

Perovskite Nanocrystals Synthesis: Exploring different approaches and ligand influence: A Review

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ABSTRACT

Metal halide perovskite nanocrystals (NCs) have emerged as highly promising materials for next-generation optoelectronic, photovoltaic, sensing, and energy-related applications owing to their remarkable optical and electronic properties. These properties include tunable bandgaps, high absorption coefficients, efficient charge-carrier transport, long carrier diffusion lengths, strong light absorption, and high photoluminescence quantum yields. Their unique compositional and structural flexibility also enables their optical and electronic properties to be tailored for specific technological applications. Despite these advantages, the practical utilization of perovskite nanocrystals remains limited by several challenges, including surface defects, ion migration, poor environmental stability, ligand instability, and degradation under exposure to moisture, oxygen, heat, intense illumination, and electrical stress.

In this regard, surface capping ligands play a fundamental role in controlling the nucleation and growth of perovskite nanocrystals and in regulating their surface chemistry, morphology, crystallinity, optical properties, and colloidal stability. This review presents a comprehensive assessment of recent advances in the design, synthesis, characterization, and application of ligand-capped metal halide perovskite nanocrystals. Particular emphasis is placed on the roles of conventional organic ligands, inorganic ligands, polymers, and emerging bio-derived ligands in controlling nanocrystal size and shape, reducing surface defects, improving charge-carrier dynamics, and enhancing photoluminescence efficiency and stability. Furthermore, recent developments in understanding ligand binding mechanisms, surface chemistry, ligand–nanocrystal interactions, and dynamic surface reconstruction are critically discussed. Strategies including ligand exchange, ligand engineering, controlled ligand density, surface passivation, and cross-linking are examined as approaches for improving charge transport, resistance to environmental degradation, and overall device performance while minimizing the formation of insulating surface layers.

Particular attention is also given to the emerging use of sustainable and naturally derived bioligands as environmentally friendly alternatives to conventional synthetic surface modifiers. Despite significant progress, challenges associated with ligand loss, surface reconstruction, reproducibility, toxicity, processing compatibility, and large-scale synthesis remain unresolved. Overall, a deeper understanding and precise control of ligand–nanocrystal interactions are essential for developing highly stable, efficient, and environmentally sustainable perovskite nanocrystals. Continued advances in ligand engineering are therefore expected to facilitate the broader integration of these materials into light-emitting diodes, solar cells, photodetectors, sensors, photocatalytic systems, and other advanced optoelectronic and energy-conversion technologies.

Keywords: Perovskite nanocrystal, ligand exchange, metal halide, optoelectronics, photoluminescence quantum yields

INTRODUCTION

The rapid development of nanoscience and nanotechnology has profoundly transformed materials science and has enabled the emergence of advanced materials with properties that differ significantly from those of their bulk counterparts. Nanomaterials, generally characterized by at least one dimension within the nanoscale regime, possess unique physicochemical characteristics arising from quantum confinement, high surface-to-volume ratios, increased surface energy, and size-dependent electronic structures. These distinctive properties have stimulated extensive research into their synthesis, surface modification, characterization, and technological applications. Consequently, nanomaterials have become increasingly important across a broad range of scientific and industrial fields, including cosmetics, medicine, biotechnology, catalysis, energy conversion and storage, environmental remediation, electronics, and optoelectronics ^[1,2]. In biomedical applications, for example, nanomaterials have been investigated for biosensing, bioimaging, drug delivery, diagnostics, and therapeutic applications because their optical, electrical, and surface properties can be tailored at the nanoscale ^[3,4]. Similarly, advances in nanoscale semiconductor materials have contributed substantially to the development of electronic and optoelectronic technologies, including light-emitting devices, displays, photodetectors, optical sensors, and next-generation communication systems ^[5,6].

A particularly important class of nanomaterials is **semiconductor nanocrystals (NCs)**. Semiconductor NCs are nanoscale crystalline materials whose dimensions are sufficiently small for their electronic and optical properties to become strongly influenced by quantum confinement and surface effects. Unlike conventional bulk semiconductors, their band structures, charge-carrier dynamics, optical absorption, and emission characteristics can be modified through control of particle size, shape, composition, and surface chemistry. These characteristics have resulted in considerable interest in semiconductor NCs for applications involving light harvesting, light emission, photocatalysis, sensing, and energy conversion. Among their most important characteristics are high extinction coefficients, efficient charge generation and separation, favorable charge-transport properties, tunable optical responses, and, for many compositions, good chemical and thermal stability^[7,8]. Furthermore, many semiconductor NCs can be synthesized using solution-based methods, offering advantages such as relatively low processing temperatures, scalable fabrication, compositional flexibility, and compatibility with various substrate types.

The surface of semiconductor NCs plays a particularly important role in determining their physicochemical behavior. Because nanocrystals possess a high fraction of surface atoms relative to bulk atoms, unsatisfied coordination sites and surface defects can significantly influence their electronic and optical properties. These surface sites can act as trapping centers for charge carriers, thereby promoting non-radiative recombination and reducing the efficiency of light-emitting or light-harvesting processes. To minimize such effects and stabilize nanocrystals during synthesis and subsequent processing, solution-phase synthesis commonly employs organic or inorganic surface-active molecules known as **capping ligands**. Capping ligands interact with specific surface atoms or crystallographic facets and can regulate nucleation, crystal growth, particle size, morphology, colloidal stability, and interparticle interactions. They also provide a protective interface between the nanocrystal surface and the surrounding environment, thereby reducing undesirable aggregation, surface degradation, and uncontrolled chemical reactions.

Importantly, ligand–surface interactions are not merely a means of stabilizing nanocrystals. They constitute a fundamental component of nanocrystal surface chemistry and can directly determine the final properties and functionality of the material. The chemical nature, binding strength, molecular structure, chain length, polarity, steric characteristics, and concentration of a ligand can influence precursor conversion, nucleation kinetics, crystal growth, surface defect passivation, colloidal stability, and charge transfer between neighboring nanocrystals. Consequently, rational control of ligand chemistry has emerged as an essential strategy for tailoring semiconductor NCs for specific technological applications. However, the presence of strongly insulating organic ligands may also introduce undesirable barriers to charge transport, particularly when nanocrystals are assembled into solid-state films. Therefore, achieving an appropriate balance between surface passivation, colloidal stability, processability, and electronic coupling remains an important challenge in nanocrystal research.

Within the broader family of semiconductor nanomaterials, **metal-halide perovskites (MHPs)** have emerged as one of the most intensively investigated classes of materials in contemporary materials science. MHPs generally possess the ABX_3 perovskite crystal framework, in which A represents a monovalent cation, B is typically a divalent metal cation, and X is a halide anion. Their exceptional optoelectronic properties have generated substantial interest because these materials combine strong light absorption, efficient charge generation, favorable charge-transport characteristics, long carrier diffusion lengths, defect-tolerant electronic structures, and highly tunable band gaps^[8–10]. The ability to systematically vary the A-site cation, B-site metal, and halide composition provides considerable flexibility for controlling their structural, electronic, and optical properties. In particular, halide substitution and compositional engineering enable the optical band gap to be adjusted over a broad spectral range, making MHPs highly attractive for applications requiring specific absorption or emission wavelengths.

The remarkable optoelectronic characteristics of MHPs have resulted in their rapid adoption in a variety of emerging technologies. They have been extensively investigated for photovoltaic solar cells, light-emitting diodes (LEDs), photodetectors, lasers, optical sensors, and other optoelectronic devices^[12–15]. Their strong optical absorption enables efficient utilization of incident light, while their favorable carrier-generation and transport characteristics facilitate the extraction and manipulation of photogenerated charge carriers. In light-emitting applications, the combination of high radiative recombination efficiency and compositionally tunable emission has made perovskite materials particularly promising for next-generation display and lighting technologies. Nevertheless, despite these advantages, conventional bulk and thin-film MHPs remain susceptible to several limitations, including sensitivity to moisture, oxygen, heat, illumination, and electrical bias. These stability challenges have stimulated extensive research into nanoscale forms of perovskite materials, where surface engineering and controlled nanocrystal architectures can provide additional opportunities for improving their performance and stability.

Metal-halide perovskite nanocrystals (MHP NCs) have consequently attracted considerable attention as a distinct and highly versatile class of nanoscale semiconductors. The reduction of perovskite materials to the nanocrystal regime introduces size-dependent properties and provides additional control over their optical and electronic behavior. MHP NCs can often be synthesized through relatively simple and facile solution-based approaches, including hot-injection, ligand-assisted reprecipitation, solvothermal, microwave-assisted, and other colloidal synthesis routes. Compared with many conventional semiconductor nanomaterials, these approaches can offer relatively low fabrication costs, mild processing conditions, rapid reaction kinetics, and substantial control over particle size and composition^[16,17]. Furthermore, MHP NCs can exhibit exceptionally high photoluminescence quantum yields (PLQYs), narrow emission linewidths, high absorption coefficients, and intense size- and composition-dependent optical responses. These characteristics make them particularly attractive for applications in displays, LEDs, lasers, photodetectors, solar-energy technologies, and photocatalysis.

One of the most significant advantages of MHP NCs is their **exceptional band-gap tunability**. The optical properties of these materials can be modified through changes in elemental composition, halide concentration, crystal dimensions, and structural characteristics^[18,19]. In mixed-halide systems, for instance, systematic variation of the halide composition can substantially alter the band gap and consequently shift the absorption and photoluminescence wavelengths. Similarly, quantum-confinement effects associated with nanocrystal dimensions can influence the electronic structure and optical transitions, particularly as the crystal dimensions approach characteristic excitonic length scales. Such tunability enables MHP NCs to be designed for specific portions of the ultraviolet, visible, and near-infrared spectral regions. This compositional and dimensional flexibility represents a major advantage for the development of wavelength-selective optoelectronic devices and multifunctional nanomaterial platforms.

Despite the impressive intrinsic properties of MHP NCs, their performance is strongly dependent on their **surface chemistry**. The large surface-to-volume ratio of nanocrystals means that a substantial proportion of atoms are located at or near the surface, where defects, vacancies, under-coordinated ions, and dangling bonds can occur. Such defects may introduce electronic states within the band gap and promote non-radiative recombination, thereby reducing photoluminescence efficiency and compromising charge-carrier dynamics. Surface defects may also provide pathways for chemical reactions with environmental species, contributing

to structural degradation and loss of optical performance. Consequently, controlling the surface chemistry of MHP NCs is essential for obtaining high-quality nanocrystals with desirable optical, morphological, and stability characteristics.

Ligand engineering therefore represents one of the most important strategies for controlling the synthesis and functionality of MHP NCs. During colloidal synthesis, ligands can coordinate with surface ions and precursor species, thereby modifying precursor reactivity, nucleation rates, crystal growth kinetics, and the development of specific crystal facets. By controlling these processes, ligands can influence nanocrystal size distribution, morphology, crystallinity, and colloidal stability. Following synthesis, surface-bound ligands can passivate defect sites, suppress non-radiative recombination, prevent aggregation, and protect the nanocrystals against environmental degradation. The identity and concentration of the ligand system can consequently have a direct influence on the photoluminescence quantum yield, emission linewidth, absorption behavior, charge-carrier lifetime, and long-term stability of MHP NCs.

However, ligand engineering presents an important trade-off. Although long-chain and strongly binding ligands may provide excellent colloidal stabilization and surface passivation, their insulating nature can hinder charge transport between adjacent nanocrystals. This limitation becomes particularly important when colloidal MHP NCs are processed into solid-state films for optoelectronic applications. Conversely, insufficient ligand coverage may result in poor colloidal stability, increased surface defect densities, particle aggregation, and accelerated degradation. Thus, the optimization of ligand composition, surface coverage, binding strength, and ligand exchange is critical for simultaneously achieving high-quality colloidal dispersions and efficient solid-state electronic transport.

In addition to influencing nanocrystal growth and final device performance, ligands can substantially affect the **purification and post-synthetic processing** of MHP NCs. Purification is necessary to remove unreacted precursors, excess ligands, solvent residues, and other synthesis by-products. Nevertheless, conventional purification procedures may unintentionally strip essential surface ligands from the nanocrystal surface or induce aggregation and structural degradation. The choice of antisolvent, solvent polarity, centrifugation conditions, washing cycles, and ligand concentration can therefore determine the balance between chemical purity and surface integrity. An optimized purification strategy must remove unwanted molecular species while retaining an appropriate ligand shell capable of maintaining surface passivation and colloidal stability. This aspect is particularly important because changes in surface ligand density during purification can subsequently influence film formation, interparticle coupling, charge transport, and device performance.

The relationship between **ligand structure, nanocrystal surface chemistry, and macroscopic device properties** therefore represents a critical area of contemporary perovskite research. When MHP NCs are assembled into thin films, the surface ligands form interfaces between neighboring nanocrystals and consequently influence the extent of electronic coupling and charge-carrier transport. Long insulating ligands may preserve individual nanocrystal properties but increase interparticle separation, whereas shorter or more strongly electronically coupled ligands may improve charge transport at the expense of colloidal stability. Ligand exchange and surface-treatment strategies have consequently been explored to modify the interfacial chemistry of MHP NC films and improve their electrical and optoelectronic properties. Understanding these competing effects is essential for translating the excellent properties of individual colloidal MHP NCs into high-performance solid-state devices.

Although substantial progress has been made in the synthesis and application of MHP NCs, several challenges remain unresolved. These include the precise identification of ligand binding configurations, control of surface defect populations, preservation of nanocrystal integrity during purification, prevention of ligand-induced degradation, optimization of interparticle charge transport, and development of environmentally and chemically stable ligand systems. Moreover, differences in ligand chemistry can produce significant variations in nucleation, growth, morphology, optical properties, purification behavior, film formation, and device stability. A comprehensive understanding of these interconnected processes is therefore required to establish rational principles for ligand selection and surface engineering.

Accordingly, this review provides a comprehensive and critical assessment of the **surface chemistry of metal-halide perovskite nanocrystals and the role of ligand modification in controlling their synthesis, growth, morphology, optical properties, purification, stability, and device performance**. Particular emphasis is placed on the mechanisms through which ligand–surface interactions influence nucleation and crystal growth, particle size and morphology, surface-defect passivation, photoluminescence behavior, colloidal stability, and environmental resistance. The review further examines how ligand composition and post-synthetic ligand modification affect purification processes and the subsequent formation and performance of MHP NC films. Finally, the relationship between surface-ligand engineering and the operational stability and optoelectronic performance of MHP NC-based devices is critically discussed. By integrating these aspects, this review seeks to provide a coherent framework for understanding the role of surface ligands in MHP NC chemistry and to highlight promising directions for the rational design of stable, efficient, and application-oriented perovskite nanocrystal systems.

LIGANDS

Ligands are molecules, ions, or molecular species capable of coordinating to metal atoms or ions through one or more donor atoms to form coordination complexes. In colloidal nanocrystal synthesis, ligands play a fundamental role in determining the nucleation, growth, surface structure, colloidal stability, and final physicochemical properties of the resulting nanocrystals (NCs) ^[20]. Their importance becomes particularly pronounced at the nanoscale because NCs possess a very high surface-to-volume ratio and, consequently, a large proportion of atoms are located at or near the surface. Surface atoms may exhibit incomplete coordination, high surface energy, and a greater susceptibility to interactions with surrounding molecules and environmental species. Without adequate surface stabilization, these characteristics can promote uncontrolled growth, aggregation, dissolution, defect formation, and chemical degradation.

In metal-halide perovskite (MHP) NCs, ligands perform several interconnected functions during and after synthesis. They can coordinate with precursor species in solution, regulate precursor reactivity, influence nucleation and crystal-growth kinetics, selectively bind to specific crystallographic facets, control particle size and morphology, and stabilize the resulting NCs against aggregation. Following synthesis, surface-bound ligands can passivate under-coordinated surface sites and ionic defects, thereby suppressing non-radiative charge-carrier recombination and improving photoluminescence efficiency.

Ligand shells can also provide a protective barrier against moisture, oxygen, heat, and other environmental factors that can destabilize perovskite structures. Thus, ligands should not be regarded merely as passive capping agents; rather, they constitute an integral component of the surface chemistry of MHP NCs and can strongly influence their structural, optical, electronic, and stability characteristics.

Classification of Ligand–Surface Interactions

The chemical interaction between a ligand and a nanocrystal surface can range from predominantly ionic or electrostatic interactions to stronger covalent or coordination interactions. One useful framework for describing these interactions is the **Covalent Bond Classification (CBC) model**, introduced by Green, which classifies ligands according to the number and nature of electrons formally donated to a metal center ^[20,21]. Within this framework, ligands are commonly described as **L-type, X-type, or Z-type**, although mixed and multifunctional coordination modes can occur in real nanocrystal systems.

L-type ligands are neutral two-electron donor species that coordinate to electron-deficient surface metal centers through lone-pair donation. Typical examples include amines, phosphines, phosphine oxides, and related Lewis bases. Their coordination can alter the electronic environment of surface metal ions and can influence precursor conversion and crystal growth. X-type ligands, in contrast, are formally anionic species that form interactions with surface cations. Carboxylates and halides are particularly important examples in MHP NC chemistry. These ligands can compensate surface charge, occupy under-coordinated sites, and contribute significantly to defect passivation and colloidal stabilization ^[20–22]. Z-type ligands are Lewis-acidic species that accept electron density from the nanocrystal surface. Although less commonly discussed in

conventional MHP NC synthesis than L- and X-type ligands, Z-type interactions provide an important conceptual framework for understanding more complex surface coordination chemistries.

The CBC classification is particularly useful because the surface of a perovskite NC is chemically heterogeneous rather than being a perfectly defined molecular surface. Metal cations, halide anions, vacancies, antisite defects, and different crystallographic facets may present chemically distinct binding sites. Consequently, a single ligand molecule may interact with the surface through different coordination configurations depending on the local chemical environment. In addition, ligand binding can be dynamic, with adsorption and desorption occurring continuously during synthesis, purification, storage, and device fabrication. Such dynamic behavior is particularly relevant to MHP NCs because their relatively soft ionic lattices can undergo surface reconstruction or compositional changes in response to changes in ligand concentration, solvent composition, temperature, and chemical environment.

Conventional Organic Ligands for MHP Nanocrystals

Among the most extensively investigated organic ligands for the synthesis of MHP NCs are **carboxylic acids and amines** ^[22]. These ligand classes are frequently used together because they can provide complementary functions during nucleation, crystal growth, and surface stabilization. Typical ligands contain a polar functional group capable of interacting with the nanocrystal surface and a hydrophobic organic segment that provides steric stabilization in non-polar solvents.

Carboxylic acids contain a polar carboxyl functional group capable of participating in acid–base reactions and surface coordination. Under typical colloidal synthesis conditions, carboxylic acids can interact with metal-containing precursors and may subsequently form carboxylate species that bind to positively charged surface sites. Their coordination can influence the concentration and reactivity of precursor species, thereby affecting nucleation and crystal growth. The hydrophobic alkyl chains of long-chain carboxylic acids also generate steric barriers between neighboring NCs, reducing attractive interparticle interactions and suppressing aggregation. Consequently, carboxylic-acid ligands can contribute simultaneously to surface passivation and colloidal stabilization.

Amines represent another major class of ligands employed in MHP NC synthesis. The nitrogen lone pair enables amines to act as Lewis bases and coordinate with Lewis-acidic sites associated with metal ions or under-coordinated surface centers. Primary, secondary, and tertiary amines can exhibit different binding strengths and steric characteristics, and these differences can influence precursor complexation, nucleation rate, crystal growth, and final NC morphology. Amines may also participate in acid–base equilibria with carboxylic acids, resulting in the formation of ammonium carboxylates. Such dynamic ligand interactions contribute to the complex equilibrium that governs MHP NC formation.

The relative concentrations and chemical characteristics of carboxylic acids and amines can therefore have a pronounced effect on NC synthesis. An increase in ligand concentration may suppress uncontrolled growth and produce smaller particles, whereas insufficient surface coverage may result in aggregation and broad particle-size distributions. Conversely, excessive ligand concentrations can inhibit precursor conversion or produce an overly insulating organic shell. The optimization of ligand concentration is consequently essential for achieving a balance between nanocrystal growth control, surface passivation, colloidal stability, and subsequent charge transport.

Monodentate Ligands

Monodentate ligands contain a single principal donor group capable of interacting with the NC surface. Long-chain carboxylic acids and amines are representative examples frequently used in colloidal MHP NC synthesis. These ligands typically consist of a polar head group and an organic tail, with the head group responsible for surface coordination and the tail contributing to steric or solvophobic stabilization.

The advantage of monodentate ligands lies in their synthetic simplicity, dynamic surface binding, and compatibility with colloidal processing. Their relatively dynamic adsorption and desorption can facilitate

surface restructuring during nanocrystal growth and may also permit post-synthetic ligand exchange. However, the same dynamic behavior can result in ligand loss during purification, washing, heating, or prolonged storage. Loss of surface ligands may expose defect-rich sites and promote NC aggregation or degradation. Therefore, while monodentate ligands are highly effective for controlling colloidal synthesis, their binding strength and long-term surface retention must be carefully considered.

The length and structure of the organic ligand tail can further affect NC behavior. Increasing alkyl-chain length generally increases steric separation between particles and can improve colloidal stability. However, long hydrocarbon chains also increase the thickness of the insulating organic barrier between adjacent NCs. In solid-state films, this can reduce electronic coupling and hinder charge transport. Consequently, ligand chain length represents an important design parameter when translating colloidal NCs into functional optoelectronic devices.

Bidentate and Multidentate Ligands

In contrast to monodentate ligands, **bidentate and multidentate ligands** possess two or more functional groups capable of coordinating simultaneously with surface atoms or ions^[22]. Multiple binding sites allow these ligands to establish stronger and, in some cases, more persistent interactions with the NC surface. Their multidentate coordination can improve surface coverage, reduce ligand desorption, and enhance colloidal stability.

Multidentate ligands may also influence the structural integrity of the NC surface by coordinating with multiple adjacent surface sites. This can reduce the probability of ligand detachment and minimize exposure of highly reactive surface defects. As a result, multidentate ligands have attracted attention as potential alternatives to conventional long-chain monodentate ligands where enhanced surface stability is required.

However, strong multidentate binding can also influence the dynamics of crystal growth. Excessively strong coordination may reduce the mobility of surface species and interfere with the controlled addition or removal of ions during crystal growth. Therefore, the binding strength and molecular geometry of multidentate ligands must be optimized to obtain effective surface passivation without excessively restricting the growth or restructuring of the perovskite lattice.

Branched and Sterically Modified Ligands

The molecular architecture of a ligand can be as important as its chemical functional group. **Branched ligands**, for example, introduce steric complexity around the nanocrystal surface and can modify the accessibility of neighboring surface sites. Compared with straight-chain ligands, branched molecules may provide enhanced steric stabilization and can influence nucleation and growth by modifying the local chemical environment surrounding developing NC surfaces.

The use of branched ligands can contribute to improved control over NC size distribution and morphological uniformity. Their three-dimensional structure may reduce close approach between NCs and inhibit aggregation more effectively than some linear ligands. In addition, steric hindrance can alter ligand packing density and surface organization, potentially affecting the accessibility of surface defects and the interaction between neighboring NCs.

Nevertheless, increased steric bulk can also reduce the ability of the ligand functional group to approach certain surface sites. Consequently, the relationship between ligand branching, surface coverage, binding strength, and NC morphology must be considered when designing ligand systems for specific applications.

Zwitterionic Ligands

Zwitterionic ligands contain both positively and negatively charged functional groups within the same molecular structure while maintaining an overall electrically neutral character. These ligands have attracted significant interest because their multiple ionic functionalities can interact simultaneously with complementary charged sites on the NC surface^[22].

The simultaneous interaction of different functional groups can produce strong surface anchoring and provide effective passivation of charged surface defects. Zwitterionic ligands may also improve colloidal stability by creating a highly organized interfacial layer around the NC. Because the molecular architecture can provide multiple points of interaction with the surface, these ligands may be less susceptible to complete desorption than weakly bound monodentate species.

Furthermore, zwitterionic surface chemistry offers an opportunity to regulate the electrostatic environment surrounding MHP NCs without necessarily introducing a large net charge to the colloidal particle. This characteristic may be particularly useful in systems where surface charge, ionic interactions, and defect passivation must be simultaneously controlled.

Ionic and Inorganic Ligands

In addition to molecular organic ligands, MHP NC surfaces can be stabilized by **ionic and inorganic species**, including halide ions and other anionic or cationic species ^[21,22]. Examples include halides, sulfide-related species, thiocyanate (SCN^-), amide-derived species, and other ions capable of interacting with surface sites. Such species are particularly important because the perovskite lattice itself is composed of ionic constituents, meaning that surface termination and charge balance can strongly influence the electronic properties of the NC.

Halide ions are especially important surface species in metal-halide perovskites. Surface halide vacancies can generate electronically active defects that serve as trapping sites for charge carriers. Appropriate halide-rich surface chemistry can therefore reduce the density of these vacancies and improve optical properties. Similarly, anionic species may coordinate with under-coordinated metal centers, while cationic species can interact with negatively charged surface sites.

