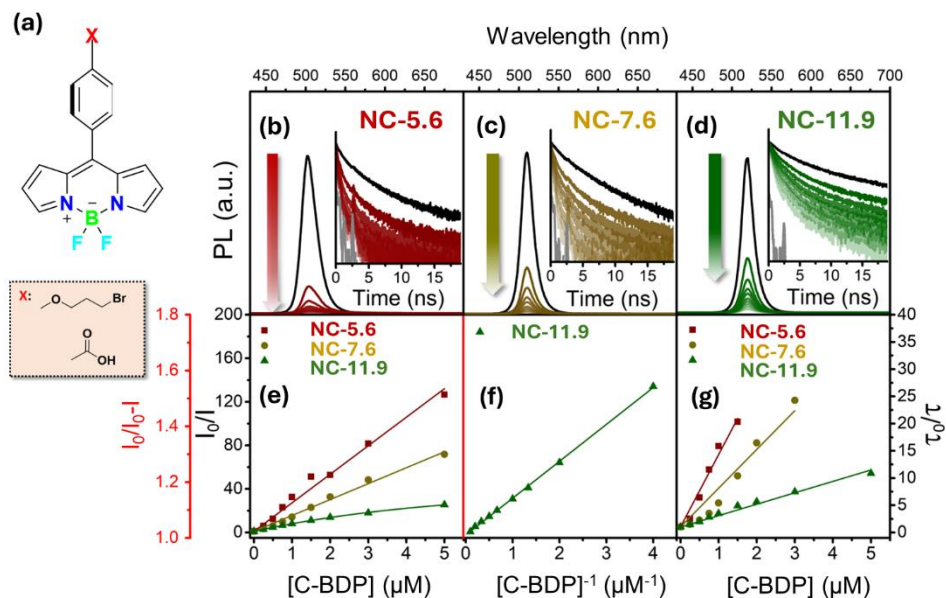


Figure 3.2. (a) Molecular structures for BODIPY dyes used in this study; X = $-\text{O}-(\text{CH}_2)_3-\text{Br}$ (Br-BDP); X = $-\text{COOH}$ (C-BDP). PL spectra of a toluene dispersion of NCs (22 nM) at different concentrations of C-BDP (0–5 μM) recorded at 420 nm excitation wavelength for NC-5.6 (b), NC-7.6 (c), and NC-11.9 (d). Inset: PL decay traces of NCs with increasing concentration of C-BDP (0–3 μM). SV plots obtained for all nanohybrids according to equations 3.1 (e), 3.2 (f), and 3.3 (g).

All quenching constant parameters extracted from the linear fit and quenching efficiency (Φ_Q) at only 1 μM C-BDP are tabulated in **Table 3.1**.

Table 3.1. Quenching constants obtained according to equations 3.1–3.3.

Entry	$K_{\text{SV}} \times 10^6$ [M^{-1}]	$K_a \times 10^6$ [M^{-1}]	α	$K_D \times 10^6$ [M^{-1}]	$k_q \times 10^{15}$ [M^{-1} s^{-1}]	Φ_Q (%) ^a
1	26.2±0.1	-	-	13.3±0.6	2.6±0.2	97
2	14.62±0.03	-	-	7.1±0.5	1.4±0.1	93
3	-	7.5±0.1	0.99	2.1±0.1	0.11±0.01	88

^a The quenching efficiency was calculated at 1 μM of C-BDP dye.

The Φ_Q was surprisingly high at this very low quencher concentration when compared to another reported system comprised of NCs and Rhodamine B.⁸⁰ Evidently, the extent of NC PL quenching follows a trend: the smaller the NC size, the highest PL quenching. The reasons for this observation are: (1) the higher surface-to-volume ratio of the more confined NCs leads to enhanced interaction with the surrounding environment (more C-BDP dyes attached per NC) and (2) the lower donor-acceptor distance, the higher rate constant for energy and charge transfer processes. However, an opposite effect was found for CdSe QDs and Nile red, where larger-sized nanoparticles led to higher FRET efficiency.¹¹³ This is likely due to the different composition and molecular structure of the donor and acceptor systems, which are known to play a significant role in ET between nanoparticles and dyes,²¹⁴ and the distinct size and shape of the nanoparticles, which imply a different extent of surface organic ligand packing and orientation of the molecular dipole.²¹⁵

The higher quenching rate constant determined for all nanohybrids than the diffusion rate constant (ca. $10^{10} \text{ M}^{-1}\text{s}^{-1}$) suggested a close interaction between the NC and C-BDP dyes, thus corroborating that most of the quencher was either bound to the NC surface or encapsulated within the organic ligand shell. Alongside NC quenching, the fluorescence lifetime of C-BDP after sensitization increased from unmeasured values (below our TCSPC setup resolution, IRF = 200 ps) up to 2.14, 0.87 and <0.2 ns for NC-5.6, NC-7.6 and NC-11.9, respectively, consistent with the degree of NC quenching.²¹⁶ Therefore, altering the NC surface shell would deeply impact the nanohybrid excited-state properties.⁶⁹ It has been reported that ligand exchange from OA/OAm ligand pair to a bulkier ligand system, such as didodecyldimethylammonium bromide (DDAB), raises the Φ_{PL} of NCs and provides a bulkier and more stable surface compared to pristine NCs (two long alkyl chain/ligand).⁶⁶ Thus, to evaluate the important role of the NC surface in our nanohybrid, the NC-5.6 nanohybrid, which exhibited the highest quenching among the series, was accordingly modified with DDAB and PbBr_2 by using a ligand

exchange strategy. While the size and morphology of NCs were preserved after the post synthetic treatment (TEM not shown here), recombination kinetics of NCs showed a significant decrease in the nonradiative pathways and therefore the PLQY boosted close to 100 % by reduction of surface trap states.¹³¹ Indeed, the Φ_Q of NC@DDAB-5.6 was considerably much lower compared to pristine NC-5.6 ($K_{SV} = 0.7 \cdot 10^6 \text{ M}^{-1}$), thus highlighting that the nature of the organic ligand shell played a key role in the approach efficiency of C-BDP to the NC surface. However, the fluorescence lifetime of C-BDP was considerably lengthened up to 3.8 ns compared to the freely diffusing C-BDP despite the extremely low NC quenching, revealing that C-BDP dye reduced its rotational freedom when encapsulating within the organic ligand shell, but without playing any role in the photophysical interaction with the perovskite.

3.3.3. Mechanism of quenching of the excited state

To confirm the type of quenching mechanism of the perovskite excited state, the PL excitation (PLE) spectra of the acceptor in the nanohybrid were recorded. The matching of the PLE and absorption spectra conclusively provides strong evidence that the excitation of the donor results in sensitized emission from the acceptor, thereby confirming the occurrence of ET from the NC to the C-BDP dye. **Figure 3.3a,b,c** shows the normalized absorption and PLE (emission wavelength at 650 nm) spectra of the three NC@C-BDP nanohybrids.

The excitation features of the NC in the PLE spectra support the ET mechanism, as confirmed by the downhill in energy from the NC to C-BDP dye (2.41 and 2.38 eV, respectively). Furthermore, estimation of the extent of ET (Φ_{ET}) was found to be 85, 70 and 20 % for NC-5.6, NC-7.6 and NC-11.9, respectively. They all agree with the highest quenching and larger contribution of SET for the more confined NC as per to all these results. The other plausible competitive mechanism for exciton deactivation of the NC (15, 30 and 80 % for NC-5.6, NC-7.6 and NC-11.9,

respectively) could potentially be a hole transfer (hT) pathway from the NC VB to the HOMO level of the C-BDP dye, as shown in **Figure 3.3d**. This hT process has previously been found to be also dependent on the surface ligands as well.²¹⁷

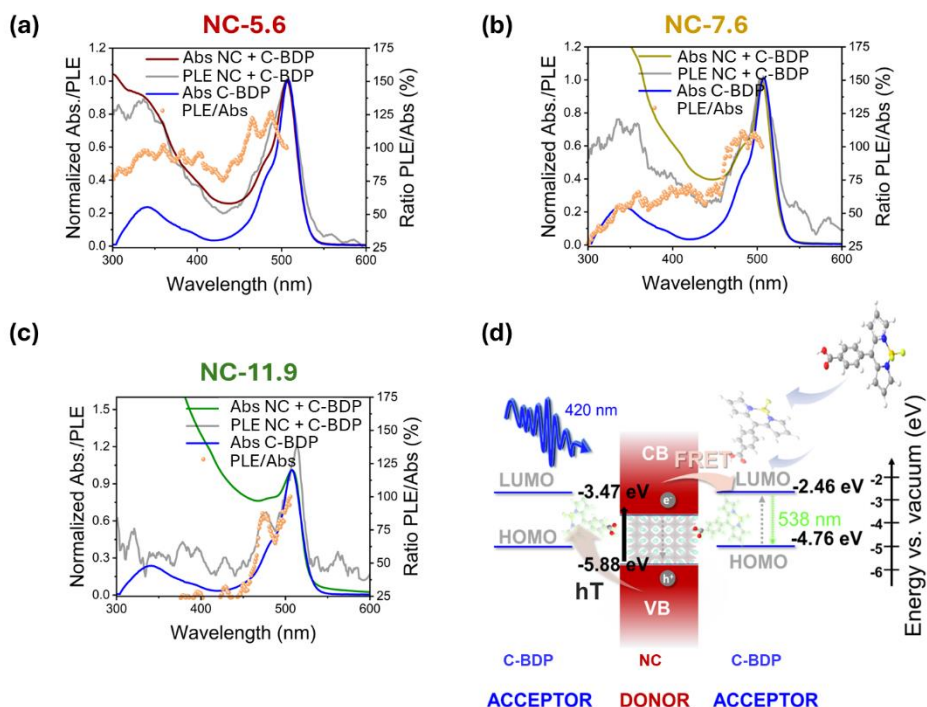


Figure 3.3. Normalized absorption and PLE spectra of nanohybrids, along with that of the dye absorption and the excitation energy transfer efficiency plot for the NC with different sizes: NC-5.6 (a), NC-7.6 (b), and NC-11.9 (c) at 10 μM of dye concentration. (d) Schematic representation of CBM and VBM for the NC-5.6, and HOMO and LUMO energy levels for the C-BDP, showing the two deactivation pathways of the perovskite excited state (FRET and hT).

In order to disentangle between FRET or DET mechanisms, it is important to consider the energetics. According to the alignment of energy levels between the NC and C-BDP dye, which were determined by a combination of electrochemical and optical measurements, the hT pathway would only be possible, whereas not for electron transfer (eT), since the reduction potential of C-BDP is higher than that of

the NC, making the eT from the conduction band to the LUMO level of C-BDP unfavorable and discarding the DET mechanism in our nanohybrid.

On the other hand, to evaluate the importance of the anchoring group of the acceptor and thus, the effectiveness in the FRET process, we performed control experiments with 8-(4-(3-bromopropoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Br-BDP), which lacks the carboxylic acid group. Nevertheless, negligible interaction was found, thus corroborating that the ligand binding is fundamental in mediating the FRET process.²¹⁸

The high quenching constant and the key role of the anchoring group are consistent with a strong binding of the C-BDP dye to the NC surface. We elucidated this binding by ¹H-NMR and FTIR techniques, which undoubtedly confirmed the close interaction of C-BDP dye with the NC surface. The ¹H-NMR titration of the NCs with increasing C-BDP concentrations (ranging from 54 to 930 equivalents) demonstrated a significant downfield shift and broadening of the C-BDP proton signals, especially those protons near the anchoring group and the indacene moiety. The FTIR spectrum of the nanohybrid showed (i) the disappearance of the acidic -OH stretching from the phenylcarboxylic acid moiety of C-BDP, indicating the anchoring of C-BDP to the lead cations at the NC surface via the carboxylate group, (ii) the apparition of a signal at 1710 cm⁻¹, due to the partial exchange of oleate from the NC surface with C-BDP, and (iii) a drastic decrease in the intensity of the band attributed to the C=O stretching of the carbonyl group at 1660 cm⁻¹, as well as those around 1550 and 1400 cm⁻¹, while the two sharp C-O stretching bands around 1100 cm⁻¹ broadened in the nanohybrid. All these findings perfectly agree with the anchoring of C-BDP dye to the NC surface by the carboxylic group, as stated in the introduction chapter.

3.4. Conclusions

In summary, size-selective precipitation has been a prominent approach to successfully isolating three ensembles of different NC sizes. We have demonstrated that quantum-confinement effects govern the quenching efficiency from the colloidal NC to surface-anchored C-BDP dyes. The type of quenching mechanism significantly changes from smaller to larger-sized NCs. By post-synthetic treatment with bulkier DDAB ligands, we evaluated the key role of the surface organic shell in the approach efficiency of C-BDP to NC surface and thus the energy transfer. We proposed a FRET mechanism as the most plausible one to deactivate the NC excited state in NC-5.6 and NC-7.6 nanohybrids, whereas a competitive hole transfer mechanism is predominant in the NC-11.9 nanohybrid, highlighting the importance of quantum confinement. The interaction is further analyzed by ^1H -NMR and FTIR techniques, which supports the strong binding of the carboxylate group (upon deprotonation) to the NC surface.

Chapter 4.

Revealing Exciton Extraction Pathways in Perovskite-Based Nanohybrids

4.1. Introduction

Inspired by nature, recent progress in energy research, such as harnessing excited-state energy transfer to enhance light energy conversion, highlights its potential as a promising approach for developing artificial photosynthetic mimics.²¹⁹ By mimicking the energy and electron transfer processes inherent in natural photosynthesis, artificial photosynthetic systems offer a promising avenue for efficient light energy conversion and energy transduction of solar energy.²²⁰ Particularly, photosensitization processes between inorganic semiconductors and organic dyes have received increased attention for their potential applications in light-driven applications such as photovoltaics, triplet-triplet annihilation-mediated upconversion and photocatalysis, to name a few.^{78, 221} Thus, understanding the underlying mechanisms of sensitization is crucial for unlocking the full potential of light-harvesting assemblies and advancing the development of innovative solutions for energy harvesting, conversion, and utilization.

To this end, the use of perovskite-based nanohybrids is recently being investigated owing to the fact that they can be engaged either in energy transfer (via the singlet or triplet owing to the small separation of 10s of meV between the bright/dark states at room temperature) or selectively transfer electrons or holes to adsorbed molecules.⁷⁹ Besides that, modulation of the NC size and halide ion in the perovskite structure through post-synthetic halide-exchange reactions allows one to fine-tune the perovskite band gap (E_g between 1.7 and 3 eV) and redox potentials,^{82, 222} making these nanohybrids perfect candidates for light-harvesting applications.

While the number of examples reporting SET from NCs to organic dyes has increased, as indicated in the previous chapter,^{80-81, 181, 183-195} not all use ultrafast techniques, such as femtosecond transient absorption (fs-TA) spectroscopy, to

fully unveil the exciton dynamics and inspect for the presence of radicals,^{80-81, 181, 189, 191-192, 194} which is of extremely importance to finally determine the full picture of the sensitization process. Unlike SET, NC-sensitized TET has been developed as a promising route for triplet excited-state generation, from organic dyes to up to molecular antenna complexes, due to the unique properties of the NC sensitizer, such as wide absorption spectrum, extremely large molar extinction coefficient, tunable surface chemistry, superior photostability and small bright/dark state energy gap.²²³

This TET mechanism, as discussed in the introduction section, is extensively recognized to proceed via (i) concerted electron exchange (similar to Dexter),^{82, 168, 170, 172, 175, 182} and (ii) charge-separated states (less frequent).^{172-173, 178} Determining the exact mechanism of sensitization requires meticulous characterization of transient species, such as molecular triplets and cation/anion radical species. Nevertheless, this task often proves to be challenging due to the overlapping spectroscopic signatures of these species, thus obscuring the interpretation.⁸⁶ What is more, accounting for the rapid exciton spin relaxation of one of the carriers inside the nanocrystal (<2 ps for <7.5 nm-sized CsPbBr₃ NCs),²²⁴ due to the electron-hole exchange, surface scattering and spin-spin interaction with surface dangling bond spins, enables a high-yield generation of molecular triplets through charge recombination (CR) of the charge-separated states (CSS) as previously reported.^{172-173, 178} In order to overcome these challenges, a combination of different spectroscopic techniques and powerful kinetic models to deconvolute these complex spectra are desired to extract relevant information regarding transient species.

Apart from changes in semiconductor properties, such as size tuning like in the previous chapter, it has been recently demonstrated that the structural influence of acceptor moieties must be considered for both energy and electron transfer in nanocrystal-Rhodamine nanohybrids.¹⁸⁹ A widely-known strategy to

induce efficient *isc* to populate the triplet manifold in BODIPY dyes, is functionalization with heavy atoms (bromide and iodine) or transition metals (Ir, Pt, etc.).²²⁵⁻²²⁶

However, due to several factors, such as direct photoexcitation to the triplet state is a spin-forbidden process, the *isc* process from photoexcited singlet to triplet is sometimes inefficient, and the energy loss resulting from state crossing is considerable for most molecules,^{86, 221} an attractive approach is to induce the triplet excited state through a direct TET from the sensitizer to the triplet acceptor, or by a sensitization process that combines charge separation (CS) followed by CR of the carriers.²²⁷ In comparison to processes involving the transfer of a single charge carrier, direct TET requires stronger electronic coupling between the donor and the acceptor to facilitate the concerted transport of both electrons and holes.¹⁰⁵ However, only two instances of the charge-mediated mechanism were found for metal chalcogenide quantum dot and BODIPY dyes (QD@BODIPY)^{117, 200} nanohybrids. To the best of our knowledge, TET from NCs to BODIPY dyes has not been reported yet.

Given this insight into this chapter, we identified a valuable opportunity to shed light on the photosensitization mechanism of two organic dyes in nanohybrids based on CsPbBr₃ perovskite NCs functionalized with BODIPY dyes; specifically, 8-(4-carboxyphenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BDP) and 8-(4-carboxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (I2-BDP), named as NC@BDP and NC@I2-BDP, respectively, prepared by a ligand-exchange strategy. The impact of the iodine substituent on the BODIPY core on the photosensitization mechanism of the two nanohybrids has now been thoroughly investigated by employing a wide range of spectroscopic techniques and theoretical calculations, which significantly support the experimental observations and, all together, provide a complete overview of the phenomena taking place in these nanohybrids. Whereas a mainly FRET mechanism

(82 %) dominates in NC@BDP, a charge-mediated TET mechanism (64 %), that outcompetes hot exciton thermalization to the band edge and FRET processes in NC@I2-BDP, led to efficient formation of I2-BDP molecular triplets that enabled productive singlet oxygen ($^1\text{O}_2$) generation. Our findings not only deepen our fundamental understanding of the energy transfer funneling between CsPbBr₃ NCs and BDP or I2-BDP dyes in the two novel nanohybrids, but they also showcase the dual role of perovskite nanocrystals in NC@I2-BDP as highly efficient triplet photosensitizer and photocatalyst in the oxidation of α -terpinene to ascaridole.⁸³

4.2. Experimental section

Methods

4.2.1. Synthesis of lead-halide perovskite nanocrystals

The CsPbBr₃ perovskite nanocrystals (NCs) were synthesized accordingly by a previously reported hot injection method with slight modifications.⁵¹ First of all, a solution of cesium oleate (Cs-oleate, 0.125 M in 1-ODE) was prepared by mixing cesium carbonate (Cs₂CO₃, 407 mg, 1.24 mmol) and OA (1.25 mL, 3.53 mmol) in 1-ODE (20 mL) in a 50 mL three-neck round-bottom flask and the mixture was degassed under vacuum (0.49 mbar) at 120 °C for 1 h. Then, the mixture was heated up to 150 °C under N₂ atmosphere until Cs₂CO₃ was completely dissolved (ca. 30 min) obtaining a clear solution. Afterward, the solution was slowly cooled down to room temperature and stored under N₂ atmosphere for being used. On the other hand, lead bromide (PbBr₂, 72 mg, 0.196 mmol), OAm (0.71 mL, 1.5 mmol) and OA (0.53 mL, 1.5 mmol) were loaded into a 50 mL three-neck round-bottom flask with 1-ODE (4.8 mL) and degassed under vacuum (1 mbar) at 100 °C for 30 min. Then, the valve of the Schlenk line was changed to N₂ flow and after 15 min, it yielded a colorless solution. At the same time, the Cs-oleate solution was heated up to 120 °C under N₂ atmosphere. After complete solubilization of the lead bromide salt, the

reaction temperature was raised to 190 °C and Cs-oleate solution (0.6 mL, 0.075 mmol) was swiftly injected through a purged syringe and, 5 sec later, the reaction was quenched through an ice/water bath (bath temperature ca. -2 °C) and the NCs were finally subjected to purification. The crude dispersion was first diluted with 5 mL of toluene and transferred to a 50 mL centrifuge tube to initiate the isolation process. The crude was first centrifuged at 2500 rpm for 10 min (15 °C). The supernatant was carefully pipetted out and transferred to another 50 mL centrifuge tube. Anhydrous MeOAc (8 mL) was added to the supernatant to help the precipitation of smaller NCs and then it was centrifuged at 5000 rpm for 10 min (15 °C). This second precipitate was redispersed in 2 mL of toluene. This dispersion was finally filtrated out through a 0.2 µm membrane filter to yield highly colloidal, homogeneous CsPbBr₃ NCs dispersion. Based on the molar extinction coefficient for 6.5 nm-sized CsPbBr₃ NCs, a concentration of ca. 1.2 µM was obtained.

4.2.2. Synthesis of 8-(4-carboxyphenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

8-(4-carboxyphenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BDP) dye was synthesized according to the reported procedures.²²⁸ First, 4-carboxybenzaldehyde (0.6 g, 4.0 mmol) was added to a 500 mL round-bottom flask in 200 mL of anhydrous DCM. Then 2,4-dimethyl pyrrole (8.97 mmol, 0.92 mL) was added followed by the addition of TFA (30 µL) and the solution was stirred overnight under Ar atmosphere at room temperature. After the addition of a solution of DDQ (4 mmol, 0.9 g) in DCM (100 mL) to the reaction mixture, stirring was continued for 10 min. Then 8 mL of TEA and 8 mL of BF₃·OEt₂ were successively added. After 12 h, the reaction mixture was treated with water (300 mL). Then the mixture was extracted into DCM. The organic layer was dried over anhydrous Na₂SO₄. The solvent was then evaporated and the residue was purified by silica gel

column chromatography (DCM:MeOH = 30:1 v/v, and Hex:AcOEt = 3:1 v/v). The BDP was obtained as a red solid with a chemical yield of 13 %.

4.2.3. Synthesis of 8-(4-carboxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

Synthesis of 8-(4-carboxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (I2-BDP) was also synthesized according to a reported method.²¹³ To the solution of BDP (100 mg, 0.27 mmol) in 20 mL of EtOH, iodine (171 mg, 0.68 mmol) and iodic acid (95 mg, 0.54 mmol) were dissolved in 1 mL of water. The reaction mixture was stirred at 60 °C for 2 h. Then, a saturated Na₂SO₄ solution was added, and EtOH was removed under reduced pressure. The residue was extracted with DCM. The organic layer was dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography using DCM:MeOH = 30:1 v/v) as eluent to give rise to I2-BDP as a deep red solid with a chemical yield of 80 %.

4.2.4. Preparation of perovskite-BODIPY nanohybrids

An aliquot of the as-synthesized NCs in toluene was evaporated and then redispersed in hexane because of the better solubility of both dyes in toluene compared to hexane. Overall, dye powders (484 nmol) were added to a 1.5 mL NCs dispersion in hexane (0.24 nmol) optically matched at 0.64 OD at 450 nm in 1 cm pathlength cuvette in a molar dye/NC ratio of ca. 2000. The mixtures were stirred for 15 min and then filtrated through a 0.2 µm membrane filter to remove the unreacted solid and/or formed aggregates. The dyes in the final hexane dispersion were bound/encapsulated to the NC surface.

Instrumentation

4.2.5. Femtosecond transient absorption spectroscopy

Femtosecond transient absorption (fs-TA) spectroscopy was used to probe the early time exciton dynamics of NCs. Fs-TA experiments were performed on a Helios spectrometer (Ultrafast Systems) with an IRF of ca. 250 fs. The IRF of the system was assumed to be equal to that of the pump-probe cross-correlation determined from the measurement of the instantaneous stimulated Raman signal from the pure solvent (in a 2 mm cuvette). To avoid photodegradation, the solutions were in movement using a motorized translating sample holder. An optical delay line of up to 7 ns was employed. An excitation flux of $50 \mu\text{Jcm}^{-2}$ was employed for all measurements. Data analysis was made on Surface Xplorer and GloTarAn software.²²⁹ The data was globally analyzed by using a parallel kinetic model. To fit the data, we based on a parallel kinetic model because of the complexity of the photophysical picture, where every component decays independently resulting in decay-associated spectra (DAS). The basic principle of DAS in Global analysis is to decompose simultaneously by using the kinetic model of the time-resolved spectra into a set of kinetic components, each associated with a specific decay time constant.

4.2.6. Spectroelectrochemical measurements

Spectroelectrochemistry (SEC) was used to study the changes of the absorption features as a function of a bias. A three-electrode electrochemical system comprised of an Ag wire, Pt wire and ITO substrate as the pseudo-reference, counter and working electrode was used in a quartz home-made cell. The I2-BDP dye was drop-casted onto the transparent ITO substrate. An electrolyte solution of 0.5 M TBAPF₆ was prepared in anhydrous ACN. This quartz cell was placed along the optical path of the UV-vis spectrophotometer. A chronoamperometry

measurement of 2 min was applied for a given potential during the acquisition of the UV-vis spectrum.

4.2.7. Quantum electronic calculations

All theoretical calculations were based on the density functional theory (DFT) type, using GAMESS-US version R3.²³⁰ All the structures in the ground and excited state were fully optimized without any symmetry restriction using LC-BPBE ($w = 0.20 \text{ au}^{-1}$) level of theory in toluene as solvent. The nature of the stationary points determined by geometry optimization was verified by vibrational frequency calculations carried out at the same level of theory. All the reported geometries corresponded to minima. In time-dependent DFT (TD-DFT) calculations of Franck-Condon (FC) excitations, the dielectric constant of the solvent was split into a “bulk” component and a fast component, which is essentially the square of the refractive index. In “adiabatic” conditions only the static dielectric constant is used. A 6-31G** basis set was used in either DFT or TD-DFT calculations. The results obtained with the LC-BPBE(20) functional are essentially unscaled raw data from calculations; for the $S_0 \rightarrow S_n$ transitions, a small correction, which results in the subtraction of 0.05 eV, to account for the difference between zero point and the first vibronic level, was considered. For the resulting optimized geometries, TD-DFT calculations (using the same functional and basis set as those in the previous calculations) were performed to predict the vertical electronic excitation energies. Molecular orbital contours were plotted using the ChemCraft 1.7 program. Frequency analysis for each compound was also computed and did not yield any imaginary frequencies, indicating that the structure of each molecule corresponds to, at least, a local minimum on the potential energy surface.

4.2.8. Photocatalytic reactions

The synthesis of ascaridole through photooxidation of α -terpinene promoted by NC@I2-BDP nanohybrids was conducted by using 0.0001 μmol NC,

0.17 μmol I2-BDP, 614.4 μmol α -terpinene in 0.65 mL deuterated benzene (C_6D_6). The α -terpinene was previously purified through column chromatography giving rise to a 98 % and 2 % purity of α -terpinene and *p*-cymene, respectively. The reaction was carried out under O_2 -saturated air atmosphere, 2 h of continuous irradiation under visible-light LED excitation at 450 nm, and 15 $^\circ\text{C}$. The conversion was calculated based on product generation. Chemical yield of ascaridole and *p*-cymene products was calculated by using CHCl_3 as the intern standard.

4.3. Results and discussion

4.3.1. Steady-state and time-resolved optical properties of perovskite-BODIPY nanohybrids

First of all, CsPbBr_3 NCs were synthesized by the conventional hot-injection approach in the weak quantum confinement regime (6.4 ± 0.6 nm) considering the better ability of ET, as previously seen.^{82, 206} Two BODIPY dyes were synthesized, namely, BDP and I2-BDP, according to procedures found in the literature.^{213, 228} The NC@BODIPY nanohybrids were prepared on this occasion by a ligand-exchange protocol, and purified by filtration.

