

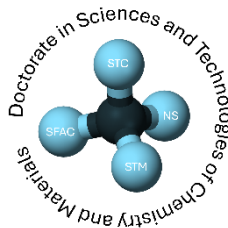


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Cycle XXXVIII

Curriculum: Chemical Sciences and Technologies



Study on the organic components in the Hot-
injection method: a useful approach for
(nano)crystal synthesis

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Chapter I

An overview on
semiconductor nanocrystals



Chapter I: An overview on semiconductor nanocrystals

Abstract: *Owning their properties lies in between conductor and insulator, semiconductor materials became centrally in a huge amount of technologies and, then, focalized lot of interest of the researcher community, especially in the field of material science. The possibility of reducing them as nanoparticles open the windows to new properties and applications. Since the entire thesis will go across the synthesis of semiconductor, in form of nanocrystal, the Chapter I introduces the fundamental physics above them, focusing on lead halide perovskites and chalcogenide semiconductors.*

1.1 Semiconductor materials

Semiconductor materials occupy a central position in modern science and technology due to their distinctive electronic properties. This unique versatility enables their integration into a wide range of applications, including microelectronics, optoelectronics, photocatalysis, and renewable energy conversion.^{1–14} The rapid progress in semiconductor research has been driven by the ability to tailor fundamental parameters such as the bandgap, carrier mobility, defect density, and surface states through advanced techniques such as doping, heterostructure design, and nanostructuring. Precise control over these properties is essential for optimizing device performance and reaching the increasingly stringent demands of next-generation technologies.^{15–17}

Despite significant advances, several challenges remain in achieving high efficiency, long-term stability, and scalable fabrication of semiconductor-based systems. These challenges continue to motivate the exploration of new materials, architectures, and processing strategies.^{16,17}

The unique properties of semiconductors lie between those of conductors and insulators. They originate from the energy difference between the *valence band* (VB) and the *conduction band* (CB), known as *bandgap* (E_g). In conductive materials, the VB and CB overlap; under these conditions, electrons can move freely from the VB to the CB, giving the material high electrical and thermal conductivity. In contrast, in the insulators the bands are separate by a gap, usually with an energy $E_g \geq 3$ eV, meaning that electrons require a large amount of energy to pass from the VB to the CB, leading to very low conductivity.^{16,17}

Semiconductors, on the other hand, are characterized by an intermediate bandgap ranging approximately from 25 meV to 3 eV. This gives them the remarkable ability to behave as either conductors or insulators depending on external conditions, such as temperature, illumination, or applied electric field.^{16,17}

To gain a deeper understanding of semiconductor behaviour, it is essential to first discuss the fundamental origins of these electronic properties.

1.2 Physics behind semiconductor band gap

Similarly to molecular systems, the bandgap of semiconductors, and crystalline materials in general, arises from the energy difference between two specific electronic states. In molecules, these discrete states are known as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

In crystalline materials, which are composed of atoms, molecules, or ions arranged in a periodic lattice, the mutual interactions between these particles lead to the formation of energy bands. These bands originate from the splitting of discrete molecular orbitals (MOs) whose energies become so closely spaced that they effectively form *quasi-continuous energy levels* (Figure 1.1).

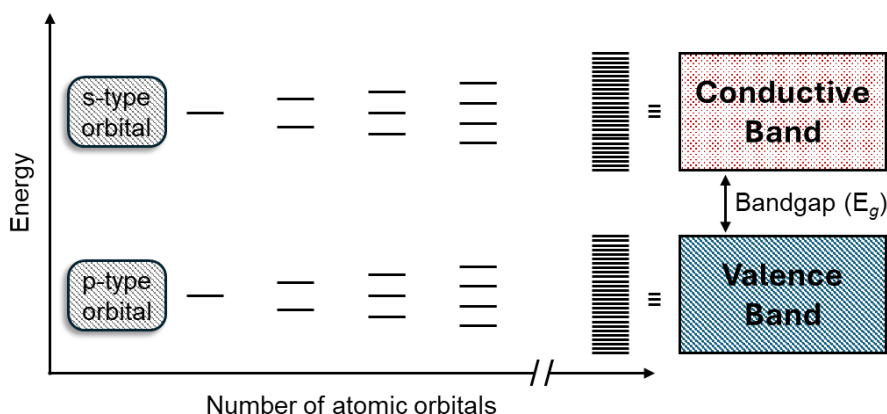


Figure 1.1 General formation of the valence and conductive band by the influences of even more particles' orbitals until achieve a quasi-continuum band of energy. The figure also represents the difference in energy between valence and conductive band, called bandgap. Figure is adapted from ref.¹⁸

To gain a deeper understanding of how electronic bands originate, it is necessary to introduce the *Schrödinger equation* (Equation 1.1), since the electronic states in semiconductors arise from the interaction between electrons and the periodic potential of the crystal lattice. The Schrödinger equation describes the wavefunction (ψ) of an electron, the Hamiltonian operator ($\hat{H}$) representing the total energy of the system, and the energy eigenvalue (E) associated with that wavefunction.