In this context, surface passivation should be understood as a process involving not only organic ligands but also the restoration or modification of local surface stoichiometry. Organic and inorganic ligands can therefore operate cooperatively, with organic ligands providing colloidal stabilization and inorganic species contributing directly to defect passivation and surface reconstruction.

Ligand Binding in Metal-Halide Perovskite Nanocrystals

The surface chemistry of MHP NCs differs from that of many conventional covalent semiconductor NCs because of the predominantly ionic and relatively soft nature of the perovskite lattice. In typical MHP systems, carboxylic acids and amines can undergo acid-base reactions that generate **carboxylate anions and ammonium cations**, respectively ^[22]. These ionic species can interact with complementary charged sites on the NC surface and contribute to surface charge compensation.

The dynamic equilibrium between protonated and deprotonated ligand species is particularly important. Changes in solvent polarity, temperature, ligand concentration, precursor composition, and reaction conditions can alter the degree of ligand protonation and consequently modify surface binding. The ligand shell should therefore be considered a dynamic interfacial structure rather than a permanently fixed coating.

This dynamic character can strongly influence NC growth. During synthesis, ligands may temporarily coordinate with precursor species, reducing their effective reactivity and modifying the rate at which constituent ions are incorporated into the developing crystal lattice. At the same time, ligand adsorption onto particular crystal facets can reduce their surface energy and alter their growth rate. Differences in the relative growth rates of individual facets can ultimately determine whether the resulting NCs are approximately spherical, cubic, plate-like, rod-like, or possess other morphologies.

Ligands and Surface Defect Passivation

One of the most technologically important functions of ligands is the **passivation of surface defects**. The high surface area of MHP NCs means that vacancies, under-coordinated metal ions, halide deficiencies, and other structural imperfections can significantly affect their electronic properties. Defect states located within or near

the band gap may trap photogenerated electrons or holes and provide pathways for non-radiative recombination.

Appropriately selected ligands can coordinate with these defect sites and reduce their electronic activity. For example, Lewis-basic ligands may interact with under-coordinated metal centers, while anionic ligands may compensate positively charged surface sites. By reducing the density of electronically active traps, surface ligands can increase radiative recombination efficiency and consequently improve photoluminescence quantum yield.

Effective defect passivation can also influence charge-carrier lifetimes and reduce photoluminescence quenching. However, ligand passivation is not necessarily permanent. Ligand desorption, chemical transformation, ion migration, and environmental exposure can gradually alter the surface composition. Therefore, long-term passivation requires consideration of both the initial ligand–surface interaction and the thermodynamic and kinetic stability of the resulting interface.

Influence of Ligands on Optical and Electronic Properties

The influence of ligands extends beyond NC synthesis and surface stabilization to the optical and electronic properties of the final material. By modifying surface defect densities, ligands can influence photoluminescence intensity, emission linewidth, carrier lifetime, and quantum yield. Strong surface passivation generally reduces non-radiative recombination pathways, resulting in improved optical efficiency.

At the same time, ligands influence interparticle charge transport when NCs are assembled into solid-state films. The organic shell separating neighboring NCs can act as a tunneling barrier for charge carriers. Long-chain ligands may provide excellent colloidal stability but can significantly increase interparticle separation, thereby reducing electronic coupling. Shorter ligands or post-synthetic ligand-exchange strategies can reduce this separation and improve charge transport.

This creates a fundamental **stability–transport trade-off** in MHP NC-based devices. Highly passivated NCs may exhibit superior optical stability and colloidal behavior but poor electrical conductivity, whereas aggressively removing or shortening ligands may enhance charge transport while exposing surface defects and increasing susceptibility to degradation. Rational ligand engineering therefore requires simultaneous consideration of colloidal stability, defect passivation, electronic coupling, environmental resistance, and device requirements.

Ligand Exchange and Post-Synthetic Surface Modification

Because the ligand requirements of colloidal NC synthesis are often different from those required for device fabrication, **post-synthetic ligand exchange** has become an important strategy for optimizing MHP NCs. The original long-chain ligands used during synthesis provide colloidal stability and growth control but may subsequently be replaced partially or completely by shorter, more conductive, ionic, or multifunctional surface species.

Ligand exchange can reduce the thickness of the insulating organic shell, decrease interparticle separation, and improve electronic coupling within NC films. At the same time, the replacement ligand must retain sufficient surface-passivation capability to prevent defect formation and degradation. Inadequate ligand exchange can lead to NC aggregation, surface damage, or loss of optical properties, whereas excessive removal of surface ligands can expose reactive sites and compromise stability.

Consequently, ligand exchange should be viewed as a controlled surface-engineering process rather than simply a purification step. The success of the process depends on the chemical compatibility between the incoming ligand, the original surface species, the perovskite lattice, and the processing environment.

Ligands as Determinants of Nanocrystal Stability

The stability of MHP NCs is closely related to the integrity and composition of their ligand shells. Perovskite NCs can be sensitive to moisture, oxygen, heat, light, and polar solvents, all of which can promote structural or chemical degradation. A sufficiently dense and stable ligand shell can provide a physical barrier that reduces direct contact between the perovskite surface and environmental species.

However, ligand protection is influenced by binding strength and ligand packing. Weakly bound ligands may desorb during purification or storage, whereas strongly bound ligands may be difficult to replace during subsequent processing. In addition, changes in temperature, solvent composition, ionic strength, and ligand concentration can disturb the equilibrium between adsorbed and free ligands. Understanding this dynamic equilibrium is therefore essential for developing MHP NCs with long-term structural and optical stability.

Overall Role of Ligands in MHP Nanocrystal Engineering

Overall, ligands represent one of the most important controllable parameters in MHP NC synthesis and application. Their effects span multiple length scales, from molecular-level coordination at individual surface sites to nanoscale control of crystal morphology and ultimately to the macroscopic performance of NC-based films and devices. The choice of ligand determines, either directly or indirectly, precursor reactivity, nucleation, crystal growth, surface termination, defect density, colloidal stability, optical behavior, purification efficiency, film formation, charge transport, and operational stability.

Therefore, ligand selection should be guided by the intended application rather than solely by their ability to stabilize colloidal NCs. Ligands suitable for producing highly luminescent colloidal dispersions may not necessarily be optimal for electrically conductive films, while ligands that promote strong electronic coupling may compromise long-term colloidal or environmental stability. The development of advanced MHP NC technologies consequently requires a rational understanding of ligand–surface interactions and the ability to independently tune surface passivation, colloidal stabilization, interparticle coupling, and environmental protection.

Figure 1 summarizes representative classes of ligands employed for the stabilization and surface modification of MHP NCs, highlighting the structural diversity of monodentate, multidentate, branched, zwitterionic, and ionic ligand systems. The molecular structures illustrate how differences in functional groups, molecular architecture, charge distribution, and number of coordinating sites can produce distinct interactions with MHP NC surfaces.

Such structural differences are directly related to ligand binding strength, surface coverage, defect passivation, colloidal stability, and ultimately the optical, electronic, and structural properties of the resulting nanocrystals.

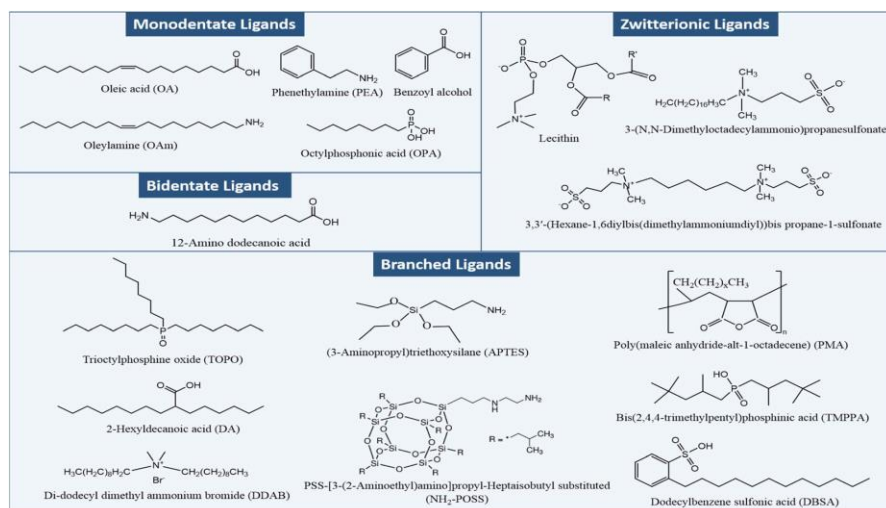


Figure 1. Chemical structures and representative classifications of capping ligands employed for the stabilization and surface modification of metal-halide perovskite nanocrystals (MHP NCs).

Quantitative Comparison of Ligand Classes: Stability–Conductivity–Device Performance

The central limitation of ligand-capped perovskite nanocrystals (PeNCs) is not simply whether a ligand can passivate surface defects, but whether the ligand can simultaneously provide surface protection, high photoluminescence quantum yield (PLQY), adequate charge transport, and operational stability after film formation. Surface chemistry is therefore a critical bridge between nanocrystal synthesis and device application¹⁶. In CsPbX₃ nanocrystals, ligand binding is dynamic rather than permanently fixed, meaning that purification, solvent exposure, heating, and film processing can change the surface composition¹⁶.

Conventional long-chain ligands such as oleic acid (OA) and oleylamine (OAm/OLA) provide effective colloidal stabilization but create relatively large organic barriers between neighbouring nanocrystals. These barriers can suppress interparticle charge transfer and carrier injection. Conversely, reducing ligand length can improve electronic coupling but may increase the susceptibility of the surface to ligand loss and reconstruction^{12; 59}

The following comparison therefore emphasizes representative experimental case studies rather than treating each ligand class as having a single universal performance.

Comparative performance of conventional organic ligand strategies

Ligand strategy	Representative system	Reported optical/device result	Stability evidence	Charge-transport implication	Device metric	Approximate ligand length
Long-chain conventional	OA/OAm–CsPbBr ₃	High-quality colloidal NCs; strong surface passivation	Good colloidal stability, but dynamic ligand loss remains an issue	Relatively poor interparticle transport because of long organic chains	Device metric	C18
Mixed long/short chain	OA/OLA + octanoic acid/octylamine–CsPbI ₃	PLQY reported at approximately 94%	Stability reported for >180 days	Shorter ligands improve charge transport	Lower than optimized short-ligand systems	C8/C18
Short-chain QAB	QAB–CsPbBr ₃	Improved surface passivation	Improved stability relative to OA/OAm control	Carrier transport increases as ligand chain length decreases	PCE increased from 7.76% to 11.87%	Short-chain alkyl
Zwitterionic ligand exchange	Zwitterionic ligand–	Retained 90% initial PLQY at	80% PLQY retained after 16 h	Improved charge transport compared with	EQE = 9.71%	Intermediate/functionalized

	perovskite NCs	353 K and 80% RH	UV irradiation	conventional surface chemistry		
					EQE = 23.36 %; T_{50} = 1.6 h at 5000 cd m^{-2}	

The short-chain CsPbI₃ study provides direct evidence for the stability–conductivity trade-off. Chen et al. (2019) reported that combining OA/OLA with shorter octanoic acid/octylamine ligands produced CsPbI₃ quantum dots with approximately 94% PLQY and improved stability while increasing the photovoltaic PCE from 7.76% to 11.87%. The authors attributed the improvement partly to enhanced charge transport associated with the shorter ligand environment.

A complementary study systematically examined quaternary ammonium bromide ligands with different chain lengths and showed that reducing ligand length increased charge-carrier transport without substantially changing the optical properties. The optimized CsPbBr₃ nanocrystal LEDs achieved an EQE of 9.71%, approximately 16 times that of the OA/OAm reference device⁵⁹. This result demonstrates that ligand length is not merely a colloidal-synthesis parameter; it is a direct device-engineering variable.

More recently, zwitterionic ligand engineering has demonstrated that high charge transport and stability can be achieved simultaneously when ligand architecture rather than chain length alone is optimized. A zwitterionic ligand strategy produced films retaining 90% of their initial PLQY at 353 K and 80% relative humidity and 80% after 16 h of 254-nm ultraviolet irradiation. The resulting QLEDs achieved an EQE of 23.36%, although their reported operational T_{50} remained only 1.6 h at 5000 cd m^{-2} ¹¹². Thus, excellent material-level stability should not automatically be interpreted as long-term operational device stability.

Representative Inorganic and Ionic Ligand Strategies

Strategy	Representative system	Main advantage	Main limitation	Device evidence
Metal-halide/inorganic surface treatment	ZnBr ₂ -treated perovskite NCs	Surface-defect passivation and reduced organic barrier	Surface stoichiometry must be carefully controlled	Improved optoelectronic performance reported
Short ionic ligands	Quaternary ammonium bromides	Reduced interparticle distance	Excessive shortening can compromise surface protection	CsPbBr ₃ LED EQE up to 9.71%
Phosphonium/ionic ligand engineering	Phosphonium-treated PQDs	Strong ionic interactions and reduced insulating character	Optimum ligand density is required	High-efficiency PeLEDs reported

Zwitterionic ligands	Zwitterion-functionalized PQDs	Stronger surface anchoring plus ionic stabilization	Long-term operational lifetime remains unresolved	EQE up to 23.36%
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Inorganic and ionic ligand systems are attractive because they can reduce the thickness of the electronically insulating organic shell. The broader literature shows that short-chain quaternary ammonium ligands can significantly improve carrier transport and device performance relative to conventional OA/OAm-capped CsPbBr₃ nanocrystals⁵⁹. The central design challenge is nevertheless surface stoichiometry: because metal-halide perovskites possess soft ionic lattices, an inappropriate ligand concentration can remove surface ions or induce structural reconstruction.

Polymer and Cross-Linking Strategies

Strategy	Primary function	Effect on stability	Effect on transport	Representative device result
Polymer ligand	Immobilize/stabilize surface ligands	Suppresses ligand loss and improves film integrity	Depends strongly on polymer thickness and composition	Device performance is system-dependent
Ligand cross-linking	Convert mobile ligands into a network	Improves solvent and processing resistance	Can improve interparticle coupling if the network is sufficiently thin	CsPbI ₃ NC LED EQE = 5.7%
Photo-crosslinkable ligand	Spatially controlled network formation	Enhances film stability and patternability	Maintains device-compatible charge transport	Patterned PeLED EQE up to 6.8%
Conjugated ligand/cross-linker	Combine passivation with electronic coupling	Reduces ligand loss	Potentially improves electronic coupling	Increasingly promising for high-EQE devices

Cross-linking provides a fundamentally different solution to the stability–conductivity dilemma. Instead of completely removing the ligand shell, the strategy immobilizes the surface ligands within a network. This can reduce ligand loss during washing, solvent exposure, and multilayer processing⁴⁰.

Li et al. (2016) demonstrated a universal cross-linking strategy for perovskite nanocrystals and obtained an EQE of 5.7% from a cross-linked red-emitting CsPbI₃ device, more than an order of magnitude higher than the corresponding non-cross-linked device. More recent optical patterning work using ligand cross-linkers produced patterned perovskite LEDs with EQEs reaching 6.8%⁴⁵.

The principal limitation is that excessive cross-link density can simply replace a molecular insulating barrier with a polymeric insulating barrier. Consequently, future cross-linking research should optimize not only chemical stability but also the **electronic permeability of the cross-linked network**.

Bioligand Strategies and Current Evidence

Bioligand strategy	Primary function	Current evidence	Device-performance status	Research gap
Amino acids	Surface passivation and defect coordination	Improved optical/environmental stability reported	Device data remain limited	Quantitative mobility measurements
Peptides	Multidentate surface interaction	Potentially strong surface binding	Limited device demonstrations	Binding-energy and transport correlations
Phospholipids/lecithin	Amphiphilic stabilization	High PLQY and strong environmental stability reported in recent work	More evidence needed for PeLED/PV devices	Direct mobility/EQE/PCE comparison
Bio-derived multifunctional ligands	Combined passivation and environmental protection	Emerging research direction	Insufficient quantitative data	Standardized device testing

Bioligands represent an emerging strategy because their functional groups can provide multiple interactions with the nanocrystal surface, including coordination, electrostatic interactions and hydrogen bonding. However, the literature currently contains substantially more evidence for their influence on PLQY and colloidal stability than for charge mobility and operational device lifetime. Therefore, claims that bioligands already outperform synthetic ligands in device conductivity would be premature.

The most useful future direction is the development of **multifunctional bioligands** containing both strong anchoring groups and short electronic pathways. Such molecules could combine the environmental advantages of biological materials with the transport characteristics required for practical devices.

Core Stability–Conductivity Dilemma

The fundamental challenge in ligand engineering can be expressed as:

Increasing ligand coverage or molecular length → improved colloidal stability and defect passivation → increased interparticle separation → reduced charge tunnelling and extraction.

Conversely:

Reducing ligand length or ligand density → improved interparticle coupling and conductivity → increased ligand loss, surface vacancies and environmental degradation.

This relationship has been experimentally demonstrated in several perovskite nanocrystal systems. Chen et al. (2019) showed that shorter ligands improved charge transport and increased solar-cell PCE, whereas Park et al. (2019) found that decreasing quaternary ammonium ligand chain length enhanced charge-carrier transport and produced a 9.71% EQE CsPbBr₃ LED.

The correct objective is therefore not simply to identify the **shortest ligand**, but to identify the **minimum electronically resistive surface architecture that still provides sufficient binding strength, defect passivation and resistance to environmental displacement**.

Ligand Exchange

Ligand exchange addresses the dilemma by separating the requirements of **colloidal synthesis** from those of **device fabrication**. Long-chain OA/OAm ligands can be used to control nucleation and maintain colloidal stability, after which they can be partially or completely replaced by shorter, ionic, zwitterionic or electronically active ligands before device fabrication.

This approach can substantially reduce interparticle spacing and improve charge extraction. However, aggressive ligand exchange can remove surface species, create vacancies, and alter the surface stoichiometry of the perovskite lattice. Consequently, exchange efficiency should not be used as the sole optimization parameter. Surface composition, residual ligand density, binding energy and charge transport must be evaluated simultaneously^{16,59}.

The recent zwitterionic-ligand study illustrates the potential of this strategy. The treated films retained substantial PLQY under thermal, humid and UV stress, while QLEDs reached 23.36% EQE¹⁰⁹. Nevertheless, the relatively short operational T_{50} demonstrates that **material stability and device stability are not equivalent quantities**.

Cross-Linking

Cross-linking takes the opposite approach. Instead of removing the ligand shell completely, it converts mobile ligands into a more permanent network.

The benefits include:

- reduced ligand desorption;
- improved solvent resistance;
- reduced nanocrystal migration;
- improved mechanical integrity;
- improved multilayer processing compatibility; and
- preservation of surface passivation during device operation.

The universal cross-linking strategy reported by Li et al. (2016) produced a CsPbI₃ NC LED with 5.7% EQE, demonstrating that stabilizing the ligand environment can simultaneously improve device performance. Subsequent ligand-cross-linking approaches have further demonstrated the compatibility of cross-linked nanocrystal films with optical patterning and electroluminescent devices⁴⁵.

Inorganic Ligands

Inorganic and ionic ligands attack the transport problem more directly by replacing bulky organic shells with shorter ionic surface species. Their principal advantage is the possibility of reducing the tunnelling distance between adjacent nanocrystals.

However, because perovskites possess highly dynamic ionic surfaces, inorganic ligand concentrations must be carefully controlled. Excessive surface treatment can alter the halide-to-metal ratio, generate vacancies, or induce structural reconstruction. The appropriate strategy is therefore **controlled surface stoichiometry rather than maximum ligand removal**.

Bioligands

Bioligands provide a distinct strategy based on multifunctional molecular interactions. Amino acids, peptides, phospholipids and other bio-derived molecules may simultaneously provide surface coordination, hydrogen bonding, electrostatic stabilization and environmental protection.

However, bioligand research remains less mature from a device perspective. Most studies report PLQY, dispersion stability or surface chemistry, whereas systematic measurements of carrier mobility, ligand density, binding energy and operational EQE remain limited.

The central research question should therefore become:

Can a bioligand be molecularly engineered so that its anchoring group provides strong surface binding while its molecular structure permits efficient interparticle charge transfer?

This question represents a more meaningful research direction than simply determining whether a particular bioligand increases PLQY.

Ligand Binding Energy, Desorption and Degradation Mechanisms

Ligand binding should be treated as a **dynamic thermodynamic equilibrium rather than a permanent attachment**. De Roo et al. (2016) demonstrated that the surface chemistry of CsPbBr₃ nanocrystals involves dynamic ligand interactions and that ligand composition can change during processing and purification.

Nuclear magnetic resonance (NMR), including diffusion-ordered spectroscopy (DOSY) and related techniques, is particularly valuable for distinguishing free and surface-associated ligand populations. X-ray photoelectron spectroscopy (XPS) can provide complementary information about surface elemental composition and chemical states, whereas Fourier-transform infrared spectroscopy (FTIR) can reveal changes in functional-group coordination ¹⁶

The degradation sequence can therefore be represented as:

ligand desorption → exposed/under-coordinated surface sites → vacancy formation or surface reconstruction → enhanced ionic migration → phase/chemical instability → non-radiative recombination → PLQY/EQE loss.

Relationship between Ligand Loss and Degradation

Ligand/surface event	Chemical consequence	Structural consequence	Device consequence	Recommended technique
Ligand desorption	Exposes under-coordinated ions	Surface reconstruction	PLQY/EQE loss	In-situ NMR, XPS
Halide-ligand displacement	Increases surface halide vacancies	Increased ionic mobility	Spectral instability	XPS, operando PL
Thermal ligand rearrangement	Reduced surface coverage	Growth/agglomeration	Luminance decay	FTIR, NMR, TEM

Moisture-induced ligand displacement	Surface hydration/chemical decomposition	Phase degradation	PL quenching	FTIR, XPS, XRD
Light-induced redistribution	Changes local surface chemistry	Possible halide segregation	Emission shift	Operando PL, XPS
Electrical bias	Ion redistribution and interface modification	Surface/interface reconstruction	Reduced lifetime	Bias-dependent XPS, PL, impedance
Excessively thick ligand layer	Low electronic coupling	Large interparticle distance	Low current injection/PCE/EQE	Conductivity, UPS, GIWAXS

The importance of directly measuring dynamic ligand binding is underscored by the NMR studies of De Roo et al. (2016), which demonstrated that ligand binding on CsPbBr₃ nanocrystals is highly dynamic. Such measurements are essential because static post-mortem characterization can miss transient ligand redistribution occurring during illumination, heating or electrical operation.

Batch Reproducibility and Process Control

Reproducibility should be treated as a separate technological challenge because ligand density is itself a hidden process variable. Two nominally identical syntheses can produce different ligand coverage, surface stoichiometry, defect concentrations and therefore different PLQYs and device efficiencies. The current review literature identifies ligand concentration, ligand type, chain length and processing conditions as variables capable of altering nanocrystal size, morphology, purification behaviour and electronic properties⁵⁹. A minimum batch-release specification should therefore include:

1. mean nanocrystal diameter and standard deviation;
2. PLQY;
3. emission maximum and FWHM;
4. ligand-to-Pb ratio;
5. surface halide/Pb ratio;
6. residual free-ligand concentration;
7. nanocrystal concentration;
8. film conductivity;
9. device EQE or PCE; and
10. accelerated-aging performance.

Design-of-experiments (DoE) approaches should replace one-factor-at-a-time optimization. The objective should be to identify the interaction between ligand concentration, precursor ratio, reaction temperature, purification severity and surface chemistry rather than optimizing each parameter independently.

Lead Toxicity and Restriction of Hazardous Substances (RoHS) Considerations

Lead-containing perovskite nanocrystals present an important obstacle to commercialization. This issue should therefore be integrated into ligand and device design rather than treated only as an environmental footnote.

The European Union Restriction of Hazardous Substances (RoHS) framework restricts lead to 0.1% by weight in homogeneous materials for covered electrical and electronic equipment, subject to specific exemptions (European Parliament & Council of the European Union, 2011). Consequently, future PeNC technology must consider lead containment, recycling, recovery and, where technically feasible, lead-free alternatives.

Three complementary strategies are recommended:

1. **Lead containment:** Develop encapsulation and barrier structures that minimize Pb release.
2. **Lead recovery:** Develop collection and recycling systems for end-of-life devices.
3. **Lead-free substitution:** Investigate Sn-, Bi-, Sb- and double-perovskite systems.

Lead-free alternatives should not be judged solely by initial PCE or PLQY. Their assessment should include efficiency, lifetime, toxicity, recyclability, material availability and manufacturing cost.

Scaling Toward Kilogram-Scale Production

Laboratory hot-injection synthesis can provide excellent control over nucleation and crystal growth but presents challenges for large-scale manufacturing because rapid precursor injection, heat transfer, mixing and temperature control become increasingly difficult as reactor volume increases. Continuous-flow and microfluidic methods provide an alternative because they allow better control over mixing and residence time. The development of continuous-flow synthesis therefore represents an important route toward reproducible scale-up⁵⁹.

A credible scale-up pathway should progress through:

batch optimization → parallel reactors → continuous flow → reactor numbering-up → integrated purification → automated ligand exchange → inline surface/optical quality control → kilogram-scale production.