The optical properties of NC@BDP and NC@I2-BDP nanohybrids were compared with the pristine NC and BODIPY controls under the same conditions, i.e., the same absorption at the excitation wavelength. UV-vis absorption spectra and TEM images of NC@BDP and NC@I2-BDP nanohybrids are shown in **Figure 4.1a,b**. The lowest-energy exciton absorption peak of the NC at 496 nm confirms a weak quantum confinement regime of NCs. It is noteworthy that the size and morphology of the NC in the nanohybrid are preserved after the ligand exchange post-treatment. The absorption profile of NC@BDP showed a completely linear combination of NCs and BDP dye. The slight mismatch around the exciton peak is ascribed to the subtle

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exciton shift upon anchoring the BDP dye to the NC surface. By contrast, the introduction of two iodine atoms directly appended to the BODIPY core strongly impacts the optical properties of the dye, producing a ca. 50 nm-redshift of the absorption peak (540 nm),²³¹ thus improving the light-harvesting properties in the visible spectral windows.

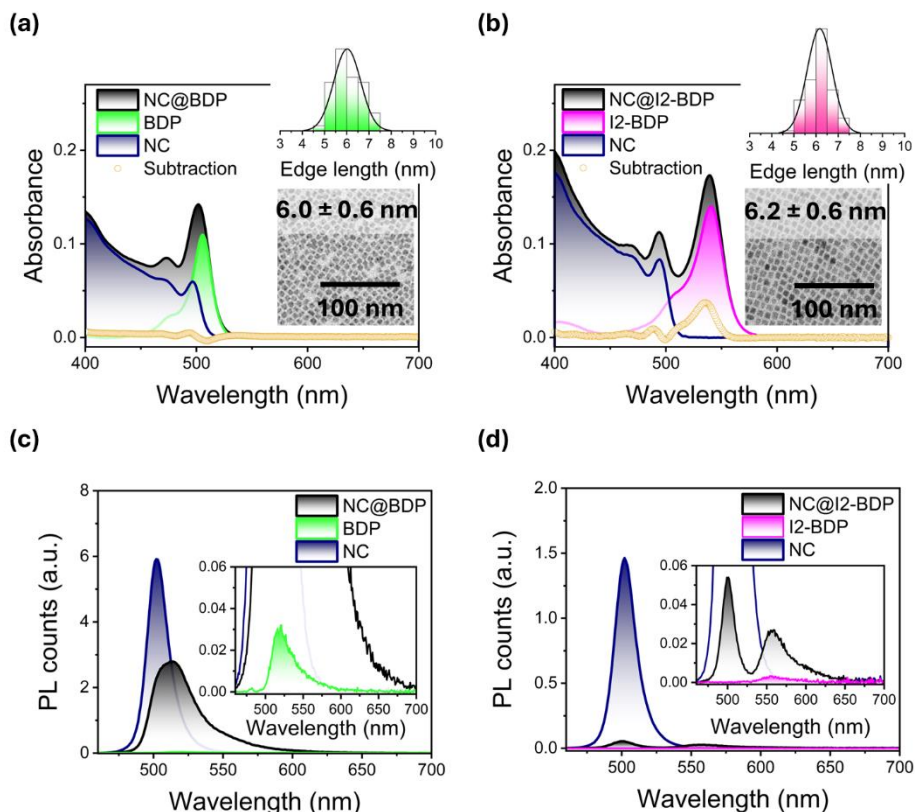


Figure 4.1. Absorption spectra of (a) NC@BDP and (b) NC@I2-BDP nanohybrids along with their corresponding controls in toluene. The subtraction spectrum is shown (orange dots). Both insets show histograms (top) accounting for 100 nanocrystals from TEM images (bottom). The scale bar is 100 nm. Steady-state PL spectra of (c) NC@BDP and (d) NC@I2-BDP along with their respective controls under 420 and 450 nm excitation, respectively. Both insets show enlarged emission windows.

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Based on the molar extinction coefficient, the dye/NC molar ratios of 80 and 250 were determined for NC@BDP and NC@I2-BDP, respectively. The considerable increase and blueshift of the I2-BDP absorption peak in the NC@I2-BDP is assigned to surface crowding of the I2-BDP, accounting for the better interaction of I2-BDP with the NC surface with respect to BDP.

The excited-state properties were evaluated by selectively exciting the NCs, being 420 and 450 nm for NC@BDP and NC@I2-BDP, respectively. Interestingly, the presence of methyl groups directly appended to the BODIPY core at the 1,7-positions significantly increased the intrinsic Φ_F owing to the free rotation blocking along the single bond between the phenyl and BODIPY core moieties.²⁰⁶ Nevertheless, the presence of iodine atoms directly attached to the BODIPY core favored the *isc* pathway via the heavy-atom effect. In this respect, the Φ_F of BDP and I2-BDP was 52 and 3 %, respectively. Regarding the excited-state properties of the NC in the nanohybrids, a strong PL quenching of NCs (maximum at 502 nm) concomitantly with a fluorescence enhancement (50-fold registered at 600 nm, where NC scarcely emits) of BDP (maximum at 520 nm) in the NC@BDP was observed, thereby suggesting a clear photosensitization process (**Figure 4.1c**). Although the Φ_Q could not precisely be determined due to the overlapping of sensitized fluorescence with that of the NC PL, a significant degree of PL quenching is anticipated given the substantial intensity of the sensitized fluorescence. Conversely, a Φ_Q of 97 % was calculated for the NC@I2-BDP, but only a 9-fold fluorescence enhancement was noticed (**Figure 4.1d**), thereby suggesting that CT outcompetes ET.^{117, 199}

TCSPC was used to study the complex band edge recombination dynamics of NCs in the nanohybrids. The decay trace of NCs was best fit to a triexponential function as a consequence of the surface trap-assisted and direct electron-hole recombination states.²³²⁻²³³ The shortest time component was significantly quenched (81 %) with a time constant of 154 ps in the NC@BDP compared to the

others, while the fluorescence of BDP at 570 nm raised with an evident rise time component of 110 ps, which was absent in the BDP control. While this observation appears to support the sensitization process by the NCs. It is worth noting that this lifetime is below the resolution limit of the TCSPC setup (IRF ca. 150 ps). On the other hand, the PL decay of NCs was completely quenched in the NC@I2-BDP (below setup resolution), but the rise time component of I2-BDP (registered at 600 nm) was unaffected, thus highlighting SET does not prevail in this nanohybrid or occurs rapidly on an earlier time scale.

4.3.2. Ultrafast properties of perovskite-BODIPY nanohybrids

Limitations in our TCSPC setup may impede a thorough analysis of PL lifetimes. To explore the hot- and band-edge excitons dynamics and the evolution of charge carriers, fs-TA was performed. **Figure 4.2a,b** shows two-dimensional (2D) pseudocolor plots of the NC and NC@BDP as a function of probe wavelength and delay time following 420 nm pump excitation (3 eV) under relatively low excitation fluence ($0.5 \mu\text{Jcm}^{-2}$).

The 2D pseudocolor plot shows several features: (i) a strong exciton bleaching (XB) centered close to the average E_g at 498 nm due to state-filling effects at the edges of the valence and conduction bands; (ii) a weak and broad excited-state absorption (ESA 1) extending above the E_g at 485 nm, ascribed to transitions to higher energy levels, and (iii) a sub-band gap, short-lived excited-state absorption (ESA 2) at 510 nm related to intraband cooling from hot states to the band edge.^{121, 234} Multiexponential fitting of the XB band yielded the following time constant parameters: 0.28 ps (rise), and 151 ps (5 %) and 3.57 ns (95 %) assigned to vibrational cooling, surface trapping, and electron-hole direct radiative recombination, respectively.

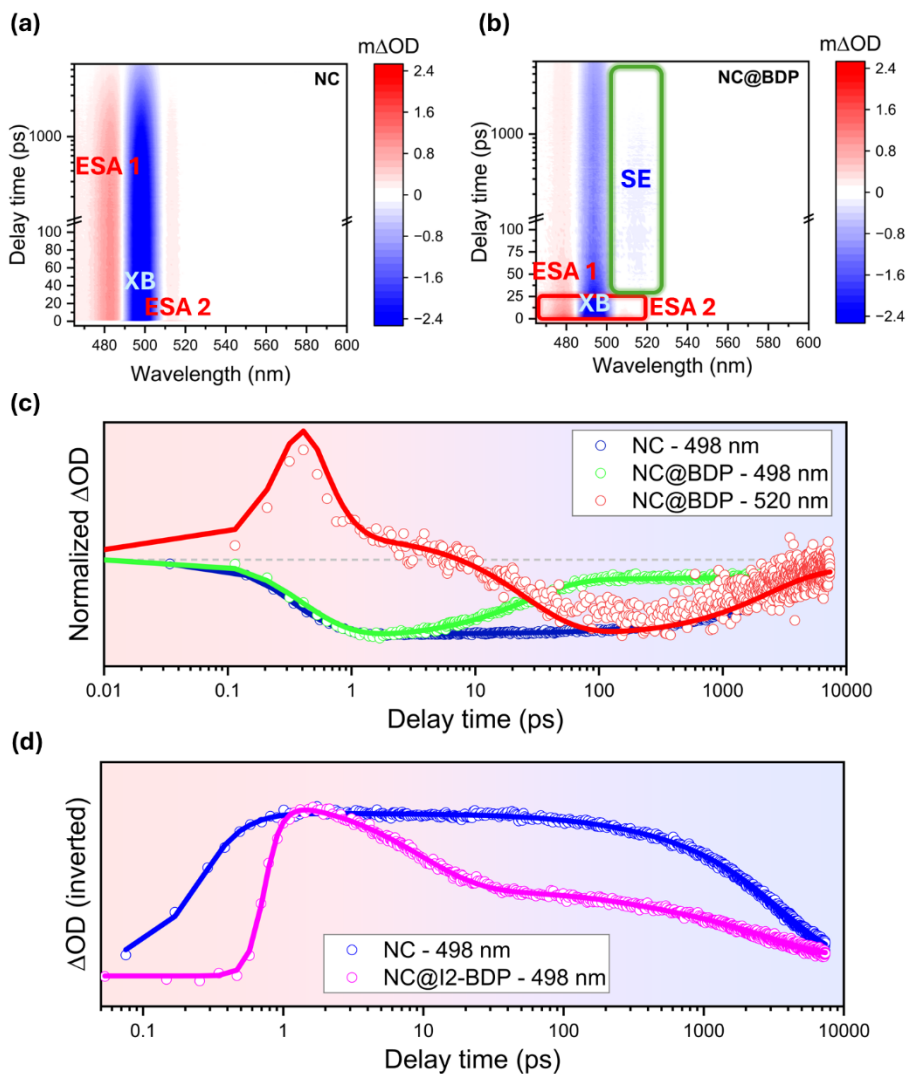


Figure 4.2. 2D pseudocolor TA plots of (a) NCs and (b) NC@BDP nanohybrids in toluene. (c) Kinetic traces of the pristine NC and NC@BDP nanohybrid (hollow circle) probed at wavelengths of 498 and 520 nm, respectively, and the best multiexponential fittings (solid line). (d) Inverted kinetic traces of the pristine NC and NC@I2-BDP nanohybrid (hollow circle) probed at 498 nm, and the best multiexponential fittings (solid line). The kinetics are normalized for better comparison.

A strong quenching of the XB and ESA 1 features was observed concomitantly with the apparition of a negative band centered at 520 nm, indicative of exciton dissociation due to the creation of a new nonradiative pathway. The new negative band perfectly matches the sensitized fluorescence of the BDP dye. Multiexponential fitting of the XB band of NC@BDP yielded 0.29 ps (rise), 26 (85 %) and 7 ns (15 %), respectively, which perfectly matches with that of the fluorescence rise of BDP at 520 nm. Therefore, this new component confirms the direct SET from the NC to BDP dyes as the main deactivation channel with a rate constant of $3.8 \times 10^{10} \text{ s}^{-1}$, being higher than that of a recent CsPbBr₃ nanoplatelet-BODIPY system ($3.8 \times 10^9 \text{ s}^{-1}$),¹⁹⁴ and the solvent diffusion rate constant (ca. 10^{10} s^{-1}),¹⁹⁶ highlighting that the BDP dye is tightly anchored to the NC surface by the carboxylate group.

On the other hand, NC@I2-BDP yielded a rather different photophysical picture. Quenching of the XB feature was even faster than that of the NC@BDP, along with a noisy band between 520 and 560 nm, where the GSB of the I2-BDP dye was expected to appear. The pump wavelength was adjusted to 450 nm to selectively excite the NCs. Although the photoexcitation of NCs at 450 nm yielded the same components as the NC excited at 420 nm, there was a shortening of the carrier cooling time from 0.28 to 0.22 ps, in agreement with the reported dependence of this process with the excitation wavelength.²³⁵ Multiexponential fitting analysis of the XB feature of the NC@I2-BDP showed the following time constant components: 0.18 ps (rise), 9.5 ps (55 %), 273 ps (11 %) and 2.8 ns (34 %) and an infinite component (which extends beyond our 7 ns time resolution). Firstly, there is a shortening of the hot-exciton state compared to the pristine NC (from 0.22 to 0.18 ns). Therefore, we attributed this process to a charge transfer event with a rate constant of $1 \times 10^{12} \text{ s}^{-1}$ from hot states, thereby competing vibrational cooling.²³⁶ This ultrafast rate constant of charge transfer is in the order of other hot charge carrier transfers from NC to 4-mercaptophenol, benzoquinone and phenothiazine.²³⁶⁻²³⁷ This observation is particularly intriguing as the vibrational

cooling of hot carriers from higher-energy to band-edge states usually represents a significant energy loss pathway in solar cells, thus impacting the Shockley-Queisser efficiency that constrains their potential photovoltaic application.²³⁸

To have a deeper understanding of the rest of the photophysical processes, the data was evaluated by Global analysis using a parallel kinetic model, where the number of monoexponentially decaying independent components provided decay-associated spectra (DAS) as seen in **Figure 4.3a,b**. Global analysis results showed the same number of components as those obtained by single wavelength analysis. The shape of the spectrum of the first component (hot state of the NC) confirms the nature of such species, which was accelerated compared to the pristine NC (from 0.21 ps to 0.16 ps), whereas the second component of 10 ps with an excited-state absorption band around 544 nm and the XB feature was detected, supporting the charge separation on a previous stage (ultrafast scale), and subsequently leading to charge recombination in 10 ps. Charge recombination in 50 ps has previously been found in BODIPY-C₆₀ dyads.²³⁹ It is worth noting that both electron and hole transfer are possible given the energy level alignment of the NC and I2-BDP. The third component of 204 ps exhibited two components: XB and I2-BDP fluorescence features, ascribed to the short lifetime of the sensitized fluorescence of I2-BDP dyes due to the heavy-atom effect. The fourth component of 2.4 ns corresponds to the fraction of NCs that does not recombine to give any species of I2-BDP since the XB feature was only present. The fifth component (fixed to 49 μ s) was determined based on the extended lifetime of GSB of I2-BDP, which exceeds the resolution limit of our setup. Additionally, it was corroborated by the population of the triplet excited state of the I2-BDP dye, as measured in nanosecond transient absorption (ns-TA) spectroscopy and singlet oxygen (¹O₂) phosphorescence experiments (not shown here).

We tentatively assigned the charge-separated state to an ultrafast hole transfer from NC-hot states to the HOMO level of the I2-BDP dye based on (i) the

acceleration of the carrier cooling time in the NC@I2-BDP compared to the pristine NC (0.16 ps vs 0.21 ps, respectively), and (ii) the presence of an excited-state absorption at 544 nm associated to I2-BDP radicals (either cation or anion radical) at 10 ps. Although, it has been reported that hole carrier extraction is easier than the electron,²⁴⁰ it still needs a careful study to assign the 544 nm feature to the I2-BDP cation radical.

To go a step further and decipher the nature of the CSS, spectroelectrochemistry (SEC) was conducted on I2-BDP dyes to identify the absorption spectrum of the cation/anion radical of I2-BDP. It can be seen from **Figure 4.3c**, the apparition of a band below 560 nm (overlapped with the absorption peak of I2-BDP when an anodic bias of + 1.4 V is applied), clearly absent under a cathodic bias of - 0.9 V (**Figure 4.3d**), thus agreeing well with the excited-state absorption observed in the DAS at 544 nm. Besides that, theoretical calculations predicted optical transitions in the ground state at 572 nm (HOMO-9 to LUMO) with an oscillator strength (f) of 0.092 for the cation radical of I2-BDP (I2-BDP^{•+}). Notably, no band was observed in that region for the radical anion and the neutral species (not shown here). Accordingly, all the experimental data and theoretical predictions mentioned above strongly support the formation of I2-BDP^{•+} as an intermediate state in the photosensitization process of I2-BDP within the NC@I2-BDP system.

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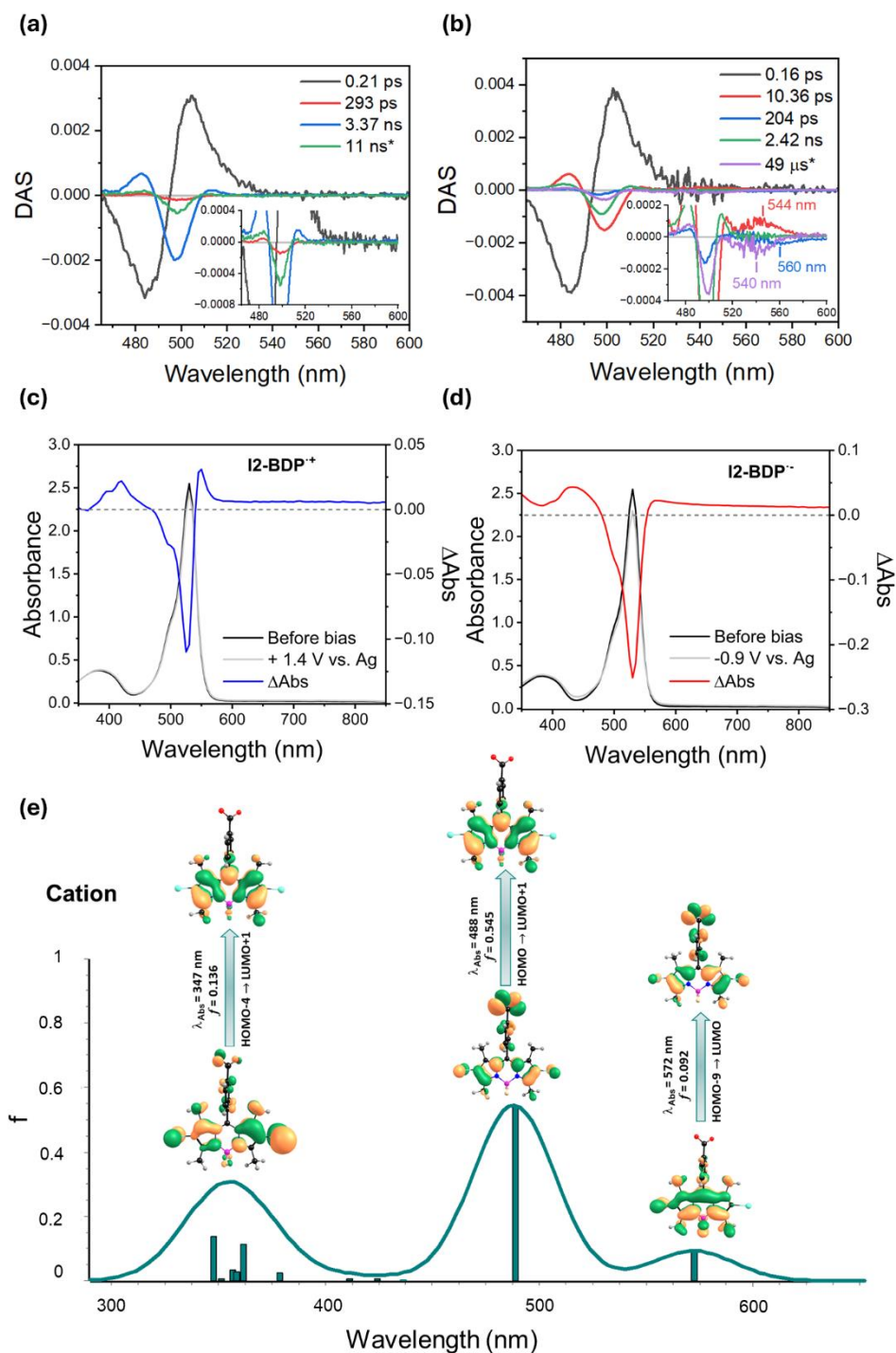


Figure 4.3. DAS obtained using Global analysis for (a) NC and (b) NC@I2-BDP under 450 nm pump excitation in toluene. Absorption spectra (before and after applying a bias) and the difference spectra of I2-BDP dye under anodic (c) and cathodic bias (d). (e) TD-DFT electronic absorption spectra and surfaces of NTOs of the probe I2-BDP cation radical in toluene.

4.3.3. Probing the sensitization mechanisms

Iodine substitution on the BODIPY core strongly impacts the sensitization mechanism of I2-BDP in the NC@I2-BDP, as it was demonstrated in the previous section. The extent of NC features in the PLE spectrum of the nanohybrids dictates the amount of ET from NCs to the dyes. Accordingly, we estimated the contribution of ET in each nanohybrid (not shown here) to be 82 % and 36 % for NC@BDP and NC@I2-BDP, respectively as shown in **Figure 4.4a,b** (right pathway). The significantly higher Φ_{ET} obtained for NC@BDP compared to NC@I2-BDP is consistent with the greater J of $2.4 \cdot 10^{15} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$ with respect to $6.6 \cdot 10^{14} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$ between the NC donor emission and dye acceptor absorption for NC@BDP and NC@I2-BDP, respectively. Interestingly, the extent of ET in NC@BDP calculated by this methodology (82 %) agrees well with the contribution of the 26 ps component in fs-TA (85 %). In order to discern between FRET or DET mechanisms, it was studied elsewhere that the FRET mechanism prevailed in CsPbBr₃ and Rhodamine B systems with $J > 2.04 \cdot 10^{14} \text{ nm}^4 \text{M}^{-1} \text{cm}^{-1}$.⁸⁰ Thus, given the relatively high J observed in both nanohybrids compared to the previously reported value, and the improbable for DET mechanism due to the higher energy of the LUMO level of the BDP dye compared to the CB of the NC for the simultaneous electron exchange, we inferred a pure FRET mechanism for both systems.

Therefore, the remanent deactivation pathway of the NC excited state in both nanohybrids is likely to be a charge transfer mechanism, specifically hole transfer (hT). In the NC@I2-BDP nanohybrid, there is a clear predominant contribution from this nonradiative pathway, i.e., a combination of hot and

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thermalized hole transfer, as previously discussed and supported by the energetics illustrated in **Figure 4.4b** (left pathway). Charge transfer processes from different states have already been shown in reported systems.²⁴¹⁻²⁴³ This assertion was further corroborated by fs-TA measurements, SEC studies, and theoretical calculations. According to the energy level alignments (**Figure 4.4a**), the formation of the BDP^{**} as a consequence of the charge transfer from the NC to the BDP in the NC@BDP (18%) was proposed.

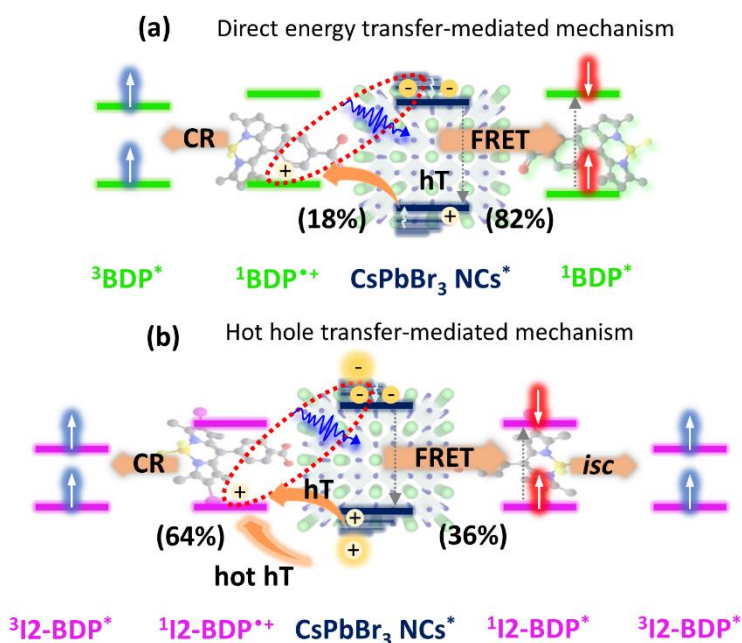


Figure 4.4. Schematic diagrams of the proposed photosensitization mechanisms for (a) BDP and (b) I2-BDP dyes in NC@BODIPY nanohybrids. The OA and OAm ligands are not shown for clarity.

Interestingly, CR of the CSS to populate the triplet excited state manifold has ultimately been investigated in different quantum dots-organic systems due to the ill-defined spin quanta configuration of the quantum dot as a consequence of

the small bright-dark energy splitting and the rapid spin relaxation of the remaining carrier in the nanocrystal.^{101, 178, 224, 244} Consequently, to confirm such a triplet excited state population through NC sensitization, $^1\text{O}_2$ phosphorescence experiments were performed. Overall, BODIPYs do not efficiently undergo *isc* to the triplet excited state.²⁴⁵ However, BODIPYs functionalized with heavy atoms in the core, such as iodine, can enhance the *isc* quantum yield (Φ_{isc}) by increasing the spin-orbit coupling (SOC) effect.²⁴⁶ Surprisingly, optically matched solutions (0.1 OD) of I2-BDP and NC@I2-BDP dispersions, with excitation wavelengths of 550 nm and 450 nm to selectively excite the I2-BDP and NC, respectively, exhibited nearly identical intensities of $^1\text{O}_2$ phosphorescence emission, thereby suggesting an efficient population of the I2-BDP triplet state sensitized by NCs. However, NC@BDP produced a small, but detectable amount of $^1\text{O}_2$ emission when selectively excited at 420 nm, unlike directly exciting at 515 nm. This indicates that selective photoexcitation of NCs resulted in a minor contribution from the triplet state in the BDP dye, which was not achievable via direct excitation of BDP at 515 nm. Thus, this triplet sensitization in NC@BDP is assumed to take place by the residual charge-mediated pathway (18 %), as occurred in the NC@I2-BDP. Additional control experiments were conducted to discard the possibility of sensitization by the pristine NCs and dyes at 420 and 450 nm.

The above-mentioned results clearly indicate that the photon absorbed by the NC in the NC@I2-BDP can be used to trigger photochemical reactions involving long-lived triplet excited states, such as that of the I2-BDP. Thus, NC@I2-BDP can be used as an energy transfer photocatalyst for the oxidation of α -terpinene to ascaridole (24.5 % yield) and *p*-cymene (23.4 %), as typical conversion under visible-light excitation. As proof-of-concept, the synthesis of ascaridole, using a very small amount of NC (0.1 nmol), 2 h of irradiation at 450 nm, and O_2 -saturated air atmosphere, has been here demonstrated. Control experiments revealed that in

the absence of any NC and photocatalyst, ascaridole was not formed and *p*-cymene was obtained with ca. 20 %.