The objective should not simply be to produce more material but to maintain **the same ligand density, particle-size distribution, PLQY and surface composition as production volume increases.**

Technology Roadmap to 2030

Five Priority Unresolved Problems, Characterization Strategies and Proposed 2030 Targets

Priority problem	Why it matters	Recommended characterization	Proposed 2030 target
1.Stability conductivity trade-off	Long ligands stabilize NCs but inhibit charge transport	Operando PL, TRPL, impedance, XPS, NMR	PeLED EQE >30% with T₈₀ >1,000 h in air
2. Ligand desorption and surface reconstruction	Causes vacancies, ion	In-situ NMR, FTIR, XPS, GIWAXS, operando PL	<5% ligand loss during 1,000-h accelerated operation

	migration and instability		
3. Batch-to-batch reproducibility	Prevents reliable manufacturing	Inline spectroscopy and automated single-particle PL	PLQY variation <5% between batches
4. Lead toxicity and regulation	Can restrict commercial deployment	ICP-MS, Pb-leaching tests, lifecycle assessment	Demonstrated containment/recycling pathway and regulatory compliance
5. Manufacturing scale-up	Laboratory synthesis does not guarantee industrial reproducibility	Process analytical technology (PAT), DoE, inline PL/UV-Vis	≥ 1 kg day ⁻¹ reproducible synthesis with PLQY >95%

The $T_{80} > 1,000$ h target should be explicitly described as a **proposed 2030 research target**, not as a current performance level of bioligand PeLEDs. Current studies can reach high EQEs and strong material-level stability, but operational lifetime remains much shorter in many cases. For example, a recent zwitterionic-ligand QLED reached 23.36% EQE but had a reported T_{50} of 1.6 h at 5000 cd m⁻²(111). This large gap demonstrates why future studies must measure both material stability and device operational stability.

Perspectives: From Ligand Screening to Ligand Engineering

The next generation of ligand research should move beyond the traditional question:

“Which ligand gives the highest PLQY?”

The more important question is:

“Which surface architecture simultaneously optimizes binding energy, ligand density, interparticle coupling, defect density, ionic mobility and operational lifetime?”

No single ligand class currently maximizes all of these parameters simultaneously. Conventional organic ligands remain valuable for colloidal synthesis; short ligands and ligand exchange improve electronic coupling; inorganic ligands reduce insulating barriers; polymers and cross-linking improve film integrity; and bioligands provide an emerging platform for multifunctional and potentially more sustainable surface chemistry.

The technological objective should therefore be the development of **hybrid ligand architectures** in which different regions of the surface perform different functions: **strong anchoring group** → **defect-passivation region** → **short/conductive pathway** → **protective/cross-linked outer network**.

Such architectures could potentially overcome the conventional stability–conductivity trade-off rather than merely shifting the optimum from one extreme to another.

Solid-State Ligand Engineering

Ligands should increasingly be regarded as **functional solid-state interfaces** rather than merely molecular shells. Their orientation, packing, dipole alignment, π – π interactions and cross-link density can determine both charge transport and surface stability.

Recent ligand-engineering studies demonstrate that controlled modification of the surface can substantially improve charge symmetry and device performance. For example, recent PCA-mediated surface engineering produced MHP-NC LEDs with an EQE of 31.7%⁵⁹

Bio-derived multifunctional ligands

Bioligands should evolve from simple amino-acid additives toward deliberately designed multifunctional structures containing:

- strong anchoring groups;
- short charge-transfer pathways;
- hydrophobic environmental barriers;
- hydrogen-bonding networks;
- ionic defect-passivation sites; and
- polymerizable or cross-linkable groups.

This would allow bioligands to be evaluated not only as environmentally attractive surface modifiers but as **engineered electronic interfaces**.

Perspectives: From Laboratory Ligands to Practical Perovskite Nanocrystals

The most important conclusion of this review should not be that one ligand class is universally superior. Rather, the evidence demonstrates that **surface chemistry must be optimized as a coupled stability–transport problem**.

Conventional organic ligands remain valuable for controlled colloidal synthesis, whereas short-chain and ionic ligands improve interparticle charge transport. Cross-linking provides an effective route to stabilizing surface ligands during processing, while bioligands offer an emerging platform for multifunctional and potentially sustainable surface engineering. However, no strategy has yet simultaneously solved colloidal stability, high carrier mobility, high PLQY, long operational lifetime, environmental safety and kilogram-scale reproducibility.

Future research should therefore focus on a measurable structure–property–device relationship in which:

ligand identity + binding energy + ligand density + molecular length + surface stoichiometry → PLQY + mobility + ion migration + device efficiency + operational lifetime.

The review should consequently move from simply describing ligand classes toward establishing **quantitative design rules and technology targets**. Such an approach can help to bridge the gap between laboratory-scale perovskite nanocrystal chemistry and practical LEDs, solar cells, photodetectors and other optoelectronic technologies.

Perovskite Nanocrystals (Pncs)

Metal-halide perovskite nanocrystals (MHP NCs or PNCs) have emerged as an important class of semiconductor nanomaterials because of their distinctive structural flexibility, composition-dependent electronic properties, high optical absorption coefficients, efficient charge-carrier generation and transport, and outstanding photoluminescence characteristics. Since the rapid development of colloidal perovskite nanocrystals, considerable attention has been devoted to understanding how their crystal structure, dimensionality, composition, size, morphology, and surface chemistry determine their optical and electronic behavior. These characteristics are particularly relevant to the development of light-emitting diodes (LEDs),

solar cells, photodetectors, lasers, sensors, photocatalytic systems, and other emerging optoelectronic technologies^[16,23].

Unlike many conventional semiconductor nanocrystals, whose properties are frequently dominated by strong covalent bonding, metal-halide perovskites possess relatively soft and dynamically responsive ionic lattices. Their surfaces can therefore undergo reconstruction, ion exchange, defect formation, and ligand-induced structural modification. As a consequence, the properties of PNCs are strongly coupled to their surface chemistry. In particular, the nature and concentration of surface ligands can influence precursor conversion, nucleation, crystal growth, surface termination, defect passivation, colloidal stability, optical emission, charge transport, and environmental stability. A detailed understanding of the structural and optoelectronic characteristics of PNCs is therefore essential for rationalizing the role of ligands in their synthesis and application.

Crystal Structure of Metal-Halide Perovskites

Metal-halide perovskites generally possess the chemical formula ABX_3 , where A is a relatively large monovalent cation, B is a smaller metal cation, and X is a halide anion, typically chloride (Cl^-), bromide (Br^-), or iodide (I^-). The archetypal three-dimensional (3D) perovskite structure consists of a continuous framework of corner-sharing BX_6 octahedra. Within this structure, the B-site metal cation occupies the center of each octahedron and is coordinated by six halide ions, whereas the A-site cation occupies the larger cuboctahedral cavity formed between neighboring BX_6 octahedra.

The structural arrangement is primarily governed by the relative sizes and charges of the constituent ions. The A-site cation contributes to the overall structural stability by occupying the cavities within the anionic BX_6 framework, while the B–X interactions determine the connectivity and electronic characteristics of the inorganic lattice. Changes in the A-, B-, or X-site components can therefore produce substantial modifications in lattice dimensions, octahedral tilting, band structure, phase stability, and optical properties.

The flexibility of the ABX_3 structure is one of the principal reasons for the exceptional versatility of MHPs. Substitution of the A-site cation, B-site metal, or halide anion allows the physicochemical properties of the material to be systematically tuned. At the nanoscale, this compositional flexibility is complemented by size- and surface-dependent effects, providing an additional level of control over the structure and properties of PNCs.

Lead-Based Perovskite Nanocrystals

The most extensively investigated MHP NCs are based on **Pb^{2+} as the B-site cation**. Lead-halide perovskite (LHP) NCs have attracted considerable attention because of their combination of high absorption coefficients, efficient charge-carrier transport, long carrier diffusion lengths, high photoluminescence quantum yields (PLQYs), narrow emission linewidths, and facile compositional tunability^[23].

Based on the nature of the A-site cation, LHP NCs can broadly be categorized into **hybrid organic–inorganic, all-inorganic, and mixed-cation perovskites**. Hybrid organic–inorganic LHPs contain organic ammonium cations such as methylammonium (MA^+) and formamidinium (FA^+). These materials can exhibit favorable optoelectronic properties but may be relatively sensitive to thermal and environmental conditions because of the chemical and structural characteristics of the organic components.

All-inorganic LHP NCs, by contrast, employ inorganic monovalent cations, most commonly Cs^+ , although other inorganic cations can also be incorporated. Representative systems include $CsPbCl_3$, $CsPbBr_3$, and $CsPbI_3$. These materials have attracted particular interest for colloidal nanocrystal applications because of their strong and compositionally tunable optical emission and comparatively favorable thermal characteristics.

Mixed-cation perovskites incorporate two or more A-site cations. Combining organic and inorganic cations can provide additional control over lattice structure, phase stability, band gap, carrier dynamics, and environmental resistance. Similarly, mixed-halide systems provide a powerful means of tuning the optical band gap across a broad spectral range.

Lead-Free and Reduced-Toxicity Perovskite Nanocrystals

Although Pb-based PNCs exhibit exceptional optoelectronic performance, concerns regarding the toxicity and environmental implications of lead have stimulated the development of alternative **lead-free or reduced-lead perovskite materials**. Several metal cations have been investigated as alternatives to Pb^{2+} , including Sn^{2+} , Ge^{2+} , Bi^{3+} , Sb^{3+} , In^{3+} , Cu^{+} , and Ag^{+} [23].

Among these alternatives, tin-based perovskites have received considerable attention because Sn^{2+} can occupy a crystallographic position analogous to Pb^{2+} in several perovskite structures. However, Sn^{2+} is readily oxidized to Sn^{4+} under ambient conditions, which can generate defects and adversely affect the optical and electronic properties of the resulting materials. Similar challenges arise in other lead-free systems, including difficulties in controlling phase formation, precursor chemistry, defect densities, crystal growth, and long-term stability. Bismuth- and antimony-based materials can exhibit improved environmental characteristics but may form structures with reduced dimensionality or electronic properties that differ substantially from conventional Pb-based perovskites. Consequently, while lead-free PNCs represent an important direction for sustainable materials development, achieving performance comparable to optimized Pb-based systems remains challenging.

This challenge highlights the importance of **surface and ligand engineering**. Appropriate ligands may help suppress oxidation, stabilize reactive surface sites, regulate nucleation, and control defects in lead-free PNCs. Therefore, ligand chemistry may become increasingly important in the development of environmentally improved perovskite nanomaterials.

Polymorphs and Phase Stability

Metal-halide perovskites can exist in several structural polymorphs, with the most commonly discussed 3D phases being **cubic, tetragonal, and orthorhombic**. These phases differ primarily in the degree of distortion and tilting of the BX_6 octahedra. At sufficiently high temperatures, many perovskites adopt structures approaching the highly symmetric cubic phase. Upon cooling, lattice distortions can produce tetragonal or orthorhombic structures. The phase adopted by a particular MHP depends on several factors, including temperature, composition, pressure, particle size, surface energy, strain, and environmental conditions. Importantly, nanoscale dimensions can significantly modify the thermodynamic balance between competing phases because surface contributions become increasingly important as particle size decreases.

Consequently, phase stability in PNCs cannot always be predicted solely from bulk-phase behavior. Surface ligands may selectively stabilize certain crystallographic facets or modify surface energies, thereby altering the relative stability of different polymorphs. This phenomenon is particularly important for metastable perovskite compositions whose desired optically active phases are unstable under ambient conditions.

Goldschmidt Tolerance Factor and Octahedral Factor

The structural stability of perovskites can be estimated using geometrical descriptors such as the **Goldschmidt tolerance factor (t)** and **octahedral factor (μ)** [24]. The **Goldschmidt tolerance factor (t)** describes the extent to which the **A-site cation fits within the structural cavity created by the BX_6 octahedral framework** in a perovskite structure. It is expressed as:

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

where:

t = Goldschmidt tolerance factor

$r_{\text{Ar_A}}$ = ionic radius of the A-site cation

$r_{\text{Br_B}}$ = ionic radius of the B-site cation

r_{Xr_X} = ionic radius of the anion (usually halide or oxygen)

For ideal cubic perovskites, the tolerance factor approaches unity. Deviations from unity generally produce structural distortions because the A-site cation is either too small or too large to fit optimally within the cavity. In simplified treatments, perovskite structures are often associated with tolerance factors within an approximate range of **0.8–1.0**, although the precise stability range depends on composition, temperature, bonding character, and other structural factors.

The octahedral factor is given by:

$$\mu = \frac{r_B}{r_X}$$

and provides an estimate of whether the B-site cation is appropriately sized to form a stable BX_6 octahedral coordination environment. A commonly cited approximate range for stable octahedral coordination in perovskite-related structures is about **0.41–0.89** [24].

These geometric factors are useful for predicting structural trends but should not be considered absolute predictors of phase stability. Real MHPs exhibit dynamic lattices, partial covalency, temperature-dependent behavior, compositional disorder, surface effects, and kinetic stabilization, all of which can cause deviations from simple geometric predictions.

Metastability of $CsPbI_3$ and $FAPbI_3$

The importance of structural stability is particularly evident in **$CsPbI_3$ and $FAPbI_3$** . Both materials possess highly desirable band gaps for photovoltaic and optoelectronic applications, yet their photoactive 3D phases can be thermodynamically unstable at room temperature under certain conditions.

For $CsPbI_3$, the relatively small ionic radius of Cs^+ produces a tolerance factor below the ideal cubic value. Bulk $CsPbI_3$ therefore tends to transform from its high-temperature perovskite phases toward non-perovskite yellow phases at room temperature. However, reducing the crystal dimensions to the nanometer scale can modify the surface-energy contribution sufficiently to stabilize the desired perovskite phase. Surface ligands can further contribute to this stabilization by selectively interacting with specific crystal facets and lowering the surface energy of the photoactive structure.

$FAPbI_3$ presents a related but distinct structural problem. The relatively large FA^+ cation can promote structural distortion and transformation between different polymorphs. The desired photoactive α -phase can transform toward a non-perovskite δ -phase under unfavorable conditions. Nanocrystal size, surface chemistry, strain, composition, and ligand coordination can all influence the phase equilibrium.

The stabilization of otherwise metastable phases in nanocrystals demonstrates that **surface chemistry can become a thermodynamic variable at the nanoscale**. This principle is highly relevant to ligand engineering because the ligand shell can influence the relative surface energies of competing polymorphs.

Low-Dimensional Perovskite Nanocrystals

In addition to conventional 3D perovskites, reduced-dimensionality perovskite structures have been developed through compositional engineering and control of crystal growth. Depending on the connectivity of the metal-halide octahedra, perovskite materials can exhibit **0D, 1D, 2D, and 3D structural dimensionalities**.

In 3D perovskites, each BX_6 octahedron is connected to neighboring octahedra in all three spatial directions through shared corners. In 2D structures, octahedral connectivity is restricted primarily to two dimensions, producing inorganic sheets separated by spacer species. In 1D systems, octahedra form extended chains, whereas in 0D structures the inorganic octahedra or clusters are isolated from one another.

These structural differences substantially influence charge-carrier confinement, excitonic interactions, dielectric screening, lattice dynamics, and environmental stability. Lower-dimensional perovskites can exhibit

stronger quantum and dielectric confinement and may possess enhanced resistance to moisture because hydrophobic or bulky spacer species separate the inorganic components.

From a stability perspective, lower-dimensional structures may therefore offer advantages over conventional 3D perovskites. However, their reduced structural connectivity can also limit charge transport. As a result, 3D PNCs remain particularly attractive for applications requiring efficient charge transport, whereas lower-dimensional structures are increasingly investigated where enhanced excitonic confinement and environmental stability are desired.

Compared to 3D perovskites, the connectivity of the octahedra in lower dimensions is presented in Figure 2b. Low-dimensional NCs are usually more stable than 3D NCs against environmental factors such as moisture.

The stability of perovskite structures can be predicted using the tolerance factor (t), which assesses whether the A-site cation fits within the voids of the framework.

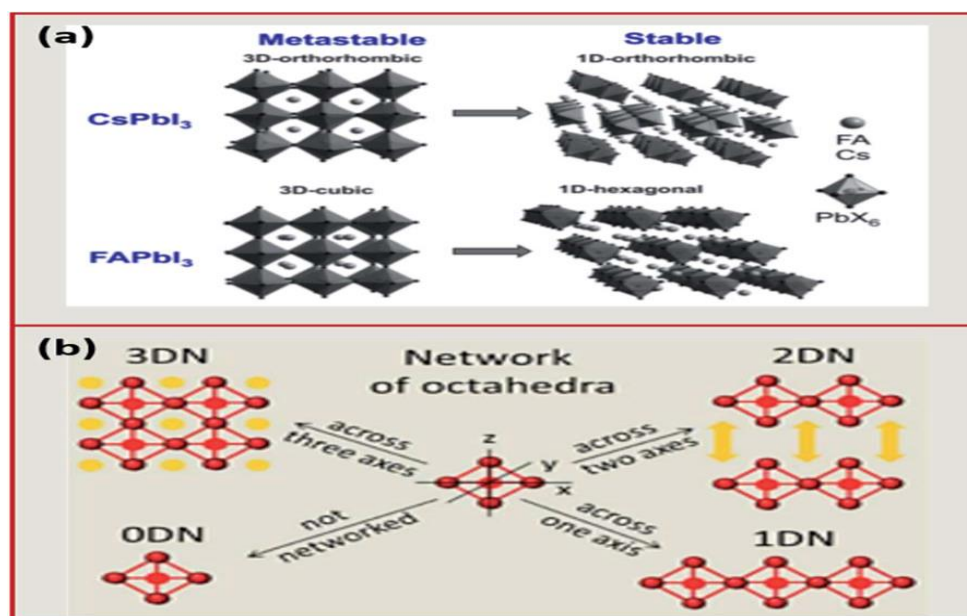


Figure. 2 (a) Illustration of the 3D to 1D phase transition in CsPbI_3 and FAPbI_3 . Reproduced with permission from et ref.²⁵. (b) Schematic presenting the differences between the different dimensionalities (0DN, 1DN, 2DN and 3DN) depending on the connectivity of the octahedra. Reproduced with permission from ref.²⁶.

Morphological Diversity of Perovskite Nanocrystals

Control of crystal dimensionality is accompanied by significant morphological diversity. Depending on precursor composition, solvent, temperature, ligand concentration, reaction kinetics, and surface chemistry, PNCs can be obtained as approximately spherical quantum dots, nanocubes, nanowires, nanorods, nanoplatelets, nanosheets, and other anisotropic structures.

The formation of a particular morphology is strongly influenced by the relative growth rates of different crystallographic facets. Ligands can selectively adsorb onto specific facets and alter their surface energies and growth kinetics. Strong adsorption onto a particular facet can suppress its growth, while weaker adsorption elsewhere allows other facets to grow more rapidly. Consequently, ligand selection provides an important route for controlling nanocrystal morphology.

This facet-selective interaction is particularly important because morphology determines the exposed surface area, surface-defect distribution, excitonic behavior, charge transport pathways, and interactions with the surrounding environment. Therefore, morphology control and surface-ligand engineering are closely interconnected aspects of PNC synthesis.

Optoelectronic Properties of Perovskite Nanocrystals

The exceptional optoelectronic properties of MHP NCs are among the principal reasons for their rapid development in contemporary materials research. These properties include strong and tunable optical absorption, intense photoluminescence, high PLQYs, narrow emission linewidths, long carrier diffusion lengths, favorable carrier mobilities, and composition-dependent band gaps ^[16,23].

The combination of these characteristics enables PNCs to function effectively as light absorbers, emitters, and charge-transporting materials. Importantly, many of these properties can be modified through composition, size, morphology, crystal dimensionality, and surface chemistry. Ligand engineering therefore provides an additional means of tailoring PNCs for specific applications.

Absorption and Photoluminescence

The absorption and photoluminescence (PL) properties of LHP NCs are strongly dependent on their halide composition. In the widely studied all-inorganic CsPbX₃ system, where X represents Cl, Br, or I, increasing the halide ionic size from Cl⁻ to Br⁻ and then to I⁻ generally decreases the band gap and shifts the optical response toward longer wavelengths.

Accordingly, CsPbCl₃ NCs typically exhibit emission toward the blue/near-blue region, CsPbBr₃ NCs emit predominantly in the green region, while CsPbI₃ NCs exhibit emission at longer wavelengths toward the red region^[16]. This broad compositional tunability provides a convenient strategy for generating different emission colors from closely related perovskite compositions.

Mixed-halide compositions provide even greater flexibility. By varying the relative proportions of chloride, bromide, and iodide, the band gap and corresponding absorption and emission wavelengths can be continuously adjusted over a broad portion of the visible spectrum. Similar compositional tuning can be achieved in MA- and FA-based perovskite NCs ^[27,28].

The ability to control the emission wavelength through composition is particularly advantageous for display and lighting technologies. However, mixed-halide PNCs may experience light-induced halide segregation under certain conditions, resulting in the formation of iodide- or bromide-rich domains with different band gaps. Surface ligands and passivation strategies can influence the susceptibility of these materials to such compositional instability, making ligand engineering relevant not only to initial optical properties but also to their long-term operational behavior.

The absorption and emission of the NCs can be further tuned over the entire visible range by using halide mixtures and changing their ratios in CsPbX₃ NCs ¹⁶. Similarly, the variation of the halide content from Cl to Br to I red-shifts the emission in MA perovskite NCs ²⁷ and FA-based perovskite NCs ²⁸ in Figure 3b.

The electronic structure of lead halide perovskites is presented in Figure 3b. The conduction band (CB) is formed from the antibonding mixing between Pb 6p orbitals and halide outer p orbitals with the major contribution from Pb 6p. The valence band (VB) is composed of the antibonding orbitals from the hybridization of the halide valence p orbitals with Pb 6s orbitals ²⁹.

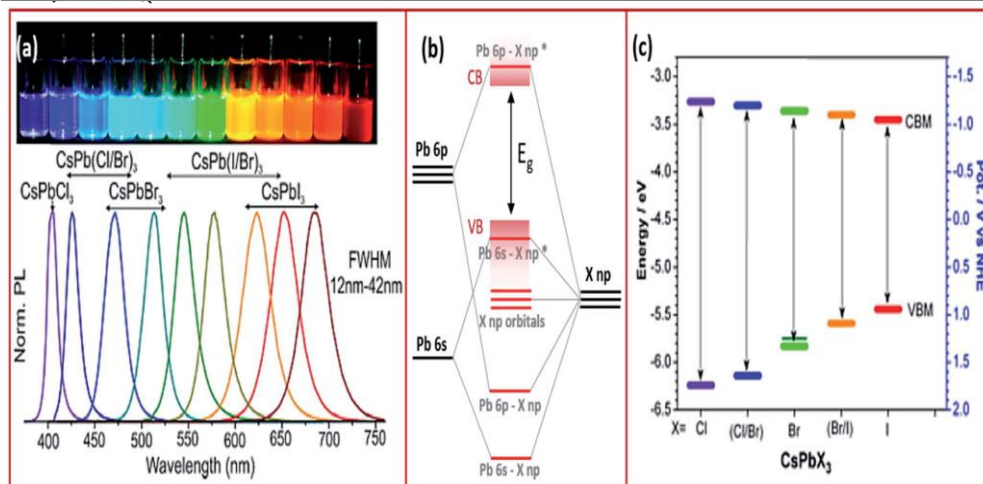


Figure. 3 (a) The PL spectra of CsPbX₃ NCs with variable halide content with the corresponding image of the different NC solutions in toluene under UV illumination. Reproduced with permission from¹⁶. (b) A schematic representing the electronic structure of lead halide perovskites. (c) Band edge energies (conduction band CBM and valence band VBM) of CsPbX₃ NCs extracted from cyclic voltammetry measurements with a scan rate of 50 mV s⁻¹ of the NCs dispersed in tetra-butyl ammonium perchlorate electrolyte in a mixture of acetonitrile and toluene. Modified with permission from³⁰

Electronic Structure of Lead-Halide Perovskites

The electronic properties of lead-halide perovskites originate from the interaction between the orbitals of the metal and halide components. In Pb-based MHPs, the **valence-band maximum (VBM)** is primarily associated with antibonding interactions between Pb 6s and halide p orbitals, while the **conduction-band minimum (CBM)** has a major contribution from Pb 6p orbitals and halide p orbitals^[29].

The relatively favorable electronic structure contributes to the efficient absorption and emission characteristics of lead-halide perovskites. Because the band-edge states involve both metal and halide orbitals, modification of the halide composition can substantially influence the band gap. This provides a direct connection between chemical composition and optoelectronic response.

At the nanocrystal scale, the electronic structure is further affected by quantum confinement and surface states. When NC dimensions become sufficiently small, spatial confinement of charge carriers can modify the energy levels and excitonic transitions. Surface defects can introduce localized electronic states within the band gap, providing pathways for carrier trapping and non-radiative recombination. Surface ligands are therefore critical because they can alter the chemical and electronic environment at these band-edge and defect sites.

Quantum Confinement and Excitonic Effects

The nanoscale dimensions of PNCs can produce quantum-confinement effects when the crystal size approaches characteristic carrier or exciton length scales. Quantum confinement restricts the spatial motion of electrons and holes and can modify the electronic energy levels, absorption spectrum, and photoluminescence.

The magnitude of confinement depends on the relationship between the NC dimensions and the exciton Bohr radius. Stronger confinement generally produces larger shifts in the optical transition energy. However, the magnitude of this effect in MHP NCs depends strongly on composition, dielectric environment, crystal size, and surface chemistry.

The surrounding ligand shell can also modify the dielectric environment of the NC. Because organic ligands generally possess dielectric constants different from those of the inorganic perovskite lattice, changes in ligand composition and surface coverage can influence excitonic interactions and charge-carrier behavior. Thus, the ligand shell represents not only a chemical interface but also an important component of the nanoscale dielectric environment.

Photoluminescence Quantum Yield and Charge-Carrier Recombination

A major advantage of many PNCs is their ability to exhibit high PLQYs. High PLQY indicates that a large fraction of excited charge carriers undergo radiative recombination rather than being lost through non-radiative pathways. Surface defects are among the important factors that can reduce PLQY because they provide trapping sites that facilitate non-radiative recombination.

Ligand passivation can reduce the density or activity of such surface traps. For example, ligands containing Lewis-basic functional groups may coordinate to under-coordinated metal centers, whereas anionic species can compensate positively charged surface defects. Effective surface passivation can therefore increase radiative recombination efficiency and improve PL intensity and PLQY.

However, excessively strong ligand binding or thick insulating ligand shells can negatively influence charge transport. Consequently, maximizing PLQY does not necessarily produce the highest device efficiency. The optimum ligand chemistry depends on whether the target application emphasizes light emission, charge extraction, photocatalysis, or another functional property.

Charge Transport and Band-Edge Engineering

Efficient charge transport is essential for PNC-based optoelectronic devices. In an individual nanocrystal, charge carriers can exhibit favorable transport characteristics; however, when NCs are assembled into films, the organic ligand shell between neighboring particles can become a major transport barrier.

Long-chain ligands increase interparticle separation and can suppress electronic coupling. Although such ligands are highly effective for colloidal stabilization, they can reduce carrier mobility across NC films. Short-chain ligands, ionic ligands, or post-synthetic ligand-exchange approaches can decrease the interparticle distance and facilitate electronic coupling.

Therefore, the design of PNC films requires a compromise between **surface passivation and charge transport**. The ligand system must be sufficiently robust to protect the NC surface and suppress defect-mediated recombination while simultaneously allowing efficient carrier movement between neighboring particles.

Environmental and Operational Stability

Despite their excellent optoelectronic properties, MHP NCs remain vulnerable to several environmental and operational stressors. These include moisture, oxygen, elevated temperature, intense illumination, electric fields, polar solvents, and chemical interactions with surrounding materials.

Moisture can penetrate the ligand shell and initiate hydration or decomposition processes, while oxygen can participate in photoinduced reactions that accelerate degradation. Heat can promote ligand desorption, ion migration, phase transformation, and structural decomposition. Illumination can induce changes in halide distribution and surface chemistry.

Surface ligands can provide a first line of defense against these degradation pathways. A densely packed and appropriately bound ligand shell can reduce the direct contact of the perovskite surface with water and oxygen and can suppress surface reactions. However, ligand protection is not absolute. Ligand desorption, chemical instability, defects, and incomplete surface coverage can create pathways through which environmental species reach the perovskite lattice.

Consequently, the long-term stability of PNCs depends on a combination of intrinsic lattice properties and extrinsic surface engineering. Ligand composition, binding strength, surface coverage, molecular architecture, and resistance to environmental conditions must all be considered when designing stable PNC systems.

Relationship Between Structure, Surface Chemistry, and Optoelectronic Performance

The structural, optical, and electronic properties of PNCs are strongly interconnected. Changes in crystal composition can alter the lattice structure and band gap; changes in dimensionality can modify carrier confinement and excitonic interactions; changes in morphology can alter surface-area-to-volume ratios and facet exposure; and changes in ligand chemistry can influence all of these properties through surface interactions.

This interdependence means that the optimization of PNCs cannot be achieved by considering crystal structure or ligand chemistry independently. For example, a ligand that promotes the formation of small, highly luminescent NCs may not necessarily be suitable for producing electrically conductive films. Similarly, a strongly bound ligand may improve environmental stability but interfere with ligand exchange or charge extraction.

A comprehensive understanding of PNCs must therefore integrate **bulk crystal structure, surface chemistry, nanoscale morphology, defect physics, optical behavior, charge transport, and environmental stability**. Such an integrated perspective provides the foundation for rational ligand engineering and for the development of PNCs with application-specific properties.

Relevance of Perovskite Nanocrystals to Ligand Engineering

The remarkable sensitivity of PNC properties to their surface environment makes them particularly suitable for ligand-based engineering. During synthesis, ligands influence precursor complexation and nucleation kinetics; during crystal growth, they regulate facet development and particle morphology; following synthesis, they passivate surface defects and maintain colloidal stability; and during device fabrication, they determine interparticle coupling, film formation, and charge transport.

Consequently, ligand chemistry provides a versatile means of controlling PNCs across multiple stages of their life cycle. The rational selection of ligands requires consideration of their functional groups, binding modes, molecular architecture, chain length, polarity, charge, and binding strength. Furthermore, the ligand concentration and ligand-to-precursor ratio can be as important as the chemical identity of the ligand itself.

This multifunctionality explains why ligand engineering has become a central strategy in the development of high-performance PNCs. Rather than treating ligands simply as stabilizing molecules, contemporary approaches increasingly regard the ligand shell as an active component of the nanocrystal that determines surface structure, defect chemistry, optical behavior, stability, and interparticle electronic interactions.

SUMMARY

Perovskite nanocrystals combine the structural versatility of metal-halide perovskites with nanoscale control over optical and electronic properties. Their ABX_3 crystal framework permits extensive compositional modification at the A-, B-, and X-sites, while reduction to the nanoscale introduces additional control through quantum confinement, surface effects, and morphology. Lead-based PNCs, particularly $CsPbX_3$ systems, remain among the most extensively studied because of their excellent optical properties and broad compositional tunability, while lead-free alternatives continue to be investigated to address environmental concerns.

The structural stability of PNCs is influenced by ionic size, octahedral connectivity, temperature, composition, particle size, surface energy, and ligand interactions. Similarly, their absorption, emission, carrier dynamics, and stability are closely related to surface-defect chemistry. These characteristics establish a direct relationship between PNC structure and surface chemistry.

Accordingly, ligands occupy a central position in the synthesis and application of PNCs. Their ability to regulate nucleation, crystal growth, morphology, surface defects, phase stability, colloidal behavior, and interparticle interactions makes them powerful tools for materials engineering. A detailed understanding of

the interplay between PNC structure and ligand chemistry is therefore essential for developing stable and high-performing nanocrystal systems for optoelectronic, energy, sensing, and photocatalytic applications.

Quantum Confinement

In addition to compositional engineering, **quantum-size effects** provide an important mechanism for controlling the electronic and optical properties of metal-halide perovskite (MHP) nanocrystals (NCs) [23]. When the dimensions of a semiconductor crystal become comparable to or smaller than the characteristic exciton Bohr radius, the motion of electrons and holes becomes spatially confined. This phenomenon, commonly referred to as **quantum confinement**, modifies the electronic energy levels and can result in an increase in the effective band gap and a corresponding shift of the absorption and photoluminescence (PL) spectra toward shorter wavelengths.

The exciton Bohr radius represents the characteristic spatial extent of an electron–hole pair, or exciton, within a semiconductor. For Wannier–Mott excitons, which are characterized by relatively weak Coulombic interactions and spatially extended wave functions, the Bohr radius depends on the dielectric properties and effective masses of the charge carriers. When the NC dimensions are significantly larger than the exciton Bohr radius, the electronic states approach bulk-like behavior and quantum confinement is relatively weak. Conversely, when the NC dimensions become comparable to or smaller than the exciton Bohr radius, confinement becomes increasingly pronounced.

For lead-halide perovskites, the estimated exciton Bohr diameters are approximately **5, 7, and 12 nm** for **CsPbCl₃, CsPbBr₃, and CsPbI₃**, respectively [16]. These values indicate that the extent of quantum confinement depends not only on NC size but also on halide composition. Because many colloidal LHP NCs are commonly synthesized with dimensions of approximately 4–15 nm, some systems may exhibit weak or intermediate confinement, whereas NCs with dimensions approaching or below the corresponding excitonic length scale can exhibit much stronger quantum-size effects.

The influence of quantum confinement can be observed experimentally through changes in absorption and PL spectra. As the dimensions of CsPbBr₃ NCs decrease, the optical absorption edge and PL maximum generally shift toward shorter wavelengths, producing a **blue shift** of the emission [16]. This shift originates from the increased energy required to confine the electron–hole pair within the smaller crystallite. Figure 4a illustrates this size-dependent behavior, demonstrating that NC dimensions provide an additional route for tuning the optical response independently of compositional modification.

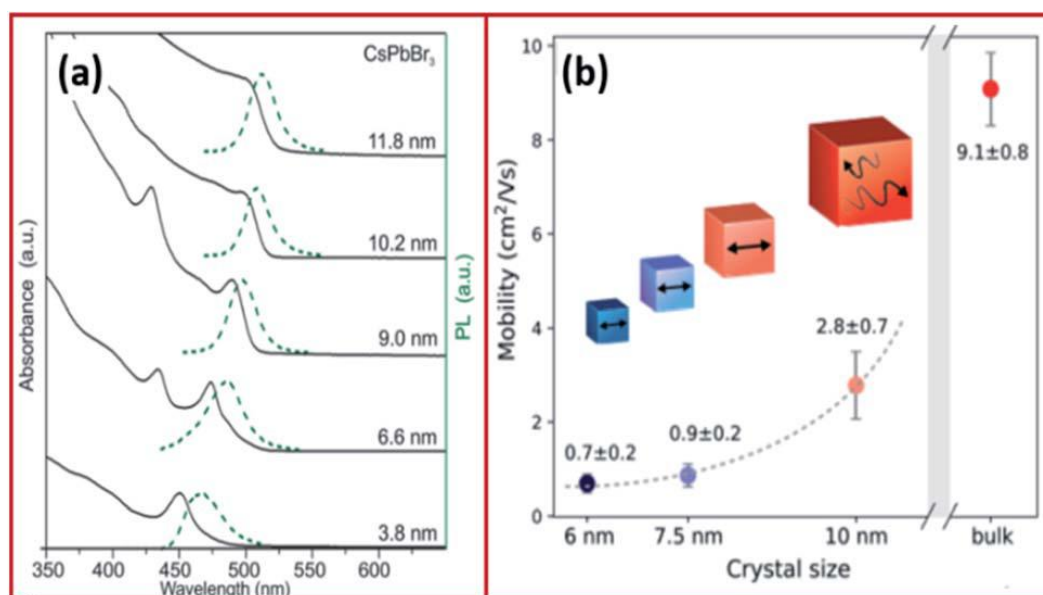


Figure. 4 (a) Absorption and emission of CsPbBr₃ NCs with variable size demonstrating quantum-size effects. (b) Size dependence of effective charge-carrier mobility of CsPbBr₃. Panels (a) and (b) are reproduced with permission from [16] and [31], respectively

Quantum Confinement in Low-Dimensional Perovskite Nanostructures

Quantum confinement becomes particularly important in anisotropic PNCs, including **nanosheets, nanoplatelets, nanowires, and nanorods**. Unlike approximately cubic NCs, these structures can possess one or more dimensions that are substantially smaller than the exciton Bohr diameter. Consequently, charge carriers may become strongly confined along specific crystallographic directions.

For example, ultrathin perovskite nanosheets consisting of only a few inorganic layers can exhibit strong confinement perpendicular to the plane of the sheet. Similarly, nanowires with diameters below approximately 10 nm can experience significant radial confinement^[23]. Such structures may display optical properties that differ substantially from those of bulk perovskites or weakly confined nanocubes.

Ligand chemistry plays an important role in producing these low-dimensional structures. Long-chain ligands can selectively bind to particular crystallographic facets and inhibit growth along specific directions. This facet-selective growth can promote the formation of thin nanosheets or anisotropic nanowires. Therefore, the effects of ligand chemistry and quantum confinement are closely interconnected: ligands influence the dimensions and morphology of the NC, while the resulting dimensions determine the degree of quantum confinement.

The ability to control confinement through ligand-directed synthesis provides an important strategy for tailoring the absorption and emission characteristics of PNCs. However, strong confinement may also alter charge-carrier transport and exciton dynamics. Consequently, the optimum degree of confinement depends on the intended application.

Quantum Confinement and Exciton Binding

An important consequence of nanoscale confinement is modification of the interaction between electrons and holes. In bulk-like MHPs, the relatively high dielectric constants and small carrier effective masses contribute to extended excitonic states and relatively weak exciton binding energies. As the dimensions of the NC approach the exciton Bohr radius, spatial confinement increases the overlap between electron and hole wave functions.

This increased overlap can enhance excitonic interactions and modify the energy required to create or dissociate excitons. The surrounding dielectric environment also becomes important at the nanoscale. Because the perovskite NC is surrounded by an organic ligand shell and solvent or another matrix, dielectric mismatch at the NC interface can modify Coulombic interactions between charge carriers.

Thus, the ligand shell is not merely a chemical coating. It can contribute to the **local dielectric environment** experienced by confined charge carriers. Changes in ligand composition, surface coverage, molecular polarity, and packing can consequently influence excitonic properties in addition to their effects on surface defects and colloidal stability.

Charge-Carrier Dynamics

The generation, transport, trapping, and recombination of charge carriers determine the suitability of MHP NCs for optoelectronic and energy-related applications. Although many of the fundamental electronic properties of MHP NCs are related to their bulk counterparts, charge transport in an NC assembly is significantly influenced by nanoscale dimensions, interparticle interfaces, surface ligands, and defects.

In bulk and polycrystalline perovskite films, charge carriers can migrate over relatively extended distances through interconnected crystalline domains. In contrast, films prepared from colloidal NCs consist of individual nanocrystallites separated by organic or inorganic surface species. Consequently, charge carriers must frequently cross NC–NC interfaces to move through the film. The ligand shell at these interfaces can act as a potential energy barrier and can strongly influence electronic coupling between neighboring NCs.

Studies of CsPbBr₃ NC films have demonstrated that charge carriers can exhibit a more localized character compared with those in polycrystalline perovskite films [32]. The degree of localization becomes more pronounced as the NC dimensions decrease. As illustrated in Figure 4b, the effective charge-carrier mobility decreases with decreasing NC size [31,32]. This behavior can be associated with stronger quantum confinement, increased excitonic effects, greater interfacial contributions, and the increasing relative influence of the barriers separating neighboring NCs.

The transport properties of an NC film are therefore determined not only by the intrinsic mobility within individual NCs but also by the **interparticle coupling**. Shorter ligands can reduce the physical separation between adjacent NCs and facilitate charge tunneling, whereas long-chain organic ligands can increase interparticle distance and suppress electronic coupling. Consequently, ligand length and surface coverage represent critical parameters in determining the effective mobility of PNC films.

Photoluminescence Dynamics and Charge-Carrier Recombination

Photoluminescence measurements provide important information about the fate of photoexcited charge carriers in PNCs. Following optical excitation, electrons and holes are generated and subsequently undergo processes that may include thermalization, trapping, radiative recombination, non-radiative recombination, or charge transfer to neighboring particles or external materials.

The **photoluminescence quantum yield (PLQY)** is an important parameter for evaluating the efficiency of radiative recombination. A high PLQY indicates that a large proportion of excited carriers recombine radiatively, whereas a low PLQY may indicate substantial non-radiative losses. However, PLQY alone does not completely describe the carrier dynamics of a PNC system.

Time-resolved photoluminescence measurements provide complementary information by determining the temporal evolution of the emission following excitation. PL decay lifetimes can provide insight into the relative contributions of radiative and non-radiative recombination processes and can help identify the presence of trap-mediated pathways [23]. Combining PLQY measurements with time-resolved PL therefore provides a more comprehensive assessment of surface quality and defect-related carrier losses.

Ligand engineering is directly relevant to these measurements because surface ligands can modify the density and electronic activity of surface defects. Effective passivation may reduce trap-assisted recombination and increase PLQY, whereas ligand loss or incomplete surface coverage can expose defect sites and accelerate non-radiative recombination.

Defect Tolerance and Surface Passivation

One of the distinctive characteristics frequently associated with metal-halide perovskites is their **defect tolerance** [33]. In semiconductor materials, defects can introduce electronic states within the band gap and act as trapping or recombination centers. Defect tolerance describes the ability of a semiconductor to maintain relatively favorable electronic properties despite the presence of certain structural imperfections.

However, defect tolerance should not be interpreted to mean that defects are completely harmless. Rather, it reflects the tendency of many intrinsic defects in MHPs to produce relatively shallow electronic states or to have limited influence on carrier recombination compared with deep defects in conventional semiconductors. The electronic consequences of a particular defect depend on its chemical identity, charge state, local structural environment, concentration, and position within the lattice or at the surface.

Under conditions close to the ideal stoichiometric composition, **Schottky-type point defects**, including cation and anion vacancies, have been predicted to possess relatively low formation energies in many lead-halide perovskites [33]. These intrinsic vacancies can therefore occur relatively readily. In contrast, certain interstitial and antisite defects can possess higher formation energies and may generate deeper electronic states, although their concentrations depend strongly on synthesis conditions and chemical potentials.

The relatively soft ionic lattice of MHPs can also accommodate structural imperfections such as dislocations, grain boundaries, stacking faults, and twin boundaries ^[23]. At the nanoscale, the large surface-to-volume ratio introduces an additional category of defects associated with surface termination, under-coordination, vacancies, reconstruction, and local compositional imbalance.

Electronic Consequences of Defects

The electronic consequences of defects depend strongly on whether they produce **shallow or deep electronic states**. Shallow states occur close to the valence- or conduction-band edges and may have relatively limited effects on charge transport under certain conditions. Deep states, by contrast, can trap charge carriers for longer periods and facilitate non-radiative recombination.

This distinction helps explain the comparatively strong optical performance of many MHPs despite the presence of structural imperfections. Several theoretical and experimental studies have indicated that important intrinsic defects in lead-halide perovskites can exhibit relatively shallow electronic character rather than introducing highly detrimental mid-gap states ^[34–37]. This defect tolerance contributes to the high PLQYs and favorable charge-carrier properties observed in many MHP systems. It also distinguishes MHPs from certain conventional semiconductor quantum dots, including some metal chalcogenide systems, where surface defects can introduce deep trap states that substantially reduce luminescence efficiency.

Nevertheless, the high surface area of NCs means that surface defects require particular attention. The electronic behavior of a PNC is therefore governed not only by the intrinsic defect tolerance of the bulk lattice but also by the chemical condition of its surface.

Surface Defects in Perovskite Nanocrystals

The surface of an MHP NC contains atoms and ions with coordination environments that differ from those in the interior of the crystal. Surface termination can therefore produce under-coordinated metal ions, halide vacancies, dangling coordination sites, and local deviations from ideal stoichiometry.

These sites can interact strongly with the surrounding environment and can serve as locations for adsorption, ion migration, chemical reactions, and charge trapping. Consequently, surface chemistry becomes increasingly important as NC size decreases.

Although intrinsic defect tolerance reduces the severity of many defects, surface defects can still influence PL intensity, carrier lifetime, charge transfer, and stability. In particular, ligand loss can expose previously passivated surface sites, leading to changes in the optical properties and chemical stability of the NC.

Role of Ligands in Surface Passivation

Surface ligands provide an important mechanism for controlling the electronic and chemical properties of PNC surfaces. A ligand can coordinate to an under-coordinated surface site, compensate local charge imbalance, or otherwise modify the electronic environment of a surface defect.

Lewis-base ligands can interact with under-coordinated metal centers, whereas anionic species such as halides and carboxylates can interact with positively charged surface sites. Through these interactions, ligands can reduce the density or activity of electronically active trap states and suppress non-radiative recombination.

Effective passivation can consequently increase PLQY, improve carrier lifetimes, and enhance the stability of PNCs. However, the effectiveness of passivation depends on ligand identity, binding strength, surface coverage, defect type, and the chemical environment.

This distinction is important because **strong ligand binding is not necessarily synonymous with optimal device performance**. A ligand may provide excellent surface passivation while simultaneously producing a thick insulating barrier that reduces charge transport. Therefore, ligand engineering requires optimization rather than maximization of surface coverage.

STABILITY OF METAL-HALIDE PEROVSKITE NANOCRYSTALS

Despite their exceptional optoelectronic properties, the practical implementation of MHP NCs remains constrained by their susceptibility to environmental and operational degradation^[23]. The relatively soft and ionic nature of the perovskite lattice makes these materials sensitive to external stimuli, including moisture, oxygen, heat, intense illumination, electric fields, and chemically aggressive solvents.

The stability problem becomes particularly important at the nanoscale because the high surface-to-volume ratio increases the fraction of atoms exposed to the surrounding environment. Surface defects, incomplete ligand coverage, and ligand desorption can provide pathways for environmental species to interact with the perovskite lattice.

Solvent-Induced Instability

MHP NCs are particularly sensitive to **polar and coordinating solvents**. Such solvents can interact strongly with the ionic components of the perovskite lattice and may disturb the surface ligand shell. In severe cases, solvent-induced interactions can cause NC aggregation, dissolution, phase transformation, or decomposition.

This sensitivity presents a challenge during purification and device fabrication. Although washing steps are necessary to remove excess ligands and unreacted precursors, aggressive purification conditions may remove beneficial surface species and expose the NC surface. Similarly, solvents used in subsequent film-processing steps may interact with the perovskite or disrupt the ligand shell.

Therefore, purification and processing procedures must be carefully designed to achieve chemical cleanliness while preserving sufficient surface protection.

Moisture, Oxygen, Light, and Thermal Stability

Moisture is one of the most important degradation factors affecting MHP materials. Water molecules can interact with the ionic lattice and surface species, potentially initiating hydration, structural transformation, ion redistribution, and eventual decomposition. Oxygen can also participate in photoinduced chemical reactions that accelerate degradation under illumination.

Temperature is another important factor because heating can promote ligand desorption, ion migration, phase transformation, and decomposition. Elevated temperatures may therefore simultaneously affect both the inorganic lattice and the organic ligand shell.

Illumination can produce additional instabilities. In mixed-halide PNCs, prolonged illumination under certain conditions can promote **halide segregation**, generating regions with different halide compositions and therefore different band gaps. This process can alter the PL spectrum and reduce the long-term stability of optoelectronic devices.

The combined effects of moisture, oxygen, heat, and illumination demonstrate that stability is a multidimensional property rather than a single material parameter.

Strategies for Improving PNC Stability

Several approaches have been developed to improve the stability of MHP NCs. These strategies include surface-ligand engineering, inorganic or ionic surface passivation, encapsulation, compositional modification, incorporation into polymer matrices, and integration with protective inorganic materials.

Embedding PNCs within **polymers** can provide a physical barrier against moisture and oxygen while improving mechanical integrity. Similarly, incorporation into **silica or alumina matrices** can provide protective interfaces that reduce environmental exposure^[23]. Carbon-based materials such as graphene and related two-dimensional materials have also been investigated as protective or functional components.

Two-dimensional materials may provide additional advantages by combining barrier properties with electrical or optical functionality. However, the compatibility between the PNC surface and the host material must be carefully considered to prevent degradation during integration. Among these approaches, surface-ligand engineering remains particularly attractive because it can simultaneously influence synthesis, defect passivation, colloidal stability, environmental protection, and electronic coupling.

Stability–Performance Trade-Off

An important challenge in PNC engineering is the relationship between **stability and optoelectronic performance**. Increasing ligand coverage may improve colloidal and environmental stability by creating a more effective protective shell. However, excessive ligand coverage can increase inter particle separation and reduce charge transport in solid-state films.

Conversely, aggressive ligand removal may enhance electronic coupling and carrier mobility but expose surface defects and increase susceptibility to moisture, oxygen, and other degradation pathways. Therefore, optimum device performance requires a balance between surface protection and electronic accessibility.

This trade-off provides a strong scientific basis for ligand-exchange strategies. Instead of completely removing the original ligand shell, carefully selected shorter, multifunctional, ionic, or electronically favorable ligands can be introduced to maintain surface passivation while reducing transport barriers.

Integrated Relationship Between Quantum Confinement, Defects, Charge Dynamics, and Stability

Quantum confinement, charge-carrier dynamics, defect chemistry, and stability should not be considered independent properties of PNCs. They are strongly interconnected through crystal dimensions and surface chemistry. Reducing NC size increases the relative contribution of surface atoms and can simultaneously enhance quantum confinement and the influence of surface defects.

Likewise, ligand-controlled morphology can determine the dimensions of a nanostructure and therefore its degree of confinement. The resulting surface area and facet distribution influence defect populations and ligand binding. These surface characteristics subsequently affect carrier recombination, PLQY, charge transport, and environmental stability.