4.4. Conclusions

In conclusion, nanohybrids based on CsPbBr₃ NCs and BODIPY dyes have successfully been prepared through a ligand exchange post-synthetic strategy. The nanohybrids prepared by this strategy enabled an efficient deactivation of the perovskite excited state by surface-anchored BODIPY dyes by using a combination of steady-state and time-resolved absorption and PL spectroscopy. Our findings demonstrate that the incorporation of iodine atoms directly onto the BODIPY core profoundly influences the sensitization mechanisms of BODIPY dyes in the nanohybrids. According to the in-depth analysis, the main quenching mechanism for NC@BDP is FRET (82 %). The relatively low intensity of ¹O₂ phosphorescence emission can be attributed to the limited occurrence of the hole transfer process (18 %) from the NC VB to the HOMO level of the BODIPY dye. Subsequent CR of the CSS generates molecular triplets, which are not accessible by direct excitation due to inefficient *isc* in BDP. Thus, accessibility to the triplet manifold in BDP dyes is successfully addressed through this sensitization approach. On the other hand, a predominant charge-mediated TET mechanism (64 %) is found for the NC@I2-BDP, where hot and thermalized hole charge carriers are transferred from the NC VB to the HOMO level of the BODIPY dye resulting in a CSS (64 %), which subsequently recombines leading to molecular triplets in I2-BDP dye, given the low-lying energy of the I2-BDP triplet excited state (1.62 eV) with respect to the CSS in toluene and the rapid spin flip of the carriers inside the NC (<2 ps). This CSS was confirmed by (i) the detection of an ultrafast hot hole extraction component (0.16 ps), (ii) the presence of an excited state absorption at 544 nm, and (iii) the use of spectroelectrochemistry and theoretical calculations to support the formation of

the radical cation of the I2-BDP dye. The remaining contribution to the I2-BDP sensitization (36 %) stems from a FRET mechanism to yield I2-BDP molecular singlets, given the relatively high J , which further evolves to the triplet excited state owing to the efficient *isc* induced by the heavy-atom effect. In the end, the effective generation of the I2-BDP molecular triplets, confirmed by $^1\text{O}_2$ measurements, enabled the utilization of the NC@I2-BDP as an energy transfer photocatalyst for the oxidation of α -terpinene to ascaridole, yielding moderate results.

Chapter 5.

Unraveling the Dexter Energy Transfer Mechanism in Perovskite- Phthalocyanine Nanohybrids

5.1. Introduction

The rational design and development of materials that mimic biological systems to efficiently harvest visible photons is still a challenging task since it requires a great light-harvesting capability, precise control over the material electronic structure and proper molecular interactions to successfully transduce the solar energy by means of energy transfer cascade processes.²²⁰ Over the past decade, phthalocyanine (Pc) dyes have become key light-harvesting materials for low-temperature, solution-processed photovoltaic cells, including DSSCs.²⁴⁷⁻²⁴⁸ Their structural similarity to chlorophylls in natural photosynthetic systems and their strong, tunable absorption in the visible spectrum make Pc derivatives widely used as sensitizers in DSSCs.²⁴⁹

In particular, Zn-carboxyphthalocyanine (ZnPc, TT1) dyes have attracted increasing attention owing to the optical and redox chemistry associated with both the 18 π -electron system of the Pc macrocycle and the central metal ion,²⁵⁰ displaying a strong absorption (ca. $10^5 \text{ M}^{-1}\text{cm}^{-1}$) in the 650 – 700 nm region, high-chemical and -thermal stability, good carrier mobility and facile synthesis through their appropriate design, making them a robust charge selective layer, passivation layer or both in perovskite solar cells.^{247, 251} However, the low absorption coverage in the entire green region greatly limits its light-harvesting efficiency. By contrast, nanoscale-based light-harvesting systems have rapidly grown in the past few years to tackle these issues.

Traditional chalcogenide quantum dots (QDs) are found to be very promising light harvesters due to their size-, shape-, and composition-dependent electronic properties as previously introduced.¹⁶ Special attention has recently been given to metal-halide perovskite nanocrystals (NCs), which have shown to exhibit several advantages over traditional QDs such as (i) superior molar extinction

coefficient, (ii) higher Φ_{PL} due to the defect-tolerance nature, and (iii) tunable CB and VB by halide alloying, among others.³⁹ Therefore, nanohybrids based on NCs and organic molecules such as Pc dyes could have attractive implications for panchromatic light harvesting and visible-light photocatalysis.²⁵² Previous works have investigated the interaction between NCs and porphyrin dyes, which share a central macrocyclic structure similar to phthalocyanines.²⁵³ CsPbBr₃ NCs enhance the light-harvesting efficiency and photoresponse of zinc porphyrin (ZnP) via a FRET process with over 70 % efficiency.²⁵⁴ Ultrafast hot hole transfer from CsPbBr₃ to 5,10,15,20-tetra(4-pyridyl) porphyrin (TpyP) was observed, achieving 42 % efficiency at 370 nm excitation due to proper energy band alignment.²⁴³ A 50 % FRET efficiency to porphyrazine (Pz) was also noted.²⁵⁵ Most studies focus on FRET and charge-transfer mechanisms, while limited examples concerning Dexter energy transfer (DET) mechanisms exist with perovskites. Particularly, a Dexter-like mechanism (mediated by charge-separated states instead of a concerted process) was also demonstrated in CsPbBr₃ interacting with triisopropylsilylethynyl pentacene carboxylic acid (TIPS-Pc), initiated by an ultrafast hole transfer followed by a slower electron transfer from the nanocrystal to TIPS-Pc, yielding the TIPS-Pc singlet state.⁸¹ By contrast, the Dexter mechanism predominated in hybrid assemblies of CsPbX₃ and Rhodamine B (RhB) upon halide alloying with chloride, resulting in chloride-rich CsPb(Br_{1-x}Cl_x)₃ perovskites, thus promoting the Dexter energy transfer (DET) mechanism rather than FRET in the hybrid assembly,⁸⁰ but an in-depth study was lacking. Interestingly, the measured ET rate constant significantly deviated from the value predicted by FRET, thus indicating the presence of an additional ET mechanism, but without confirming the absence of CSS over time.

Although many examples of QD-Pc donor-acceptor assemblies successfully demonstrate FRET-based processes at the interface,²⁵⁶⁻²⁷³ a few of them noticed substantial discrepancies: i) between the experimental and

estimated rate constants, ii) in the efficiency based on the FRET theory, and iii) deviation of the linear dependence of the spectral overlap on the efficiency. These issues were attributed to the oversimplification of the FRET for QDs,²⁷⁴ surface-related processes, due to the interdigitization of the Pc linker chain into the QD capping ligand,²⁷⁵ and the involvement of QD surface states in the energy transfer process from the QDs to the energy acceptor.²⁷⁶

Alternatively, dye aggregation issues, caused by hydrogen bonding, π - π stacking, electrostatic interactions, van der Waals forces, etc., are an initial motive for the efficiency loss of PCE in DSSCs,²⁷⁷ and the low production of singlet oxygen for photodynamic therapy (PDT) applications due to triplet excited state quenching.^{262, 278} Therefore, the use of appropriate ligands on the NC surface to prevent dye aggregation in solution is an appealing notion to enhance the optical and electronic properties of such dyes.²⁷⁹ The X-type surface ligands in perovskites, such as oleate and oleylammonium ions, have a highly dynamic binding to the NC surface atoms.⁶³ Consequently, the ligand exchange strategy to bind new dyes to the NC surface might cause the loss of some native organic ligands, leading to the formation of new surface trap states that can compromise NC properties.²⁸⁰

Hence, understanding excited-state interactions, such as energy or charge transfer processes, is of great importance for the design of such efficient light-harvesting systems, which require both the generation of an exciton by absorption of light and the subsequent funneling of the excitation energy through energy/charge transfer cascade processes.⁷⁸ Thus, the fundamental knowledge of these photophysical processes is crucial for the development of efficient light-harvesting systems for their potential applications in photovoltaics, photocatalysis, TTA-UC and PDT.^{78, 281}

Considering this information, we have reported the first example of pure Dexter energy transfer (DET) mechanism from the CsPbBr₃ NC to surface-anchored Zn-carboxyphthalocyanine (ZnPc) dyes in NC@ZnPc nanohybrids and

demonstrated the key role of the NC surface chemistry in the dye aggregation-disaggregation phenomena at the NC-ZnPc interface. Particularly, we found a synergistic interaction of both systems, which resulted in (i) the sensitization (>100-fold) of the ZnPc singlet excited state by selective excitation of the NC, (ii) the higher molar extinction coefficient of the ZnPc dye, and (iii) the lengthening of the ZnPc triplet excited state >40 μ s, both as a result of the disaggregation effect on the NC surface. While an Φ_{ET} of only 45 % was achieved as an upper limit in the NC@ZnPc, a detailed temporal analysis of the energy transfer process, by using a combination of time-resolved techniques such as time-resolved PL, fs-TA, ns-TA, and μ s-TA spectroscopies, concomitantly with a target kinetic model, revealed the formation of a new dark trap state upon ligand exchange with ZnPc molecules, which dissipated the rest of the excitation energy (55 %) and was responsible of the other nonradiative pathway. This study provides a comprehensive assessment of the exclusive energy transfer pathway that operates in the complex excited state dynamics of the NC@ZnPc nanohybrid under selective excitation of the NC.

5.2. Experimental section

Methods

5.2.1. Synthesis of the phthalocyanine dye

Synthesis of carboxyphthalocyanine TT1, hereafter ZnPc, was carried out by Prof. Tomas Torres from the Autonomous University of Madrid, according to their previously reported protocol.²⁸² Zinc oxide (0.4 mg, 0.005 mmol) and potassium hydroxide (2.8 mg, 0.05 mmol) are placed in an oven-dried tube, which is placed in a Radley carousel. The tube is three times subjected to vacuum and then N₂ gas. Vacuum is applied again, and the carousel heated to 170 °C for 1 h. Then the tube is refilled with N₂ gas. Anhydrous and degassed mesitylene (1 mL) is added by syringe and the mixture heated to reflux. Hydroxyl derivative phthalocyanine (0.05

mmol, 40 mg) that previously is dissolved in degassed mesitylene (1 mL) is added dropwise by syringe, and the reaction is stirring under a flow of N₂ for 24 h at 170 °C. The mixture is cooled down to room temperature and the mesitylene is evaporated under vacuum. The precipitate is acidified with 2 mL of 16 % aqueous hydrochloric acid. The aqueous layer is extracted with ethyl acetate (3x5 mL). The combined organic layers are dried over anhydrous Na₂SO₄ and concentrated in vacuum to give the ZnPc as a pure compound in 96 % yield (38 mg).

Instrumentation

5.2.2. Femtosecond and nanosecond transient absorption spectroscopy

Femtosecond and nanosecond transient absorption (fs/ns-TA) spectroscopy was used to probe the early and late time exciton dynamics of NCs and the energy transfer funneling from the NC to Pc dyes. Specifically, ultrafast transient absorption experiments were conducted using an Astrella-F-1K amplified Ti:sapphire femtosecond laser system from Coherent, operating at a repetition rate 1kHz, 5.5 W power (5 mJ pulse energy), pulse duration of 80 fs, with TA pump/probe Helios and EOS detection systems from Ultrafast Systems. White light was generated by focusing a fraction of the fundamental 800 nm output onto a 2 mm sapphire crystal (Helios). A 1.2 mJ fraction of the fundamental is used for pump beam generation by a TOPAS Prime from Light Conversion with standard NirUVis extension. The pump energy was varied between 150 and 1000 nJ. The laser spot diameter was estimated to be 0.5 cm. Therefore, assuming a spherical shape, the area was ca. 0.196 cm². A depolarizer was placed in the pump beam to avoid rotational dynamics. Bandpass filters with ± 5 or ± 10 nm were used to ensure low spectral width and to exclude 800 nm photons. All measurements were conducted in a 2 mm quartz cuvette under Ar atmosphere, using solutions with absorbances of 0.5 – 0.7 under continuous stirring. To analyze transient absorption data, we used

a suggested procedure.²⁸³ We started with single value decomposition (SVD) and Global analysis, using an all-sequential decay model that provides evolution-associated spectra (EAS) of potentially intervening species, to determine the number of decaying species that participate in the decay cascade. However, this does not necessarily yield differential spectra with genuine physicochemical meaning. Afterward, a target analysis was applied, using specific target models that result in species-associated difference spectra (SADS) with true physicochemical meaning. Obtained data were treated by SVD, global and target analyses using the R-package TIMP and GloTarAn.^{229, 283-284}

5.3. Results and discussion

5.3.1. Steady-state optical properties and evidence of energy transfer

Primarily, CsPbBr₃ NCs were synthesized according to the same strategy as the previous chapter, yielding similar NC size and optical properties, thus demonstrating the reproducibility of this methodology.⁸³ As an energy acceptor, we used the asymmetric Zn-carboxyphthalocyanine (ZnPc), which was previously synthesized by Torres et al.²⁸² It is noteworthy that the presence of a carboxylic acid as an anchoring group is essential to ensure the close interaction of the ZnPc with the NC surface as previously demonstrated for C-BDP.²⁰⁶ The NC@ZnPc nanohybrid was prepared by titration experiments (similar to *Chapter 3*) in which increasing concentrations of the ZnPc dye (2.5, 5.0, 7.5 and 10 μM) to a fixed concentration NC dispersion in toluene (0.25 μM) were added, leading to the corresponding 1:10, 1:20, 1:30 and 1:40 NC:ZnPc ratios, respectively. Regarding the steady-state absorption properties of the nanohybrid, apart from the strong and wide absorption of the NC in the 300 – 500 nm range, new absorption features appeared at 350 nm and in the

550 – 700 nm range, corresponding to the Soret and Q-bands of the ZnPc, respectively, then exhibiting a panchromatic effect, as observed in **Figure 5.1a**.

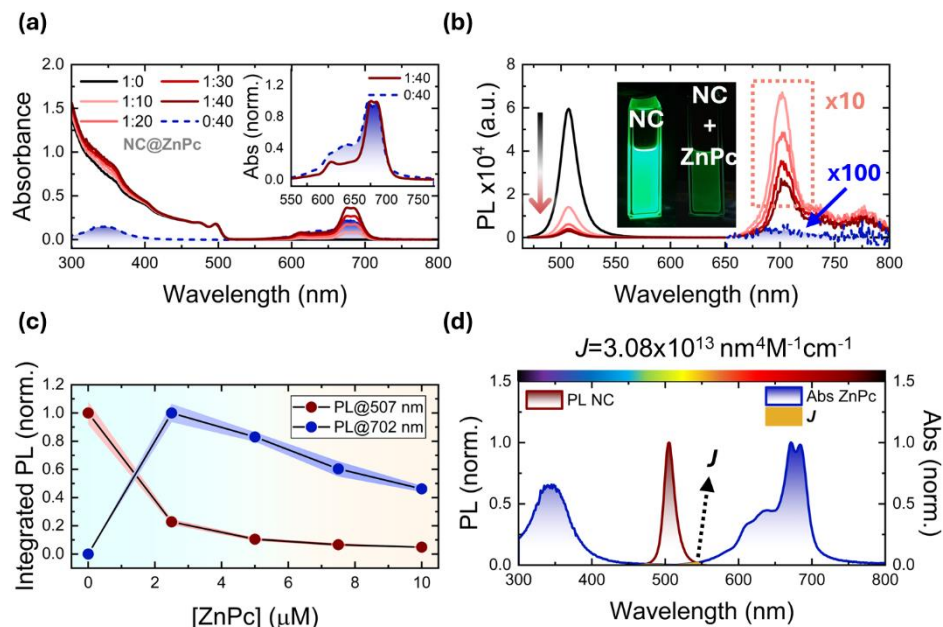


Figure 5.1. (a) Steady-state absorption spectra of NCs in the presence of variable concentrations of ZnPc [0 – 10 μM]. Inset: normalized absorption spectra of the Q-band absorption of the NC@ZnPc (1:40) and ZnPc. (b) Steady-state PL spectra of NCs in the presence of variable concentrations of ZnPc [0 – 10 μM] under 460 nm photoexcitation. Photosensitized fluorescence of ZnPc in NC@ZnPc and the intrinsic fluorescence of ZnPc are multiplied by a factor of 10 and 100, respectively. Inset: Digital photographs of NCs and NC@ZnPc (1:40) nanohybrids under 365 nm photoexcitation. (c) PL evolution at the NC and ZnPc maxima at 507 and 702 nm, respectively. (d) Spectral overlap integral (J) between the normalized NC PL and ZnPc absorption.

Scrutiny of the absorption spectrum of the NC@ZnPc clearly indicates the intercomponent electronic interactions in the ground state and ZnPc disaggregation effect on the NC surface. Notably, the shoulder at 637 nm decreased upon surface anchoring, while the highest-energy peak of the Q-band

intensified and redshifted from 671 to 676 nm, supporting the disaggregation effect. This is further corroborated by increasing the NC concentration on a fixed concentration ZnPc solution. Notably, significant PL quenching of the NC was noted in **Figure 5.1b** upon increasing the concentration of the ZnPc dyes (Φ_Q up to 95 % for 1:40 NC@ZnPc) under 460 nm excitation, where the ZnPc dye negligibly absorbs. This strong quenching was accompanied by the concomitant formation of a new emission band centered around 702 nm, assigned to the ZnPc fluorescence from the (S_1) singlet excited state (**Figure 5.1c**). Surprisingly, the intensity of this new emission band was >100-fold higher than that of the ZnPc fluorescence in control experiments, suggesting the involvement of an energy transfer process in NC@ZnPc nanohybrids.

Energy transfer efficiencies were estimated according to the methodology already employed in previous works.^{83, 206} However, a plateau of 45 % at 5 μ M ZnPc was observed (not shown here), indicating that other nonemissive processes compete with the ET process (charge transfer or formation of new trap states), which dissipates the energy. Control experiments with ZnPc_{ref} dyes, which presented the same electronic structure but without any anchoring group, showed negligible effects on the excited-state properties of the NC. This underscores again the fundamental role of the carboxylic acid anchoring group in facilitating dye attachment to the NC surface and thereby driving forward the energy transfer process. However, the poor spectral overlap integral value ($3.08 \times 10^{13} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$) excludes the FRET mechanism as a candidate to deactivate the perovskite excited state, as seen in **Figure 5.1d**.⁸⁰ This finding, in conjunction with the need for an anchoring group to bring closely the energy acceptor, supports a through-bond Dexter energy transfer (DET) mechanism for ZnPc sensitization. Nonetheless, to obtain a comprehensive understanding of the ET mechanism and demonstrate the exclusivity of the DET mechanism in deactivating the perovskite excited state, time-

resolved PL and TA spectroscopy were employed across various time scales, from femtoseconds to microseconds.

5.3.2. Time-resolved photoluminescence properties

With the aim to probe the band-edge exciton properties of the NC, TCSPC experiments were performed at 460 and 507 nm excitation and emission wavelengths, respectively (**Figure 5.2a**). The NC was well-fitted to the typical triexponential decay function with time constants and corresponding contributions of 2.1 ns (16 %), 5.0 (76 %) and 17.7 ns (8 %). A lengthening of all time constants was observed due to the use of concentrated dispersions for TCSPC measurements (similar conditions to TA). As highlighted in *Chapter 5*, the short-, medium- and long-time components correspond to shallow trap-mediated exciton (STX, τ_{STX}), direct electron-hole exciton (X, τ_x), and deep trap-mediated exciton recombination processes (DTX, τ_{DTX}), respectively.¹³⁴ These trap-mediated exciton recombination processes can be attributed to surface defects and multiple trapping and detrapping of charge carriers,²³² accompanied by spontaneous electron-hole recombination, respectively.

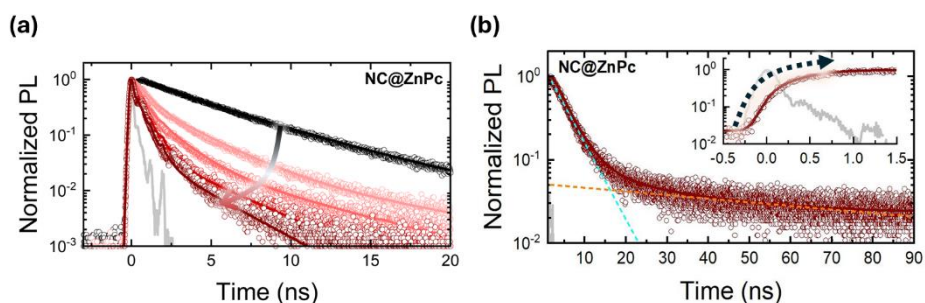


Figure 5.2. (a) Time-resolved PL of NCs in the presence of variable concentrations of ZnPc [0 – 10 μM] under 460 nm pulsed laser photoexcitation and 507 nm detection. (b) Sensitized emission of ZnPc in NC@ZnPc (1:40) at 702 nm under 460 nm pulsed laser photoexcitation. Inset: Early time scale of the sensitized ZnPc fluorescence in NC@ZnPc (1:40) illustrating the rise dynamics.

In the presence of ZnPc dyes, all time components of the NC were gradually shortened. For the 1:40 NC@ZnPc, time constants of 0.33 ns (65 %), 1.93 ns (30 %) and 7.92 ns (5 %) for (STX), (X) and (DTX), respectively, were obtained, indicating that the three exciton states were involved in the interfacial ET process from the NC to surface-anchored ZnPc dyes. Thus, the energy transfer rate constants (k_{ET}) and quantum yields (Φ_{ET}) calculated from TCSPC measurements are $2.56 \cdot 10^9 \text{ s}^{-1}$ and 84 %, $0.32 \cdot 10^9 \text{ s}^{-1}$ and 61 % and $0.07 \cdot 10^9 \text{ s}^{-1}$ and 55 % for (STX), (X) and (DTX), respectively. Therefore, three different time scales for the ET process can be highlighted: below 1 ns, between 1 – 5 ns, and above 10 ns for (STX), (X) and (DTX), respectively. The higher values for the surface-mediated ET highlight the importance of surface states in mediating the ET process.

In order to monitor the S_1 formation of the ZnPc, the detection wavelength was turned to 702 nm (fluorescence maximum for ZnPc). For ZnPc control, the fluorescence resulted in the characteristic monoexponential decay with a 2.77 ns lifetime. However, the time constants of 0.61 ns, 3.67 ns (79 %) and 22.27 ns (21 %) were found for 1:40 NC@ZnPc nanohybrids. Interestingly, the first component appeared as a rise, providing unequivocal evidence of the faster ET process associated with surface states, being very close to the (STX) component of 0.33 ns, as clearly observed in **Figure 5.2b**. In contrast, the other two decaying components with lifetimes longer than that of the S_1 singlet excited state (2.77 ns) indicated a slower ET process from (X) and (DTX) states. In principle, the FRET mechanism can be excluded because the estimated FRET rate constant was $0.067 \cdot 10^9 \text{ s}^{-1}$ based on the FRET theory, i.e. ca. 40-fold lower than the experimentally determined by the TCSPC technique, excluding again this type of ET mechanism.

5.3.3. Inspection of the transient absorption properties

TA experiments in the femtosecond, nanosecond and microsecond time scales were performed. First, fs-TA spectroscopy was used to shed light on the ultrafast excited-state dynamics. For these experiments, we maintained the 460 nm

excitation like in the former experiments. Considering an optical band gap of ca. 2.5 eV, which was measured from the second derivative of the steady-state absorption spectrum of NCs, an energy excess of ca. 0.2 eV was used along with a high pump energy of 1 μ J. This resulted in the population of a great number of hot exciton states, which considerably had an impact on the early-time dynamics. Related transient absorption features to those found in the previous chapter can in principle be identified from **Figure 5.3a**: exciton bleaching (XB) features at 477 and 498 nm, concomitantly with excited-state absorption (ESA) features below 450 nm and a broad ESA feature over the 515-750 nm range, was immediately observed (1 ps) upon excitation due to the cooling of hot excitons;²³⁴ in the next 10 ps, suppression of the 477 nm XB and 515 nm ESA bands by a redshift in the ESA feature up to 460 nm and the apparition of a negative band around 520 nm, respectively; followed by narrowing down the XB feature in 25 ps; and at time delays longer than 100 ps, a remanent XB feature with ESA features on both sides, in which the intensity progressively decays, are ascribed to the exciton recombination process (determined by TCSPC). Inspection at two representative wavelengths (**Figure 5.3b**), specifically 498 nm and 688 nm, allowed probing of the XB and GSB features of the NC and ZnPc, respectively. It is noteworthy that no signal was present at 688 nm for NCs after 1 ns. The fs-TA properties of the ZnPc under 670 nm excitation (1 μ J) revealed a deep negative signal attributed to ground-state bleaching (GSB) and stimulated emission (SE), superimposed with a broad ESA covering the entire visible range. Nevertheless, a quenching of the NC features together with the delayed formation of the GSB around 688 nm due to the singlet sensitization of ZnPc was noticed in **Figure 5.3c**. A detailed examination of the 688 nm kinetic revealed that the GSB of ZnPc grew before 1 ns (**Figure 5.3d**), as confirmed by TCSPC data.

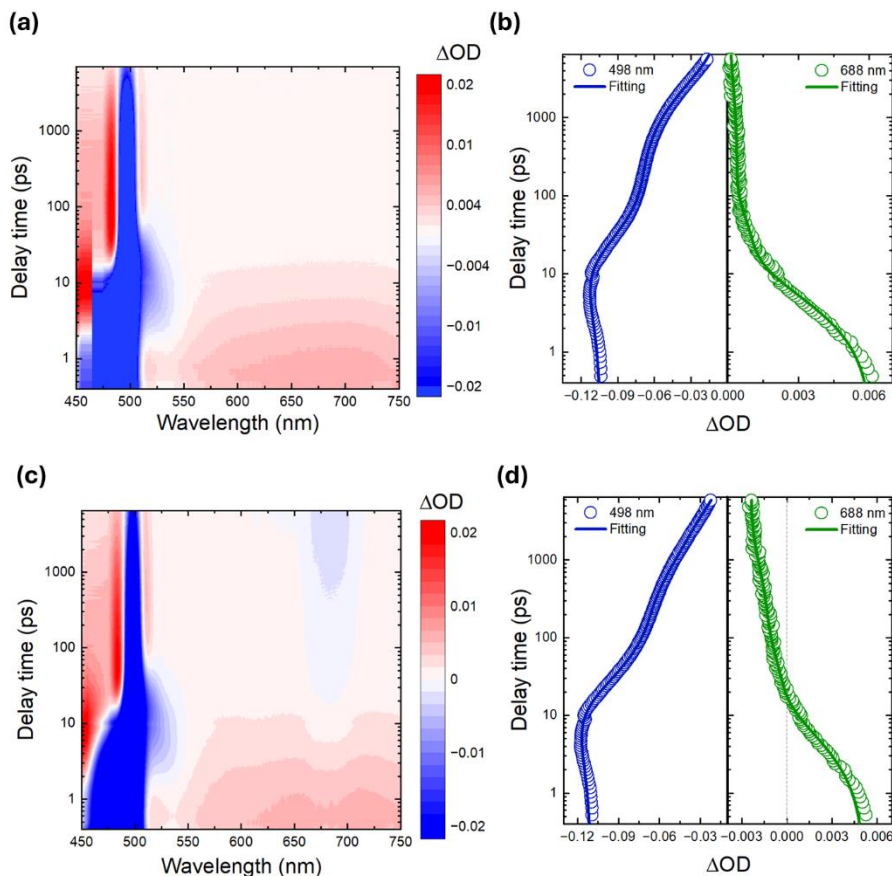


Figure 5.3. 2D pseudocolor plot for (a) NCs and (c) NC@ZnPc (1:40) nanohybrids under 460 nm pump excitation. Representative decay traces and fitting at 498 and 688 nm for XB of NCs and GSB of ZnPc dyes, respectively, for (c) NCs and (d) NC@ZnPc (1:40) nanohybrids.