This interconnected behavior is particularly important when designing PNCs for practical applications. A nanocrystal exhibiting excellent PLQY in solution may not necessarily produce an efficient solid-state device if its ligand shell strongly suppresses charge transport. Similarly, a highly conductive NC film may suffer from rapid degradation if excessive ligand removal exposes the perovskite surface.

Therefore, rational PNC design requires simultaneous optimization of size, composition, morphology, defect density, surface ligand chemistry, interparticle coupling, and environmental protection.

Implications for Ligand Engineering

The properties discussed above demonstrate why ligand engineering is central to the synthesis and application of MHP NCs. Ligands influence the dimensions of NCs and therefore quantum confinement; they modify surface coordination and defect populations; they determine interparticle separation and charge transport; and they provide protection against environmental degradation.

The ideal ligand system is therefore application-dependent. For highly luminescent colloidal NCs, strong surface passivation and colloidal stability may be the primary Objectives. For LEDs, photodetectors, and other electrically driven devices, the ligand system must additionally facilitate efficient charge transport. For long-term environmental stability, the ligand must provide sufficient resistance to moisture, oxygen, heat, and illumination.

The challenge is consequently to develop ligand systems that provide strong but appropriately reversible surface binding, effective defect passivation, controlled nanocrystal growth, adequate colloidal stability,

favorable electronic coupling, and resistance to environmental degradation. Achieving this balance represents one of the central challenges in the development of next-generation perovskite nanocrystal technologies.

Synthesis Of Novel Perovskite Nanocrystals

The synthesis of metal-halide perovskite (MHP) nanocrystals (NCs) is a critical determinant of their structural, morphological, optical, electronic, and stability characteristics. Unlike bulk perovskites, where the primary objective is often to obtain a continuous crystalline film or bulk crystal, the synthesis of PNCs requires precise control over nucleation, crystal growth, particle size, morphology, surface composition, and colloidal stability. Small changes in precursor concentration, reaction temperature, solvent polarity, reaction time, ligand concentration, ligand identity, and precursor-to-ligand ratio can produce substantial changes in the resulting NCs.

The development of colloidal PNC synthesis has been particularly important because it enables the production of highly crystalline nanoparticles with controllable dimensions and compositions under relatively mild chemical conditions. Depending on the desired material and application, synthetic methods can broadly be classified into colloidal (non-template) and non-colloidal or template-assisted approaches. Colloidal methods involve direct nucleation and growth of NCs in solution, whereas template-assisted methods employ a pre-existing matrix, scaffold, substrate, or confined environment to regulate crystal formation.

Among colloidal approaches, **hot injection (HI)** and **ligand-assisted reprecipitation (LARP)** are two of the most extensively investigated techniques for producing MHP NCs. Both methods rely heavily on ligand chemistry, but they differ considerably in reaction temperature, nucleation mechanism, solvent environment, scalability, and control over crystal morphology.

Colloidal Synthesis

Colloidal synthesis is a solution-phase approach in which molecular or ionic precursors are converted into crystalline nanoparticles in the presence of surface-active ligands. During the reaction, the precursors undergo chemical transformation, supersaturation, nucleation, and subsequent crystal growth. The newly formed nanocrystals are stabilized by ligands that adsorb or coordinate at their surfaces and prevent uncontrolled aggregation.

A major advantage of colloidal synthesis is the ability to independently manipulate nucleation and growth conditions. By controlling the concentration of reactive species and the rate at which supersaturation is achieved, it is possible to influence the number of nuclei generated during the early stage of the reaction. Subsequent growth of these nuclei determines the final particle dimensions and morphology.

The general colloidal synthesis process can therefore be considered as a sequence involving:

- precursor dissolution and complexation;
- formation of reactive precursor species;
- generation of supersaturation;
- nucleation;
- crystal growth;
- surface passivation by ligands; and
- isolation and purification of the resulting NCs.

Among the various colloidal approaches, HI and LARP have become particularly important because they can produce highly crystalline PNCs with relatively narrow size distributions.

Hot-Injection Synthesis

The **hot-injection (HI) method** is one of the most established approaches for synthesizing monodisperse colloidal semiconductor NCs. The methodology originated from earlier work on conventional semiconductor quantum dots, particularly II–VI materials, and was subsequently adapted to metal-halide perovskites. A landmark contribution was the report by Protesescu et al. in 2015, which demonstrated the colloidal synthesis of all-inorganic CsPbX_3 ($X = \text{Cl, Br, I}$) PNCs.

The principal advantage of the HI approach is the ability to generate a short, intense nucleation event by rapidly introducing one precursor into a hot solution containing the remaining precursor components and ligands. This temporal separation between nucleation and growth can promote relatively uniform particle formation.

General Procedure

In a typical HI synthesis, one precursor is rapidly injected into a reaction mixture containing the remaining precursors, ligands, and an appropriate solvent maintained at an elevated temperature. For CsPbX_3 synthesis, for example, a cesium precursor is introduced into a hot solution containing lead-halide precursors and surface ligands such as oleic acid (OA) and oleylamine (OAm), commonly using 1-octadecene (ODE) as a high-boiling solvent.

The sudden introduction of the precursor rapidly changes the chemical equilibrium of the reaction mixture and generates a transient state of high supersaturation. When the concentration of reactive species exceeds the critical supersaturation required for nucleation, numerous nuclei can form within a relatively short period.

The ligands simultaneously interact with precursor species and nascent crystal surfaces. These interactions influence precursor reactivity, nucleation kinetics, surface energy, crystal growth rates, and colloidal stability. Consequently, the ligand system is an integral component of the HI synthesis rather than merely a post-synthesis stabilizing agent.

Nucleation and Crystal Growth

The formation of PNCs through the HI approach can be described in terms of nucleation followed by crystal growth. Immediately after precursor injection, rapid supersaturation promotes the generation of numerous small nuclei. If the concentration of reactive species subsequently decreases below the nucleation threshold, formation of additional nuclei is suppressed and the existing nuclei preferentially consume the remaining precursors.

This temporal separation between nucleation and growth is important for achieving narrow particle-size distributions. Ideally, a large number of nuclei are generated during a short nucleation period, followed by controlled growth of those nuclei.

However, the separation between nucleation and growth is not always complete. Continued precursor availability, temperature fluctuations, ligand dynamics, and surface reactions can result in secondary nucleation or particle ripening.

At longer reaction times, **Ostwald ripening** may become significant. In this process, smaller particles or less stable crystallites dissolve partially and their constituent species contribute to the growth of larger particles. Excessive ripening can broaden the size distribution and alter the morphology of the NC population.

Therefore, rapid termination of the reaction at an appropriate stage can be important for preserving a narrow size distribution.

Synthesis of CsPbX₃ Nanocubes by Hot Injection

The successful application of HI synthesis to CsPbX₃ PNCs by Protesescu et al. represented an important milestone in the development of colloidal metal-halide perovskite nanomaterials. In the reported approach, cesium oleate was rapidly injected into a hot solution containing PbX₂, OA, OAm, and ODE.

The resulting CsPbX₃ NCs exhibited well-defined cubic morphologies and relatively narrow size distributions. Depending on the halide composition and reaction conditions, particles with dimensions approximately within the nanometer regime could be obtained.

A major advantage of this system was the simultaneous control of **composition and size**, allowing the optical properties to be tuned through both halide substitution and nanoscale dimensions. CsPbCl₃, CsPbBr₃, and CsPbI₃ exhibited progressively red-shifted optical responses as the halide was changed from Cl⁻ to Br⁻ and I⁻.

The resulting NCs also exhibited narrow PL emission bands and high PLQYs, demonstrating the potential of colloidal PNCs for light-emitting and other optoelectronic applications.

The optical performance of these NCs was associated with their high crystallinity, relatively uniform dimensions, favorable electronic structure, and effective surface stabilization by the ligand shell.

Optical Properties of Hi-Synthesized Pncs

The optical properties of CsPbX₃ NCs are highly sensitive to composition, particle size, and surface condition. In the pioneering CsPbX₃ synthesis, the NCs exhibited narrow PL emission with reported full widths at half maximum (FWHM) in the range of approximately **12–42 nm**, together with PLQYs of approximately **50–90%**, depending on composition and preparation conditions ^[16].

The narrow emission linewidths are particularly attractive for display and lighting applications because they enable highly saturated colors. Furthermore, the emission wavelength can be systematically adjusted by modifying the halide composition.

The optical performance of the NCs is not determined solely by the inorganic lattice. Surface defects can create non-radiative recombination pathways, while the ligand shell can influence surface passivation and the dielectric environment. Consequently, differences in ligand composition or surface coverage can result in substantial variations in PLQY and carrier lifetime even when the bulk crystal composition remains nominally unchanged.

Extension of Hi Synthesis to Other Perovskite Compositions

Following the development of all-inorganic CsPbX₃ PNCs, the HI method was extended to hybrid organic–inorganic perovskites. For example, methylammonium lead halide NCs (MAPbX₃) can be prepared by introducing methylammonium-containing precursors into suitable lead-halide reaction mixtures ^[40].

The extension of HI synthesis to different A-site cations demonstrates the adaptability of the method. However, the different chemical properties of organic and inorganic precursors require modification of reaction conditions, ligand composition, solvent environment, and injection temperature.

Similarly, mixed-halide and mixed-cation systems can be synthesized through appropriate adjustment of precursor ratios. Such compositional control enables systematic tuning of the band gap and emission wavelength.

Control of Size, Size Distribution, and Morphology in the Hi Method

The ability to control NC dimensions and morphology is one of the major advantages of colloidal synthesis. In the HI method, several parameters determine the final characteristics of the NCs, including:

- reaction temperature;
- injection temperature;
- precursor concentration;
- precursor ratio;
- ligand identity;
- ligand concentration;
- ligand-to-precursor ratio;
- reaction time;
- solvent composition;
- halide concentration; and
- rate of precursor injection.

These parameters influence nucleation and growth kinetics, surface energies, and the relative growth rates of different crystallographic facets.

Effect of Temperature

Reaction temperature is one of the most important parameters governing PNC nucleation and growth. Increasing temperature generally increases precursor conversion and can modify nucleation and surface-reaction kinetics. It can also influence the relative growth rates of different crystal facets and thereby alter morphology.

For example, temperature-dependent synthesis of $\text{Cs}_3\text{Sb}_2\text{I}_9$ has demonstrated that different morphologies can be obtained by changing the reaction temperature, with nanoplatelets reported under lower-temperature conditions and nanorod-like structures under higher-temperature conditions^[41].

The influence of temperature is particularly pronounced in systems exhibiting competing growth pathways. At different temperatures, changes in precursor reactivity and ligand binding can alter the balance between isotropic and anisotropic growth.

For CsPbX_3 , particle dimensions can be strongly influenced by the injection and reaction temperatures because the nucleation event and subsequent growth occur rapidly. Consequently, reaction temperature can provide an effective means of controlling NC size without requiring prolonged reaction times.

Temperature-Induced Anisotropic Growth

Temperature can also influence the dimensionality of PNCs. Lower reaction temperatures may favor anisotropic growth under suitable ligand and precursor conditions, resulting in two-dimensional nanoplatelets or nanosheets rather than three-dimensional nanocubes.

Bekenstein et al. demonstrated temperature-dependent morphological evolution in CsPbBr_3 NCs. Green-emitting CsPbBr_3 nanocubes could be produced at approximately 150 °C, whereas lower-temperature conditions favored the formation of thinner nanoplatelet structures. At approximately 90–100 °C, particularly thin blue-emitting nanoplatelets with lamellar structures could be obtained^[45,46].

This behavior demonstrates the close relationship between reaction kinetics and morphology. At lower temperatures, certain ligands can preferentially adsorb on specific crystal facets and suppress growth along

selected directions. The resulting anisotropic growth produces thin structures with strong quantum confinement.

Thus, temperature and ligand chemistry should not be considered independent parameters. Their combined effect determines the relative rates of precursor conversion, nucleation, facet stabilization, and crystal growth.

Effect of Reaction Time

Reaction time provides another route for controlling NC morphology and dimensions. After nucleation, continued exposure to reactive precursors allows the nuclei to grow. However, prolonged reaction times may also promote secondary processes such as Ostwald ripening, aggregation, phase transformation, or morphological reconstruction.

In CsPbBr₃ systems, the evolution from nanocubes toward more extended structures has been reported with increasing reaction time under particular reaction conditions^[48]. Very thin nanoplatelets can also exhibit changes in their lateral dimensions while maintaining relatively controlled thickness.

The ability to independently manipulate thickness and lateral dimensions is particularly valuable for preparing two-dimensional PNCs because the optical properties of these structures are strongly dependent on thickness. Reducing the thickness can enhance quantum confinement and shift the emission toward higher energies.

Consequently, reaction time should be optimized according to the desired morphology rather than simply maximized to increase crystallinity.

Effect of Initial Precursors and their Concentrations

The identity and concentration of the starting precursors are fundamental determinants of PNC formation. The precursor concentration influences the degree of supersaturation achieved during injection and therefore affects nucleation density and subsequent particle growth.

Increasing the concentration of reactive species can produce a greater degree of supersaturation, potentially increasing the nucleation rate. However, excessive precursor concentrations may also accelerate growth or promote aggregation if the ligand concentration is insufficient to stabilize the resulting NCs.

Additional halide sources have also been employed to improve control over CsPbBr₃ NC synthesis. For example, incorporation of ZnBr₂ or alkylammonium bromide can modify the bromide chemical potential and influence nucleation and growth, resulting in improved control over NC size and size distribution^[49,50].

This observation demonstrates that precursor chemistry extends beyond simply providing the required elements. Precursors can also act as chemical regulators of reaction kinetics and surface composition.

Role of Ligands in Hot-Injection Synthesis

Ligands are fundamental to the successful synthesis of colloidal PNCs. In conventional HI synthesis, long-chain organic acids and amines—particularly OA and OAm—serve several simultaneous functions. They can interact with precursor species, modify their solubility and reactivity, adsorb on growing crystal surfaces, regulate crystal growth, prevent uncontrolled aggregation, and passivate surface defects^[23].

The multifunctionality of ligands makes it difficult to separate their individual roles completely. For example, an amine can participate in precursor complexation while also interacting with the crystal surface. Similarly, a carboxylic acid can influence precursor solubility and simultaneously provide colloidal stabilization after NC formation. The final characteristics of PNCs therefore depend on the chemical equilibrium between ligands, precursors, solvent, and crystal surfaces.

Effect of Ligand Chain Length

The molecular structure of a ligand, including its alkyl-chain length, can significantly affect NC nucleation and growth. Changing chain length modifies steric interactions, solubility, ligand packing, surface coverage, and the strength and dynamics of ligand–surface interactions.

Studies of CsPbBr₃ NCs have shown that shortening the alkyl chain of carboxylic-acid ligands, while maintaining the amine component, can increase the resulting NC size under high-temperature synthesis conditions^[52]. This behavior may be related to differences in ligand packing and surface stabilization, which alter the balance between precursor attachment and surface growth.

The alkyl chain of the amine ligand can likewise influence morphology. When OA is maintained at a fixed concentration while the amine chain length is varied, substantial changes in morphology can occur. Under appropriate conditions, nanoplatelets can form, whereas specific combinations of ligand chain length and elevated temperature can favor nanocube formation^[52].

These observations indicate that ligand effects are not simply determined by the functional group that directly coordinates to the surface. The **entire molecular architecture**, including hydrophobic chain length and steric bulk, can influence crystal growth.

Effect of Ligand Concentration

Ligand concentration is another critical parameter in HI synthesis. Increasing ligand concentration can increase surface coverage and modify precursor complexation, nucleation kinetics, and growth rates. However, the relationship between ligand concentration and NC size is not necessarily linear.

Almeida et al. demonstrated that reducing the concentrations of OA and OAm toward the minimum level required to solubilize the PbBr₂ precursor could suppress Ostwald ripening and produce CsPbBr₃ nanocubes with relatively narrow size distributions^[54].

This observation emphasizes an important distinction between **surface stabilization and excessive ligand-mediated growth suppression**. Excess ligands can strongly alter precursor equilibria and surface dynamics, whereas insufficient ligand concentrations can result in aggregation or uncontrolled growth. The optimum concentration is therefore dependent on the precursor chemistry, solvent, reaction temperature, and desired morphology.

Effect of Ligand Type

The chemical identity of the ligand can produce significant changes in PNC morphology and surface chemistry. Conventional OA/OAm ligand pairs have been extensively employed, but alternative ligands—including branched ammonium compounds, phosphines, thiols, zwitterions, carboxylates, and other functional molecules—have been investigated.

Park et al. examined the replacement of conventional OA/OAm surface species with branched quaternary ammonium bromide ligands in CsPbBr₃ NCs. Both ligand systems could produce monodisperse nanocubes, demonstrating that different ligand chemistries can support similar overall morphologies while potentially producing different surface compositions and stability characteristics^[55].

This distinction is important because morphological similarity does not necessarily imply identical surface chemistry. Two NC populations may have comparable dimensions and crystal structures while exhibiting different defect densities, ligand-binding configurations, PLQYs, charge-transfer characteristics, or environmental stability.

Consequently, characterization of the ligand shell should accompany structural characterization whenever ligand effects are being investigated.

Ligand-Assisted Reprecipitation (LARP)

The **ligand-assisted reprecipitation (LARP)** method provides an alternative colloidal route for synthesizing MHP NCs. Unlike HI synthesis, which generally requires elevated temperatures, LARP can often be conducted under relatively mild conditions, including room temperature. This feature makes LARP attractive because it can reduce energy consumption, simplify experimental procedures, and facilitate rapid synthesis [56].

The fundamental principle of LARP is the controlled generation of **supersaturation**. Perovskite precursors are initially dissolved in a solvent in which they have relatively high solubility. The precursor solution is then introduced into a second solvent in which the precursor components or newly formed perovskite have substantially lower solubility.

The abrupt change in solvent environment generates a highly supersaturated state, promoting rapid nucleation and subsequent formation of nanoscale crystalline particles.

General Larp Mechanism

In a typical LARP synthesis, precursor salts such as MX_2 , CsX , MAX , or FAX , where X represents a halide, are dissolved in a polar solvent such as **DMF or DMSO**. This precursor solution is then rapidly introduced into a miscible nonpolar or weakly coordinating antisolvent such as toluene or hexane in the presence of surface ligands.

The miscibility of the two solvents results in a rapid reduction in precursor solubility. Consequently, the system moves from a relatively stable dissolved state toward a strongly supersaturated state. Once the critical supersaturation level is reached, nuclei form rapidly.

The ligands interact with the emerging crystal surfaces and regulate subsequent growth and aggregation. Because nucleation can occur extremely rapidly, LARP can produce small PNCs under relatively mild conditions.

The final particle size and morphology depend on the magnitude and rate of supersaturation, precursor concentration, solvent ratio, injection or mixing rate, temperature, ligand concentration, ligand type, and purification conditions.

Versatility of the Larp Method

The LARP technique was initially demonstrated for the synthesis of highly crystalline MAPbBr_3 nanoparticles. Schmidt et al. reported the production of approximately 6 nm MAPbBr_3 nanoparticles using a room-temperature reprecipitation strategy [60].

The method was subsequently extended to a wide variety of MHP compositions and morphologies, including nanocubes, nanoplatelets, nanowires, and nanorods [17,56]. This versatility arises from the fact that supersaturation and surface chemistry can be independently manipulated through solvent composition and ligand selection.

Compared with HI synthesis, LARP can offer several advantages, including: lower reaction temperatures; simpler experimental equipment; relatively rapid synthesis; reduced energy consumption; compatibility with temperature-sensitive components; and potential for facile scale-up and continuous processing.

However, LARP can also present challenges associated with rapid nucleation, batch-to-batch reproducibility, solvent sensitivity, and control of particle aggregation.

Role of Ligands in Larp Synthesis

Ligands play a particularly important role in LARP because nucleation and precipitation occur rapidly. Without adequate surface stabilization, the newly generated nuclei can readily aggregate or undergo uncontrolled growth.

Zhang et al. investigated MAPbBr₃ NC formation under different ligand conditions and demonstrated that ligand composition strongly influences particle size and colloidal stability^[61].

When amines were excluded, NC formation could still occur, demonstrating that amines are not strictly required for crystallization. However, the absence of amines reduced the ability to control particle size. This observation suggests that amines can influence the kinetics of nucleation and crystal growth. Conversely, eliminating carboxylic acids resulted in pronounced aggregation, indicating that the acid component contributes significantly to colloidal stabilization^[61].

These observations support a functional distinction in which amine-containing ligands can strongly influence **crystallization kinetics**, while carboxylate-containing species can contribute substantially to **surface stabilization and aggregation suppression**. Nevertheless, these roles are not completely independent because acid–base equilibria and ligand exchange can produce multiple surface species during synthesis.

Effect of Ligand Type and Concentration in Larp

The concentration and chemical identity of the ligand strongly influence the supersaturation-driven nucleation process. At higher ligand concentrations, newly formed nuclei may become rapidly passivated, restricting further precursor attachment and thereby producing smaller NCs.

Conversely, insufficient ligand concentrations may result in uncontrolled particle growth and aggregation. Therefore, an appropriate ligand-to-precursor ratio is necessary to balance nucleation, growth, and stabilization. The effect of ligand concentration can also depend on the type of ligand employed. Strongly coordinating ligands may exert a greater influence on precursor complexation and surface growth than weakly interacting ligands. Ionic ligands can additionally alter the surface charge and colloidal interactions between NCs.

Consequently, ligand concentration should be considered together with ligand binding strength and molecular structure rather than as an isolated parameter.

Effect of Ligand Chain Length in Larp

Ligand chain length affects NC formation by modifying steric interactions, surface packing, solvent compatibility, and the accessibility of precursor species to growing surfaces. Increasing the alkyl-chain length can increase steric hindrance around the nanocrystal and alter the kinetics of precursor attachment.

Studies have shown that increasing ligand concentration in LARP generally reduces NC dimensions. Similarly, increasing alkyl-chain length can promote smaller dimensions in at least one direction under many LARP conditions^[62]. This effect is particularly significant in the synthesis of two-dimensional PNCs. Long-chain ligands can preferentially bind to selected facets, suppressing growth along a particular crystallographic direction while allowing lateral growth to continue. This anisotropic growth mechanism can produce ultrathin nanoplatelets and nanosheets. Thus, ligand chain length provides a molecular-level means of controlling the dimensionality and degree of quantum confinement of PNCs.

Comparison of Hi and Larp Synthesis

Although HI and LARP are both colloidal approaches, they differ fundamentally in their mechanisms and practical requirements.

Parameter	Hot Injection (HI)	Ligand-Assisted Reprecipitation (LARP)
Reaction temperature	Generally high	Usually room temperature or mild
Main driving force	Rapid precursor injection and supersaturation	Solubility change and antisolvent-induced supersaturation
Typical solvents	High-boiling organic solvents	Polar solvent/antisolvent combinations
Nucleation	Rapid after precursor injection	Very rapid after reprecipitation
Equipment	Heating and inert/controlled atmosphere often useful	Relatively simple
Reaction control	Strong control through temperature and injection	Strong control through solvent and ligand parameters
Morphology	Nanocubes, NPLs, NRs, NWs	NCs, NPLs, NWs, NRs
Ligand importance	High	Very high
Energy requirement	Relatively high	Relatively low
Major challenge	High temperature, air sensitivity, purification	Rapid nucleation, reproducibility, solvent effects
Scale-up potential	Possible but technically demanding	Attractive, particularly for continuous approaches

Neither method is universally superior. The appropriate synthesis route depends on the desired NC composition, morphology, particle size, optical properties, production scale, and application.

Ligand-Dependent Synthesis: A Unifying Perspective

The preceding discussion demonstrates that ligand chemistry represents one of the most important variables connecting the synthesis conditions to the final properties of PNCs. Ligands influence the system at several stages:

Precursor stage → Nucleation → Crystal growth → Surface passivation → Purification → Film formation → Device operation

At the precursor stage, ligands can coordinate metal ions and modify precursor solubility and reactivity. During nucleation, they can alter the critical supersaturation and nucleation rate. During crystal growth, selective adsorption can regulate the growth rates of individual facets. After crystallization, ligands stabilize the NC surface and suppress aggregation.

Following synthesis, however, the ligand shell can become a double-edged factor. Long-chain ligands provide excellent colloidal stability but may impede charge transport when NCs are assembled into films. Conversely, short-chain or weakly bound ligands can improve interparticle electronic coupling but may provide insufficient surface protection.

This trade-off explains why ligand engineering has become a major research direction in PNC science.

Limitations of Conventional Colloidal Synthesis

Despite their advantages, conventional HI and LARP methods have several limitations. HI synthesis typically requires elevated temperatures, controlled reaction conditions, and precise timing of precursor injection and reaction termination. Small variations in temperature, precursor concentration, or injection rate can affect reproducibility.

LARP, although simpler and more energy-efficient, involves extremely rapid precipitation and therefore requires precise control over solvent composition, precursor concentration, mixing rate, and ligand concentration. Small variations in these parameters can produce significant changes in nucleation density and particle size.

Both approaches also require post-synthetic purification. Washing with antisolvents is often necessary to remove excess ligands, unreacted precursors, and soluble by-products. However, excessive purification can remove beneficial ligands from the NC surface, expose surface defects, induce aggregation, or reduce colloidal stability.

Therefore, synthesis and purification should be considered interconnected processes rather than independent experimental stages.

Purification and its Influence on Pnc Quality

Purification is particularly important for colloidal PNCs because excess free ligands and precursor residues can influence optical measurements, surface chemistry, and device performance. However, the removal of these species must be carefully balanced against the need to retain an adequate protective ligand shell.

Aggressive antisolvent precipitation, centrifugation, or repeated washing can cause ligand stripping and irreversible aggregation. Such changes can result in reduced PLQY and altered surface defect densities.

Consequently, optimized purification protocols are required to obtain PNCs that are simultaneously chemically clean, colloidally stable, and sufficiently passivated.

This issue is especially important when comparing literature reports because apparently different optical or structural properties may arise not only from differences in synthesis but also from differences in purification and ligand retention.

Emerging Direction: Sustainable Synthesis of PNCs

Although conventional colloidal methods have produced excellent PNCs, concerns regarding the use of high-boiling organic solvents, toxic precursors, large quantities of ligands, and energy-intensive processing have stimulated interest in more sustainable synthesis strategies.

Current research increasingly explores greener solvents, lower-temperature processes, aqueous or partially aqueous approaches, bio-derived ligands, mechanochemical routes, microwave-assisted synthesis, and solvent-minimized techniques. These approaches seek to reduce environmental impact while maintaining control over particle size, morphology, crystallinity, and optical performance.

Bio-derived and multifunctional ligands are particularly promising because a single natural molecule may simultaneously provide precursor coordination, surface passivation, colloidal stabilization, and environmental protection. Such strategies are especially relevant to the development of sustainable PNCs for photocatalytic and environmental applications.

Concluding Remarks on Pnc Synthesis

The synthesis of metal-halide perovskite nanocrystals has progressed from conventional high-temperature colloidal methods toward increasingly versatile, low-temperature, morphology-controlled, and surface-engineered approaches. Hot injection and ligand-assisted reprecipitation remain two of the most important colloidal strategies because they provide substantial control over nucleation, crystal growth, composition, particle size, and morphology.

However, the final properties of PNCs are determined not by the synthesis method alone but by the interaction between precursors, solvent, temperature, reaction kinetics, crystal structure, and ligand chemistry. In particular, ligand identity, concentration, molecular architecture, and binding behavior can alter precursor conversion, nucleation rate, facet growth, particle dimensions, surface defects, optical properties, colloidal stability, and subsequent charge transport.

A central challenge is therefore to design ligand systems that simultaneously provide adequate surface passivation and colloidal stability without creating excessive barriers to charge transport. This challenge becomes even more important when PNCs are transferred from solution into solid-state films.

The synthesis literature consequently establishes an important foundation for understanding the subsequent **influence of ligands on PNC growth, purification, surface chemistry, optical properties, stability, and device performance**. A systematic investigation of these relationships is essential for developing PNCs with controlled physicochemical properties and improved practical functionality.

Morphological Properties of Mapbbr₃ Nanoplatelets

The morphology of metal-halide perovskite nanocrystals is strongly governed by the interplay between precursor chemistry, solvent environment, reaction kinetics, and ligand–surface interactions. In particular, ligand concentration and molecular structure are critical parameters for controlling the thickness, lateral dimensions, and dimensionality of perovskite nanoplatelets (NPLs). This effect is particularly evident in MAPbBr₃ NPLs synthesized using the ligand-assisted reprecipitation (LARP) method.

Cho et al. (2018) systematically investigated the influence of alkylamine concentration and chain length on the morphology of MAPbBr₃ NPLs. Their results demonstrated that both parameters exerted a pronounced influence on NPL thickness. Increasing either the alkylamine concentration or alkyl-chain length promoted the formation of thinner NPLs ^[62].

The observed behavior can be explained in terms of selective ligand adsorption and steric stabilization. Long-chain alkylamines possess a hydrophilic functional group capable of interacting with the perovskite surface and a hydrophobic alkyl segment that provides substantial steric protection. When the concentration of such ligands is increased, surface coverage becomes more extensive. Preferential adsorption on particular crystallographic surfaces can inhibit attachment of additional precursor species to those surfaces.

In the case of NPLs, suppression of crystal growth in the vertical direction while allowing relatively unrestricted lateral growth results in structures with large lateral dimensions and extremely small thicknesses. The resulting anisotropic morphology can produce strong quantum and dielectric confinement, leading to optical properties that differ substantially from those of three-dimensional perovskite NCs.

The relationship between ligand concentration and NPL thickness therefore provides an important example of how molecular-scale surface interactions can be translated into nanoscale morphological control. Rather than functioning solely as stabilizing agents, ligands act as **growth-directing molecules** that determine which crystallographic directions remain accessible during crystal formation.

Effect of Ligand Concentration on Crystal Structure and Composition

In addition to influencing particle size and morphology, ligand concentration can determine the crystal phase and chemical composition of the resulting PNCs. This effect is particularly important in LARP synthesis

because the high degree of supersaturation generated during reprecipitation can produce multiple competing crystalline phases.

Chen et al. (2019) demonstrated that increasing the amount of OA and OAm in the precursor solution could induce a substantial change in the products obtained from the synthesis of CsPbX_3 . Under relatively low ligand concentrations, a three-dimensional perovskite phase could be formed, whereas increasing ligand content favored the formation of a lower-dimensional Cs_4PbX_6 phase [63].

The transition can be understood in terms of ligand-mediated steric and coordination effects. At elevated ligand concentrations, the organic molecules surrounding the inorganic precursor species can hinder close approach and assembly of PbX_6^{4-} octahedral units. This restriction can prevent the formation of the extended corner-sharing three-dimensional perovskite framework and instead favor structures in which the inorganic octahedra have reduced connectivity. This phenomenon demonstrates that ligand concentration can function as a phase-selection parameter rather than merely a particle-size control variable.

The effect is particularly significant because different perovskite phases can possess markedly different optical and electronic properties. Consequently, small variations in ligand concentration during synthesis may result in substantial changes in absorption, photoluminescence, carrier transport, and stability.

Differential Role of Oleylamine and Oleic Acid in Phase Control

Although OA and OAm are frequently used together, they do not necessarily exert identical effects on perovskite crystallization. Experimental studies indicate that OAm can have a particularly strong influence on phase evolution in some Cs–Pb–halide systems [64].

The stronger influence of OAm has been associated with the coordination ability of the nitrogen-containing head group. The lone pair of electrons on the amine nitrogen can interact with ionic species present in the precursor solution and at the developing crystal surface. Such interactions can modify the spatial distribution of the inorganic components and influence the connectivity of PbX_6^{4-} octahedra. Increased OAm concentration may therefore promote stronger separation or stabilization of specific inorganic units, favoring the formation of lower-dimensional structures under appropriate reaction conditions.

However, the behavior of OA and OAm should not be interpreted as completely independent. Acid–base reactions between OA and OAm can generate ammonium carboxylate species, while dynamic ligand exchange and ion pairing can occur during nucleation and growth. The effective surface chemistry is therefore determined by the overall equilibrium among free ligands, ionic species, ligand-derived salts, solvent molecules, and the NC surface. This dynamic behavior is one reason why ligand concentration and ligand ratio must be carefully controlled when attempting to reproduce PNC syntheses.

Modifications to the Larp Technique

Although conventional LARP provides a simple and versatile route for producing PNCs, several modifications have been introduced to improve control over nucleation, morphology, surface passivation, optical properties, and colloidal stability.

One important modification involves introducing **auxiliary ligands** into the reaction mixture. Rather than relying exclusively on conventional OA and alkylamine ligands, auxiliary molecules can be incorporated to modify precursor coordination and surface chemistry.

For example, benzoyl alcohol has been employed alongside OA and octylamine in modified LARP systems. The additional ligand can participate in precursor coordination and influence the kinetics of crystal formation, while also contributing to improved surface passivation. Such modifications have been associated with enhanced PLQY of the resulting NCs [65].

The use of auxiliary ligands illustrates an important principle in PNC synthesis: ligand systems can be designed to perform different functions simultaneously. One ligand may primarily regulate precursor

reactivity, another may control crystal growth, while another provides surface passivation and colloidal stability.

Peptide and Bifunctional Ligands

The search for alternative ligand systems has led to the investigation of molecules containing multiple functional groups capable of interacting with PNC surfaces. Such ligands can provide stronger and more versatile surface interactions than conventional monodentate ligands.

For example, **12-aminododecanoic acid**, which contains both amino and carboxylic-acid functional groups, has been employed as a capping ligand in the synthesis of MAPbBr₃ NCs [66].

The presence of two chemically distinct functional groups within a single molecule provides the possibility of simultaneous interactions with different surface species. The amino group can interact strongly with the inorganic framework, while the carboxyl-containing end can contribute to surface coordination and colloidal stabilization. Such bifunctional molecules may reduce the complexity associated with using mixtures of independent ligands because both growth regulation and surface stabilization can potentially be achieved using a single molecular species. The concept also provides a foundation for developing multifunctional and bio-inspired ligands for PNC synthesis.

Adamantylammonium Bromide as a Surface-Passivating Ligand

Ammonium-based ligands have received considerable attention because of their strong interactions with halide-perovskite surfaces. One notable example is **2-adamantylammonium bromide (ADBr)**, which has been employed as a single capping ligand for MAPbBr₃ NC synthesis using LARP.

The reported use of ADBr resulted in exceptionally high PLQY, reaching approximately 100% under the reported experimental conditions [67]. Such high PLQY indicates that non-radiative recombination pathways associated with surface defects can be strongly suppressed.

The effectiveness of ADBr can be associated with its molecular architecture. The ammonium group provides strong ionic interaction with the perovskite surface, while the rigid adamantyl group provides substantial steric protection. This combination can result in effective surface coverage and reduced accessibility of defect sites to environmental species. The example demonstrates that ligand structure can be deliberately engineered to achieve both strong surface binding and steric stabilization.

Nevertheless, extremely strong ligand binding may also create challenges during subsequent ligand exchange or charge transport. Therefore, maximizing PLQY alone does not necessarily identify the optimal ligand for device applications. The ideal ligand must provide an appropriate balance among surface passivation, colloidal stability, processability, and electronic coupling.

Branched Ligands for Morphological Control

Branched ligands represent another important class of surface-active molecules investigated for PNC synthesis. Unlike conventional linear ligands, branched molecules contain multiple alkyl or functional branches around their coordinating groups. This architecture can provide greater steric bulk and different surface-packing behavior.

Luo et al. investigated the use of branched ligands, including (3-aminopropyl)triethoxysilane (APTES) and amino-functionalized polyhedral oligomeric silsesquioxane (POSS) derivatives, for the synthesis of MAPbX₃ NCs [68]. The use of these branched ligands resulted in smaller and more uniform NCs compared with systems employing conventional linear ligands. The improved uniformity was attributed to the greater steric influence and surface interactions of the branched molecules.

Branched ligands can occupy a larger effective volume near the NC surface, thereby limiting the ability of precursor species to approach and attach to growing crystal surfaces. This effect can suppress excessive growth and improve size uniformity.

Aptes-Dependent Size Control

The amount of APTES used during LARP synthesis has been shown to influence the size of MAPbX₃ nanocubes [68]. Increasing the APTES concentration resulted in smaller nanocubes.

This behavior can be interpreted through a steric-growth mechanism. As the concentration of APTES increases, greater surface coverage and steric hindrance can develop around the growing NCs. This reduces the frequency with which reactive monomers or precursor species reach the crystal surface. Reduced monomer transport consequently decreases the growth rate and limits the final crystal dimensions.

The phenomenon illustrates how ligand concentration can influence not only nucleation but also the mass-transfer stage of crystal growth. Thus, ligand-mediated size control can involve both chemical interactions at the surface and physical limitations on precursor diffusion.

Emulsion Ligand-Assisted Reprecipitation

An important modification of conventional LARP is **emulsion ligand-assisted reprecipitation (emulsion-LARP)**. Conventional LARP generally relies on two miscible solvents, whereas emulsion-LARP uses precursor solutions distributed between two immiscible phases [69–71].

In a typical emulsion-LARP process, the precursor components and ligands are separately dissolved or dispersed in two immiscible solvents. When the two phases are mixed, an emulsion containing numerous microscopic droplets is generated.

These droplets provide localized reaction environments in which the precursor components can interact. The subsequent addition of a de-emulsifying solvent disrupts the emulsion and changes the solubility conditions. The resulting increase in supersaturation triggers rapid nucleation and crystallization of the PNCs [70]. This approach provides an additional level of control because the interfaces between the immiscible phases can influence mass transfer and precursor mixing.

Synthesis of Mapbbr₃ Using Emulsion-Larp

Huang et al. demonstrated the application of emulsion-LARP to MAPbBr₃ NC synthesis [69]. In their approach, an aqueous or polar phase containing MABr and PbBr₂ dissolved in DMF was combined with an oil phase containing OA and n-octylamine in hexane. The resulting mixture formed an emulsion containing the precursor and ligand components. Addition of an appropriate de-emulsifying solvent disrupted the emulsion and rapidly changed the solubility environment, initiating recrystallization and PNC formation. Acetone and tert-butanol have been employed as de-emulsifying or antisolvent components capable of initiating the precipitation process [70,71].

The method has subsequently been applied to different perovskite compositions, including CsPbX₃, MAPbX₃, and FAPbBr₃, and has produced different morphologies, including spherical quantum dots, nanocubes, nanoplatelets, and nanowires [72–74].

Advantages of Emulsion-Larp

The major advantage of emulsion-LARP is that it does not require the precursor-containing solvents to be mutually miscible. This distinguishes it from conventional LARP and creates additional opportunities for controlling the local reaction environment. The use of immiscible phases can influence: precursor transport; nucleation rate; interfacial reactions; local concentration; ligand distribution; crystal growth; and particle aggregation. The droplet environment can effectively act as a confined reaction domain, potentially limiting uncontrolled crystal growth.

However, emulsion-LARP also introduces additional variables, including droplet size, phase ratio, emulsification energy, interfacial tension, de-emulsifier concentration, and mixing conditions. Consequently, reproducible synthesis requires careful optimization of these parameters.

Polar-Solvent-Controlled Ionization

Another variation of solution-based PNC synthesis involves **polar-solvent-controlled ionization**. This approach differs from conventional LARP because the precursor species are initially maintained in a relatively nonpolar medium rather than being completely dissolved in a strongly polar solvent. In this strategy, precursors such as metal oleates and alkylammonium halides are dispersed in a nonpolar solvent such as hexane. A polar solvent is subsequently introduced, inducing ionization or dissociation of the precursor species. The newly generated ionic species then undergo rapid interaction and crystallization, resulting in PNC formation^[74].

An important advantage of this approach is the reduced quantity of polar solvent required compared with conventional LARP. Minimizing the amount of strongly coordinating polar solvent can be beneficial because polar solvents may interact strongly with the perovskite lattice and can sometimes compromise NC stability.

CsPbX₃ NCs synthesized using this strategy have demonstrated PLQYs exceeding 80% and composition-dependent emission spanning a substantial portion of the visible spectrum^[74]. This approach therefore represents an interesting compromise between conventional nonpolar colloidal synthesis and polar-solvent-driven reprecipitation.

Other Colloidal Synthetic Approaches

Beyond HI and LARP, several additional colloidal approaches have been developed to simplify PNC production and improve scalability. These include heat-up synthesis, ultrasonication-assisted synthesis, microwave-assisted synthesis, and other rapid energy-assisted methods.

Such approaches generally seek to avoid the requirement for instantaneous precursor injection while maintaining sufficient control over nucleation and crystal growth.

In the **heat-up method**, all or most of the precursor components, ligands, and solvent are initially combined and subsequently heated under controlled conditions. Unlike HI synthesis, there is no requirement for rapid injection of one precursor into a preheated reaction mixture.

As the temperature increases, precursor conversion gradually occurs, followed by nucleation and crystal growth. The resulting particles can be stabilized by carboxylic-acid and alkylamine ligands.

Heat-up synthesis offers several practical advantages. It can simplify experimental operation, reduce sensitivity to injection timing, and facilitate scale-up. Some studies have demonstrated gram-scale synthesis under atmospheric conditions while maintaining high PLQYs^[75,76]. The gradual heating process, however, changes the kinetics of nucleation compared with HI synthesis. Since precursor conversion occurs progressively during heating, nucleation may take place over a longer period. Consequently, the resulting particle-size distribution can be strongly dependent on heating rate, precursor reactivity, ligand concentration, and reaction temperature. Optimization of the heating profile is therefore essential for achieving reproducible particle dimensions.

Ultrasonication-Assisted Synthesis

Ultrasonication provides another means of accelerating precursor mixing and promoting nucleation. Acoustic cavitation generated during sonication can produce localized regions of high temperature and pressure and can enhance mixing between precursor components. In PNC synthesis, ultrasonication may accelerate the formation of supersaturation and reduce the time required for nucleation. It can also improve precursor dispersion and promote more homogeneous reaction conditions.

However, the effect of sonication depends strongly on acoustic power, frequency, duration, solvent properties, and reaction volume. Excessive sonication may also produce undesirable heating or mechanical effects. Therefore, ultrasonication should be regarded as a kinetic-control tool rather than simply an alternative energy source.

Microwave-Assisted Synthesis

Microwave-assisted synthesis has attracted attention because microwave irradiation can provide rapid and volumetric heating of reaction mixtures. Compared with conventional heating, microwave irradiation can significantly reduce reaction times and potentially improve the uniformity of thermal energy distribution.

In PNC synthesis, microwave irradiation can influence nucleation and crystal growth by rapidly increasing the reaction temperature. The resulting control over heating rate and reaction duration can be used to tune particle size and morphology.

Microwave-assisted routes are also attractive for rapid and potentially scalable synthesis. Nevertheless, the interaction between microwave radiation, solvent properties, precursor composition, and reaction vessel geometry must be considered when comparing microwave synthesis with conventional thermal methods.

Comparative Assessment of Modified Colloidal Methods

The development of modified colloidal techniques demonstrates that PNC synthesis is moving from simple particle formation toward increasingly precise control over surface chemistry and crystal growth.

Synthetic approach	Primary control mechanism	Major advantage	Major limitation
Hot injection	Rapid precursor injection	Excellent control of nucleation and size	High temperature and timing sensitivity
LARP	Antisolvent-induced supersaturation	Mild conditions and simple operation	Rapid nucleation and reproducibility challenges
Emulsion-LARP	Interfacial supersaturation	Immiscible solvents and confined reaction environments	More complex processing
Polar-solvent-controlled ionization	Controlled precursor dissociation	Reduced polar-solvent requirement	Sensitive to solvent and precursor interactions
Heat-up	Gradual thermal precursor conversion	Simple operation and scale-up potential	Less distinct nucleation/growth separation
Ultrasonication-assisted	Acoustic mixing/cavitation	Rapid reaction and improved mixing	Sonation parameters strongly affect reproducibility
Microwave-assisted	Rapid volumetric heating	Short reaction time	Requires careful control of microwave conditions

Critical Role of Ligands Across Synthesis Methods

Comparison of these synthesis approaches reveals that ligand chemistry represents a common controlling factor across apparently different synthetic strategies. Regardless of whether supersaturation is generated through precursor injection, solvent exchange, emulsion disruption, thermal activation, or controlled ionization, ligands interact with the resulting crystal surfaces and influence the subsequent growth pathway.

Ligands can affect PNC synthesis through at least five interconnected mechanisms:

(i) Precursor complexation

Ligands can coordinate metal ions and modify precursor solubility, reactivity, and availability. This changes the concentration of reactive monomers participating in nucleation and growth.

(ii) Nucleation regulation

Ligands can alter the critical supersaturation required for nucleation. Strong precursor–ligand interactions can delay precursor conversion, whereas weaker interactions can facilitate rapid formation of reactive species.

(iii) Facet-selective adsorption

Ligands may preferentially bind to specific crystallographic surfaces. Such selective adsorption can suppress growth along one direction while allowing growth along another, producing anisotropic structures.

(iv) Surface passivation

Ligands can coordinate under-coordinated surface atoms and compensate for surface defects. Effective passivation reduces non-radiative recombination and can increase PLQY.

(v) Colloidal stabilization

The organic portion of the ligand shell generates steric and/or electrostatic repulsion between NCs, reducing aggregation and maintaining colloidal dispersibility.

These functions are interconnected. A ligand that strongly passivates the surface may simultaneously suppress precursor attachment and slow crystal growth. Similarly, a ligand that produces excellent colloidal stability may create an insulating barrier between NCs when the particles are assembled into films.

Synthesis–Ligand–Property Relationship

The collective findings from HI, LARP, emulsion-LARP, polar-solvent-controlled ionization, and heat-up synthesis demonstrate a fundamental structure–property relationship:

Synthesis conditions → Ligand–precursor interactions → Nucleation kinetics → Crystal growth → Surface chemistry → Morphology → Optical/electronic properties → Stability

This relationship is particularly important for the rational design of novel PNCs. Modification of only one parameter can influence several stages of the synthesis simultaneously. For example, increasing alkylamine concentration may change precursor complexation, increase surface coverage, reduce crystal growth, modify morphology, alter the surface defect density, and consequently change PLQY.

Therefore, ligand engineering should not be treated as an isolated aspect of PNC synthesis. It is a central strategy for controlling the complete physicochemical behavior of the nanocrystal.

Implications for Green and Bio-Ligand-Assisted Synthesis

The understanding gained from conventional ligands provides a useful framework for developing sustainable ligand systems. Natural molecules containing functional groups such as hydroxyl, carboxyl, amino, carbonyl, phosphate, and other donor groups can potentially interact with perovskite precursor species and crystal surfaces.

Bio-derived ligands may provide multiple functions within a single molecular framework, including precursor coordination, nucleation regulation, surface passivation, steric stabilization, and environmental protection. Such multifunctionality could reduce the requirement for multiple synthetic additives.

However, the application of bio-ligands requires careful characterization because natural extracts can contain numerous chemically active constituents whose concentrations may vary between batches. For reproducible PNC synthesis, the relationship between functional-group composition, ligand concentration, binding behavior, and resulting NC properties must therefore be established systematically.

This consideration is particularly important for developing green PNC synthesis protocols intended for photocatalytic, sensing, environmental, and optoelectronic applications.

Concluding Remarks

The development of modified colloidal synthesis techniques has substantially expanded the ability to control the size, morphology, crystal phase, composition, and surface properties of metal-halide perovskite nanocrystals. In MAPbBr₃ and CsPbX₃ systems, ligand concentration, chain length, molecular architecture, and chemical functionality can strongly influence crystal growth and phase selection.

Longer and more concentrated alkylamines can promote thinner nanoplatelets by increasing surface passivation and suppressing growth along selected crystallographic directions. Increased concentrations of OA and OAm can also alter phase stability and, under appropriate conditions, favor lower-dimensional perovskite-related phases. Bifunctional, branched, ammonium-based, and auxiliary ligands provide additional mechanisms for controlling nucleation, morphology, surface defects, and optical performance.

Modifications such as emulsion-LARP and polar-solvent-controlled ionization further demonstrate that the nucleation environment can be engineered by manipulating solvent compatibility and precursor ionization. Heat-up, ultrasonication-assisted, and microwave-assisted routes provide additional opportunities for simplifying synthesis, reducing reaction times, and improving scalability.

Despite these advances, an important challenge remains in balancing **surface passivation, colloidal stability, crystal-growth control, and electronic transport**. Strongly bound and bulky ligands may improve stability and PLQY but can hinder charge transfer between neighboring NCs. Conversely, insufficient surface coverage can result in defect formation, aggregation, and degradation.

Future research should therefore focus on multifunctional ligands capable of providing strong but controllable surface interactions while maintaining efficient charge transport. Particular attention should be given to sustainable and bio-derived ligands whose molecular structures can be rationally correlated with precursor chemistry, crystal growth, surface defect passivation, and long-term stability. Such developments are essential for translating laboratory-scale PNC synthesis into reproducible, scalable, and environmentally responsible technologies.

Solvothermal Method

The solvothermal method represents an important alternative route for the synthesis of metal halide perovskite nanocrystals (MHP NCs), particularly where controlled thermal treatment, precursor concentration, and reaction time are required to regulate crystal nucleation and growth. In contrast to conventional hot-injection synthesis, the solvothermal approach generally involves placing the precursor mixture and ligands in a sealed autoclave, where the reaction proceeds under elevated temperature and autogenous pressure. The closed

reaction environment can promote efficient precursor conversion while limiting solvent evaporation and providing relatively uniform thermal conditions throughout the reaction system.

Chen et al. (2020) demonstrated the solvothermal synthesis of CsPbX_3 NCs using caesium carbonate or caesium acetate and PbX_2 salts in the presence of suitable surface ligands. The reaction was conducted in an autoclave under controlled heating conditions ^[76]. Interestingly, the morphology of the resulting NCs was strongly dependent on the initial state of the precursors.