Subsequently, ns-TA spectroscopy was used to provide further details about the singlet sensitization process on longer time scales and to investigate the excited-state dynamics in NC@ZnPc nanohybrids. Curiously, while the XB feature was completely quenched, the GSB of ZnPc persisted for the whole experimental window ($>40 \mu\text{s}$). This is quite surprising considering the short triplet excited-state (T_1) lifetime ($0.67 \mu\text{s}$) of the ZnPc control under same conditions (aggregated state

of ZnPc in toluene) and was attributed to the ZnPc disaggregation on the NC surface caused by the native organic ligands.²⁸⁵

5.3.4. Target analysis and proposed model

To better understand the complex photophysical processes in NC@ZnPc nanohybrids, a target kinetic model was used for data analysis. Target analysis of the pristine NC on the fs-TA afforded five states with time constants of 5.8 ps, 11 ps, 34 ps, 1.0 ns and 4.4 ns, which were associated with hot excitons (hot-X), multiexcitons (MX), biexcitons (XX), (STX) and (X) exciton states, respectively, accompanied by an infinite offset accounting for the long-lived exciton recombination. Due to the elevated pump energy and excess energy employed, slower cooling times are typically observed compared to those found in the previous chapter, which is attributed to the hot-phonon bottleneck effect.¹²⁷ Additionally, many-body interactions manifested at that pump energy, such as MX and XX are clearly observed. We tentatively assigned the 11 ps component to a MX state. Meanwhile, the 34 ps component was attributed to a biexciton, as its differential absorption spectrum resembles those reported in the literature for similar NC sizes.²⁸⁶ For ZnPc, fs-TA dynamics exhibited two time components of 16 ps and 1.9 ns corresponding to vibrationally-hot S_1 and S_1 states, respectively, accompanied by an infinite offset ascribed to the triplet excited state population. However, target analysis of the 1:40 NC@ZnPc nanohybrid identified six states accompanied by an infinite offset: 5.5 ps, 12 ps, and 30 ps, corresponding to hot-X, MX, and XX, respectively. These states exhibited negligible changes relative to the NC, suggesting that none of them were involved in the ET process and indicating that the ET process occurs at a later stage. The other three states of 0.25 ns, 2.4 ns and 2.8 ns were assigned to the (STX), (X) and S_1 states, respectively. In this case, the infinite offset was ascribed to the long-lived exciton and T_1 excited states. The assignment of these states from target analysis is based on the shape of the differential absorption spectrum for each component.

Target analysis of the NC on the ns-TA, on the other hand, exhibited four components: 2.1, 4.9, 17.7 and 100 ns, ascribed to (SXT), (X), (DXT) and a dark trap state (DT), which is nonemissive in nature. That is the reason why this dark state was undetected by TCSPC. For ZnPc, two components were obtained, with 2.6 ns and 0.69 μ s, assigned to S_1 and T_1 states, respectively. Meanwhile for the NC@ZnPc, a more complex evolution of the excited-state dynamics was observed, and consequently, seven components accompanied by an infinite offset were included for the global fitting, which included the four NC components (STX), (X), (DTX) and (DT), the S_1 and T_1 states of ZnPc, and an additional dark trap (DT'), which was absent in NC control, and whose lifetime was 1.3 μ s. We attributed this (DT') to a new nonemissive NC state linked to surface defects due to the unique contribution of the XB feature. This state is associated with the loss of native surface ligands during ligand exchange with ZnPc dyes, a process previously observed in quantum dots (QDs) and organic dyes,^{280, 287} and agrees well with the remaining 55 % deactivating the NC excited state. Interestingly, the absence of cation/anion radical species of ZnPc in the entire time scale of TA unequivocally indicates the absence of sequential electron/hole transfer pathways and thus highlights the exclusive Dexter ET pathway.

Bearing this in mind, combining information from various time scales techniques enabled us to fully unveil the complete picture of the intricate excited-state decay cascade in NC@ZnPc nanohybrids, revealing a singlet ET process facilitated by the Dexter mechanism (**Figure 5.4**).

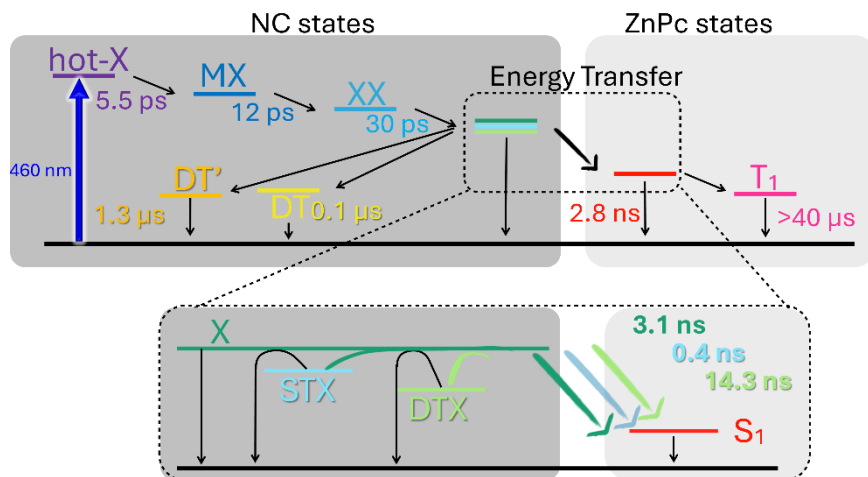


Figure 5.4. Full picture of the Dexter-mediated singlet sensitization mechanism of ZnPc in the NC@ZnPc (1:40) nanohybrid.

Following selective photoexcitation to the NC at 460 nm, the early-time processes best fitted to a sequential model until reaching the (X) state. From this point on, the (X) state population branched, feeding dark states on one hand, and undergoing ET on the other hand, and consequently, populating the S_1 state of the ZnPc, which further evolved to the T_1 state. It is noteworthy that all exciton components from TA matched reasonably well with those found in TCSPC experiments under experimental uncertainties.

5.4. Conclusions

In conclusion, this work demonstrates the crucial role of the anchoring group in ZnPc dyes in facilitating exclusive concerted electron exchange, resulting in the *first example* of a Dexter-type singlet energy transfer mechanism using CsPbBr_3 NCs as the visible light-harvesting antenna in CsPbBr_3 NC@Zn-carboxyphthalocyanine nanohybrids. A thorough analysis of the excited-state properties of the NC in the nanohybrids was conducted using a range of

spectroscopic techniques across different time scales, including time-resolved PL, fs-TA, and ns-TA. We specifically observed the disaggregation of ZnPc molecules upon dye attachment to the NC surface through steady-state absorption properties and the prolonged triplet excited-state lifetime of ZnPc in the nanohybrid. A high degree of ZnPc singlet sensitization (>100-fold) was achieved, resulting in 45 % of the excitation energy being transferred from the NC to ZnPc, while the remaining 55 % was dissipated through the creation of a new dark trap state. The energy transfer process to the ZnPc originated from the three NC exciton states, occurring across three different time scales. The fastest of these processes was observed at < 1 ns, corresponding to the rise time of the ZnPc after sensitization. Finally, the significant extension of the ZnPc triplet excited state in the nanohybrid, higher than the experimental window (>40 μ s), further confirms the previously discussed disaggregation phenomenon.

Chapter 6.

Lengthening of Exciton Dynamics in Linear Upconversion-Perovskite Hybrid Assemblies

6.1. Introduction

The ability to control PL lifetimes and adapt them to target technological applications, such as optoelectronics, photonics, displays and imaging, is achievable by rationalizing the excited-state interactions.³⁸ A promising approach is by using upconversion nanoparticles (UCNPs), which are lanthanide-doped inorganic matrices that are able to absorb two or more low-energy photons by a nonlinear optical process, and consequently, converting them into high-energy photons.^{288,289}

The inorganic matrix is optically inactive (e.g., β -NaYF₄) but becomes optically active when is doped with lanthanide ions which can act as a sensitizer, such as Yb³⁺, which absorbs low-energy photons), and the activator, such as Tm³⁺ and Er³⁺, emitter of the high-energy photon.²⁸⁸ The mechanism of the process completely relies on the energy-transfer upconversion (ETU),²⁹⁰ in which one low-energy photon is absorbed by the sensitizer, and subsequent transfer the energy from neighboring sensitizer ions to the nearby activator, thus resulting in the population of a highly excited state from which upconversion emission takes place.²⁹¹ This is made possible thanks to the electronic structure of lanthanide ions with 4f orbitals (Laporte-forbidden 4f-4f electronic and spin-forbidden transitions),²⁸⁹ ladder-like arrangements,²⁹² and the shielding effect by the closed 5s² and 5p⁶ shells,²⁹³ which features characteristic narrow emission bandwidths and prolonged PL lifetime of lanthanide excited states, thereby facilitating the sequential absorption of multiple photons.

Long lifetimes and NIR absorption of UCNPs make these materials very appealing in biosensing and bioimaging applications,²⁹¹ as well as to circumvent NIR photon losses of the total solar irradiance in solar cells (SCs).²⁹⁴ This is possible by converting photons below a semiconductor band gap into high-energy photons,

thus generating additional photocurrent.²⁹⁵ In fact, there have been reported hybrid assemblies of UCNPs with other materials to yield novel functional materials, among which perovskite materials have gained great interest in photovoltaic technology due to their strong absorption capabilities, easy modulation of optical properties in the whole visible range by easy anion exchange, high charge carrier mobility and outstanding PCEs exceeding 25 % nowadays.²⁹⁶⁻²⁹⁷ Nevertheless, perovskites exhibit weak multiphoton excitation efficiency, thereby impeding their practical use for NIR harvesting. By contrast, UCNPs are considerably more efficient in NIR harvesting and could potentially address this problem.²⁹⁸

In this context, UCNPs and perovskites have previously been assembled in devices aimed at improving the PCE.²⁹⁹⁻³⁰¹ The physical mixture of $\text{LiYbF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ @ LiYF_4 core-shell UCNPs and CsPbX_3 NCs when excited by a 980 nm CW laser, primarily led to a radiative energy transfer process (trivial mechanism) from UCNPs to the NCs. This was deduced since the Tm^{3+} emission lifetime was nearly unchanged, most likely due to the unfavorable shell structure, which limits distance-dependence nonradiative processes (r_{DA}^{-6}).²⁹⁸ Additionally, UCNPs have been embedded in MAPbBr_3 wires to facilitate the close interaction of both systems, thereby increasing the efficiency of nonradiative energy transfer up to 29 % between UCNPs and the perovskites (termed as lanthanide resonance energy transfer, LRET) when compared with the simple mixture of UCNPs and MAPbBr_3 wires separately. However, the sensitized PL of perovskites through energy transfer was absent in the emission spectrum.³⁰²

An attractive way to further enhance the LRET process is through the preparation of a nanohybrid where nanoparticles are in close proximity. In fact, the first example of colloidal nanohybrids was successfully reported by our group,³⁰³ where MAPbBr_3 NCs were efficiently anchored on the $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ UCNP surface using cucurbit[7]uril (CB[7]) to firmly and closely attach the NCs to the UCNPs. This led to an outstanding LRET of ca. 100 % efficiency under NIR excitation,

using NIR multiphoton laser scanning (NIR-MLS) microscopy, and resulted in the apparition of the perovskite PL centered at 525 nm. The *In-situ* growth of CsPbBr₃ NCs@OAm in the presence of sub-10 nm-sized BaYF₅:Yb³⁺,Tm³⁺ UCNPs@OA also enabled an overall 100 % energy transfer, but only 35 % was attributed to LRET process.³⁰⁴ On the other hand, building directional superlattices of nanocrystals is a research area of great interest,³⁰⁵ as it provides valuable insights into the collective properties of these materials and also it would allow to bring UCNPs and NCs in close proximity to enable efficient NIR harvesting.

In addition, our group has assembled MAPbBr₃ NCs within a linear PbBr₂ polymer leading to long, 1D MAPbBr₃ NCs arrays, when deposited on carbon-coated surfaces.³⁰⁶ Although this linear assembly resulted in poor stability since it coiled up into a ball when placed onto a glass substrate. Another general strategy employing lead sulfate (PbSO₄) molecular clusters enables nanoparticles to be assembled into a linear peapod-like superstructure through solvent-induced association interactions. This cluster-assisted assembly process applies to various metallic, semiconductor, and magnetic NCs of different sizes and shapes, including perovskites.^{116, 307}

Therefore, a linear assembly of both NaYF₄:Yb³⁺,Tm³⁺ and NaYF₄:Yb³⁺,Er³⁺ core and NaYF₄:Yb³⁺,Tm³⁺/NaYF₄ core/shell, along with the co-assembly with CsPbX₃ (X: Cl, Br, I) was prepared for the first time by using the above-mentioned PbSO₄ cluster-induced assembly approach. This resulted in novel and promising superstructures that exhibit NIR harvesting properties, with significant potential for photovoltaic applications. The effective formation of the linear co-assembly was further demonstrated by (i) single photon counting measurements using a low-power 980 nm diode laser-pulsed excitation, which revealed an importance reduction in the Tm³⁺ emission lifetime, concomitantly with the sensitized and lengthened PL lifetime of NCs, more pronounced in solid film (37 %) than solution (7 %) sample; and (ii) the NIR-MLS microscopy employing a high-power,

femtosecond-pulsed 980 nm laser, which manifested in the dramatic quenching of the Tm^{3+} PL (out of temporal range) and observation of the NC green emission.³⁰⁸

6.2. Experimental section

Methods

6.2.1. Synthesis of core upconversion nanoparticles

The oleate-capped core $\text{NaYF}_4:\text{Yb}^{3+}(31\%),\text{Tm}^{3+}(0.3\%)$ and $\text{NaYF}_4:\text{Yb}^{3+}(20\%),\text{Er}^{3+}(2\%)$ UCNPs (UC_{Tm} and UC_{Er}) were synthesized by following a previously reported method with some modifications.³⁰⁹ Briefly, a mixture of the adequate proportion of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (20 mmol in total), OA (160 mL) and 1-ODE (300 mL) was stirred at 160 °C under N_2 in a 1 L three-necked round-bottom flask until complete dissolution of the lanthanide salts. Subsequently, the mixture was kept under vacuum for 30 min at 160 °C. Then, the solution was cooled to room temperature and 70 mL of a methanol solution of NaOH (0.05 mol) and NH_4F (0.08 mol) was added to the flask. Methanol was removed at 100 °C under N_2 flow and vigorous stirring. Afterwards, an Allihn condenser was added to the setup and the flask was heated to 305 °C under N_2 flux for one hour. The solution was allowed to cool down to room temperature and then an excess of ethanol was added to precipitate the corresponding UCNPs, which were separated by centrifugation (7012 g, 8 min, 25 °C). Three centrifugation/redispersion cycles were performed first with chloroform and ethanol and secondly with cyclohexane and acetone to purify the UCNPs. Finally, UCNPs were dispersed in cyclohexane.

6.2.2. Synthesis of core/shell upconversion nanoparticles

The oleate-capped core-shell $\text{NaYF}_4:\text{Yb}^{3+}(16\%),\text{Tm}^{3+}(0.2\%)/\text{NaYF}_4$ UCNPs ($\text{UC}_{\text{CS,Tm}}$) were synthesized by following a previously reported method with some

modifications.³¹⁰ First of all, a shell precursor solution was prepared by heating until complete dissolution a 1:1 OA:1-ODE solution containing $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mmol) under N_2 atmosphere. Then the solution was allowed to cool down to room temperature and a methanol solution of NaOH (25 mmol) and NH_4F (40 mmol) was added. Finally, the precursor was heated to 120 °C under N_2 and vigorous stirring to remove the methanol and residual water. Once the precursor was prepared, an aliquot of the cyclohexane-dispersed UC_{Tm} core (500 mg UC_{Tm}) was added to a three-necked 500 ml flask containing OA (65 mL) and 1-ODE (150 mL). The mixture was heated to 70 °C to remove the cyclohexane under N_2 and stirred gentle. An Allihn condenser was added to the setup without losing the inert atmosphere, and the temperature was raised to 320 °C. At that temperature two 15 min-spaced additions of 10 mL of the shell precursor solution were added by dripping. After the second addition, the solution was kept 30 min at 320 °C. Then, the mixture was allowed to cool down. The purification procedure involved the same centrifugation/redispersion cycles described for the core synthesis.

6.2.3. Synthesis of lead-halide perovskite nanocrystals

The CsPbX_3 ($\text{X} = \text{Br}, \text{I}$) NCs were synthesized by following the procedure described in the literature with slight modifications.⁵¹ First, a solution of cesium oleate (0.125 M) was prepared by mixing Cs_2CO_3 (407 mg, 0.12 mmol) and OA (1.25 mL, 1.77 mmol) in 1-ODE (20 mL) in a 100 mL round-bottom flask and the mixture was degassed under vacuum at 120 °C for 1 h. The reaction was heated to 150 °C under N_2 flux until Cs_2CO_3 was dissolved and then the solution was cooled to room temperature and stored in an inert condition. For the synthesis of CsPbBr_3 , PbBr_2 (69 mg, 0.19 mmol) and 1-ODE (5 mL) were loaded into a 50 mL 2-necked round-bottom flask and the mixture was degassed under vacuum at 120 °C for 1 h. Then, OA (0.5 mL) and OAm (0.5 mL) were added to the above-mentioned mixture in N_2 atmosphere. The mixture was heated to 180 °C followed by the injection of a cesium oleate solution (0.4 mL, 0.125 M in 1-ODE). Finally, the solution was cooled to room

temperature in a water-ice bath and the NCs were purified by centrifugation (10,956 g, 25 °C, 5 min), and the first solid was then redispersed in toluene.

6.2.4. Synthesis of lead sulfate molecular clusters

Lead sulfate (PbSO_4) molecular clusters were prepared by following a previously reported method with some modifications.¹¹⁶ Firstly, a lead-oleate precursor solution (0.062 M) was prepared by mixing PbCl_2 (139 mg, 0.50 mmol) with OAm (8 mL) and OA (0.1 mL). The mixture was heated to 150 °C under N_2 flux for one hour to form a clear solution. This solution was stored in an inert condition. Then, the PbSO_4 cluster was prepared by mixing lead-oleate precursor solution (0.4 mL of 0.062 M), tetrabutylammonium hydrogensulfate (TBAHS) or cyclohexanemethylammonium hydrogensulfate (CHMAHS) organic salt (5.3 mg, 0.025 mmol) and OA (0.4 mL) in chloroform (10 mL) by stirring. The cluster was obtained after precipitation by addition of 30 mL ethanol and centrifugation (10,956 g, 20 °C, 5 min). The white solid obtained was dissolved in chloroform or hexane (2.5 mL).

6.2.5. Preparation of the linear assembly/co-assembly

The preparation of the UCNP assembly/polymer was carried out following a similar procedure described in the literature.¹¹⁶ First, a freshly-prepared PbSO_4 cluster solution in chloroform (0.3 mL) was added to an UCNP dispersion (0.2 mg mL^{-1}) in hexane (2 mL). The mixture was incubated at room temperature and for different times without stirring. The UCNP assemblies were separated by centrifugation (185 g, 20 °C, 5 min) and redispersed in hexane.

The preparation of NC assembly/polymer was carried out following a similar procedure to that described above. A freshly prepared PbSO_4 cluster solution in hexane (0.3 mL) was added to a CsPbBr_3 perovskite NC dispersion (2 mL, 2.8 mg mL^{-1}) in hexane. The mixture was incubated at room temperature for 24 h

without stirring. The NC assemblies were separated by centrifugation (185 g, 20 °C, 5 min) and redispersed in hexane.

The co-assembly/co-polymer of UC_{Tm}-NC was prepared by addition of a freshly prepared PbSO₄ cluster solution in hexane (0.3 mL) to a binary mixture of NCs (2.8 mgmL⁻¹) and UC_{Tm} (0.2 mgmL⁻¹) in 2 mL of hexane. The mixture was incubated during 24 h without stirring. Finally, the assembly was separated by centrifugation (185 g, 20 °C, 5 min) and redispersed in hexane.

The UC_{Tm}-NC film was prepared by using the centrifugal casting method.³¹¹ Briefly, four copolymer dispersions were mixed in hexane (1.2 mL) in order to obtain a concentrated assembly sample. The mixture was centrifuged (15,777 g, 20 °C, 5 min) on a glass substrate (1.1 x 0.9 cm) immersed in a centrifugal tube (50 mL). Finally, the supernatant was removed, and the solid coassembly film was allowed to dry under a hexane atmosphere for 2 h.

Instrumentation

6.2.6. Photoluminescence spectroscopy using NIR laser excitation

Steady-state emission spectra were recorded with an Aminco Browman series 2 (AB2) spectrometer, equipped with a Xenon lamp (150 W) and a CW 980 nm diode laser (CNI Optoelectronics Tech. Co. MDL-H-980nm-5W-17111142, a power density of 1.5 kWcm⁻²) as an excitation source for UCNPs.

Time-resolved kinetics of assemblies dispersed in hexane and solid films were recorded in a FLS1000 photoluminescence spectrometer (Edinburgh Instruments) coupled with a 2 W CW 980 nm diode laser (PSU-III-LED, CNI Optoelectronics Technology Co. Ltd.) in a time range of 0–8000 ms with 8 ms of step.

6.2.7. X-ray diffraction spectroscopy

X-ray diffraction (XRD) spectroscopy was used to determine the crystal structure and phase of the nanomaterials prepared in this thesis. The power XRD (PXRD) diffractograms were registered in a powder diffractometer D8 Advance A25 model Bruker, with a powder diffractometer θ - θ configuration, X-ray tubes on a lineal receiver Cu radiation. DIFFRAC EVA Data assessment program was used to register the data.

6.2.8. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to provide information regarding the morphology of clusters, nanocrystals and assemblies. The SEM images of assemblies deposited on glass were obtained using a HITACHI S-4800 with a spotlight of field emission gun and an acceleration voltage of 15 kV.

6.2.9. NIR multiphoton laser scanning microscopy

NIR multiphoton laser scanning (NIR-MLS) microscopy was used to study the multiphoton absorption properties of UCNPs and to track the ET evolution. The emission images and emission lifetimes of the UCNPs were recorded on an Olympus FV1000MPE coupled to an Olympus BX61WI upright microscope, provided of a Mai Tai HP Deep See multiphoton laser (pulse width of 100 fs) as excitation source and focused over the sample at 980 nm (excitation power of 1.12 W). The images were acquired by means of a 25x1.05 N.A. Olympus dipping lens, appropriated emission filters and a dwell time of 8 μ s pixel⁻¹ and a resolution of 1024x1024 pixels. The emission was detected in a 4-channel visible-range detector (420–500, 515–580, 590–650, 660–740). The samples were prepared by spin coating (12 sec at 500 rpm, then 30 sec at 4500 rpm) 100 μ L of assembled nanoparticles dispersed in hexane on top of a microscope glass cover slips (22x22 mm).

6.3. Results and discussion

6.3.1. Preparation of the linear upconversion-perovskite co-assembly

UCNPs, specifically core $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ (UC_{Tm}) and $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ (UC_{Er}) and core/shell $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}/\text{NaYF}_4$ ($\text{UC}_{\text{CS,Tm}}$) were synthesized by a slightly-modified thermal decomposition strategy.³⁰⁹ On the other hand, OAm-ligated PbSO_4 molecular clusters were first prepared by using a previously reported method,¹¹⁶ leading to the formation on lamellar ribbons comprising two stacking layers of OAm ligands stabilizing PbSO_4 clusters.³¹² This methodology traditionally consisted of mixing the previously-prepared lead-oleate in OAm with an alkylammonium salt such as TBAHS at room temperature, and the resulting solid was dispersed in hexane yielding lamellar ribbons (cloudy dispersion). The addition of an aliquot of UC_{Tm} into these freshly prepared lamellar ribbons and subsequent incubation for a certain period of time led to the formation of 1D UC_{Tm} superlattices. Although this UC_{Tm} assembly was rather inhomogeneous so that we decided to optimize the homogeneity of this linear assembly by using the cyclohexanemethylammonium hydrogen sulfate (CHMAHS) organic salt as we mentioned earlier, on the basis of the successful formation of MAPbBr_3 NCs inside the PbBr_2 polymer.³⁰⁶ Peculiarly, the cyclohexyl moiety has been shown to increase the stability of the structures through van der Waals stacking interactions.³¹³ Considering this new strategy, we efficiently prepared UC_{Tm} and UC_{Er} assemblies for the first time as shown in **Figure 6.1a,b**. These assemblies had lengths and widths of up to 1.2 μm and 35 nm, respectively. In parallel with this, CsPbBr_3 perovskite NCs were synthesized by a hot-injection approach with slight modifications,⁵¹ and then subjected to be assembled with PbSO_4 clusters as previously described. Interestingly, NCs preserved its morphology after deposition on a glass substrate unlike was observed for the MAPbBr_3 NCs inside the PbBr_2 polymer.³⁰⁶

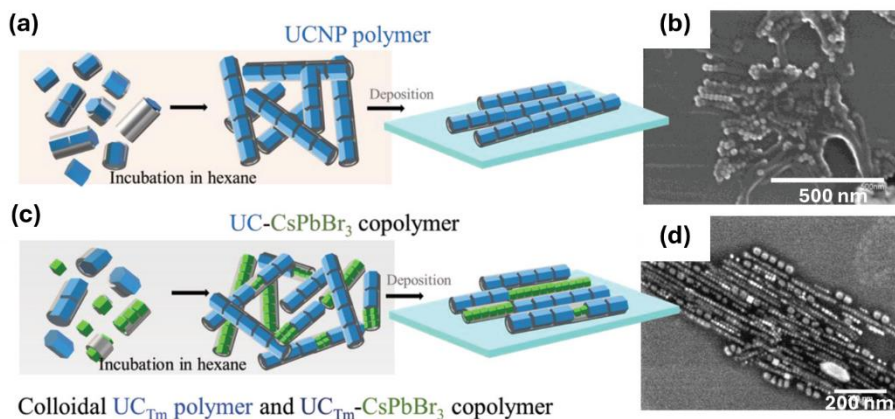


Figure 6.1. (a) Schematic representation of the growth and deposition of an UCNP polymer. (b) SEM image of UC_{Tm} polymer deposited on glass (scale bar: 500 nm). (c) Schematic representation of the growth and deposition of an UC_{Tm}-NC copolymer. (d) SEM image of UC_{Tm}-NC copolymer deposited on glass (scale bar: 200 nm).

After successfully preparing linear assemblies of UCNPs and NCs, we proceed with the co-assembly of both entities, following the same strategy, in which the resulting co-assembly showed a block-type arrangement (**Figure 6.1c,d**). Once prepared, our aim was to study the potential of this co-assembly to sensitize the perovskite emission under NIR excitation. This approach leverages the strong absorption features of the perovskite in the visible range and the good spectral overlap between the upconversion PL and the perovskite absorption of NCs.

6.3.2. Photophysical study using single photon counting

UCNPs exhibit characteristic narrow PL bands in the blue or green spectral region depending on the activator composition (Tm³⁺ or Er³⁺). Regarding UC_{Tm}, five intense PL bands in the blue region below 500 nm are observed corresponding to 290 nm (¹I₆ → ³H₆), 345 nm (¹I₆ → ³F₄), 368 nm (¹D₂ → ³H₆), 450 nm (¹D₂ → ³F₄) and 475 nm (¹G₄ → ³H₆) transitions under low-power CW 980 nm excitation (up to 10 Wcm⁻²). Upon assembly with PbSO₄ clusters, UCNPs experienced a significant increase in

upconversion PL. However, a deeper analysis of the emission time constants of UCNPs revealed that these constants remained nearly unchanged. This suggests that the observed enhancement in upconversion PL is not due to an increase in the emission rate constant, but likely due to other factors influenced by the assembly process with PbSO_4 clusters.

Remarkably, in the presence of NCs in the co-assembly, a quenching of the Tm^{3+} PL intensity concomitantly with the apparition of a PL band centered around 514 nm was noticed, thereby matching the PL maximum of NCs. *A priori*, this is consistent with an efficient ET process from the UC_{Tm} to the NC due to the co-alignment of both entities in the assembly and the good spectral overlap properties of the co-assembly. Control experiments indicated the absence of upconversion PL of NCs in the assembly under the same conditions, further corroborating the need of the UC_{Tm} entity. Generality of this assembly strategy was demonstrated by the preparation of $\text{UC}_{\text{Tm}}\text{-CsPbCl}_3$, $\text{UC}_{\text{Tm}}\text{-CsPbCl}_{1.75}\text{Br}_{1.25}$, $\text{UC}_{\text{Tm}}\text{-CsPbBr}_{1.25}\text{I}_{1.75}$ co-assemblies. All of them showed efficient sensitized PL of NCs through NIR-induced ET.

According to PL lifetimes of UC_{Tm} , the emission decay trace at 475 nm was conveniently recorded under a microsecond-pulsed 980 nm laser diode excitation in order to determine the involvement of the LRET mechanism. The decay trace of UC_{Tm} in the co-assembly fitted to a biexponential function with a short (τ_1) and long (τ_2) decay components of 361 μs (37 %) and 603 μs (63 %), respectively. The shorter and longer time constants are attributed to Tm^{3+} ions closer to the surface and those located inner the core, respectively. However, these components are a way shorter than those obtained for UC_{Tm} in the assembly (396 μs (37 %) and 646 μs (63 %)), indicating the partial LRET mechanism. Although the average LRET efficiency was calculated to be only 7 %. The typical ns-lifetime of NCs greatly lengthened under selective NIR excitation of the UC_{Tm} , further proving the emergence of ET in the co-assembly. Notwithstanding, the sensitized lifetime of NCs was still so different from

that of the UC_{Tm} donor, meaning that enhancement in upconversion PL was likely due to radiative energy transfer rather than nonradiative mechanisms (LRET). Interestingly, a considerable enhancement of the efficiency in LRET up to 37 % was noticed when the co-assembly was deposited as solid films, where both entities are now brought closer in comparison to the colloid as shown in **Figure 6.2a,b**. In addition, the sensitized PL of NCs showed now closer time constants to those of the UC_{Tm} assembly (**Figure 6.2c**).

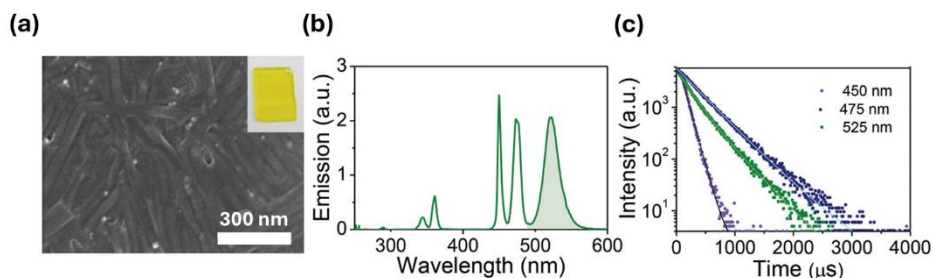


Figure 6.2. (a) SEM image of a UC_{Tm}-NC co-assembly film prepared by the centrifugal casting method. Inset: digital photograph of the film. (b) Emission spectrum under 980 nm CW laser excitation. (c) PL decay traces under 980 nm laser excitation recorded at 450, 475, and 525 nm of the UC_{Tm}-NC co-assembly film.

6.3.3. Photophysical study using NIR-MLS microscopy

The efficient ET mechanism was further corroborated by the NIR-MLS microscopy technique, which employed a high-power, femtosecond-pulsed 980 nm laser. For this technique, the microscope images of UC_{Tm}, UC_{Tm} assembly and UC_{Tm}-NC co-assembly under 20.1 MWcm⁻² excitation were recorded on two channels (1: 450 – 505 nm and 2: 515 – 560 nm) with a dwell time of 8 μs as shown in **Figure 6.3a**. The UC_{Tm} exhibited characteristic emission tails in the channel 1 as previously observed,³⁰³ owing to the long PL lifetime of the UC_{Tm} whereas negligible PL emission was detected in channel 2 since UC_{Tm} scarcely emit in this channel (**Figure 6.3b,c**). The analysis of the PL tail indicated a lifetime of 338 μs under these

conditions. The UC_{Tm} assembly led to similar PL tails in channel 1 because of the similar lifetimes (**Figure 6.3d,e**). However, analysis of the decay trace was unfeasible, even though the UC_{Tm} assembly sample was very diluted. In contrast, the UC_{Tm}-NC co-assembly exhibited a strong quenching of the upconversion PL in channel 1, accompanied by the appearance of a bright emission in channel 2 attributed to the perovskite (**Figure 6.3f,g**). Control experiments showed that under identical conditions, the direct two-photon absorption of NCs in the assembly resulted in negligible emission. Therefore, these facts clearly demonstrated the effectiveness of the LRET in the UC_{Tm}-NC co-assembly using this technique with these high-power conditions.

The power dependence of the PL intensity of the perovskite in the NC assembly and UC_{Tm}-NC co-assembly was also analyzed, but at high irradiance (10^6 – $2.9 \times 10^7 \text{ Wcm}^{-2}$), recording the 515–560 nm emission (channel 2) after excitation at 980 nm (not shown here). The ln–ln plots of PL intensity versus excitation power showed a slope of ca. 2 in the NC assembly, which is in agreement with the previously reported two-photon absorption behavior of NCs.³¹⁴

On the contrary, the UC_{Tm}-NC co-assembly exhibited a slope of 2.5, indicating the involvement of at least three-photon processes. This observation aligns with the hypothesis that the perovskite excited state is populated via LRET from the UC_{Tm}.

Finally, the chemical stability of the perovskite in the co-assembly in direct contact with water increased due to the semi-open peapod-like shell (not shown here), which partly isolates from the environment, offering new opportunities for practical applications of perovskite-based materials.

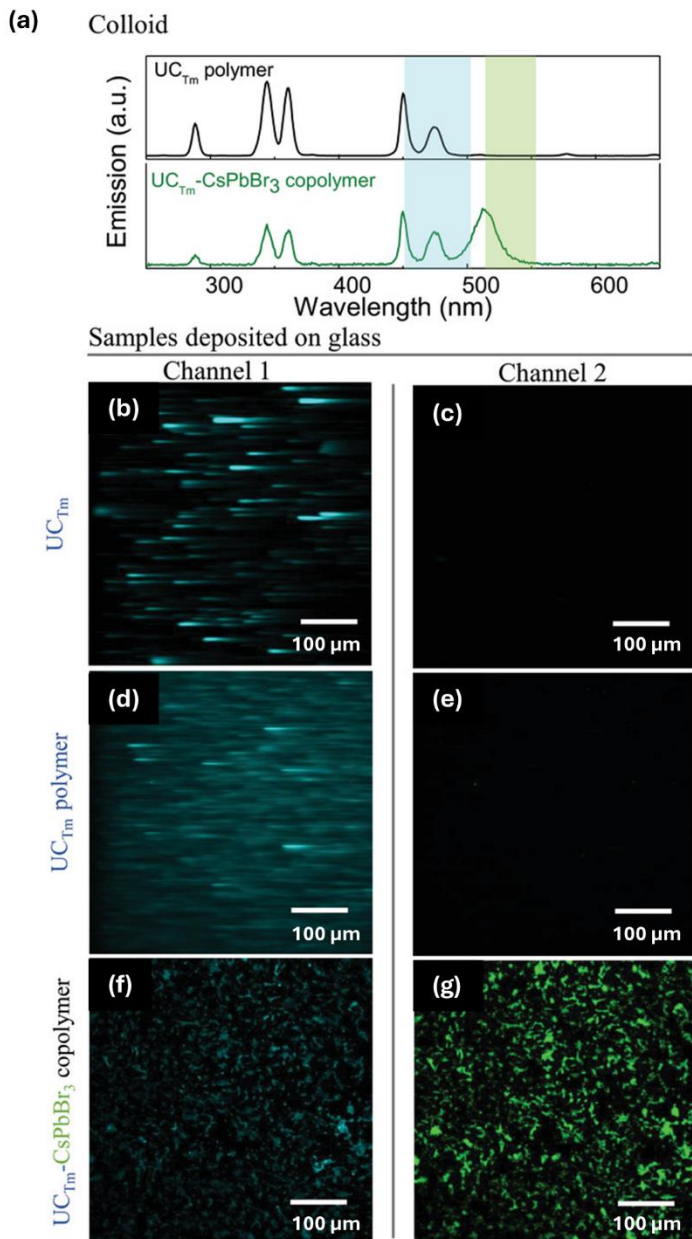


Figure 6.3. (a) PL spectra of the colloidal UC_{Tm} assembly and the UC_{Tm}-NC coassembly are shown here to guide the reader as to the emissive species under 980 nm excitation in each

channel (either the UCNP or the NC); the blue and green bands represent the emission range analyzed by multiphoton microscopy (channels 1 and 2, respectively). Confocal images of **(b,c)** UC_{Tm}, **(d,e)** UC_{Tm} assembly, and **(f,g)** UC_{Tm}-NC co-assembly; acquired under 980 nm pulsed excitation (20.1 MW cm^{-2}), under 450–505 nm (channel 1) and 515–560 nm (channel 2); 8 μs per pixel.

6.4. Conclusions

In summary, we have efficiently prepared the linear UCNP assembly and block-type UC_{Tm}-CsPbX₃ co-assembly by using this cluster-assisted process for the first time. The preferred use of CHMAHS instead of TBAHS optimized the linear assembly due to the better interaction between cyclohexyl moieties. The sensitization mechanism of the NC from UCNP under NIR excitation has been proved by two different techniques, i.e, (i) single photon counting using a low-power excitation source, which demonstrated that the LRET mechanism does not compete with the radiative energy transfer, and (ii) NIR-MLS microscopy employing a high-power excitation source, in which the predominant sensitization mechanism was attributed to LRET due to the strong shortening of the Tm³⁺ PL lifetime below the resolution limit of our setup. The higher efficiency in terms of LRET in the solid film resulted from the close proximity of both entities in the co-assembly than in solution. Power-dependent studies shed light on the number of photons involved in populating a target excited state, where a slope of 2 and 2.5 were found for NC assembly and UC_{Tm}-NC co-assembly, respectively, which indicates that at least three-photon processes occurred in the latter case. Finally, the chemical stability of the co-assembly was further demonstrated as a consequence of the stabilizing effect of the semi-open peapod-like structure.

Chapter 7.

The Power of *N,N*-Disubstituted Amino Moieties on the Emissive Properties of Push-Pull Systems

7.1. Introduction

Organic molecules with a delocalized π -system of electrons have emerged as attractive candidates for advanced functional materials due to their unique optical and electronic properties. Concerning this matter, push-pull systems or donor-acceptor organic compounds are pivotal here, which are conjugated organic molecules characterized by the presence of electron-donating and electron-withdrawing moieties linked through a π -conjugated system, thereby facilitating this charge delocalization across the entire molecule. This delocalization of the electron cloud between the donor and acceptor moieties is also known as intramolecular charge transfer (ICT),³¹⁵ and ICT materials have extensively been used as potential sensitizers in DSSCs,³¹⁶⁻³²¹ and as HTMs in PSCs,³²²⁻³²⁴ for instance, owing to their high molar absorption coefficient, long exciton diffusion length and efficient hole mobility, respectively, which potentially might lead to high values of open-circuit voltage.³²⁵ In addition, these materials have successfully been integrated into organic light-emitting diodes (OLEDs) due to their high Φ_F .³²⁶⁻³³⁰

Push-pull systems typically exhibit strong fluorosolvatochromism as a result of the large dipole moment in the excited state compared to that in the ground state.³³¹⁻³³² This large Stokes shift stems from an intramolecular relaxation process in an electronically excited state upon increasing solvent polarity, leading to a new energetic minimum that is significantly lower in energy compared to the initially excited structure. This relaxation process typically accompanies not only changes in bond lengths and bond angles but also structural changes due to rotation around a single bond.³³³

In this context, pyrimidine derivatives have extensively been used as the electron-withdrawing group in push-pull systems due to the significant π -deficient character of diazine rings. However, these systems substituted with electron-

donating fragments through π -conjugated linkers are highly fluorescent and sensitive to external stimuli, making them suitable for various optoelectronic applications.³³⁴ This situation is based on the classic use of 4-(dimethylamino)benzonitrile (DMABN) to illustrate a push-pull system. This relatively simple molecule has gathered significant attention due to its intriguing behavior under photoexcitation and the subsequent ICT processes, which makes it an ideal candidate for both empirical and theoretical studies. Despite extensive research, the exact mechanisms leading to its lower-energy emission remained under debate due to the complexity of the relaxation process, with several models proposed to explain these phenomena. On the one hand, the twisted intramolecular charge transfer (TICT) model was proposed by Grabowski et al. to elucidate the dual fluorescence consisting of a broad, red-shifted band emitted from an ICT state and a blue-shifted band attributed to a locally excited (LE) state, observed for DMABN in polar solvents.³³⁵⁻³³⁷ According to this model, after electronic excitation, a charge transfer occurs simultaneously with a significant structural change – a rotation around a single bond, typically by about 90°. This rotation electronically disconnects the donor and acceptor moieties in the excited state, thereby impacting the optical and photophysical properties. The driving force for this sort of stabilization emerges from the minimization of the Coulomb interaction of the two unpaired electrons.³³⁵ On the other hand, Zachariasse et al. proposed the planarized intramolecular charge-transfer (PLICT) model to explain the opposite effect in which a rotation of ca. 90° leads to a planarization of the donor and acceptor moieties in the excited state instead.³³⁸⁻³⁴⁰ Although both mechanisms lead to a redshift in the fluorescence properties, the Φ_F associated with the TICT process is typically weakened whereas the Φ_F is even maintained for the PLICT process.³⁴¹

The importance of electron-donor and acceptor groups, conjugation in the excited state, and the nature of π -bridges (particularly thiophene) has been

investigated in the literature for indolo[2,3-*b*]quinoxaline-based dyes, aryl-substituted indolo [2,3-*a*]carbazole derivatives synthesized and indeno [1,2-*b*]indole donor derivatives.³⁴²⁻³⁴⁴ Thus, rationalizing the excited-state properties of these push-pull materials provides valuable insights into the design of novel functional materials with tailored optical properties for various applications.³⁴⁵

With this perspective, we aimed to unravel the underlying mechanisms of fluorosolvatochromism in biphenyl derivatives that govern their optical and photophysical properties. Particularly, push-pull systems that comprise a dialkylamino or diarylamino as the electron-donor and a pyrimidine as the electron-acceptor moieties, respectively, were studied by employing steady-state and time-resolved fluorescence techniques, supported with theoretical calculations, which accurately explain the main findings. This finding contributes significantly to expanding knowledge about the photochemical behavior and properties of push-pull systems and enhances the understanding of the relationship between the molecular structure of the amino donor, the solvent environment and the fluorescence properties. Finally, we foresee that these materials could pave the way for innovative applications in OLEDs and perovskite-based optoelectronic devices.³⁴⁶

1.3 Experimental section

Methods

7.1.1. Synthesis of push-pull systems of biphenyl derivatives

The 4-[4-(4-*N,N*-dimethylaminophenyl)phenyl]-2,6-diphenylpyrimidine (D1) and 4-[4-(4-*N,N*-diphenylaminophenyl)phenyl]-2,6-diphenylpyrimidine (D2) push-pull systems were synthesized by Dr. Carolina Aliaga from the University of Santiago de Chile, by following their previously reported protocol. In brief, a microwave vial

(10 mL) was charged with bromophenyl-4-pyrimidines (0.7 mmol), Pd(PPh₃)₄ (41 mg, 0.035 mmol, and 5 mol%), K₂CO₃ (97 mg and 0.7 mmol), DMF (5 mL), and 4-(*N,N*-dimethyl)phenylboronic acid (139 mg and 0.84 mmol) for D1 or the 4-(*N,N*-diphenyl)phenylboronic acid (243 mg and 0.84 mmol) for D2. The resulting reaction mixture was heated for 1 h at 100 °C. Upon the end of the reaction (as observed on TLC, n-hexanes:EtOAc, 5:1), the crude was diluted with water (25 mL) and extracted with EtOAc (3×15 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, and all the volatile components were removed by evaporation. The respective products were purified by column chromatography (n-hexane: EtOAc, 20:1 → 5:1).

1.1.10. Sample purging

A measure of 3 mL contained optically matched D1 or D2 solutions at 0.1 OD at an excitation wavelength (365 nm) was purged with nitrogen directly from the cylinder for 5 min by placing a syringe needle through the septum into the bottom and another into the air space above the sample as a vent with a flow rate of dry nitrogen so that bubbles are observable in the sample. In case the solvent was evaporated upon bubbling, the cuvettes were refilled with extra purged solvent. Immediately after this procedure, samples were placed in the instrument for measurement. Cuvettes of 1 cm optical path length were used for spectroscopy studies.

Instruments

7.1.2. Thermal measurements

The thermal properties of D1 and D2 were examined under a nitrogen atmosphere, with a heating rate of 10 °C/min up to 950 °C.

7.1.3. Computational details

The singlet ground state (S_0) was optimized using DFT calculations. The first excited singlet state (S_1) was also optimized at the TD-DFT level of theory. All the calculations were performed based on the exchange-correlation Becke's three-parameter (B3LYP) functional,³⁴⁷⁻³⁴⁸ and the split-valence triple-zeta 6-311G** basis set,³⁴⁹ without imposing any symmetry restriction. Calculations were carried out using Gaussian 16 software (Rev. A.03).³⁵⁰ Solvent effects (hexane, toluene, ACN, and DMSO) were implicitly considered by employing the polarizable continuum model (PCM) method.³⁵¹ For this reason, all the excited state geometries were obtained at the LR-PCM TD-DFT level of theory. Nevertheless, solvent effects on the photophysical processes (absorption and emission) can be inadequately reproduced using LR-PCM.³⁵² To solve this problem, single vertical point calculations were employed, at the optimized LR-TD-DFT geometries, using the corrected linear response (CLR-PCM) method.³⁵³⁻³⁵⁴ This approach allows to relax the interaction between the solvent and the solute molecule in the excited-state minima, thus improving the description of the excited states from an energetical point of view. All the energies discussed in the main text refer to PCM-CLR TD-DFT energies. The optimizations must be carried out at the LR-PCM TD-DFT level of theory because CLR-PCM TD-DFT is only implemented for single-point calculations. The ORCA 5.0.1 code was additionally used,³⁵⁵ employing the same computational approach (B3LYP/6-311G**) and simulating the solvent effects with CPCM methodology,³⁵⁶ to characterize the minimum energy paths (MEPs) connecting two singlet excited-state minima belonging to the same potential energy surface (PES). This was accomplished by employing the climbing image nudged elastic band (CI-NEB) method.³⁵⁷ The energy of the so-obtained MEPs was then re-computed using Gaussian 16 as described previously. The computation of natural transition orbitals (NTOs) and the Mulliken population analysis were performed as implemented in Gaussian 16.³⁵⁸⁻³⁵⁹

7.2. Results and discussion

7.2.1. Steady-state and time-resolved optical properties

The synthesis of D1 and D2 was first carried out using a previously reported procedure found elsewhere (see **Figure 7.1a,b** for molecular structures).³⁶⁰ The optical and photophysical properties of D1 and D2 were investigated in a battery of solvents with different solvent optical dielectric constants (ϵ_{op}) from nonpolar solvents such as hexane up to highly polar solvents such as DMSO, as can be seen in the photographs in **Figure 7.1c,d**. According to the ground-state absorption properties, both systems are characterized by only slight differences in the absorption features, which involve two major absorption bands, 260 – 285 nm and 355 – 380 nm for the high- and low-energy bands, respectively, along with a small shoulder at approximately 303-307 nm for D2. The shape and energy of the high-energy absorption band in both systems are nearly independent of the solvent polarity, whereas the low-energy band shows a weak dependent on solvent polarity, being redshifted in DMSO compared to hexane. This suggests a low molecular dipole moment in the ground state (**Figure 7.1e,f**). On the contrary, the solvent dependence on the fluorescence properties under 365 nm excitation is fairly complex but interesting. As the dielectric constant of the solvent increases, a strong positive fluorosolvatochromism is observed, indicating that the excited state has a larger dipole moment than that in the ground state. This significant redshift in the excited-state properties suggests a charge transfer origin between the donor and acceptor moieties in the emitting excited state. Specifically, the fluorescence spectrum of both systems in hexane showed well-resolved vibronic bands associated with a structured emission due to the small solute-solvent interaction. Nevertheless, the fluorescence band progressively redshifts, broadens and loses its vibrational fine structure as the dielectric constant of the solvent is increased (Stokes shifts of 50 – 250 nm between hexane and DMSO), as observed in **Figure**

7.1e,f. Lippert-Mataga analysis was also performed to investigate the dependence of the Stokes shift ($\Delta\lambda$) as a function of the orientation polarizability (Δf) of the solvent.³⁶¹⁻³⁶² The linear behavior observed for both compounds clearly shows the higher dipole moment in the excited state compared to that of the ground state, supporting the ICT nature of the excited state (**Figure 7.1g,h**). The higher slope for D1 compared to D2 indicates a more pronounced charge-transfer process in the former. Interestingly, it is noteworthy that the deviation of the linearity in hexane for both compounds supports the coexistence of partial contribution of the LE state.

According to the emissive properties, both systems displayed marked differences in terms of fluorescence efficiency. They exhibited high Φ_F in nonpolar solvents such as hexane, which is explained by the weak solute-solvent interaction. However, Φ_F of D1 was significantly diminished in polar solvents such as DMSO, whereas D2 even maintained the high Φ_F observed in nonpolar solvents. In the case of solvents with intermediate polarity, other factors such as solvent polarizability (π^*) and hydrogen-bonding ability of the solvent (α'') also play significant roles and thus, explain the complex solvent-dependent optical behavior observed.³⁶³

Chapter 7. The Power of *N,N*-Disubstituted Amino Moieties on the Emissive Properties of Push-Pull Systems

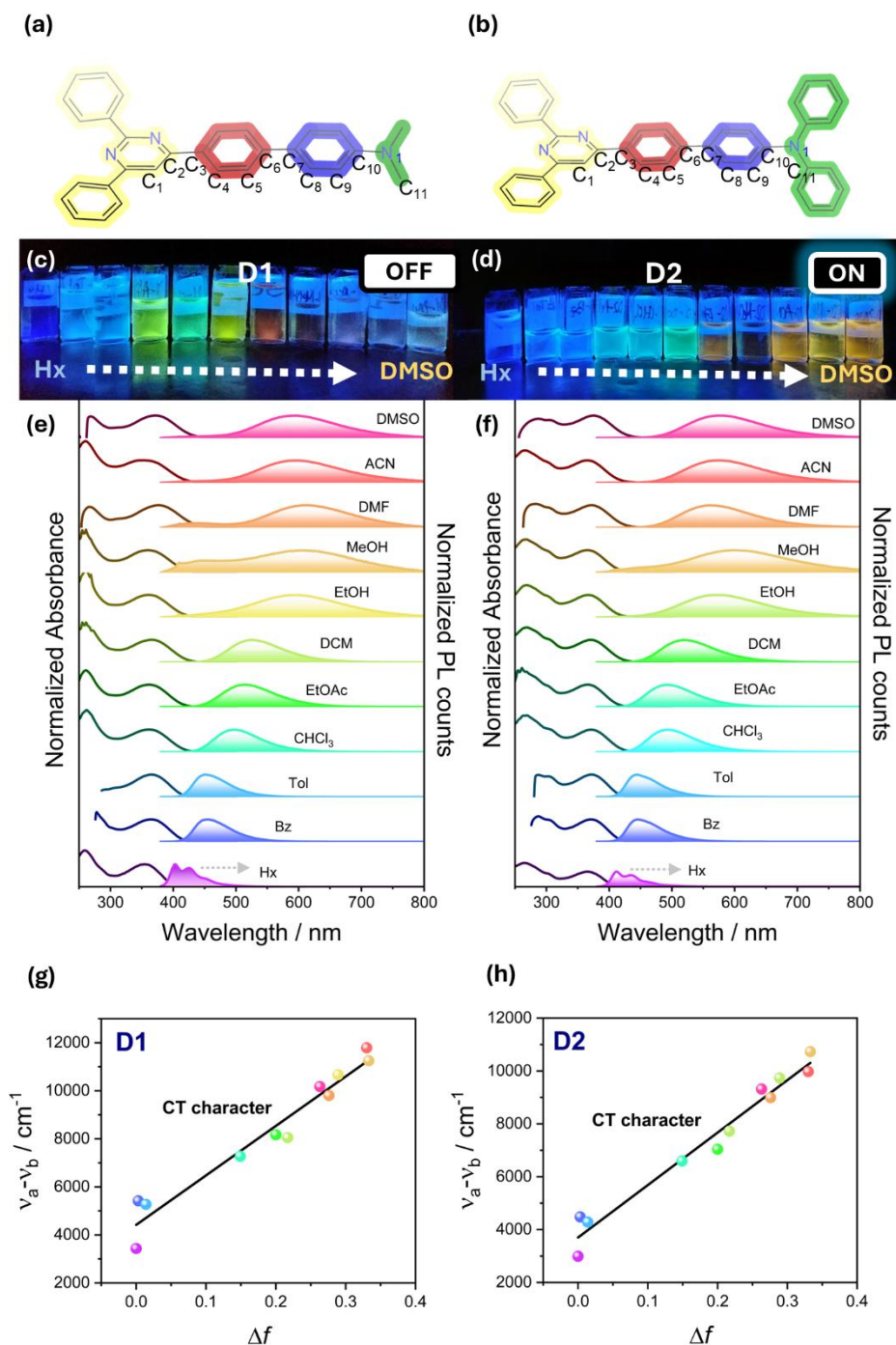


Figure 7.1. Molecular structures for **(a)** D1 and **(b)** D2, and atomic numbering used to define the dihedral angles in the optimized geometries. Digital photographs for **(c)** D1 and **(d)** D2 in solvents with an increasing dielectric constant from hexane to DMSO under 365 nm excitation. Normalized absorption and fluorescence spectra for **(e)** D1 and **(f)** D2 in the solvents shown previously under anaerobic conditions. Lippert-Mataga plots for **(g)** D1 and **(h)** D2.

All data regarding the absorption, fluorescence, and efficiency properties are summarized in **Table 7.1**.

Table 7.1. Optical data (absorption and fluorescence maxima, Stokes shift and absolute fluorescence quantum yield (Φ_F) of D1 and D2 systems in solvents with decreasing dielectric constant (ϵ_{op}) under anaerobic conditions.

Sample	Solvent dielectric constant, ϵ	Abs. max. (nm)	Fluor. max. (nm)	Stokes shift, $\Delta\lambda$ (nm)	Fluor. quantum yield, Φ_F (%)	Nature of the solvent
D1	Dimethylsulfoxide (DMSO, $\epsilon = 46.7$)	265, 376	410, 436, 609	233	16	Polar aprotic
	Acetonitrile (ACN, $\epsilon = 37.5$)	260, 349	418, 593	244	19	
	Dimethylformamide (DMF, $\epsilon = 36.7$)	265, 373	410, 438, 588	215	29	
	Methanol (MeOH, $\epsilon = 32.7$)	260, 361	410, 445, 608	247	2	Polar protic
	Ethanol (EtOH, $\epsilon = 24.5$)	261, 364	410, 595	231	7	
	Dichloromethane (DCM, $\epsilon = 8.9$)	261, 369	525	156	82	Medium polar
	Ethyl acetate (AcOEt, $\epsilon = 6.0$)	261, 362	514	152	54	
	Chloroform (CHCl ₃ , $\epsilon = 4.8$)	262, 365	497	132	41	
	Toluene (Tol, $\epsilon = 2.4$)	286, 365	452	87	87	Nonpolar
	Benzene (Bz, $\epsilon = 2.3$)	278, 365	455	90	96	

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	Hexane (Hx, $\epsilon = 1.9$)	259, 354	403, 425, 454	49	87	
	Dimethylsulfoxide (DMSO, $\epsilon = 46.7$)	287, 307, 374	411, 574	200	79	
	Acetonitrile (ACN, $\epsilon = 37.5$)	265, 303, 365	411, 574	209	78	Polar aprotic
	Dimethylformamide (DMF, $\epsilon = 36.7$)	279, 306, 372	411, 559	187	87	
	Methanol (MeOH, $\epsilon = 32.7$)	265, 304, 365	411, 447, 600	235	3	Polar protic
	Ethanol (EtOH, $\epsilon = 24.5$)	268, 305, 367	411, 571	204	31	
D2	Dichloromethane (DCM, $\epsilon = 8.9$)	269, 307, 371	520	149	91	
	Ethyl acetate (AcOEt, $\epsilon = 6.0$)	257, 304, 366	493	127	82	Medium polar
	Chloroform (CHCl ₃ , $\epsilon = 4.8$)	266, 308, 372	493	121	84	
	Toluene (Tol, $\epsilon = 2.4$)	286, 306, 373	444	71	96	
	Benzene (Bz, $\epsilon = 2.3$)	287, 307, 371	455	74	69	Nonpolar
	Hexane (Hx, $\epsilon = 1.9$)	267, 303, 366	411, 434, 465	45	75	

Regarding time-resolved properties, fluorescence decay traces showed a correlation of the lifetime parameter with solvent polarity only for D2, with lifetimes spanning from 1.51 to 4.64 ns from hexane to ACN, consistent with a stabilization of the excited state. Nevertheless, this correlation was absent in D1, suggesting a more complex process in the latter. Nearly all decays displayed monoexponential fitting, except for D1 in DMF, ACN and DMSO, which showed a biexponential

behavior owing to the coexistence of two-emitting species: localized-excited (LE) and ICT states. The LE state likely arises from the H-bond interaction of the amine group of D1 with the solvent. Interestingly, the fluorescence lifetime in polar protic solvents such as methanol was significantly quenched for both compounds because of the strong hydrogen-bonding ability of this type of alcohol. However, in the case of D2 in ethanol, this quenching is partially suppressed, which suggests a less effective interaction of ethanol molecules with the electron pair of the amine due to the steric hindrance introduced by the phenyl substituents of D2.