When the precursors were introduced directly into the autoclave without prior dissolution, the products predominantly exhibited nanocubic morphology. In contrast, predissolving the precursors before the solvothermal reaction increased the concentration and availability of ionic precursor species. The resulting increase in the concentration of reactive species promoted the formation of a larger number of nuclei during heating and ultimately favored the formation of CsPbX_3 nanowires (NWs) ^[76].

This observation demonstrates that precursor dissolution is not merely a preparative step but can fundamentally alter the nucleation pathway. A higher concentration of dissolved precursor species increases the degree of supersaturation achieved during heating, thereby influencing the nucleation rate and the competition between nucleation and subsequent crystal growth.

Reaction duration also plays an important role in determining the final morphology. Extended solvothermal treatment has been reported to favor nanowire formation even when the precursors were not predissolved^[77]. This behavior suggests that prolonged exposure to the reaction conditions allows initially formed nuclei to undergo anisotropic growth, ripening, and structural rearrangement.

The solvothermal method therefore provides several variables for controlling PNC morphology, including precursor concentration, dissolution state, temperature, reaction duration, solvent composition, ligand concentration, and autogenous pressure. However, the sealed nature of the reaction can make real-time observation and kinetic control more difficult than in open or injection-based systems.

From a scalability perspective, solvothermal synthesis is attractive because the procedure can accommodate relatively large reaction volumes. Nevertheless, reproducibility requires careful control of autoclave filling ratio, heating rate, precursor concentration, ligand composition, and cooling conditions. These parameters can significantly affect nucleation and crystal growth and should therefore be reported explicitly in reproducible research.

Ultrasonication-Assisted Synthesis

Ultrasonication-assisted synthesis is another energy-assisted approach that has been developed for the rapid production of metal halide perovskite nanocrystals. Unlike conventional thermal synthesis, this method employs acoustic energy to facilitate precursor mixing, nucleation, and crystal growth.

Tong et al. (2019) demonstrated a single-step ultrasonication-assisted method for producing CsPbX_3 NCs with different halide compositions and morphologies^[75]. In this approach, ultrasonic energy was applied directly to the reaction mixture, allowing rapid interaction among the precursor species and promoting the formation of PNCs.

An important feature of the method is the possibility of controlling morphology through reaction time. CsPbBr_3 nanocubes formed during the initial stages of the reaction could progressively transform into nanowire-like structures when the reaction was prolonged ^[75]. This observation indicates that ultrasonication does not simply accelerate crystal formation but can influence the subsequent growth and restructuring processes.

The precursor ratio is another important parameter. Modification of the $\text{CsCO}:\text{PbX}$ ratio was found to influence the size, morphology, and fluorescence characteristics of the resulting CsPbX_3 NCs ^[75]. Changes in precursor stoichiometry alter the relative availability of cationic and anionic species and consequently modify the chemical environment during nucleation and growth.

Ultrasonication can also affect the dispersion of ligands and precursor molecules. The mechanical and acoustic effects generated during sonication can improve mixing and facilitate more uniform interaction between the ligands and newly formed crystal surfaces. Consequently, ligand concentration remains an important variable even when acoustic energy rather than conventional heating is used.

The method has also been applied to MAPbBr_3 systems, where increasing OAm concentration produced changes in NC morphology^[79]. This result reinforces the broader observation that ligand-mediated surface interactions remain important across different synthesis strategies.

Mechanistic Considerations

The effectiveness of ultrasonication can be associated with acoustic cavitation. During sonication, microscopic bubbles can form, grow, and collapse within the liquid medium. Bubble collapse can generate localized regions of intense energy, promoting rapid mixing and enhancing mass transfer. For PNC synthesis, improved mass transfer can accelerate the interaction between precursor species and reduce concentration gradients within the reaction mixture. This can promote more homogeneous nucleation and potentially improve particle uniformity.

However, the effect of ultrasonication is highly dependent on experimental conditions. Parameters such as ultrasonic frequency, acoustic power, sonication duration, probe position, solvent properties, precursor concentration, and reaction temperature can all influence the resulting NCs. Excessive sonication may also promote unwanted heating or structural degradation. Consequently, ultrasonication-assisted synthesis should be optimized rather than regarded simply as a faster version of conventional synthesis.

Microwave Irradiation Method

Microwave-assisted synthesis has emerged as a rapid approach for preparing metal halide perovskite nanocrystals with tunable size and morphology. The method relies on microwave irradiation to rapidly heat the reaction mixture, potentially reducing reaction times compared with conventional conductive heating.

Several researchers have adapted microwave irradiation for the synthesis of CsPbX_3 NCs with different morphologies^[80]. A major advantage of the method is the ability to manipulate particle properties by varying microwave irradiation time and power.

Long et al. (2020) demonstrated that increasing microwave irradiation time initially transformed irregular CsPbI_3 nanocubes into larger and more regular nanocubes^[80]. Continued irradiation resulted in progressive particle growth until excessive irradiation eventually caused destruction or degradation of the CsPbI_3 NCs.

This observation illustrates the importance of defining an optimum irradiation window. Insufficient irradiation may result in incomplete precursor conversion or poorly developed crystals, whereas excessive energy input may destabilize the perovskite lattice. Microwave power also influenced the PLQY of the resulting NCs^[80]. The dependence of optical properties on microwave power can be associated with changes in nucleation rate, crystal quality, defect concentration, and surface chemistry.

ROLE OF LIGANDS IN MICROWAVE-ASSISTED SYNTHESIS

Ligands remain important even under microwave-assisted conditions. In particular, changing the concentration of OAm has been shown to modify the morphology of CsPbX_3 NCs^[80].

This observation confirms that microwave irradiation and ligand chemistry operate cooperatively. Microwave energy determines the thermal and kinetic environment, whereas ligands influence precursor coordination, surface adsorption, crystal growth, and stabilization.

Therefore, morphology cannot be attributed exclusively to irradiation conditions. A given microwave power may produce different NC structures depending on the ligand concentration, ligand type, precursor ratio, and solvent environment.

An optimized microwave synthesis should consequently consider both **energy input and surface chemistry**. This is particularly relevant when the resulting NCs are intended for applications where particle size, surface defect density, and PLQY are critical.

Indirect Two-Step Synthesis from Nanocrystal Seeds

In addition to direct colloidal synthesis, indirect two-step strategies have been developed in which preformed nanocrystals serve as seeds for the subsequent growth of metal halide perovskite NCs ^[81,82].

In seed-mediated synthesis, a parent NC is first prepared under controlled conditions. The resulting seeds are then introduced into a second reaction containing additional precursor species capable of forming the desired perovskite phase.

For example, pre-synthesized CsX NCs have been employed as seeds for the formation of CsPbBr₃ by reaction with Pb-oleate^[81]. Similarly, PbI₂ NCs have been reacted with methylammonium iodide or alkylammonium species to generate two- and three-dimensional lead-halide perovskite structures ^[82].

The principal advantage of seed-mediated synthesis is that the dimensions and morphology of the parent NCs can be established before the perovskite-forming reaction. Consequently, the size of the final PNCs can be influenced by controlling the seed dimensions and the subsequent growth conditions.

This strategy can also facilitate the formation of complex morphologies that may be difficult to obtain through direct nucleation ^[81]. Because nucleation and growth are partially separated into different stages, the researcher gains additional control over the final crystal architecture.

The approach is therefore particularly attractive for rational morphology engineering. However, the surface chemistry of the seed particles must be carefully controlled because seed-bound ligands may influence precursor attachment, interfacial reactions, and the final structure.

Template-Assisted Synthesis

Template-assisted synthesis represents a fundamentally different strategy for controlling PNC morphology. Instead of relying primarily on ligand-mediated growth control, a nanoscale porous matrix is used as a physical host within which the perovskite material forms ^[83].

The porous matrix contains nanosized open cavities that can accommodate the perovskite material. Infiltration of precursor species into these pores restricts crystal growth according to the dimensions and geometry of the template.

This approach can therefore provide strong spatial confinement and potentially generate nanostructures with controlled dimensions. The pore size, connectivity, surface chemistry, and interaction between the precursor and template can all affect the resulting PNC structure.

Although template-assisted methods provide valuable morphological control, they are less directly relevant to ligand-focused investigations because the template itself performs much of the growth-regulating function. Consequently, colloidal approaches remain particularly important when the objective is to understand how molecular ligands control PNC growth, surface chemistry, purification, and optoelectronic properties.

Purification and Surface Chemistry of Perovskite Nanocrystals

Post-synthetic purification is an essential stage in colloidal PNC synthesis. Immediately after synthesis, the reaction mixture generally contains the desired NCs together with excess ligands, unreacted precursors, precursor-derived species, solvent molecules, and reaction by-products. Removal of these components is necessary before the NCs can be reliably characterized or incorporated into devices ^[84].

A conventional purification procedure involves precipitation of the NCs using an appropriate polar/nonpolar solvent combination, followed by centrifugation, removal of the supernatant, and redispersion of the purified NCs in a suitable nonpolar solvent ^[25,81].

However, purification of MHP NCs is considerably more delicate than purification of many conventional colloidal semiconductor NCs. Perovskite lattices are relatively soft and can be chemically sensitive to polar solvents. Repeated washing can therefore extract surface ligands, disrupt surface stoichiometry, dissolve part of the NCs, or induce aggregation ^[72,85].

The loss of surface ligands is particularly important because the ligand shell is directly involved in colloidal stabilization and surface-defect passivation. Excessive ligand removal may expose under-coordinated surface sites, increasing non-radiative recombination and reducing PLQY.

Therefore, purification should be considered not simply a process for removing impurities but as a **surface-chemistry engineering step**.

Effect of Purification on Nanocrystal Properties

The number and intensity of purification cycles can have a substantial effect on the final properties of PNCs. Repeated precipitation and washing may progressively alter the surface composition.

Loss of ligands can result in:

- reduced colloidal stability;
- increased NC aggregation;
- increased surface-defect density;
- reduced PLQY;
- changes in optical absorption and emission;
- reduced resistance to environmental degradation; and
- altered interparticle charge transport.

These effects demonstrate that the properties measured after purification may not necessarily be identical to those of the as-synthesized material.

A rigorous thesis or publication should therefore report the purification procedure in sufficient detail, including solvent identity, solvent ratio, centrifugation conditions, and number of washing cycles, redispersion solvent, and ligand concentration where applicable.

Surface-Ligand Interactions

Understanding the surface chemistry of PNCs is essential for explaining their remarkable optical properties and their sensitivity to purification. Several analytical techniques have been employed to investigate NC–ligand interactions, including Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS) ^[84].

FTIR spectroscopy can provide information regarding functional-group interactions and changes in chemical bonding. NMR spectroscopy provides complementary information about ligand mobility, chemical environment, and dynamic exchange processes. XPS provides information about the elemental composition and chemical states of surface-associated species.

Among these methods, ^1H NMR combined with nuclear Overhauser effect spectroscopy (NOESY) and diffusion-ordered spectroscopy (DOSY) is particularly valuable for studying dynamic ligand interactions^[84]. These methods can distinguish between free and surface-associated ligand populations and can provide insight into ligand mobility.

Such measurements are particularly important for MHP NCs because their surface ligands are not necessarily permanently attached. Instead, many ligand species participate in dynamic equilibria between free, weakly bound, and more strongly associated states.

Dynamic Surface Ligation in CsPbBr_3 Nanocrystals

Most detailed investigations of PNC surface chemistry have focused on CsPbX_3 systems, particularly CsPbBr_3 ^[84].

The surface of these NCs is generally stabilized through dynamic interactions between ionic ligand species and oppositely charged surface ions. Surface ligation may therefore involve a combination of alkyl carboxylates, halide-containing species, Cs^+ , alkylammonium ions, and neutral amines.

The precise ligand composition depends not only on the synthesis conditions but also on the purification procedure and solvent environment^[86]. This means that two samples synthesized using nominally identical conditions can possess different surface chemistries if they undergo different purification treatments. This dynamic behavior is a defining characteristic of MHP NCs and must be considered when interpreting changes in their optical or electronic properties.

Surface Ligation by Oleylammonium Bromide

De Roo et al. (2016) provided important insight into the surface chemistry of CsPbBr_3 NCs synthesized using the hot-injection method^[84]. During synthesis, reactions involving OA, OAm, PbX_2 , and related precursors generate species such as Pb-oleate and oleylammonium bromide (OAmH-Br), which can participate in surface stabilization.

Following purification with acetone and redispersion in hexane, the surface of CsPbBr_3 was found to be strongly associated with oleylammonium bromide.

OAmH-Br can function as an X-type ligand and interact with surface ionic species^[84]. DOSY measurements indicated that a substantial fraction of OAmH-Br was surface-associated, with approximately 65% reported as bound under the investigated conditions. The corresponding ligand density was estimated at approximately 2.9 nm^{-2} ^[84]. These observations demonstrate that the ligand shell of PNCs can contain reaction-derived species rather than simply the ligands initially added to the reaction mixture. This distinction is important when assigning surface chemistry. The ligand present in the synthesis flask may undergo protonation, deprotonation, ion exchange, or reaction with precursor-derived species before becoming associated with the final NC surface.

Acid–Base Equilibria and Ligand Exchange

The interaction of OAm with CsPbBr_3 provides an important example of the dynamic nature of PNC surface chemistry.

First, OAm can undergo an acid–base reaction with HBr, producing oleylammonium bromide. This species can associate with the NC surface as an X-type ligand^[84].

Second, acid–base reactions involving OA and OAm can generate oleylammonium oleate. In this situation, the oleate and oleylammonium ions can function as an ionic ligand pair associated with the NC surface.

Third, neutral OAm can coordinate directly with surface cationic sites through its nitrogen lone pair and therefore behave as an L-type ligand^[84].

These equilibria can be represented conceptually as:



The actual surface composition is consequently determined by the equilibrium among these species rather than by a single permanent ligand structure.

Ligand exchange may occur as one surface-associated species is replaced by another. Such exchange processes can be affected by ligand concentration, solvent polarity, temperature, acid–base conditions, and purification.

Labile Nature of Alkylammonium Ligands

Pan et al. (2018) further demonstrated the dynamic nature of alkylammonium and carboxylate ligands on CsPbBr₃ NCs using ¹H NMR and FTIR spectroscopy [84].

Both alkylammonium and carboxylate species were detected at the NC surface in nonpolar solvents such as toluene and hexane. However, alkylammonium species were found to be more susceptible to detachment during purification with polar solvents [84]. This finding provides an important explanation for why purification can significantly alter PNC properties. If a particular ligand population is selectively removed during washing, the surface composition changes even though the inorganic core may initially remain structurally intact. Selective ligand loss can alter surface charge balance, defect passivation, aggregation behavior, and optical properties.

The stability of a colloidal PNC dispersion should therefore be understood as a balance between the inorganic lattice and a dynamic organic/inorganic surface layer.

Surface Chemistry as a Determinant of Pnc Performance

The preceding findings establish that PNC surface chemistry is intimately connected to synthesis, purification, morphology, optical properties, and stability. The surface should therefore not be regarded as a passive boundary between the crystal and its environment. Instead, the surface represents an active chemical region where precursor-derived ions, ligands, solvent molecules, defects, and environmental species interact.

The surface ligand shell can influence: crystal growth; NC size and morphology; surface defect density; charge-carrier recombination; PLQY; colloidal stability; resistance to moisture and oxygen; solubility and processability; interparticle charge transport; and compatibility with device-processing conditions.

Consequently, rational ligand engineering provides a route for simultaneously optimizing several PNC properties.

Relationship Between Synthesis, Purification, and Surface Chemistry

The synthesis and purification stages should not be considered independent processes. The chemical environment created during synthesis determines the initial surface composition, while purification modifies that composition through selective ligand removal, ligand exchange, and solvent-dependent surface interactions. A useful conceptual relationship can therefore be expressed as: Precursor chemistry → Nucleation → Crystal growth → Surface ligation → Purification → Surface restructuring → Final NC properties

This relationship explains why identical PNC cores can exhibit different PLQYs, colloidal stabilities, and charge-transport characteristics following different purification procedures. For this reason, publication-quality studies should report not only the synthetic route but also the complete post-synthetic treatment.

Critical Comparison of the Synthetic Approaches

The different synthesis routes discussed above demonstrate that no single method provides universal control over all desirable PNC characteristics. The hot-injection method offers excellent control over rapid nucleation and can produce highly monodisperse NCs, but it requires accurate temperature and injection-time control. LARP provides a simpler and generally lower-temperature route, although its rapid supersaturation can make nucleation and aggregation highly sensitive to experimental conditions.

Solvothermal synthesis provides a sealed environment suitable for controlled thermal processing and can produce different morphologies through adjustment of precursor dissolution and reaction duration. Ultrasonication-assisted synthesis offers rapid mixing and nucleation, whereas microwave irradiation provides rapid heating and short reaction times.

Seed-mediated approaches provide additional control by separating seed formation from subsequent crystal growth. Template-assisted synthesis, meanwhile, introduces physical confinement as the primary morphological-control mechanism. Across these methods, however, ligands remain a common and fundamental factor controlling the final properties of the NCs.

Overall Significance of Ligand Engineering

The evidence discussed throughout this section demonstrates that ligand engineering is central to the rational synthesis of metal halide perovskite nanocrystals. Ligands influence precursor reactivity, nucleation, crystal growth, morphology, surface passivation, colloidal stability, purification behavior, and ultimately optoelectronic performance.

The dynamic nature of MHP surfaces further indicates that ligand identity alone is insufficient to describe surface chemistry. The ligand concentration, ligand ratio, acid–base equilibria, solvent environment, purification procedure, and binding strength must all be considered. A ligand that produces highly stable colloids may not necessarily be optimal for electronic devices because a thick organic shell can hinder interparticle charge transport. Conversely, aggressive ligand removal may improve electrical coupling but expose surface defects and decrease PLQY. The optimal surface chemistry therefore represents a compromise between **stability, passivation, processability, and charge transport**.

Relevance to the Development of Novel and Bio-Derived Ligands

The understanding of conventional OA/OAm-based surface chemistry provides an important foundation for the development of alternative ligands, including multifunctional and bio-derived molecules. A suitable bio-ligand may contain several functional groups capable of coordinating precursor ions and interacting with under-coordinated surface sites. Such molecules could potentially influence nucleation and growth while simultaneously providing surface passivation and colloidal stabilization.

However, bio-derived ligands require particularly careful chemical characterization. Natural materials can contain mixtures of organic molecules with different molecular weights, functional groups, and binding affinities. Consequently, variations in extraction conditions and composition can produce significant differences in PNC morphology and optical properties.

For a thesis investigating novel bio-ligand-capped PNCs, it is therefore important to establish correlations among: bio-ligand composition → functional groups → precursor interaction → nucleation/growth → surface binding → morphology → optical properties → photocatalytic/device performance.

Such a framework provides a scientifically rigorous basis for evaluating whether a bio-derived ligand offers genuine advantages over conventional synthetic ligands.

CONCLUDING REMARKS

The development of solvothermal, ultrasonication-assisted, microwave-assisted, seed-mediated, and template-assisted approaches has significantly broadened the synthetic toolbox available for the preparation of metal halide perovskite nanocrystals. Each method provides distinctive opportunities for controlling precursor conversion, nucleation, crystal growth, morphology, and reaction kinetics. Among these methods, solvothermal synthesis provides a controlled sealed reaction environment in which precursor dissolution and reaction time can be used to manipulate the final morphology. Ultrasonication-assisted synthesis uses acoustic energy to enhance mixing and accelerate nucleation, while microwave irradiation provides rapid heating and allows particle properties to be tuned through irradiation time and power.

Seed-mediated synthesis offers an additional level of control by separating seed formation from subsequent perovskite growth, whereas template-assisted synthesis uses nanoscale spatial confinement to regulate crystal dimensions.

Nevertheless, the final performance of PNCs is determined not solely by their inorganic crystal structure. Their surface chemistry is equally important. Post-synthetic purification can substantially alter the ligand population, and repeated washing may lead to ligand loss, aggregation, degradation, and reduced PLQY. Spectroscopic investigations using FTIR, NMR, NOESY, DOSY, and XPS have established that surface ligation in PNCs are dynamic and involve multiple ligand species and binding configurations.

In CsPbBr₃ NCs, for example, oleylammonium bromide, oleylammonium oleate, oleylamine, and carboxylate species can participate in dynamic surface equilibria. The relative abundance and binding strength of these species depend strongly on solvent, ligand concentration, acid–base chemistry, and purification conditions.

These findings establish a fundamental principle for PNC research: the nanocrystal core and its surface ligand shell constitute an integrated physicochemical system. Modification of the surface can alter not only colloidal stability but also morphology, defect chemistry, optical emission, charge transport, and environmental stability.

Accordingly, future development of high-performance and sustainable PNCs should move beyond simply identifying new synthesis routes and instead focus on rational control of the entire synthesis–surface–property relationship. In particular, multifunctional, branched, ionic, peptide-based, and bio-derived ligands represent promising platforms for simultaneously controlling crystal growth, defect passivation, environmental stability, and application-specific performance.

A systematic understanding of these relationships is essential for translating metal halide perovskite nanocrystals from laboratory-scale colloidal systems into robust materials for optoelectronics, photocatalysis, sensing, energy conversion, and other emerging technologies.

Effect of Surface Ligation on the Stability of Inorganic Perovskite Nanocrystals

The stability of metal halide perovskite nanocrystals (MHP NCs) is strongly governed by their surface chemistry. Although reduction in particle dimensions provides perovskite nanocrystals with attractive optical and electronic characteristics, the accompanying increase in surface-to-volume ratio also increases the relative contribution of surface atoms, under-coordinated ions, defects, and adsorbed molecular species. Consequently, the nature, concentration, binding strength, and dynamic behavior of surface ligands are critical determinants of colloidal stability, structural integrity, optical performance, and resistance to environmental degradation.

In colloidal CsPbX₃ nanocrystals, where X represents Cl, Br, or I, surface ligands do not necessarily form a rigid and permanently attached molecular shell. Instead, the surface is characterized by dynamic equilibria involving precursor-derived ionic species, carboxylic acids, amines, carboxylates, alkylammonium ions, and halides. These species can associate with, dissociate from, and exchange across the nanocrystal surface depending on solvent polarity, ligand concentration, acid–base equilibria, temperature, and purification conditions. Understanding these processes is therefore essential for explaining why seemingly minor changes

in purification or ligand composition can produce substantial differences in nanocrystal stability and photoluminescence.

Surface-Ligand Equilibria in As-Synthesized Nanocrystals

Grisorio et al. (2017) investigated the relationship between purification, surface ligation, and instability in CsPbX₃ nanocrystals and demonstrated that the instability of as-prepared NCs can be associated with chemical reactions occurring among residual surface species. In particular, they identified the formation of amides through condensation reactions involving carboxylic acid and amine ligands as an important pathway contributing to surface degradation^[87].

Immediately after synthesis, the NC surface contains a complex mixture of species. These may include unreacted Cs-oleate, excess oleic acid (OA), oleylamine (OAm), protonated oleylammonium species, and other precursor-derived components. Rather than existing independently, these species participate in acid–base and coordination equilibria at the nanocrystal interface.

The presence of protonated amines is particularly important. Surface-associated OAmH⁺ can participate in proton-transfer processes, resulting in an acidic surface environment. In addition, residual Lewis-acidic precursor species can remain associated with the NC surface if they are not removed during post-synthetic treatment. The combined presence of acidic species and carboxylic acid/amine ligands can promote the condensation reaction between OA and OAm, resulting in amide formation.

Conceptually, the process can be represented as: **carboxylic acid + amine → amide + water**

Although this reaction may appear to concern only the organic ligand shell, it has direct implications for the stability of the inorganic nanocrystal. The functional groups responsible for surface coordination become chemically transformed during amide formation. Consequently, the resulting organic molecules have reduced ability to interact effectively with the inorganic surface.

Amide Formation and Nanocrystal Destabilization

The formation of amides represents an important chemical pathway through which the ligand shell can progressively lose its stabilizing function. Carboxylate and amine functional groups possess strong relevance to surface coordination because they can interact with under-coordinated metal and ionic sites. When these functional groups participate in condensation reactions, their coordination capability is reduced.

As reported in several studies^[84,86,87], amide formation therefore decreases the number of available functional groups capable of maintaining effective surface passivation. The resulting reduction in ligand coverage can expose previously protected surface sites and increase the probability of nanocrystal aggregation or degradation.

This phenomenon provides an important explanation for the apparently contradictory observation that an as-synthesized NC dispersion may initially be stable but become unstable during storage. The instability may not necessarily originate from an immediate structural weakness of the perovskite lattice. Instead, gradual chemical modification of the ligand shell can progressively reduce the effectiveness of surface stabilization.

Thus, the stability of PNCs should be understood as a dynamic process involving both the inorganic core and the organic surface layer.

Molecular-Level Surface Interactions

Nuclear magnetic resonance (NMR) studies performed in non-polar solvents have provided valuable information concerning the molecular interactions occurring at the surfaces of CsPbX₃ NCs^[87]. These studies indicate that oleate species can interact strongly with under-coordinated Pb and Cs sites. Oleylamine, by comparison, exhibits weaker interactions with surface protons and uncoordinated Pb species. Carboxylic acid molecules can also participate in exchange processes with strongly bound oleate species.