From Φ_F and time-resolved measurements, the corresponding kinetic parameters can be extracted with a view to inspecting the radiative (k_r) and nonradiative (k_{nr}) rate constants. The k_r decreased in both systems as the dielectric constant raised while the k_{nr} increased considerably for D1. However, this k_{nr} remains lower in polar solvents, thus resulting in a high Φ_F even in polar solvents. The kinetic data described above perfectly correlates with the strong dependence of the emissive properties on the nature of the *N*-donor substituent of the biphenyl derivatives push-pull systems.

It is worth noting that these systems have demonstrated high stability at the typical annealing temperature required for optical device preparation (>100 °C, data not shown here).

7.2.2. Quantum-chemistry theoretical calculations

DFT and TD-DFT calculations were performed for the ground and excited states, respectively, to disentangle the different optical and photophysical behaviors of D1 and D2 in polar solvents. Specifically, geometry optimization was conducted at the DFT B3LYP/6-311G** and TD-DFT B3LYP/6-311G** levels of theory for the S_0 and S_1 , respectively, in two sets of solvents of different polarity:

hexane and toluene to represent the nonpolar solvents, while ACN and DMSO served as examples of the polar solvents to describe the polar aprotic solvents.

To define the deviations from molecular planarity and characterize the obtained minima, the $C_1C_2C_3C_4$, $C_5C_6C_7C_8$, and $C_9C_{10}N_1C_{11}$ dihedral angles, which account for the internal twisting of the pyrimidine ring, the central biphenyl unit and the amino group, respectively, were used. The $C_1C_2C_3C_4$ and $C_5C_6C_7C_8$ angles exhibited similar values for both D1 and D2 (approximately 20° and 35° , respectively) regardless of solvent polarity for the ground state, whereas the $C_9C_{10}N_1C_{11}$ dihedral angle showed drastic changes of approximately 8° and 36° for D1 and D2, respectively. The difference mostly arises from the steric hindrance caused by the phenyl groups attached to the terminal amine group in D2.

Considering the minimum-energy geometry of the S_0 state, the absorption properties of both systems were calculated. The results indicated that the previously observed low- and high-energy absorption bands correspond to vertical transitions to the S_1 and S_4 singlet excited states, respectively. Although the computed maxima for the S_1/S_4 transitions in both systems are redshifted in all solvents studied, consistent with the well-documented underestimation by B3LYP functional,³⁶⁴ the calculations accurately predicted the weak dependence of absorption on solvent polarity and the slight redshift observed when transitioning from D_1 to D_2 .

The S_1 state in both systems predominantly exhibits a charge-transfer character across the four solvents investigated. This state is described by a one-electron excitation from the HOMO to the LUMO, with the HOMO localized over the amine group, which has a substantial contribution from the biphenyl linker, and the LUMO localized on the pyrimidine group. The charge-transfer nature of the S_1 state is further supported by the calculated dipole moments (36 D for D_1 and 32 D for D_2), which are significantly larger than those of the S_0 state (6 D and 3 D, respectively).

In contrast, the S_4 state of D_1 is characterized as a π - π^* state, localized on the pyrimidine group, and is described by a one-electron transition from the HOMO-1 to the LUMO. For D_2 , however, the S_4 state retains a charge-transfer character, primarily involving the HOMO to LUMO+2 orbitals.

Concerning the geometry optimization for the emitting S_1 state, calculations predicted considerable differences, mainly in the $C_9C_{10}N_1C_{11}$ dihedral angle. In the case of D_1 , two minima were found for the lowest singlet excited state, namely, $S_{1,0}$, where the amine group is in the same plane as the adjacent phenyl ring, having a $C_9C_{10}N_1C_{11}$ dihedral angle of roughly 0° , and $S_{1,90}$, where the amine group is perpendicular to the plane of the adjacent phenyl ring, displaying a $C_9C_{10}N_1C_{11}$ dihedral angle close to 90° . Nonetheless, an overall planarization of the other dihedral angles was observed in both systems for the S_0 to S_1 transition. On the other hand, only one minimum was calculated for D_2 , $S_{1,40}$, where the amine group is significantly rotated (40 - 50°) but without being planar nor perpendicular to the phenyl ring. This stark contrast in the number of excited states is a consequence of the steric hindrance caused by the phenyl rings in D_2 . The specific values of dihedral angles for the different molecular geometries are found in **Figure 7.2**. Notably, the values of these dihedral angles are essential for understanding the optical and photophysical properties of these push-pull systems. Based on the obtained values, it can be inferred although, that the biphenyl spacer minimally affects the connection with the acceptor biphenyl pyrimidine moiety, thereby facilitating ICT. However, it significantly influences the conformation of the amine-donor group as it transitions from the S_0 to the S_1 , depending on the nature of the substituent donor and solvent polarity. In the same manner, the predicted energies for the emission maxima of both systems are redshifted with respect to those found experimentally, but accurately describe the shift observed when passing from nonpolar to polar solvents.³⁵⁶

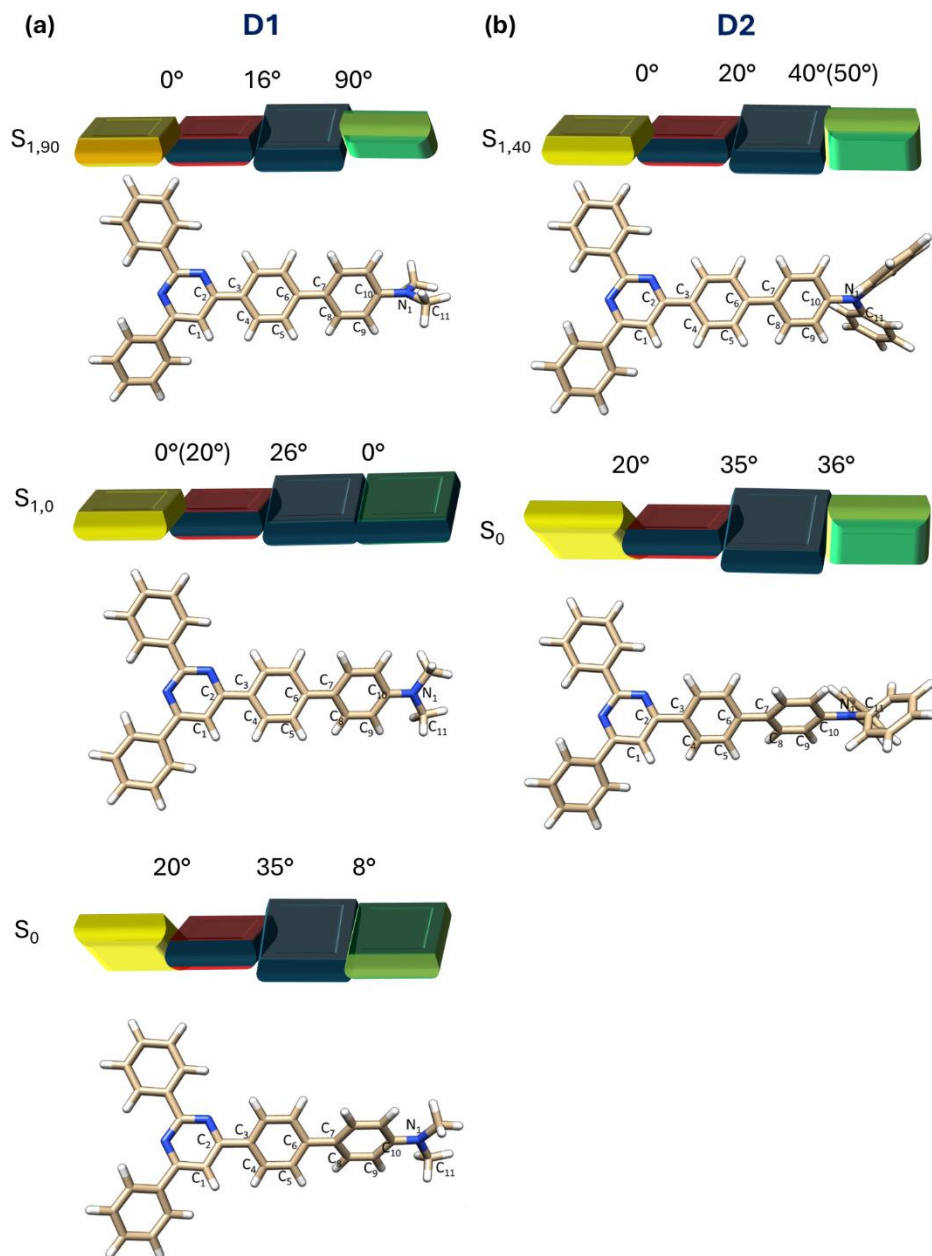


Figure 7.2. Schematic representation showing the twisting of the different molecular fragments for (a) D1 and (b) D2 along with the optimized structures.

7.2.3. Rationalizing the excited-state properties

The $S_{1,90}$ minima of D1 seem to be non-emissive, as the calculated oscillator strength for the transition to the ground state is zero. This is a consequence of the 90° rotation of the amine group, making the overlap between the HOMO and LUMO wavefunctions negligible and agreeing with the TICT process already mentioned in the introduction section. The presence of this dark state in nature appropriately explains the enormous decrease of the Φ_F of D1 in polar aprotic solvents, which is absent in D2 (see the PES in **Figure 7.3a**). In polar aprotic solvents such as ACN, the $S_{1,90}$ state represents the lowest-energy minimum of the S_1 state at 1.81 eV. As a result, this geometry is expected to evolve after the S_1 state is populated. The energy barrier between the $S_{1,0}$ and $S_{1,90}$ states is relatively small (0.25 eV), indicating that the system can easily transition to the $S_{1,90}$ state. Furthermore, the small energy difference between this dark state and the ground state (0.39 eV) favors nonradiative decay back to the ground state. These factors make D_1 highly susceptible to nonradiative deactivation in polar aprotic solvents. The situation completely changes in the case of nonpolar solvents such as toluene (see **Figure 7.3b**). In this case, the $S_{1,0}$ state now represents the lowest-energy minimum. The energy barrier for transitioning from the $S_{1,0}$ to $S_{1,90}$ states is significantly higher (0.43 eV), and the energy gap between this dark state and the ground state is much larger than before (1.76 eV). As a result, nonradiative decay is considerably reduced in this scenario. Finally, the absence of this dark state in D2 in all solvents investigated (**Figure 7.3c,d**), perfectly explains the high Φ_F recorded in both nonpolar and polar aprotic solvents. Only a redshift of the emission maxima is noticed when passing from nonpolar to polar solvents.

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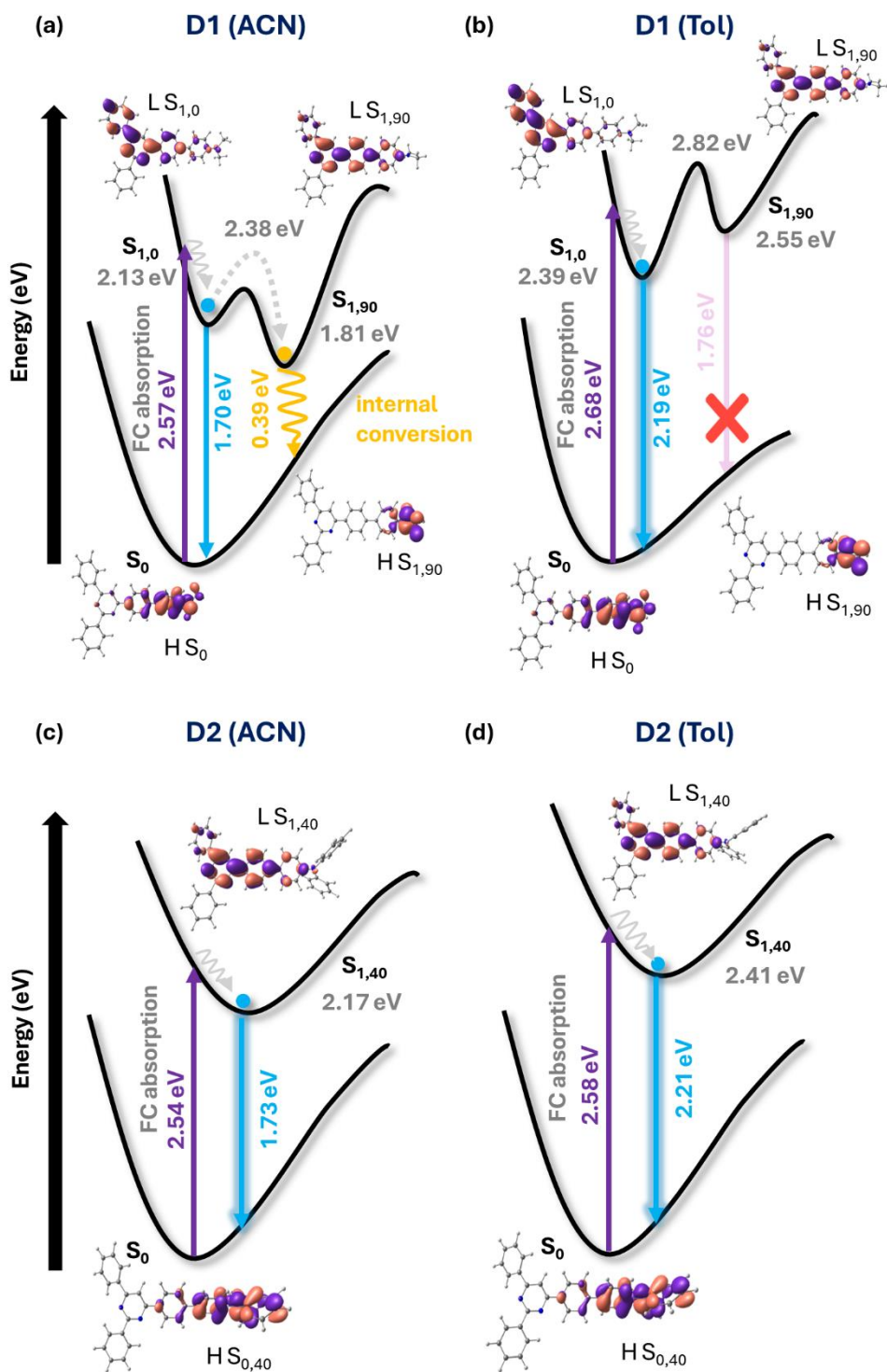


Figure 7.3. Schematic representation of the S_0 and S_1 PES for D1 in ACN **(a)** and Tol **(b)** and for D2 in ACN **(c)** and Tol **(d)** solvents.

7.3. Conclusions

In summary, the large solvatochromism observed for both D1 and D2 push-pull systems is explained based on the charge-transfer character of the S_1 excited state. The presence of either dimethylamino (D1) or diphenylamino (D2) as electron donor groups in the biphenyl derivatives completely dictates their emissive properties according to solvent polarity. While a drastic fluorescence quenching is observed in D1 in polar aprotic solvents, D2 maintains its fluorescence independently of solvent polarity, suggesting different deactivation pathways. Quantum-chemistry theoretical calculations have proven to be a key tool in shedding light on these experimental findings and supporting the presence of a twisted geometry ($S_{1,90}$) in the dimethylamino electron donor group (D1). This twisted minimum is the lowest-energy minimum in polar aprotic solvents and presents a small energy barrier to transition from the excited to the ground state, thereby promoting nonradiative decay and reducing fluorescence efficiency. While this twisted geometry is less favorable in nonpolar solvents, it explains the high Φ_F . In contrast, the absence of this twisted geometry in D2 in all solvents investigated, imposed by the steric hindrance between the phenyl rings of the diphenylamino electron donor group, explains the high-emission properties of D2 even in polar aprotic solvents. We anticipate that these systems could serve as potential candidates for hole-transporting materials in optoelectronic devices, such as perovskite solar cells, due to their hole mobility, suitable band alignment, and good thermal stability.

Chapter 8.

Conclusions

This dissertation holds promise for a relatively new class of nanomaterials: metal-halide perovskites. Metal-halide perovskite nanocrystals (NCs) have demonstrated a profound impact across various research disciplines, ranging from light harvesting to light-emitting applications, including photocatalysis. In combination with suitable molecular acceptors and accounting for precise compositional and size control over the optical and electronic properties, a great deal of singlet, triplet, and charge transfer processes can be conducted at the perovskite-molecular interface. This applies not only to excited state interactions between inorganic nanocrystals and organic molecules but also extends to interactions between inorganic nanocrystals themselves. Finally, an outlook is provided for two push-pull organic compounds to be explored as possible candidates for hole-transporting materials in perovskite solar cells. Together, these elements provide a broader scope for potential light-harvesting and photocatalytic nanosystems, opening new possibilities for innovative applications in solar energy conversion and sustainable chemical synthesis.

The conclusions of each chapter are detailed below:

- Chapter 3: provides a facile size-selective precipitation methodology to separate three different sizes of CsPbBr₃ NCs from the same synthesis batch. Titration experiments were conducted by increasing C-BDP dye concentrations to a fixed NC concentration. This is the *first example* reporting excited-state interactions between perovskites and BODIPY dyes. ¹H-NMR and FTIR experiments showed that all the C-BDP was tightly bound to the NC surface. By using a combination of steady-state absorption and photoluminescence, and time-resolved photoluminescence techniques, we were able to unravel the two main mechanisms occurring at the NC@C-BDP interface: FRET-type energy transfer and hole transfer from the NC to C-BDP. The fact that the smallest nanocrystal size is the one with the highest quenching of the perovskite excited state (97 % of quenching at only 1 μM C-BDP) and also FRET-type energy transfer efficiency (85 %)

is due to the occurrence of both (i) the higher surface-to-volume ratio, which implies a higher number of acceptor molecules on the surface and the deactivation is more effective, and (ii) the smaller nanocrystal size, which involves a smaller separation of the nanocrystal core from the molecular acceptor and therefore a higher rate of energy transfer. As the nanocrystal size increases, the hole transfer contribution rises with respect to that of energy transfer. We also demonstrated the impact of nanocrystal surface chemistry on energy transfer properties by performing a ligand-exchange strategy with a bulkier DDAB ligand, which significantly influenced the dye's approach efficiency to the surface. This work provides meaningful insights into the excited-state interactions between NCs and molecular acceptors such as C-BDP, which is essential for comprehending the sensitization mechanisms, which can lead to significant advancements in the design and optimization of hybrid assemblies. By gaining a deeper knowledge of these interactions, we can enhance the efficiency and functionality of various applications, including photovoltaic devices, optoelectronic systems, and photocatalytic reactions.

- *Chapter 4:* transfers the knowledge acquired in the previous work, in which the smallest nanocrystal size (most confined one) resulted in a higher degree of quenching. Hence, a nanocrystal in this quantum confinement regime is used this time to evaluate the strong effect of iodine substitution in the BODIPY core on the photophysical properties and photosensitization mechanisms of two nanohybrids, NC@BDP and NC@I2-BDP, by selective excitation of the nanocrystal. These nanohybrids were prepared differently compared to the previous work, using a post-synthetic ligand exchange strategy, which made it possible to obtain a highly pure nanohybrid. Using an extensive arsenal of spectroscopic techniques, such as steady-state and time-resolved absorption and photoluminescence coupled with spectroelectrochemistry and quantum-chemical theoretical calculations, enabled the confirmation of different photosensitization mechanisms of the BODIPY acceptors in the two nanohybrids, NC@BDP and NC@I2-BDP. Global analysis across the entire spectrum supports the formation of charge-separated states.

While a small, but detectable amount of sensitized triplet excited state of BDP was generated in NC@BDP, which was confirmed by singlet oxygen measurements, a highly efficient sensitized triplet excited state formation of I2-BDP was detected in NC@I2-BDP instead. The fact that the triplet excited state of BDP is not accessible by direct excitation is justified by the inefficient *isc* process to the triplet manifold. Thus, this sensitization approach, involving charge separation and subsequent charge recombination, provides access to the triplet manifold in BDP dyes that would not be accessible on its own. Effective triplet generation in I2-BDP by sensitization allows the use of the NC@I2-BDP nanohybrid as an energy transfer photocatalyst for the oxidation of α -terpinene to ascaridole, yielding moderate results due to competition of superoxide anion formation, which attacks the perovskite ligands and damages the intrinsic stability of the perovskite. Nevertheless, these findings open new avenues for the utilization of efficient hybrid materials in light-energy conversion and photocatalytic applications.

- Chapter 5: highlights the deep impact on the photosensitization mechanism achieved through selective excitation of the same NC, as in the previous work, but with a different molecular acceptor. In the present case, we turned our attention to phthalocyanine (ZnPc) dyes, in which the crucial role of the anchoring group, such as the carboxylic acid in the phthalocyanine, was confirmed in facilitating the concerted electron exchange-mediated singlet energy transfer. This is the *first example* in which concerted Dexter-type energy transfer in perovskite-based nanohybrids is extensively demonstrated using a complete range of spectroscopic techniques on different time scales and by using a target kinetic model. Detailed analysis on different time scales, by using time-resolved photoluminescence, fs- and ns-transient absorption spectroscopies, indicates that the energy transfer occurs at three distinct time scales, which are related to the different excitonic states of the perovskite. The anchoring of the phthalocyanine to the nanocrystal surface in turn produced several effects: (i) high sensitization (> 100-fold) of the ZnPc singlet by 45 % singlet energy transfer from the NC to ZnPc, (ii)

disaggregation of the dye upon dye attachment, which increased the molar extinction coefficient, and (iii) significant lengthening of the ZnPc triplet excited state in the nanohybrid than the experimental window ($>40\ \mu\text{s}$). All these observations indicate the presence of a disaggregation effect on the NC surface. Specifically, the remaining 55 % of the deactivating pathway was mitigated by the formation of new dark trap states, which arose due to the attachment of the dye. The capability to control and extend the triplet-excited state lifetime of photoactive dyes paves the way for developing advanced materials with enhanced light-energy conversion performance, triplet energy transfer photocatalysis and photovoltaic devices that require efficient charge separation.

- Chapter 6: reports the *first example* of linear co-assembly of CsPbX_3 perovskite nanocrystals (NCs) and $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}/\text{Er}^{3+}$ core ($\text{UC}_{\text{Tm}}/\text{UC}_{\text{Er}}$) and $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}/\text{NaYF}_4$ core/shell ($\text{UC}_{\text{Tm}}/\text{CS}$) upconversion nanoparticles (UCNPs) assisted by PbSO_4 molecular clusters. Once sulfate source precursors is optimized in this work by substituting the organic salt TBAHS for CHMAHS, it resulted in longer and more homogeneous linear structures that were used in the throughout study. Interestingly, the use of UCNP nanoparticles in the linear co-assembly facilitates efficient light harvesting in the NIR region, a process that is not observed with NCs and thus can enhance the PCE in PSCs. The close proximity of the two nanocrystals in the linear assembly enabled the investigation of lanthanide-resonant energy transfer (LRET) mechanism from UCNPs to NCs through NIR laser excitation by using two different techniques, (i) single photon counting using a low-power excitation source and (ii) NIR-MLS microscopy employing a high-power excitation source. The improvement of the chemical stability of NCs under wet conditions demonstrates the stabilizing effect of the PbSO_4 shell and opens interesting new avenues for developing more durable nanocrystals for use in various applications. This includes enhancing the longevity and performance of devices in challenging environments, such as in solar cells, sensors, and photocatalysts, where moisture and other environmental factors can impact

functionality. We envisage considerable enhancement in the efficiency of the LRET mechanism by using random coassembly of similar sizes.

- Chapter 7: systematically demonstrates the strong fluorosolvatochromism effect observed in biphenyl derivative push-pull systems, D1 y D2, in different environments, which is explained by the charge-transfer character of the excited state. During the study, the presence of the various substituents on the donor amino group completely dictates the emissive properties of these compounds, resulting in totally different behavior in polar solvents. The presence of two states (planar and twisted) in D1 compared to one state in D2 (partially rotated) in the excited state illustrates the importance of the substitution in the donor amino group on the excited state properties of these two push-pull derivatives. Here, theoretical calculations greatly support our findings by a simple model. Understanding the excited-state properties of these push-pull systems is crucial for evaluating their potential use as hole-transporting materials in perovskite-based optoelectronic devices, for instance, due to the charge-transfer properties and proper energy-band alignment with the previously observed CsPbBr₃ NCs. The proper design with tailormade properties and effective integration of these materials could lead to superior device efficiency, which is essential to push forward our frontier of knowledge in the field of optoelectronics.

Capítulo 9.

Resumen en Castellano

9.1. Capítulo 1. Introducción

La creciente demanda mundial de energía, impulsada por factores como el crecimiento demográfico, los avances tecnológicos y la mitigación del cambio climático, hace necesario un cambio hacia las fuentes de energía renovables. Históricamente, los combustibles fósiles han abastecido las necesidades energéticas de los países desarrollados, pero han provocado importantes problemas medioambientales, como la contaminación y el calentamiento global. Las energías renovables, especialmente la solar, ofrecen una solución prometedora. El proceso natural de la fotosíntesis, que convierte la energía solar en energía química, ha inspirado a los científicos a desarrollar materiales artificiales captadores de luz, como los semiconductores. Los nanocristales semiconductores inorgánicos como los puntos cuánticos (QDs) son especialmente prometedores debido a sus propiedades ópticas y electrónicas sintonizables, derivadas de los efectos de confinamiento cuántico que surgen cuando sus dimensiones son menores al radio del excitón de Bohr del material.

Las perovskitas de haluro metálico (MHP) emergen como materiales líderes en aplicaciones optoelectrónicas, como la fotovoltaica, los diodos emisores de luz (LED) y la fotocatalisis. Las MHP, en particular en forma de nanocristales (NCs), ofrecen propiedades ópticas superiores a las de los semiconductores convencionales QDs tales como: (i) elevados coeficientes de extinción molar; (ii) elevada y sintonizable fotoluminiscencia que abarca desde las longitudes de onda ultravioleta a las del infrarrojo cercano mediante el intercambio de haluro en la estructura; (iii) tolerancia a los defectos, (iv) fácil síntesis, entre otras. Sin embargo, los problemas de estabilidad frente a los disolventes polares, humedad, luz y la temperatura limitan algunas de sus aplicaciones.

Las interacciones que ocurren entre los ligandos y la superficie de los NCs afectan significativamente a las propiedades intrínsecas de los NCs, por lo que las

estrategias de estabilización son cruciales. La integración de NCs con moléculas orgánicas o nanopartículas puede mejorar los procesos de transferencia de energía y/o carga, ampliando las aplicaciones en conversión de energía solar, fotocátalisis y conversión ascendente de fotones. Así, comprender los mecanismos que ocurren en la interfaz NC-molécula es esencial para optimizar el rendimiento en estas diversas aplicaciones.

Los procesos de transferencia de energía entre NCs y colorantes orgánicos, en los que el NC actúa como donante de energía, requieren que la separación energética HOMO-LUMO del colorante (aceptor) sea igual o inferior a la banda prohibida del NC (donante). En este contexto, la transferencia de excitones singlete puede realizarse a través de mecanismos no radiativos como la transferencia de energía por resonancia de Förster (FRET) o la transferencia de energía de Dexter (DET). La transferencia de energía mediada por FRET es una interacción dipolo-dipolo que depende de factores como la orientación dipolar, el rendimiento cuántico de fotoluminiscencia del donante, el solapamiento espectral entre la fotoluminiscencia del donante y la absorbancia del aceptor, la distancia donante-aceptor, y está limitada a excitones singlete debido a las reglas de conservación del espín. La transferencia de energía mediada por DET, por su parte, implica la transferencia de electrones y huecos simultánea a través del solapamiento orbital, por lo que es aplicable tanto a excitones singlete como triplete. Mientras que FRET funciona a distancias mayores (hasta 10-12 nm), DET requiere una mayor proximidad donante-aceptor (1-2 nm) debido a la necesidad de solapamiento orbital. La transferencia de energía de tripletes (TET) está mediada por mecanismos DET o de transferencia de energía de triplete mediada por transferencia de carga (CT-TET). El mecanismo DET es un proceso concertado que implica la transferencia simultánea de electrones y huecos, mientras que la CT-TET implica un proceso de transferencia de carga secuencial, formando finalmente estados tripletes por recombinación del estado separado de carga.

La eficacia de los procesos de transferencia de energía y/o carga depende del número de moléculas de colorante unidas a la superficie del NC, en lo que también influyen el tamaño y la forma del NC. Aumentar el número de moléculas de colorante unidas a la superficie o utilizar ensamblajes dirigidos de nanocristales puede mejorar la eficacia de la interacción entre ambos sistemas. Sin embargo, la superposición de señales espectroscópicas a menudo dificulta la comprensión de los mecanismos de interacción exactos que subyacen en el estado excitado. Técnicas avanzadas como son la fotoluminiscencia resuelta en el tiempo y la espectroscopia de absorción transitoria, junto con métodos de análisis globales, son esenciales para deconvolucionar con precisión estos procesos y proporcionar más información sobre los mecanismos involucrados.

Las técnicas de láser pulsado, como son la fotoluminiscencia resuelta en el tiempo (TRPL) y la espectroscopia de absorción transitoria (TA), son cruciales para estudiar las interacciones de estado excitado entre NCs y colorantes orgánicos. Estos métodos permiten comprender mejor las interacciones dinámicas de los excitones con los entornos circundantes, como son las capas orgánicas, los disolventes y los estados trampa superficiales. TRPL se centra en los estados excitados emisivos, mientras que TA proporciona información de tanto las especies emisivas como de las no emisivas, ofreciendo información complementaria. Las medidas resueltas en el tiempo, como los cambios en los tiempos de vida de la fotoluminiscencia y la dinámica del TA, ayudan a revelar la transferencia de energía o de carga entre los NCs y las moléculasceptoras. Por ejemplo, si se produce una transferencia de energía, el tiempo de vida de fotoluminiscencia del NC disminuye debido a la presencia de una nueva vía no radiativa que compite con la recombinación radiativa de excitón intrínseca.

Los procesos que ocurren en el estado excitado de los NCs se producen en varias escalas temporales, empezando por la absorción de luz, que genera portadores de carga o excitones. Estos excitones, que han sido electrónicamente

excitados por el exceso de energía con respecto a la energía de la banda prohibida, se enfrían mediante relajación intrabanda hasta los bordes de banda y pueden disociarse transfiriendo alguna de sus cargas/energía a los aceptores adsorbidos o atrapándose en estados superficiales. La recombinación puede producirse por vías radiativas o no radiativas, dependiendo de las propiedades de la NC, como la composición, el tamaño y el número de defectos. Por último, la recombinación electrón-hueco, esencial para la emisión de luz, suele dar lugar a un decaimiento multiexponencial debido a la mezcla de estados emisivos.

Las MHPs son materiales prometedores para las tecnologías de conversión de energía luminosa, sobre todo en optoelectrónica. Sus principales ventajas son el bajo coste de síntesis, la procesabilidad de las dispersiones coloidales, un elevado coeficiente de extinción molar, propiedades ópticas sintonizables y una eficiente separación de cargas. Estas propiedades han impulsado avances significativos en celdas solares, fotodetectores, láseres, pantallas y fotocatalisis. Sin embargo, su naturaleza iónica limita su estabilidad bajo tensiones externas, lo que sigue siendo un reto para su fabricación a gran escala.

El paso de perovskitas de dimensionalidad volumétrica (bulk) a los nanocristales (NCs) ha abierto oportunidades para aprovechar el confinamiento cuántico y mejorar la estabilidad de éstas. Las celdas solares basadas en NCs de perovskita han demostrado su competitividad frente a las películas delgadas policristalinas, con eficiencias de conversión de potencia que alcanzan el 16.6 % en sistemas de cationes mixtos. Sin embargo, persisten problemas como la reducción de la eficiencia de transferencia de carga debida a la presencia de ligandos orgánicos. Además de las capas activas de perovskita, los materiales de transporte de carga, en particular los materiales de transporte de huecos (HTM), son fundamentales para el rendimiento y la estabilidad de los dispositivos. Se están estudiando nuevos HTM donantes-aceptores por su potencial para mejorar la

extracción de carga y la protección que ofrece a la perovskita frente a la degradación medioambiental.

Por otro lado, los NCs de perovskita también son prometedores en fotocátalisis, ya que permiten llevar a cabo reacciones químicas de gran impacto, como la producción de hidrógeno y la reducción de CO_2 . Los nanocristales ofrecen ventajas frente a los semiconductores tradicionales gracias a la separación de energía de banda prohibida sintonizable, pero su inestabilidad química intrínseca en entornos polares todavía limita su aplicación. Los esfuerzos por mejorar su estabilidad se centran en la modificación de la superficie con polímeros o capas inorgánicas, que incrementen su resistencia a la degradación.

En la fotocátalisis por transferencia de energía mediada por tripletes ofrece un enfoque más controlado evitando la corrosión (procesos redox). Estudios recientes han demostrado alta eficacia de las transformaciones químicas impulsadas por la luz utilizando NCs sin degradación. Sin embargo, es necesario seguir investigando para mejorar en la estabilidad a largo plazo, maximizando los procesos interfaciales para una conversión eficaz de la energía solar en química.

Por lo tanto, esta tesis doctoral se centra en el desarrollo de nuevos materiales captadores de luz basados en nanocristales de perovskita, inspirados en la interacción entre la luz y la materia a escala nanométrica. Los NCs de perovskita poseen propiedades excepcionales de absorción de la luz y pueden ajustarse fácilmente para aplicaciones fotovoltaicas y fotocatalíticas. Mediante el estudio de las interacciones en estado excitado entre nanocristales y aceptores moleculares de energía y/o carga utilizando diversas técnicas espectroscópicas, se pretende *profundizar en la comprensión de la dinámica de los estados excitados* en estos nanohíbridos y optimizar su potencial para las aplicaciones antes mencionadas.

A continuación, se describen los objetivos alcanzados en cada capítulo:

- **Capítulo 3:** estudio del efecto del confinamiento cuántico y química de superficie sobre la eficiencia de la transferencia de energía singlete desde los CsPbBr₃ NCs a los colorantes BODIPY anclados a su superficie.
- **Capítulo 4:** evaluación del efecto de la presencia de yodo en el núcleo del BODIPY sobre el mecanismo de fotosensibilización de nanohíbridos basados en CsPbBr₃ NCs. Se demostró que el nanohíbrido CsPbBr₃@I₂-BDP puede actuar como fotocatalizador en la oxidación de alfa-terpineno mediado por transferencia de energía de triplete.
- **Capítulo 5:** análisis exhaustivo del mecanismo de sensibilización de ZnPc en los nanohíbridos CsPbBr₃@ZnPc en distintas escalas temporales, desde femtosegundos a microsegundos, y el rol de los ligandos orgánicos del NC sobre la desagregación del ZnPc en su superficie, dando lugar a una mejora en las propiedades de sensibilización de oxígeno singlete.
- **Capítulo 6:** preparación de co-ensamblajes de perovskita-nanopartícula de conversión ascendente de los tipos CsPbX₃-NaYF₄:Yb³⁺,Tm³⁺ y CsPbX₃-NaYF₄:Yb³⁺,Tm³⁺/NaYF₄ utilizando agentes directores basados en clústeres moleculares de sulfato de plomo, junto con la investigación de las propiedades de captación de luz del infrarrojo cercano (NIR) en la transferencia de energía por resonancia de lantánidos de NaYF₄:Yb³⁺,Tm³⁺ a CsPbX₃.
- **Capítulo 7:** inspección en detalle de las propiedades de fluorosolvatocromismo de dos sistemas de tipo donor-aceptor de electrones derivados del bifenilo en una amplia gama de disolventes, y el efecto de los sustituyentes donantes sobre las propiedades fluorescentes.

9.2. Capítulo 2. Técnicas de caracterización

En esta sección se detallan las técnicas de caracterización más generales para estudiar nanomateriales y colorantes orgánicos, que se dividen en tres

grandes categorías: espectroscopia, microscopia y electroquímica. Estos métodos proporcionan información sobre sus propiedades electrónicas, estructurales y redox, ofreciendo una comprensión global de su comportamiento. Entre las técnicas de espectroscopia, se encuentran las siguientes: espectroscopia de absorción y fotoluminiscencia en estado estacionario y tiempo resuelto, resonancia magnética nuclear e infrarrojo con transformada de Fourier. Dentro de las técnicas de microscopia y electroquímica se encuentran la microscopia de transmisión de electrones y la voltamperometría cíclica, respectivamente.

9.3. Capítulo 3. Efectos de Confinamiento Cuántico en la Eficiencia de Sensibilización Singlete de un Rotor Molecular Basado en BODIPY

9.3.1. Introducción

Los NCs ofrecen propiedades ópticas y electrónicas sintonizables variando su composición, tamaño y forma, lo que permite optimizarlos para aplicaciones en fotovoltaica, optoelectrónica, detección y fotocátalisis. La sensibilización de colorantes orgánicos en los nanohíbridos basados en perovskita y colorante suele basarse en mecanismos de transferencia de energía triplete (TET), pero estudios recientes muestran un creciente interés por los mecanismos de transferencia de energía singlete (SET). Dentro de este tipo de transferencia de energía singlete se encuentran los mecanismos no radiativos, FRET y DET, y radiativo como la emisión-reabsorción (ERA). Los dos primeros mecanismos operan bajo diferentes restricciones de distancia, con FRET actuando sobre distancias más largas (10-12 nm) a través de acoplamiento dipolar, mientras que DET requiere solapamiento orbital (1-2 nm). Los ligandos superficiales de las NCs

desempeñan un papel clave en la determinación del mecanismo de sensibilización, ya que afectan a la proximidad y la unión de los aceptores de energía. Las investigaciones sobre NCs con colorantes de la familia de BODIPY, centradas en los efectos de tamaño del nanocrystal y transferencia de energía, son aún limitadas, y por tanto, merecen una mayor exploración.

En este capítulo, se demuestra cómo el confinamiento cuántico y la química superficial de los NCs afectan la transferencia de energía a los colorantes BODIPY anclados. El mecanismo de tipo FRET predomina para los NCs de menor tamaño, mientras que un mecanismo de tipo CT para los NCs de mayor tamaño. El anclaje de los colorantes BODIPY a la superficie del NC se evidenció mediante espectroscopias de ^1H -NMR y FTIR.

9.3.2. Sección experimental

Todos los nanocristales de perovskita de haluro metálico (CsPbBr_3) que se usan en este estudio se sintetizaron a partir de la estrategia de inyección en caliente. Se aislaron los diferentes tamaños de nanocrystal del mismo lote de síntesis mediante la estrategia de precipitación selectiva de tamaños, que consiste en procesos de centrifugación-redispersión, aislándose así tres tamaños diferentes.

Por otro lado, los colorantes de BODIPY, específicamente, 8-(4-carboxifenil)-4,4-difluoro-4-bora-3a,4a-diaza-s-indaceno (C-BDP) y 8-(4-(3-bromopropoxi)fenil)-4,4-difluoro-4-bora-3a,4a-diaza-s-indaceno (Br-BDP) fueron también sintetizados por métodos ya establecidos.

9.3.3. Resultados y discusión

La caracterización de los tres tipos de tamaños de nanocristales de perovskita aislados (NC-5.6, NC-7.6 y NC-11.9) confirmaron que presentaban la misma estructura cristalina. Sin embargo, los máximos de absorción del excitón y fotoluminiscencia indicaron un cambio considerable en las propiedades ópticas en función del tamaño de éstas.

Capítulo 9. Resumen en castellano

Experimentos de titulación a concentraciones mayores de C-BDP (y manteniendo fija la de NCs) mostraron una fuerte desactivación de las propiedades de estado excitado de los NCs, siendo mayor para los nanocristales más pequeños. Análisis de Stern-Volmer, tanto para intensidades de fotoluminiscencia como para tiempos de vida, indicaron una mayor desactivación de la fotoluminiscencia de la perovskita cuanto menor es el tamaño del nanocristal. La constante de desactivación de fluorescencia en todos los casos ($10^{15} \text{ M}^{-1} \text{ s}^{-1}$) fue mayor a la propia difusión del disolvente ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$). La mayor desactivación en los nanocristales más pequeños se debe a una mayor relación superficie/volumen de los NCs más confinados, que conduce a una mayor interacción con el medio circundante (más colorantes C-BDP unidos por NC), y una menor distancia donante-aceptor, que da lugar a una mayor constante de velocidad para los procesos de transferencia de energía y carga.

La mayor constante de velocidad de desactivación de la fotoluminiscencia en todos los nanohíbridos en comparación con la constante de velocidad de difusión del disolvente sugiere una estrecha interacción entre los nanocristales y los colorantes C-BDP, lo que indica que el aceptor está unido a la superficie del NC o encapsulado en la capa del ligando orgánico. La modificación de la superficie de los NC con ligandos más voluminosos, como el bromuro de didodecildimetilamonio (DDAB), preservó el tamaño de las NC al tiempo que redujo la recombinación no radiativa, aumentando significativamente el rendimiento cuántico de fotoluminiscencia. Sin embargo, la reducción en la interacción en el nuevo nanohíbrido pone de manifiesto la importancia de la capa orgánica del ligando en el control de la interacción con el colorante. Aunque el tiempo de vida de la fluorescencia del C-BDP aumentó dentro de la capa de ligando, no afectó significativamente a la disminución de la fotoluminiscencia de la perovskita, indicando una mejora en la constante de velocidad radiativa del C-BDP por esa disminución en los grados de libertad.

Los espectros de excitación de los nanohíbridos confirmaron la transferencia de energía singlete desde los NCs al C-BDP, como demuestra la coincidencia de los espectros de excitación y de absorción con eficiencias del 85 %, 70 % y 20 % para NC-5.6, NC-7.6 y NC-11.9, respectivamente, correlacionándose con el grado de desactivación y confinamiento de los NCs. Además, se propone un mecanismo competitivo de transferencia de huecos (hT), particularmente para NC-11.9, donde hasta el 80 % de la desactivación de excitones puede ocurrir a través de transferencia de hueco desde la banda de valencia del NC al HOMO del C-BDP. La vía de transferencia de electrones se descarta debido a la desfavorable alineación del potencial de reducción entre los NCs y C-BDP, descartando de esta manera el mecanismo de transferencia de energía Dexter (DET).

Los experimentos control con Br-BDP, que carece del grupo funcional ácido carboxílico, demostraron una interacción insignificante con los nanocristales, lo que confirma que el grupo de anclaje del ácido carboxílico es esencial para facilitar FRET. Los análisis de $^1\text{H-NMR}$ y FTIR corroboraron esta afirmación, mostrando una fuerte unión del colorante C-BDP a la superficie de los NC a través del grupo carboxilato. Los resultados indican desplazamientos significativos en las señales de protones y cambios en las bandas de infrarrojo específicas, todo ello coherente con el fuerte anclaje del colorante a través del grupo carboxílico a los cationes superficiales del NC.

9.3.4. Conclusiones

La precipitación selectiva por tamaño permitió aislar tres conjuntos de NCs de diferentes tamaños, demostrando que los efectos de confinamiento cuántico influyen en la eficacia de desactivación de la fotoluminiscencia de los NCs al interactuar con los colorantes C-BDP anclados en su superficie. El mecanismo de desactivación varía significativamente con el tamaño de los NCs: FRET es el mecanismo predominante en los nanohíbridos NC-5.6 y NC-7.6,

mientras que hT es más prominente en el NC-11.9. Además, el análisis mediante ^1H -NMR y FTIR confirma una fuerte interacción del C-BDP con la superficie del NC.

9.4. Capítulo 4. Evaluación del Mecanismo de Extracción de Excitones en Nanohíbridos Basados en Perovskita

9.4.1. Introducción

Los procesos de sensibilización entre semiconductores inorgánicos y colorantes orgánicos despiertan especial interés en aplicaciones como la fotovoltaica y la fotocatalisis. Comprender, por tanto, estos mecanismos de sensibilización, especialmente en los nanohíbridos basados en perovskita, es clave para optimizar su capacidad de captación de luz. Los nanocristales de perovskita de haluro metálico (NCs) son candidatos ideales para estas aplicaciones debido a la separación de banda prohibida y potenciales redox sintonizables, conseguidos mediante reacciones post-sintéticas de intercambio de haluros, y a su capacidad para transferir selectivamente energía, electrones o huecos.

La transferencia de energía de triplete (TET) de NCs a colorantes orgánicos ha surgido como un enfoque prometedor para generar estados excitados tripletes, pero determinar el mecanismo exacto sigue siendo todavía un reto. Las especies transitorias, como los tripletes moleculares y los estados de carga separada, deben caracterizarse cuidadosamente mediante técnicas espectroscópicas avanzadas. Además, no solo el tamaño de los nanocristales como se observó en el capítulo anterior, sino también los factores estructurales de las moléculasceptoras influyen tanto en la transferencia de energía como de carga. Particularmente, la inducción de estados tripletes mediante la funcionalización

con átomos pesados ha sido objeto de gran atención. Sin embargo, la transferencia de energía triplete de los NCs a los colorantes BODIPY aún no se ha estudiado, lo que supone una oportunidad para seguir investigando en esta dirección.

Este capítulo explora el mecanismo de sensibilización de nanohíbridos de CsPbBr_3 funcionalizados con colorantes BODIPY, concretamente 8-(4-carboxifenil)-1,3, 5,7-tetrametil-4,4-difluoro-4-bora-3a,4a-diaza-s-indaceno (BDP) y 8-(4-carboxifenil)-2,6-diiodo-1,3,5,7-tetrametil-4,4-difluoro-4-bora-3a,4a-diaza-s-indaceno (I2-BDP), denominados NC@BDP y NC@I2-BDP, respectivamente, preparados mediante una estrategia de intercambio de ligando. Se ha estudiado el gran impacto del sustituyente yodado en el núcleo de BODIPY sobre el mecanismo de sensibilización en los nanohíbridos. Mientras que en NC@BDP predomina principalmente un mecanismo FRET (82 %), en NC@I2-BDP predomina un mecanismo de TET mediado por cargas (64 %) que supera a la termalización de excitones calientes hacia el borde de banda y a los procesos FRET, lo que condujo a la formación eficiente de tripletes moleculares de I2-BDP en el nanohíbrido que permitieron la generación eficiente de oxígeno singlete ($^1\text{O}_2$). Nuestros hallazgos no sólo profundizan el conocimiento sobre la transferencia de energía entre los NCs y los colorantes BDP o I2-BDP en los dos nuevos nanohíbridos, sino que también muestran el doble papel de los nanocristales de perovskita en NC@I2-BDP como fotosensibilizador de tripletes altamente eficiente y fotocatalizador en la oxidación de α -terpineno a ascaridol.

9.4.2. Sección experimental

En este capítulo, se sintetizaron nanocristales de perovskita CsPbBr_3 (NCs) de 6.4 nm utilizando la estrategia de inyección en caliente. Esta técnica, previamente discutida en el capítulo anterior, demostró ser eficaz para producir nanocristales que actúan como donadores de energía de manera óptima. Por otro lado, se utilizaron las estrategias correspondientes para sintetizar los dos colorantes BODIPY utilizados en el estudio (BDP y I2-BDP).

En este caso, la preparación del nanohíbrido se llevó a cabo mediante la técnica de intercambio de ligando. Se agregó una cantidad específica de colorante a una dispersión de perovskita y la mezcla se agitó durante un tiempo determinado (15 minutos), seguido de la filtración de la mezcla y conservación del filtrado para su análisis posterior.

9.4.3. Resultados y discusión

Las propiedades ópticas de los nanocristales (NCs) de CsPbBr_3 hibridizados con dos colorantes BODIPY diferentes (NC@BDP y NC@I2-BDP) mostraron un desplazamiento significativo en su absorción debido a la introducción de átomos de yodo, mejorando las propiedades de captación de luz. Los estudios de fotoluminiscencia indican un proceso de fotosensibilización en NC@BDP , como demuestra la fuerte desactivación de la fotoluminiscencia del NC y una fluorescencia 50 veces mayor que el control BDP. Por el contrario, el NC@I2-BDP también muestra una alta eficiencia de desactivación de la fotoluminiscencia (97 %) pero sólo una fluorescencia de I2-BDP 9 veces mayor, lo que sugiere que la transferencia de carga domina sobre la transferencia de energía en este nanohíbrido. El análisis de la fotoluminiscencia resuelta en el tiempo muestra dinámicas de recombinación de excitón más rápidas en NC@BDP en comparación con la del NC, además de observarse un crecimiento en la formación de fluorescencia con un tiempo de formación de 110 ps, mientras que NC@I2-BDP muestra una desactivación completa de la fotoluminiscencia del NC y ningún retardo en la fluorescencia de I2-BDP. Las limitaciones del sistema de fotoluminiscencia resuelta en el tiempo motivaron el uso de la espectroscopia de absorción transitoria de femtosegundo para investigar la dinámica de los excitones electrónicamente excitados y relajados en los bordes de banda de los NCs en los dos nanohíbridos. El espectro de absorción transitoria de NC@BDP reveló una fuerte desactivación de la banda del NC a 498 nm, junto con la aparición de una banda negativa a 520 nm, indicativa de la disociación de los excitones y de la

creación de una vía no radiativa. Esta banda negativa coincide con la fluorescencia sensibilizada del colorante BDP, lo que confirma la transferencia directa de energía singlete de las NCs a los colorantes BDP como principal canal de desactivación. Por el contrario, las NC@I2-BDP mostraron una desactivación, incluso más rápida que la anterior, de la banda a 498 nm y presentó un estado excitónico electrónicamente excitado más corto en comparación con el control del NC. El análisis global mediante un modelo cinético paralelo identificó una componente de 10 ps asociado a una absorción de un estado excitado en 544 nm, lo que apoya la separación ultrarrápida de cargas en una etapa anterior. Tanto la transferencia de electrones como la de huecos fueron posibles debido a la favorable alineación energética del NC y con el colorante I2-BDP. Con el fin de elucidar la especie formada tras la transferencia de carga, se llevaron a cabo medidas de espectroelectroquímica que junto con cálculos teóricos confirmaron la formación del radical catiónico de I2-BDP.

El grado de transferencia de energía singlete de los NC a los colorantes en los nanohíbridos NC@BDP y NC@I2-BDP se estimó en un 82 % y un 36 %, respectivamente, a partir de la comparación del espectro de excitación de fotoluminiscencia con los espectros de absorción. Esta mayor eficiencia de transferencia de energía en NC@BDP es coherente con su mayor solapamiento espectral, lo que indica un mecanismo FRET puro para ambos híbridos. Además, se identificó la transferencia de huecos como la principal vía de desactivación no radiativa, particularmente en NC@I2-BDP, donde los mecanismos de transferencia de carga, incluyendo la transferencia de huecos electrónicamente excitados y relajados en los bordes de banda, dominan con un 64 %. La investigación de la formación del estado triplete se realizó alternativamente mediante experimentos de generación de oxígeno singlete, que mostraron que las dispersiones de I2-BDP y NC@I2-BDP presentaban intensidades similares de fotoluminiscencia de oxígeno singlete a las mismas condiciones, lo que indicaba una población eficiente del estado triplete sensibilizado. Por el contrario, las NC@BDP produjeron sólo una

pequeña cantidad de fotoluminiscencia de oxígeno singlete tras excitación selectiva del NC, lo que sugiere una baja sensibilización triplete a través de una vía mediada por cargas (18 %). Los resultados muestran que los fotones absorbidos por el NC en NC@I2-BDP pueden desencadenar reacciones fotoquímicas que implican estados tripletes de larga vida, como el del I2-BDP. Esto hace que NC@I2-BDP también sea eficaz como fotocatalizador de transferencia de energía triplete para la oxidación de α -terpineno a ascaridol bajo luz visible.

9.4.4. Conclusiones

Se prepararon con éxito dos nanohíbridos basados en CsPbBr₃ y colorantes BODIPY mediante la técnica de intercambio de ligando, logrando una eficiente desactivación del estado excitado de la perovskita por parte de los colorantes anclados en la superficie. La incorporación de yodo en el núcleo de BODIPY afecta significativamente los mecanismos de sensibilización, destacando que el mecanismo de desactivación principal en NC@BDP es FRET (82 %) con un 18 % restante de TET mediada por carga, mientras que en NC@I2-BDP predomina un mecanismo TET mediado por carga (64 %), con una contribución adicional de FRET (36 %). Esta estrategia de sensibilización permitió la generación efectiva de tripletes moleculares de I2-BDP, utilizables como fotocatalizadores para la oxidación de α -terpineno a ascaridol.

9.5. Capítulo 5. Desvelando el Mecanismo de Transferencia de Energía Dexter en los Nanohíbridos de Perovskita-Ftalocianina

9.5.1. Introducción

Los colorantes de ftalocianina (Pc), en particular la Zn-carboxi-ftalocianina (ZnPc, TT1), han sido utilizados en celdas fotovoltaicas debido a su gran absorción

y estabilidad, aunque su eficiencia en la captación de luz se encuentra limitada a la zona verde del espectro electromagnético. Para solucionar este problema, la combinación de NCs con colorantes orgánicos, como los derivados de Pc, puede mejorar la captación de luz y ser transferida por medio de mecanismos de transferencia de energía FRET y DET. No obstante, la agregación de colorantes en superficie de nanocristales en aplicaciones de fotovoltaica y terapia fotodinámica puede reducir su eficiencia desactivando el estado triplete. El uso de ligandos adecuados en los nanocristales puede evitar la agregación de colorantes y mejorar las propiedades ópticas y electrónicas, aunque el intercambio de ligandos puede introducir estados trampa en la superficie que comprometan el rendimiento cuántico de fotoluminiscencia de los NCs. Por lo tanto, comprender las interacciones de los estados excitados, como la transferencia de energía o de carga, es esencial para diseñar sistemas eficientes de captación de luz para aplicaciones en fotovoltaica, fotocatalisis y terapia fotodinámica.

En este capítulo se presenta el primer ejemplo de mecanismo DET puro desde nanocristales de perovskita CsPbBr_3 a los colorantes Zn-carboxifthalocianina (ZnPc) anclados a la superficie en nanohíbridos NC@ZnPc y se demuestra el rol clave de la química de la superficie del NC en los fenómenos de agregación-desagregación de colorantes en la interfaz NC-ZnPc. Este estudio proporciona una evaluación exhaustiva de la vía exclusiva de transferencia de energía que opera en la compleja dinámica del estado excitado del nanohíbrido NC@ZnPc bajo excitación selectiva del NC.

9.5.2. Sección experimental

Los nanocristales de CsPbBr_3 utilizadas fueron del mismo tipo que los sintetizados en el capítulo anterior, con un tamaño de nanocristal de 6.5 nm. Por otro lado, el colorante ZnPc se sintetizó según bibliografía.