This dynamic exchange is significant because the surface composition is not determined exclusively by the amount of ligand initially introduced into the reaction. Instead, the final ligand population depends on the relative binding affinities of the different species and the chemical environment established during synthesis and purification.

The distinction between strongly bound and weakly associated ligand populations is particularly important. Strongly associated species contribute to surface passivation and structural stabilization, whereas weakly associated species can undergo rapid exchange with molecules in solution. Consequently, PNC dispersion should be regarded as an equilibrium system rather than as a fixed inorganic core coated by an immutable organic layer.

Effect of Purification on Surface Stability

Purification is therefore a critical stage in controlling PNC stability. Although purification is conventionally performed to remove unreacted precursors and excess ligands, it can simultaneously alter the chemical composition of the NC surface.

Grisorio et al. (2017) showed that purification using a polar antisolvent can remove acidic species associated with the NC surface. Their removal suppresses the acid-catalyzed formation of amides from OA and OAm. Consequently, appropriate purification can preserve the chemical functionality of the ligand shell and improve the long-term stability of the NC dispersion²².

This finding emphasizes an important distinction between **insufficient purification** and **excessive purification**.

Insufficient purification can leave behind residual precursor species and acidic components that promote undesirable chemical reactions within the ligand shell. Excessive purification, on the other hand, can remove too many surface ligands, expose the inorganic surface, increase aggregation, and compromise colloidal stability. Therefore, optimum purification should remove destabilizing residual species while retaining sufficient surface ligands to maintain effective passivation

Purification and Isolation of Perovskite Nanocrystals

Purification and isolation constitute critical post-synthetic stages in the preparation of colloidal metal halide perovskite nanocrystals (MHP NCs). Following synthesis, the reaction mixture generally contains the desired nanocrystals together with unreacted metal and halide precursors, excess ligands, reaction by-products, solvent molecules, and weakly associated surface species. Removal of these components is necessary to obtain stable and reproducible nanocrystal dispersion suitable for structural, optical, and electronic characterization and for subsequent fabrication of nanocrystal-based films and devices.

Several purification strategies have therefore been developed using different antisolvents, solvent combinations, centrifugation speeds, precipitation conditions, and redispersion procedures. The appropriate purification protocol depends strongly on the chemical composition, particle size, morphology, surface-ligand chemistry, and phase stability of the nanocrystals^[60,61,84,92]. Unlike many conventional semiconductor nanocrystals, however, MHP NCs possess relatively soft and ionically bonded lattices and consequently exhibit substantial sensitivity toward their chemical environment.

A major challenge is that the same purification procedure designed to remove unwanted molecular species can simultaneously remove desirable surface ligands. Polar antisolvents can disrupt ligand–surface interactions, induce partial ligand desorption, and alter the surface stoichiometry of the nanocrystals^[84]. These changes can result in aggregation, loss of photoluminescence, increased surface-defect density, and, in severe cases, partial or complete structural transformation into photo-inactive phases.

Thus, purification of MHP NCs should not be considered merely a separation step. Rather, it represents a form of **surface-chemistry engineering** in which the balance between removal of impurities and preservation of surface passivation must be carefully maintained.

Influence of Purification on Nanocrystal Properties

The optical and colloidal properties of MHP NCs are strongly dependent on their surface ligand population. Long-chain carboxylic acids and amines provide steric stabilization and interact with surface ions to reduce the energetic penalty associated with under-coordinated surface sites. Removal of these ligands during purification exposes the inorganic surface and increases the likelihood of NC–NC interactions.

If ligand coverage becomes insufficient, the attractive forces between individual nanocrystals can overcome steric stabilization, resulting in agglomeration. Aggregation increases the effective particle size and can modify the optical response of the material through changes in scattering, electronic coupling, and defect-assisted recombination.

More severe ligand loss may destabilize the perovskite lattice itself. This is particularly important for iodide-containing perovskites, which generally exhibit greater chemical sensitivity than their chloride- and bromide-containing counterparts ^[92]. Excessive purification can therefore lead not only to colloidal aggregation but also to conversion into phases that are less suitable for optoelectronic applications.

Consequently, the objective of purification should be to achieve an optimum balance between: removal of unreacted species + preservation of surface ligands + retention of crystal structure + maintenance of optical properties.

Purification of Iodide-Based Perovskite Nanocrystals

The sensitivity of iodide-based MHP NCs to ligand loss presents a particularly important challenge. Compared with chloride- and bromide-based systems, CsPbI₃ and related iodide-rich compositions can exhibit greater susceptibility to surface restructuring, ligand desorption, aggregation, and phase transformation ^[92].

Loss of the protective ligand shell can expose the surface to environmental species and increase the probability of NC–NC contact. This can initiate aggregation and facilitate transformation from the desired photoactive perovskite phase into a less favorable structure. The purification procedure must therefore be designed to minimize the residence time of the NCs in strongly polar environments and avoid excessive precipitation/redispersion cycles.

This consideration is particularly important for applications requiring high photoluminescence quantum yield (PLQY), because ligand loss can expose non-radiative recombination centers. A reduction in PLQY following purification may therefore serve as an indirect indication of changes in surface chemistry.

Ligand-Assisted Purification

An important strategy for reducing purification-induced degradation involves maintaining an appropriate equilibrium between free and surface-bound ligands during the purification process.

De Roo et al. (2016) demonstrated that the addition of excess oleic acid (OA) and oleylamine (OAm) during purification of CsPbBr₃ NCs could manipulate the equilibrium between bound and free surface ligands. Rather than allowing the antisolvent to remove the ligand shell indiscriminately, the presence of additional ligand molecules helps maintain the chemical equilibrium necessary for surface stabilization.

Grisorio et al. (2017) subsequently adapted related purification principles to CsPbX₃ NCs containing different halides ^[87].

The underlying concept is that ligand binding on the NC surface is dynamic. Surface-bound species can continuously exchange with molecules dissolved in the surrounding solution. Increasing the concentration of free ligands can therefore shift the equilibrium toward surface coverage and reduce excessive ligand depletion. This strategy illustrates the importance of considering purification and ligand chemistry as interconnected processes rather than treating them as independent experimental steps.

Methyl Acetate-Based Purification of CsPbI₃

Swarnkar et al. (2016) developed a purification strategy for CsPbI₃ NCs based on methyl acetate (MeOAc) as the antisolvent. The method allowed unreacted precursor species to be removed while minimizing complete removal of the surface-associated species⁸⁰. This feature is particularly important for CsPbI₃ because excessive ligand stripping can result in rapid aggregation and degradation. By preserving a sufficient proportion of the surface ligand population, the MeOAc-based procedure enabled the NCs to remain dispersed following isolation.

The study illustrates a broader principle in PNC purification: the effectiveness of an antisolvent cannot be evaluated solely according to its ability to precipitate the NCs. Its interaction with the ligand shell, inorganic surface, and solvent environment must also be considered. An ideal antisolvent should therefore exhibit sufficient polarity or miscibility to remove unwanted soluble components while avoiding excessive disruption of the surface-ligand equilibrium.

Zwitterionic Ligands for Improved Purification Stability

An alternative strategy for addressing ligand loss during purification involves replacing conventional dynamic acid/amine ligand pairs with strongly bound zwitterionic ligands.

Krieg et al. (2018) demonstrated that 3-(N,N-dimethyloctadecylammonio)propanesulfonate could be used as a long-chain zwitterionic ligand for CsPbBr₃ NCs. Importantly, these NCs retained high PLQY following multiple precipitation and redispersion cycles³⁴.

Zwitterionic ligands contain both positively and negatively charged functional groups within the same molecule. This molecular architecture provides several advantages for surface stabilization.

First, the cationic and anionic groups are not dependent on the same acid–base equilibria that characterize conventional OA/OAm ligand systems. Second, simultaneous interaction of multiple functional groups with surface sites can produce stronger overall attachment. Third, the long hydrocarbon chain can provide steric protection against NC–NC aggregation. The resulting ligand shell is therefore less susceptible to complete removal during purification. This approach highlights the potential of designing ligands not only according to their initial binding affinity but also according to their resistance to the chemical stresses associated with purification and processing.

ADVANTAGES OF ZWITTERIONIC SURFACE LIGANDS

The improved stability provided by zwitterionic ligands can be attributed to two principal characteristics.

Reduced Dependence on Acid–Base Equilibria

Conventional OA/OAm ligand systems involve continuous acid–base interactions among free acids, neutral amines, ammonium ions, and carboxylates. Changes in solvent polarity or ligand concentration can shift these equilibria and consequently alter the population of surface-bound species.

Zwitterionic molecules contain oppositely charged groups within the same molecular structure. Their simultaneous presence reduces dependence on external acid–base equilibration and can provide more persistent surface attachment.

Multidentate or Chelating Surface Interaction

Zwitterionic ligands can also interact with multiple surface sites. Such interactions may provide a chelating or multidentate stabilization effect compared with simple monodentate ligands. The combination of stronger surface attachment and steric stabilization can reduce ligand loss, aggregation, and degradation during purification.

However, stronger surface binding may also create a trade-off for electronic applications because highly insulating organic ligands can impede charge transport between neighboring NCs. Consequently, the ligand that is optimal for colloidal stability may not necessarily be optimal for device performance.

Surface Manipulation for the Application of Perovskite Nanocrystal Films

Metal halide perovskite nanocrystals have attracted substantial interest for applications including lasers, photodetectors, electroluminescent devices, light-emitting diodes (LEDs), and solar cells ^[23,85]. Most of these applications require the NCs to be converted from colloidal dispersions into continuous or semi-continuous solid-state films. Although colloidal dispersions are convenient for synthesis and solution processing, they are unsuitable as final device architectures because their concentration, composition, aggregation state, and surface chemistry can change with time. Device fabrication therefore requires the deposition of nanocrystals into controlled solid-state arrangements.

The transition from colloidal NCs to solid-state films introduces a fundamental materials challenge. The long-chain ligands that provide excellent colloidal stability can become detrimental to charge transport after film formation because they create insulating barriers between adjacent nanocrystals. Surface engineering is consequently required to reconcile two competing requirements: high colloidal stability during synthesis and processing **versus** efficient electronic coupling after film formation.

Several strategies have been developed to address this challenge, including:

- ligand exchange;
- incorporation of short-chain ligands;
- use of bidentate and multidentate ligands;
- use of branched or multifunctional ligands; and
- deliberate control of surface ligand density.

Ligand Exchange

Ligand exchange involves replacing the original surface ligands of a nanocrystal with alternative ligands possessing more desirable chemical or electronic properties.

Long-chain OA and OAm are widely used during MHP NC synthesis because they provide effective colloidal stabilization. However, their extended hydrocarbon chains form relatively thick insulating barriers between adjacent NCs. When these NCs are assembled into a film, the long-chain ligands can increase the interparticle distance and reduce electronic coupling. Consequently, charge carriers experience increased resistance when moving from one NC to another. Ligand exchange provides a means of modifying the surface after synthesis without necessarily changing the inorganic core.

The ideal exchanged ligand should therefore satisfy several requirements: strong interaction with the NC surface; effective passivation of surface defects; sufficient colloidal stability during processing; reduced interparticle distance; improved electronic coupling; resistance to desorption; and compatibility with the intended device architecture.

Solution-Based Ligand Exchange

Solution-based ligand exchange is performed while the NCs remain dispersed in solution. The native surface ligands are replaced by a new ligand population before deposition of the NC film ^[86]. This approach is particularly useful for replacing long-chain OA/OAm ligands with shorter or more strongly bound species.

The process is generally governed by competitive adsorption. The incoming ligand must possess sufficient affinity for the surface to displace the native ligand without causing irreversible degradation of the perovskite core. The ligand exchange process can be particularly delicate for MHP NCs because their surface ions are labile and the perovskite lattice can undergo dissolution or reconstruction under inappropriate chemical conditions.

Mechanism of Solution-Based Ligand Exchange

Solution-based ligand exchange can involve multiple sequential processes. Initially, addition of OA can protonate OAm, producing an acid–base pair and altering the equilibrium between free and surface-bound ligands. This facilitates desorption of the native ligand species from the NC surface. A second ligand, often an X-type ligand, can then be introduced. Because of its stronger interaction with surface Pb^{2+} or Cs^+ sites, the incoming ligand can replace the remaining OA/OAm species. The success of this process depends strongly on the chemical compatibility between the incoming ligand and the perovskite surface. Direct exposure to an aggressive ligand may destabilize the NCs. Consequently, controlled sequential exchange can be preferable to direct substitution.

DDAB Ligand Exchange

Pan et al. (2018) demonstrated a representative solution-based ligand-exchange strategy using di-dodecyl dimethyl ammonium bromide (DDAB) to replace OA/OAm on CsPbX_3 quantum dots synthesized by the hot-injection method. DDAB contains a quaternary ammonium cation and bromide counterion. The bromide species possesses strong affinity for under-coordinated Pb^{2+} and Cs^+ sites at the perovskite surface.

The intermediate addition of OA was found to be important because direct introduction of DDAB could induce NC degradation^[93]. This observation highlights the importance of controlling the chemical pathway through which ligand exchange occurs.

Following exchange, DDAB-treated NCs exhibited improved colloidal stability compared with untreated NCs. The enhanced stability was associated with the steric contribution of the adsorbed dodecyl chains together with stronger ionic interactions at the surface.

Influence of DDAB on Optoelectronic Performance

The effect of ligand exchange extends beyond colloidal stability. DDAB-treated CsPbBr_3 NCs incorporated into LED architectures demonstrated external quantum efficiency (EQE) of approximately 3%, substantially exceeding the performance of untreated NC-based devices^[94].

The improved device performance was attributed to improved charge-carrier balance, enhanced film crystallinity, and reduced defect density. This finding demonstrates that ligand exchange can simultaneously modify: surface chemistry $\rightarrow$ defect density $\rightarrow$ charge transport $\rightarrow$ recombination $\rightarrow$ film quality $\rightarrow$ device efficiency. Therefore, ligand engineering represents an important bridge between colloidal nanocrystal synthesis and device engineering.

Sulfide-Based Surface Passivation

A related surface-engineering strategy involves introducing sulfur-containing species to passivate under-coordinated surface sites. Di-dodecyl dimethyl ammonium sulfide (DDAS) has been investigated as an ion-pair ligand for CsPbBr_3 NCs^[94]. Elemental analysis indicated that both the DDA^+ cation and S^{2-} species contributed to surface passivation. The sulfur-containing component is particularly relevant because sulfide ions can interact strongly with under-coordinated Pb^{2+} centers. Such interactions can reduce the density of surface traps and suppress non-radiative recombination.

Treatment with sulfur precursors increased the PLQY from approximately 49% to 70%^[95]. In addition, the treated NCs exhibited improved environmental stability under conditions of approximately 60% relative humidity. The corresponding films also demonstrated substantial resistance to continuous pulsed-laser

irradiation, remaining stable for approximately 34 h and enabling the observation of highly stable amplified spontaneous emission (ASE) ^[95]. These findings demonstrate that surface passivation can be simultaneously beneficial for optical efficiency and operational stability.

Quaternary Ammonium Ligands

Park et al. (2019) investigated the replacement of OAm in CsPbBr₃ NCs with quaternary ammonium bromide (QAB) ligands possessing different chain lengths and molecular bulkiness ^[96]. The results demonstrated that ligand architecture can substantially affect surface passivation. Less bulky QAB ligands provided improved surface coverage and resulted in higher PLQY and stability. Interestingly, ligand chain length did not produce a major change in the intrinsic optical properties of the NCs. However, it strongly affected charge transport within NC films. Shorter ligands reduce the physical distance between neighboring NC cores and consequently facilitate electronic coupling and charge-carrier transport. This distinction illustrates an important principle of ligand engineering: the ligand that optimizes the colloidal or optical properties of an isolated NC may not necessarily maximize charge transport in a solid-state film. LEDs fabricated using NCs with optimized QAB chain length and molecular bulkiness achieved an EQE of approximately 9.71%, representing a substantial improvement over conventional OA/OAm-capped CsPbBr₃NCs ^[96].

Long-Chain Ligands Versus Short-Chain Ligands

Although short-chain ligands generally facilitate charge transport, reducing ligand length can compromise surface passivation.

Ye et al. (2020) investigated the reverse ligand-exchange strategy by replacing short-chain propionic acid and butylamine ligands with longer-chain acid and amine ligands before purification ^[100]. The resulting spin-coated films exhibited improved uniformity, demonstrating that longer ligands can provide important processing advantages.

Interestingly, despite the superior charge-transport characteristics expected from shorter ligands, the NCs capped with OA/OAm exhibited the highest LED performance and thermal stability in the investigated system ^[100]. This behavior was attributed to more effective defect passivation by the longer ligands.

The result emphasizes that optimizing NC films requires balancing several competing properties:

ligand length → surface passivation → film morphology → charge transport → thermal stability → device efficiency. Therefore, simply minimizing ligand length is not necessarily an appropriate universal strategy for improving device performance.

Ligand-Induced Phase Transformation

Surface manipulation can influence not only ligand coverage but also the crystal structure of the perovskite itself. The addition of specific ligands to pre-synthesized NC dispersions can induce phase transformations accompanied by changes in morphology and dimensionality. Amines are particularly important in this regard.

For CsPbBr₃, addition of amines can promote transformation of the three-dimensional CsPbBr₃ structure into zero-dimensional CsPbBr₃ ^[99]. The transformation is associated with extraction of PbBr₃ from the original 3D lattice and subsequent complexation of the extracted Pb species by amine molecules. This process demonstrates that ligands can function as active chemical reagents rather than merely passive surface stabilizers. The interaction between amines and Pb-containing species can modify the chemical equilibrium of the perovskite lattice and drive structural reconstruction.

Reversible 3d–Od Transformation

The ligand-induced transformation can also occur in solid-state films. CsPbBr₃ NC films exposed to volatile butylamine vapor have been reported to undergo conversion into zero-dimensional CsPbBr₃ NCs. Upon removal and evaporation of the butylamine, the system can revert toward the three-dimensional CsPbBr₃

structure^[98]. This reversible transformation demonstrates the remarkable chemical responsiveness of metal halide perovskites. It also highlights the importance of controlling residual ligands and processing solvents during device fabrication. Volatile amines, residual surface species, and processing additives can potentially alter the phase composition of the final film.

Consequently, ligand selection should account not only for initial surface passivation but also for the possibility of ligand-induced structural reconstruction during storage, thermal treatment, solvent exposure, or device operation.

Integrated Perspective on Purification and Surface Manipulation

The studies discussed above demonstrate that purification and ligand exchange are interconnected aspects of PNC surface engineering. During synthesis, ligands control nucleation and crystal growth. Following synthesis, purification modifies the ligand population. During film formation, additional surface manipulation may be required to replace insulating ligands or enhance defect passivation.

The complete sequence can therefore be represented conceptually as: Synthesis → Initial ligand adsorption → Purification → Surface restructuring → Ligand exchange/passivation → Film formation → Device operation. At each stage, the ligand shell can undergo adsorption, desorption, protonation, deprotonation, exchange, or chemical transformation. The final properties of the NC film therefore depend on its entire processing history rather than solely on the original synthesis conditions.

Trade-Off Between Stability and Charge Transport

One of the central challenges in PNC surface engineering is the trade-off between colloidal stability and charge transport.

Long-chain ligands such as OA and OAm are effective at stabilizing NC dispersions because their hydrocarbon chains provide steric repulsion. However, these same long chains increase the distance between neighboring NCs and act as electrical barriers. Short-chain ligands reduce this barrier and facilitate charge transport but may provide weaker steric protection and less effective surface passivation.

Similarly, strongly bound zwitterionic or multidentate ligands can significantly improve stability but may form relatively insulating surface layers. Thus, the optimum ligand system depends on the intended application. For solution-based storage, long-chain or strongly bound ligands may be advantageous. For LEDs, photodetectors, and photovoltaic devices, the ligand system must additionally permit efficient charge injection and transport.

Implications for Optoelectronic Devices

The performance of PNC-based optoelectronic devices depends on the ability of charge carriers to move efficiently through the NC film while minimizing non-radiative recombination. Poorly passivated surfaces contain under-coordinated ions and vacancies that can act as trap states. These defects capture charge carriers and facilitate non-radiative recombination, reducing device efficiency.

Conversely, excessively thick organic ligand shells increase the interparticle barrier and reduce charge transfer. Effective surface engineering must therefore simultaneously minimize trap-assisted recombination and maintain sufficient electronic coupling. This explains why ligand exchange, halide passivation, sulfide treatment, and quaternary ammonium surface modification have attracted considerable interest in PNC optoelectronics.

Critical Consideration of Ligand Design

An effective ligand for PNC applications should ideally combine four characteristics:

- **Strong surface affinity** to prevent ligand loss during purification and operation;

- **Effective defect passivation** to suppress non-radiative recombination;
- **Appropriate molecular dimensions** to balance colloidal stability with interparticle charge transport;
- **Chemical and environmental stability** under the intended processing and operating conditions.

Multifunctional ligands are particularly attractive because a single molecule can potentially provide several of these functions simultaneously. For example, a ligand containing multiple coordinating groups may bind more strongly than a monodentate molecule, while an appropriate organic backbone can provide steric stabilization. If the ligand also possesses electronically active or ionically conductive characteristics, it may reduce the negative effect of surface insulation. This provides a strong scientific basis for continued investigation of bidentate, multidentate, zwitterionic, branched, peptide-based, and bio-derived ligands.

Relevance to the Development of Novel Bio-Derived Ligands

The challenges associated with conventional ligands provide an important motivation for exploring renewable and bio-derived surface ligands. Natural molecules frequently contain functional groups such as hydroxyl, carboxyl, amino, carbonyl, ether, and other heteroatom-containing groups capable of interacting with inorganic surfaces. Depending on their molecular structure, these functional groups may coordinate metal ions, interact with halide species, or provide steric stabilization.

A bio-derived ligand could therefore potentially perform several functions simultaneously, including: precursor coordination; nucleation regulation; crystal-growth control; surface passivation; colloidal stabilization; defect suppression; environmental protection; and modification of photocatalytic or optoelectronic behavior.

However, the use of bio-derived materials also introduces additional challenges. Natural extracts may contain several chemically distinct constituents, and their composition can vary with plant source, extraction solvent, temperature, purification method, and storage conditions.

For this reason, rigorous characterization of bio-ligands is essential. Techniques such as FTIR, NMR, UV–Vis spectroscopy, HPLC, mass spectrometry, and elemental analysis can help establish the functional groups and molecular constituents responsible for NC binding.

The development of bio-derived ligands should therefore be based on a structure–function relationship rather than simply on the assumption that a natural material will provide better stabilization.

SUMMARY AND RESEARCH OUTLOOK

Purification, ligand exchange, and surface manipulation are fundamental components of the processing of metal halide perovskite nanocrystals. Purification determines which precursor and ligand species remain associated with the NC surface, while ligand exchange provides a means of deliberately modifying this surface to meet the requirements of subsequent applications.

The susceptibility of MHP NCs to ligand loss during purification demonstrates the importance of carefully selecting antisolvents and controlling precipitation/redispersion conditions. This issue is especially pronounced in iodide-based perovskites, where excessive ligand removal can promote aggregation and phase transformation.

Strategies involving excess OA/OAm, methyl acetate purification, and zwitterionic ligands have demonstrated that preservation of surface chemistry can significantly improve NC stability.

For solid-state applications, however, conventional long-chain ligands introduce a competing problem: their insulating nature limits interparticle charge transport. Ligand exchange with shorter, ionic, halide-containing, sulfide-containing, or quaternary ammonium species can improve the balance between passivation and electronic coupling.

Studies involving DDAB, DDAS, and QAB ligands demonstrate that rational modification of surface chemistry can improve PLQY, environmental stability, charge transport, and LED efficiency. At the same time, the reverse exchange study using longer ligands demonstrates that increased ligand length can sometimes improve film uniformity, defect passivation, and thermal stability.

These apparently contrasting observations demonstrate that ligand engineering cannot be reduced to simply selecting the shortest or strongest-binding ligand. Instead, optimal surface chemistry requires simultaneous consideration of ligand binding, molecular architecture, surface coverage, defect passivation, interparticle distance, film morphology, charge transport, and environmental stability.

Furthermore, ligand-induced structural transformations such as the reversible $\text{CsPbBr}_3/\text{CsPbBr}_3$ conversion demonstrate that ligands can actively participate in the chemical equilibrium of perovskite materials. This finding reinforces the need to treat surface ligands as integral components of the material rather than as passive protective coatings.

Overall, future research should focus on multifunctional ligand systems capable of combining strong and controllable surface binding with efficient defect passivation, minimal electronic insulation, environmental resistance, and compatibility with scalable processing. In this context, zwitterionic, branched, multidentate, peptide-based, and bio-derived ligands represent promising directions for developing more stable and application-specific perovskite nanocrystals.

For sustainable PNC development, particular attention should be given to ligands obtained from renewable biological resources. Such ligands could potentially reduce dependence on petroleum-derived surface modifiers while introducing multiple functional groups capable of interacting with perovskite surfaces. Nevertheless, their effectiveness must be established through systematic correlations between ligand chemistry, surface binding, structural properties, optical response, stability, and application performance.

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