9.5.3. Resultados y discusión

El espectro de absorción del nanohíbrido mostró características correspondientes a la desagregación del ZnPc en la superficie de los NC junto con una desactivación considerable de la fotoluminiscencia de los NCs de hasta el 95 %, acompañada de una nueva banda de emisión intensa en 702 nm, lo que sugiere una transferencia de energía entre el NC y ZnPc. La eficiencia de la transferencia de energía alcanzó un límite superior del 45 %, influyendo otros procesos no radiativos. Los experimentos control excluyeron FRET como mecanismo dominante. No obstante, para obtener una comprensión global del mecanismo de transferencia de energía y demostrar la exclusividad del mecanismo DET en la desactivación del estado excitado de la perovskita, se emplearon espectroscopias de fotoluminiscencia y de absorción resuelta en el tiempo a lo largo de varias escalas temporales. Se observó que la transferencia de energía tenía lugar en tres escalas temporales diferenciadas, siendo la más rápida en 0.61 ns como componente de crecimiento de la fluorescencia del ZnPc. Mientras que las otras dos componentes se observaron como decaimientos, que resultaron ser más lentos que el decaimiento intrínseco de la fluorescencia del ZnPc.

Los estudios de absorción transitoria revelaron que la dinámica del NC en tiempos cortos no cambia, mientras que la desactivación de la banda XB del NC y el retraso en la formación de la señal de GSB de ZnPc confirmaron la sensibilización del estado singlete del ZnPc. Los experimentos a escala de nanosegundos mostraron que mientras la banda XB desaparecía rápidamente, mientras que el GSB del ZnPc persistía durante más de 40 μ s, lo que se atribuyó a la desagregación del ZnPc en la superficie del NC debido a la interdigitación con los ligandos orgánicos. Mediante la aplicación de un modelo cinético compartimental, se explica la compleja dinámica del estado excitado del nanohíbrido NC@ZnPc bajo excitación selectiva del NC. Como prueba de concepto, el nanohíbrido NC@ZnPc presentó mejores rendimientos en la formación de oxígeno singlete, lo que

presenta un potencial significativo para aplicaciones en fotocátalisis y terapia fotodinámica.

9.5.4. Conclusiones

Este trabajo destaca el papel fundamental del grupo de anclaje en los colorantes ZnPc y la planaridad de la molécula para facilitar la transferencia concertada de electrones y huecos en nanocristales de CsPbBr₃ y Zn-carboxifthalocianina. A través de un análisis exhaustivo de las propiedades del estado excitado de los NC en los nanohíbridos, utilizando técnicas espectroscópicas en distintas escalas temporales se logró una alta sensibilización del estado singlete del ZnPc (>100 veces), con un 45 % de la energía de excitación transferida al ZnPc y el 55 % restante disipado en un nuevo estado trampa oscuro. Además, la extensión del estado triplete del ZnPc en el nanohíbrido confirma su desagregación y mayor eficiencia en la generación de oxígeno singlete.

9.6. Capítulo 6. Alargamiento de la Dinámica del Excitón en Nanohíbridos Lineales de Nanopartículas de Conversión Ascendente -Perovskita

9.6.1. Introducción

Las nanopartículas de conversión ascendente (UCNP), dopadas con iones lantánidos, ofrecen una forma prometedora de controlar los tiempos de vida de la fotoluminiscencia y mejorar aplicaciones tecnológicas como la optoelectrónica y la bioimagen. Al absorber fotones de baja energía y convertirlos en emisiones de alta energía a través de la conversión ascendente por transferencia de energía, las UCNPs captan eficazmente la luz infrarroja cercana. En particular, la combinación

de UCNPs con nanocristales de perovskita (NCs) ha demostrado un gran potencial para mejorar la transferencia de energía y, por ende, la eficiencia fotovoltaica. Sin embargo, persisten desafíos para lograr una fotoluminiscencia sensibilizada óptima y una eficiente transferencia de energía no radiativa. La creación de ensamblajes direccionales de NCs mediante agentes directores es una área emergente que podría mejorar la captación en el rango NIR y las propiedades colectivas de los materiales, ofreciendo nuevas oportunidades para el avance en tecnologías de conversión de energía.

En este capítulo, se ha preparado con éxito por primera vez un nuevo ensamblaje lineal de $\text{NaYF}_4/\text{Yb}^{3+}, \text{Tm}^{3+}$ y $\text{NaYF}_4/\text{Yb}^{3+}, \text{Er}^{3+}$, así como estructuras de núcleo/capa de $\text{NaYF}_4/\text{Yb}^{3+}, \text{Tm}^{3+}/\text{NaYF}_4$, además de un co-ensamblaje lineal con nanocristales de CsPbX_3 (X: Br, I) utilizando una estrategia de ensamblaje asistido por clústeres de sulfato de plomo. Se estudió la transferencia de energía resonante de lantánido mediante dos técnicas diferentes; la espectroscopia de recuento de fotones con excitación láser a 980 nm de baja potencia y la microscopia de barrido láser de multifotón a 980 nm de alta potencia. Estas superestructuras presentan propiedades prometedoras de captación de energía NIR para potenciales aplicaciones fotovoltaicas.

9.6.2. Sección experimental

Se han llevado a cabo la síntesis de nanopartículas de conversión ascendente de tipo núcleo de distintos tipos [$\text{NaYF}_4:\text{Yb}^{3+}$ (31 %), Tm^{3+} (0.3 %) and $\text{NaYF}_4:\text{Yb}^{3+}$ (20 %), Er^{3+} (2 %) UCNPs], que tienen emisión en el azul y en el verde, respectivamente, y también de tipo núcleo-capa [$\text{NaYF}_4:\text{Yb}^{3+}$ (16 %), Tm^{3+} (0.2 %)/ NaYF_4 UCNPs], mediante la estrategia de descomposición térmica. Por otro lado, se sintetizaron los nanocristales de perovskita del tipo CsPbX_3 (X = Br, I) mediante la estrategia de inyección en caliente. Los clústeres de sulfato de plomo se prepararon a partir de una metodología ya

establecida con ligeras modificaciones, utilizando una sal orgánica hidrogeno sulfato de ciclohexanometilamonio que dio lugar a ensamblajes más homogéneos.

La preparación del ensamblaje lineal y co-ensamblaje de nanopartículas de conversión ascendente y perovskita se llevaron a cabo a partir de la incubación de la mezcla de ambas dispersiones de nanopartículas en presencia de los clústeres de sulfato de plomo recién preparados, durante diferentes intervalos de tiempo.

La película sólida del co-ensamblaje se preparó mediante centrifugación de una dispersión de concentración elevada de co-ensamblaje en presencia de un vidrio.

9.6.3. Resultados y discusión

Mediante la realización de ajustes finos en la síntesis de los clústeres de sulfato de plomo, se consiguieron preparar ensamblajes lineales más homogéneos mediante la incubación de tanto nanopartículas de conversión ascendente y nanocristales de perovskita. El hecho de preparar este ensamblaje híbrido con ambos sistemas de tipo bloque permitió estudiar la transferencia de energía resonante de lantánido desde la nanopartícula de conversión ascendente al nanocristal de perovskita bajo excitación en el infrarrojo cercano (980 nm). Para ello, se estudió la cinética de emisión de la banda del ión Tm^{3+} a 475 nm. El fenómeno de sensibilización se llevó a cabo empleando dos técnicas diferentes.

En primer lugar, se usó la técnica de recuento de fotones con un láser de 980 nm a baja potencia (hasta 10 Wcm^{-2}), en el cual, mediante la desactivación de la cinética de emisión en el co-ensamblaje con respecto al ensamblaje lineal de nanopartículas de conversión ascendente, se logró cuantificar el rendimiento en la transferencia de energía resonante de lantánido sobre un 7 %. A su vez, la fotoluminiscencia de la perovskita emergía sobre 525 nm (correspondiente a un tamaño no confinado de aproximadamente 12 nm). Sin embargo, este bajo

rendimiento cuántico aumentaba considerablemente cuando el co-ensamblaje se depositaba sobre una película de cuarzo hasta un 37 %.

En segundo lugar, se empleó la técnica de microscopia de barrido láser de multifotón, en el que, se usó una potencia superior a la de la primera técnica de hasta 20 MWcm^{-2} . En este caso, la desactivación de la emisión del Tm^{3+} fue extrema (por debajo de la resolución del microscopio) en concomitancia con la aparición de una intensa fotoluminiscencia en el canal de emisión de la perovskita.

9.6.4. Conclusiones

Se preparó un ensamblaje lineal de nanopartículas de conversión ascendente y de perovskita por separado, y a su vez, un co-ensamblaje de tipo bloque de ambos sistemas, mediante un proceso asistido por clústeres de sulfato de plomo. Al utilizar la sal de hidrogenosulfato de ciclohexanometilamonio en lugar de hidrogenosulfato de tetrabutylamonio, se optimizó el ensamblaje lineal debido a las mejores interacciones de las moléculas de ciclohexilo. Las dos técnicas utilizadas revelaron que el mecanismo de sensibilización de perovskita bajo excitación en el infrarrojo cercano está mediado por transferencia de energía resonante por lantánido que predomina bajo excitación de alta potencia y en estado sólido, lo que conduce a una mayor eficiencia.

9.7. Capítulo 7. El poder de los Grupos Amino *N,N*-disustituidos en las Propiedades Emisivas de los Sistemas Push-Pull

9.7.1. Introducción

Las moléculas orgánicas con un sistema π deslocalizado han surgido como candidatas atractivas para materiales funcionales avanzados debido a sus

propiedades ópticas y electrónicas únicas. Los compuestos orgánicos con grupos donantes y aceptores de electrones permiten la deslocalización de la carga a través de la molécula, lo que se conoce como transferencia de carga intramolecular. Estos materiales se han utilizado ampliamente como material activo en celdas solares sensibilizadas por colorante y como materiales de transporte de huecos en celdas solares de perovskita, debido a su alta absorción de luz y movilidad de portadores de huecos. También se han integrado eficazmente en diodos orgánicos emisores de luz por su alta eficiencia cuántica de emisión. Estos sistemas exhiben un comportamiento de fluorosolvatocromismo fuerte en disolución, con cambios estructurales y relajación intramolecular en estados excitados, particularmente en solventes polares. El modelo de transferencia de carga intramolecular por torsión (TICT) explica una rotación de 90 ° entre los donantes y aceptores tras la excitación electrónica, mientras que el modelo de transferencia de carga intramolecular planarizada (PLICT) sugiere la planarización de estas partes. Ambos afectan a la energía de fluorescencia, pero con diferentes intensidades. El estudio de estos mecanismos proporciona así valiosa información para diseñar nuevos materiales funcionales con propiedades ópticas ajustables para diversas aplicaciones.

Por ello, en este capítulo se investigaron los mecanismos de fluorosolvatocromismo en derivados de bifenilo con dos tipos de donantes de electrones, grupos dialquilamino y diarilamino, y aceptores de electrones de tipo pirimidina. Utilizando técnicas de fluorescencia en estado estacionario y resuelta en el tiempo, apoyadas en cálculos teóricos, se muestra cómo la estructura molecular y el entorno del disolvente significativamente influyen en sus propiedades emisivas, con un modelo sencillo.

9.7.2. Sección experimental

Se sintetizaron dos tipos de derivados de bifenilo: 4-[4-(4-*N,N*-dimetilamino)fenil]-2,6-difenilpirimidina (D1) y 4-[4-(4-*N,N*-difenilamino)fenil]-2,6-difenilpirimidina (D2) mediante un protocolo ya reportado en literatura. Los sólidos

se disolvieron en un amplio abanico de disolventes que abarca desde no polares (hexano) hasta muy polares (DMSO). Todas las propiedades se midieron a las mismas condiciones de absorbancia.

9.7.3. Resultados y discusión

Ambos sistemas presentan propiedades de absorción en el estado fundamental con ligeras diferencias, destacándose dos bandas principales. La banda de alta energía es independiente de la polaridad del solvente, mientras que la de baja energía muestra una leve dependencia, con un desplazamiento al rojo en DMSO en comparación con hexano, lo que sugiere un bajo momento dipolar en el estado fundamental. En cuanto a las propiedades de fluorescencia bajo excitación a 365 nm, se observó un fuerte fluorosolvatocromismo positivo al aumentar la constante dieléctrica del solvente, indicando un mayor momento dipolar en el estado excitado, que se incrementó más en disolventes con elevada constante dieléctrica. En términos de eficiencia de fluorescencia, ambos sistemas exhibieron un alto rendimiento cuántico de fluorescencia en disolventes no polares debido a la baja interacción soluto-solvente. Sin embargo, el rendimiento cuántico de fluorescencia del sistema D1 disminuyó significativamente en solventes polares como DMSO, mientras que D2 mantuvo un alto rendimiento cuántico incluso en entornos altamente polares.

Los cálculos teóricos demostraron que la optimización de la geometría para el estado excitado singlete mostraron diferencias significativas en el ángulo diedro entre el grupo donante de electrones de la amina y el grupo fenilo. En D1, se identificaron dos mínimos: $S_{1,0}$, con el grupo amina en el mismo plano que el anillo fenilo (ángulo de 0 °), y $S_{1,90}$, con el grupo amina perpendicular (ángulo de 90 °). Mientras que para D2, solo se encontró un mínimo, $S_{1,40}$, con el grupo amina rotado entre 40-50 °, debido al impedimento estérico de los anillos fenólicos del grupo amina. El estado $S_{1,90}$ (electrónicamente desacoplado) desactiva la fluorescencia de D1, siendo el estado de más baja energía en disolventes polares. Mientras que

D2 solo tiene un estado, lo que justifica que presente rendimientos cuánticos elevados incluso en disolventes altamente polares.

9.7.4. Conclusiones

El fuerte solvatocromismo observado en los sistemas donor-aceptor D1 y D2 se debe al carácter de transferencia de carga intramolecular en el estado excitado singlete. Mientras que D1 muestra una fuerte supresión de la fluorescencia en solventes polares, D2 mantiene su fluorescencia independientemente de la polaridad del solvente, sugiriendo diferentes vías de desactivación. Los cálculos teóricos indican que la geometría perpendicular en D1 favorece la desactivación no radiativa, mientras que la estructura de D2 evita este fenómeno, manteniendo su alta eficiencia emisiva.

9.8. Capítulo 8. Conclusiones

Esta tesis explora el potencial de los nanomateriales de perovskita de haluro metálico en aplicaciones de captura y emisión de luz, como la fotocatalisis, destacando su capacidad para realizar procesos de transferencia de energía y/o carga en la interfase perovskita-molécula aceptora. Además, se propone la investigación de compuestos orgánicos donor-aceptor de electrones como posibles materiales transportadores de huecos en dispositivos fotovoltaicos de perovskita.

A continuación, se resumen las conclusiones de cada capítulo:

- Capítulo 3: demuestra que la precipitación selectiva es una estrategia de separación efectiva para obtener nanocristales de perovskita CsPbBr_3 de diferentes tamaños. Los experimentos de titulación con el colorante C-BDP revelan por primera vez interacciones en el estado excitado entre los nanocristales de perovskita y colorantes basados en BODIPY, mostrando que el tamaño menor

de los nanocristales y, por tanto más confinado, provoca una mayor eficiencia en la transferencia de energía FRET y una mayor desactivación del estado excitado de la perovskita.

- Capítulo 4: ilustra como la sustitución con yodo en el núcleo del BODIPY mejora significativamente la formación de estados excitados triplete en los nanohíbridos NC@I2-BDP en comparación con NC@BDP. La utilización de técnicas espectroscópicas avanzadas, en combinación con otras técnicas y cálculos teóricos, confirmó la efectividad de la transferencia de energía triplete en I2-BDP, lo que abre nuevas posibilidades para aplicaciones fotocatalíticas.

- Capítulo 5: revela la inusual transferencia de energía de tipo Dexter en nanohíbridos basados en perovskita-ftalocianina mediante un análisis exhaustivo en todas las escalas temporales, destacando el papel crucial del grupo carboxílico y la planaridad de la molécula en la transferencia de energía singlete. Los resultados evidencian una alta sensibilización del ZnPc, una mayor eficiencia en la extensión del estado excitado triplete y la formación de nuevos estados trampa que compiten con la transferencia de energía. Esta extensión del triplete en el colorante facilita posibilidades para el desarrollo de materiales avanzados en fotocatálisis mediada por triplete.

- Capítulo 6: presenta el primer co-ensamblaje lineal de nanocristales de perovskita y nanopartículas de conversión ascendente, mediante el uso de clústeres moleculares de sulfato de plomo. El uso de nanopartículas de conversión ascendente, con absorción en el infrarrojo cercano, permitió la obtención de la emisión sensibilizada de las perovskitas.

- Capítulo 7: demuestra de manera sistemática el fuerte efecto de fluorosolvatocromismo en los sistemas donor-aceptor de electrones derivados de bifenilo, D1 y D2, en diferentes entornos, explicado por el carácter de transferencia de carga intramolecular en el estado excitado. La presencia de sustituyentes en el grupo amino donante gobierna completamente las propiedades emisivas de estos compuestos, resultando en comportamientos diferentes en disolventes polares,

Capítulo 9. Resumen en castellano

con D1 mostrando dos estados (plano y perpendicular) y D2 uno (parcialmente rotado).

List of abbreviations

Abbreviations

PM	→ particulate matter
AOs	→ atomic orbitals
VB	→ valence band
CB	→ conduction band
MOs	→ molecular orbitals
LCAOs	→ linear combination of atomic orbitals
QDs	→ conventional quantum dots
DOS	→ density of states
NPLs	→ nanoplatelets
NRs	→ nanorods
MHPs	→ metal-halide perovskites
LEDs	→ light-emitting diodes
PCE	→ power conversion efficiency
NCs	→ perovskite nanocrystals
AMX₃	→ perovskite general formula
A	→ monovalent inorganic cation
M	→ divalent inorganic cation
X	→ halide anion
MX₆	→ octahedra
PL	→ photoluminescence
NIR	→ near-infrared
VBM	→ valence band maximum
CBM	→ conduction band minimum
CBC	→ covalent bond classification

LARP → ligand-assisted reprecipitation technique
TTA-UC → triplet-triplet annihilation-upconversion
SET → singlet energy transfer
FRET → Förster resonance energy transfer
DET → Dexter energy transfer
ERA → emission-reabsorption
TET → triplet energy transfer
CT-TET → charge transfer-mediated triplet energy transfer
isc → intersystem crossing
RP-ISC → radical pair-intersystem crossing
SOCT-ISC → spin-orbit coupling-mediated intersystem crossing
HOMO → highest-occupied molecular orbital
LUMO → lowest-unoccupied molecular orbital
TRPL → time-resolved photoluminescence
TA → transient absorption
fs-TA → femtosecond transient absorption
OLEDs → organic-inorganic light-emitting diodes
TFTs → thin-film field-effect transistors
PSCs → perovskite solar cells
PNCSCs → perovskite nanocrystal solar cells
HTMs → hole-transporting materials
ETMs → electron-transporting materials
CW → continuous wave
OD → optical density
PMT → photomultiplier tube
MCP → microchannel plate
MCS → multichannel scaling
TCSPC → time-correlated single photon counting

IRF → instrument response function

N₂ → nitrogen

NMR → nuclear magnetic resonance

¹H-NMR → proton nuclear magnetic resonance

TMS → tetramethylsilane

FTIR → Fourier-transform infrared

ATR → attenuated total reflectance

TEM → transmission electron microscopy

CV → cyclic voltammetry

CS → charge separation

CR → charge recombination

HR-TEM → high-resolution transmission electron microscopy

FFT → fast-Fourier transform

PLE → photoluminescence excitation

hT → hole transfer

CSS → charge-separated state

DAS → decay-associated spectra

SEC → spectroelectrochemistry

DFT → density functional theory

TD-DFT → time-dependent density functional theory

DSSCs → dye-sensitized solar cells

PDT → photodynamic therapy

Ar → argon

EAS → evolution-associated spectra

SADS → specie-associated difference spectra

STX → shallow trap-mediated exciton recombination

X → direct electron-hole exciton recombination

DTX → deep trap-mediated exciton recombination

SE → stimulated emission
hot-X → hot exciton
MX → multiexciton
XX → biexciton
DT → deep-trap state
DT' → new deep-trap state
UCNPs → upconversion nanoparticles
ETU → energy transfer upconversion
LRET → lanthanide resonance energy transfer
NIR-MLS → near-infrared-multiphoton laser scanning
XRD → x-ray diffraction
SEM → scanning electron microscopy
ICT → intramolecular charge transfer
TICT → twisted intramolecular charge transfer
PLICT → planarized intramolecular charge transfer
PCM → polarizable continuum model
LR → linear response
CLR → corrected linear response
MEPs → minimum energy paths
PES → potential energy surface
CI-NEB → climbing image-nudged elastic band
NTOs → natural transition orbitals

List of symbols

$E_g \rightarrow$ energy gap

$E_F \rightarrow$ Fermi energy level

$k_B \rightarrow$ Boltzmann constant

$T \rightarrow$ temperature

$h \rightarrow$ Planck constant

$\nu \rightarrow$ photon frequency

$a_0 \rightarrow$ Bohr exciton radius

$t \rightarrow$ Goldsmith tolerance factor

$\Phi_{PL} \rightarrow$ photoluminescence quantum yield

$k_{FRET} \rightarrow$ Förster resonance energy transfer rate constant

$\Phi_D \rightarrow$ photoluminescence quantum yield of the donor

$\kappa^2 \rightarrow$ orientation factor

$\tau_D \rightarrow$ lifetime of the donor

$J(\varepsilon_m) \rightarrow$ spectral overlap integral

$n \rightarrow$ solvent refractive index

$\varepsilon_m \rightarrow$ molar extinction coefficient of the acceptor

$r_{DA} \rightarrow$ donor-acceptor distance

$k_{DET} \rightarrow$ Dexter energy transfer rate constant

$K \rightarrow$ orbital interaction

$r_0 \rightarrow$ van der Waals radii of the donor and acceptor

$k_{TET} \rightarrow$ triplet energy transfer rate constant

$\hbar \rightarrow$ reduced Planck constant

$\rho_{DA} \rightarrow$ joint density of states

$|V|^2 \rightarrow$ squared matrix element

$\frac{e^2}{\bar{r}_{12}} \rightarrow$ two-electron operator

$\psi_i \rightarrow$ initial state
 $\psi_f \rightarrow$ final state
 $\psi_{HO}^D \rightarrow$ HOMO state for the donor
 $\psi_{HO}^A \rightarrow$ HOMO state for the acceptor
 $\psi_{LU}^A \rightarrow$ LUMO state for the acceptor
 $\psi_{LU}^D \rightarrow$ LUMO state for the donor
 $k_{CT} \rightarrow$ charge transfer rate constant
 $\lambda \rightarrow$ reorganization energy
 $\Delta G_0 \rightarrow$ difference between final and initial states
 $\lambda_i \rightarrow$ inner-sphere reorganization energy contribution
 $\lambda_o \rightarrow$ outer-sphere reorganization energy contribution
 $\epsilon_0 \rightarrow$ vacuum permittivity
 $\epsilon_{op} \rightarrow$ solvent optical dielectric constant
 $\epsilon_s \rightarrow$ static dielectric constant
 $d_D \rightarrow$ diameter of the donor cavity
 $d_A \rightarrow$ diameter of the acceptor cavity
 $\alpha' \rightarrow$ absorption coefficient
 $\nu \rightarrow$ frequency of the incident light
 $K \rightarrow$ energy independent constant
 $n \rightarrow$ constant for direct or indirect electronic transition
 $\Phi_{Fl} \rightarrow$ fluorescence quantum yield
 $k_r \rightarrow$ radiative rate constant
 $k_{nr} \rightarrow$ nonradiative rate constant
 $\tau_0 \rightarrow$ average lifetime
 $\tau_i \rightarrow$ lifetime of the i th component
 $\alpha_i \rightarrow$ weight parameter of the i th component
 $\delta \rightarrow$ chemical shift
 $J \rightarrow$ coupling constant

Φ_{ET} → energy transfer efficiency

Φ_Q → quenching efficiency

λ_{exc} → excitation wavelength

I_0 → photoluminescence intensity of pristine NCs

I → photoluminescence intensity change of NCs in presence of dye

K_{SV} → Stern-Volmer quenching constant

α → fraction of the initial photoluminescence accessible to the quencher

K_α → Stern-Volmer quenching constant for this fraction

K_D → Stern-Volmer constant for dynamic quenching

k_q → bimolecular quenching rate constant

Φ_{isc} → intersystem crossing quantum yield

$\Delta\lambda$ → Stokes shift

Δf → orientation polarizability

π^* → solvent polarizability

α'' → hydrogen-bonding ability of the solvent

List of publications

Published works related to this dissertation:

Chapter 3

Cortés-Villena, A.; Caminos, D.A.; Galian, R.E.; Pérez-Prieto, J., Singlet Sensitization of a BODIPY Rotor Triggered by Marriage with Perovskite Nanocrystals. *Adv. Opt. Mater.* **2023**, *11*, 2300138.



Chapter 4

Cortés-Villena, A.; Bellezza, D.; Cunha, C.; Rosa-Pardo, I.; Seijas-Da Silva, A.; Pina, J. Abellán, G.; Seixas de Melo, J.S.; Galian, R.E.; Pérez-Prieto, J., Engineering Metal Halide Perovskite Nanocrystals with BODIPY Dyes for Photosensitization and Photocatalytic Applications. *J. Am. Chem. Soc.* **2024**, *146* (21), 14479–1449.



Chapter 5

Cortés-Villena, A.; Cadranet, A.; Azizi, K.; Torres, T.; Guldi, D.; Pérez-Prieto, J.; Galian, R.E., Deciphering the Energy Transfer Mechanism Across Metal Halide Perovskite-Phthalocyanine Interfaces. *Angew. Chem.* (under review)

Chapter 6

Estebanez, N.[‡]; **Cortés-Villena, A.[‡]**; Ferrera-González, J.; González-Bejar, M.; Galian, R.E.; Pérez-Prieto, J., Linear Coassembly of Upconversion and Perovskite Nanoparticles: Sensitized Upconversion Emission of Perovskites by Lanthanide-Doped Nanoparticles. *Adv. Funct. Mater.* **2020**, *30*, 2003766 ([‡]equal contribution).



Chapter 7

Cortés-Villena, A.; Soriano-Díaz, I.; Domínguez, M.; Vidal, M.; Rojas, P.; Aliaga, C.; Giussani, A.; Doménech-Carbó, A.; Ortí, E.; Galian, R.E.; Pérez-Prieto, J. Governing the emissive properties of 4-aminobiphenyl-2-pyrimidine push-pull systems via the restricted torsion of *N,N*-disubstituted amino groups. *Front. Chem.* **2023**, *11*, 1292541.



Other publications generated from this dissertation:

- **Cortés-Villena, A.**; Galian, R.E. Present and perspectives of photoactive porous composites based on semiconductor nanocrystals and metal-organic frameworks. *Molecules*, **2021**, 26 (18), 5620.



- Rosa-Pardo, I.; **Cortés-Villena, A.**; Galian, R.E.; Pérez-Prieto, J. Synthesis techniques of metal halide perovskites. In *Low-Dimensional Halide Perovskites: Structure, Synthesis, and Applications*; Zhan, Y., Khalid, M., Vivo, P., Arshid, N.; Elsevier: **2023**; pp 91–151.



- Rosa-Pardo, I.; Zhu, D.; **Cortés-Villena, A.**; Prato, M.; De Trizio, L.; Manna, L.; Galian, R. E.; Pérez-Prieto, J. The dark side of lead-free metal halide nanocrystals: substituent-modulated photocatalytic activity in benzyl bromides reduction. *ACS Energy Letters*, **2023**, 8 (6), 2789–2798.



- PATENT in process: Hybrid perovskite upconversion materials (EP23382748.4).

Published works prior to this dissertation:

- Arrabal-Campos, F. M.; **Cortés-Villena, A.**; Fernández, I. Building “My First NMRviewer”: A Project Incorporating Coding and Programming Tasks in the Undergraduate Chemistry Curricula *J. Chem. Educ.* **2017**, *94* (9), 1372–1376.



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