Equation 1.1 Schrödinger equation not dependent from the time.

$$\hat{H}\psi = E\psi$$

The Hamiltonian can be expressed as the sum of kinetic and potential energy terms. The first term in Equation 1.2 corresponds to the kinetic energy, where $\hbar$ is the reduced Planck constant, m is the particle mass, and ∇^2 is the Laplacian operator; the second term V represents the electrostatic potential energy of the electron.

Equation 1.2 Explicit expression of the Hamiltonian operator.

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \nabla^2 + V\right)$$

In a metallic crystal, the valence electrons are delocalized throughout the entire lattice, moving within a uniform positive background of ionic cores, a system often described by the jellium model. In this approximation, the positive background charge of the lattice is balanced by the electron-electron repulsion, so that the potential energy V can be considered negligible. Consequently, the electron's total energy depends only on the kinetic term of the Hamiltonian. Solving the Schrödinger equation under these conditions yields plane wavefunctions, representing electrons that move freely through the crystal. The corresponding electron energy follows a parabolic dispersion relation (Equation 1.3)¹⁹, shown in Figure 1.2a, where k is the wavevector related to the electron momentum in the Brillouin zone, and m_e is the electron mass.^{19,20} The Brillouin zone itself is defined as the region enclosed by the Wigner–Seitz cell in the reciprocal lattice.

Equation 1.3 Dispersion relation for a free electron obtained by the free-electron model.

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m_e}$$

However, in a real crystalline solid, the free-electron model no longer provides an accurate description, because the atomic nuclei generate a *periodic potential* along the lattice (Figure 1.2b). This potential perturbs the electron energy levels, leading to discontinuities in the energy-momentum relationship and the formation of forbidden energy regions, or bandgaps.

The behaviour of electrons in such a periodic potential is described by the *Bloch theorem* (Equation 1.4)¹⁹, which states that in an ideal crystal, the electron wavefunction $\psi(r, k)$ can be written as the product of a plane wave ($e^{jk \cdot r}$) representing free-electron motion, and a periodic function $u(k, r)$ having the same periodicity of the crystal lattice.

Equation 1.4 Bloch theorem for $\psi(r, k)$

$$\psi(r, k) = e^{jk \cdot r} u(k, r)$$

The Bloch function of $\psi(r+R, k)$ is expressed in Equation 1.5, where R is any lattice translation vector. Two points separated by R are equivalent in a periodic lattice, the periodic part of the Bloch function must also be identical; therefore, $u(k, r) = u(k, r+R)$. Hence, the second part of the Equation 1.5 can be written.

Equation 1.5 Bloch theorem for $\psi(r, k)$ translated of R .

$$\psi(r + R, k) = e^{jk \cdot (r+R)} u(k, r + R) = e^{jk \cdot r} e^{jk \cdot R} u(k, r)$$

Because the lattice is periodic, the wavefunction at two equivalent points must be the same. Therefore, the relation expressed in Equation 1.6 can be written.

Equation 1.6 Periodic relation between two Bloch functions translated by a lattice vector R

$$\begin{aligned}\psi(r + R, k) &= \psi(r, k) \\ e^{jk \cdot r} e^{jk \cdot R} u(k, r) &= e^{jk \cdot r} u(k, r) \\ e^{jk \cdot R} &= 1 \\ k \cdot R &= 2\pi n\end{aligned}$$

Therefore, this condition imposes that $k \cdot R$ must be an integer multiple of 2π . Consequently, the electron energy $\varepsilon(k)$ is periodic in the reciprocal lattice, satisfying $\varepsilon(k) = \varepsilon(k + G)$, where G is a reciprocal lattice vector. Then, the electronic states characterized by k and $k + G$ are equivalent, allowing the entire electronic structure to be described using only the first Brillouin zone.²¹

When k lies well within the Brillouin zone, the electron behaves nearly as a *free particle*, and its energy varies continuously according to the free-electron dispersion relation. However, when k approaches the zone boundary ($k \approx G/2$, or equivalently $|\pi/a|$, where a is the lattice constant), the electron's de Broglie wavelength becomes comparable to the lattice spacing, resulting in diffraction and Bragg reflection. At these points, the electron motion is *strongly perturbed* by the lattice potential, causing a flattening of the energy-momentum curve and the *appearance of discontinuities*.¹⁹

The resulting energy relation (Equation 1.7)¹⁹ incorporates a perturbative term due to the periodic potential U . λ_k represents the energy in the free-electron approximation.

Equation 1.7 Dispersion relation for an electron in the presence of a periodic potential.

$$\varepsilon(k) = \frac{1}{2}(\lambda_{k-G} + \lambda_k) \pm \left[\frac{1}{4}(\lambda_{k-G} - \lambda_k)^2 + U^2 \right]^{\frac{1}{2}}$$

Solving this modified Schrödinger equation reveals a forbidden energy range, a region where no allowed electronic states exist (Figure 1.3c). The allowed states below and above this region correspond, respectively, to the VB and the CB. The energy difference between the top of the VB and the bottom of the CB defines the E_g .

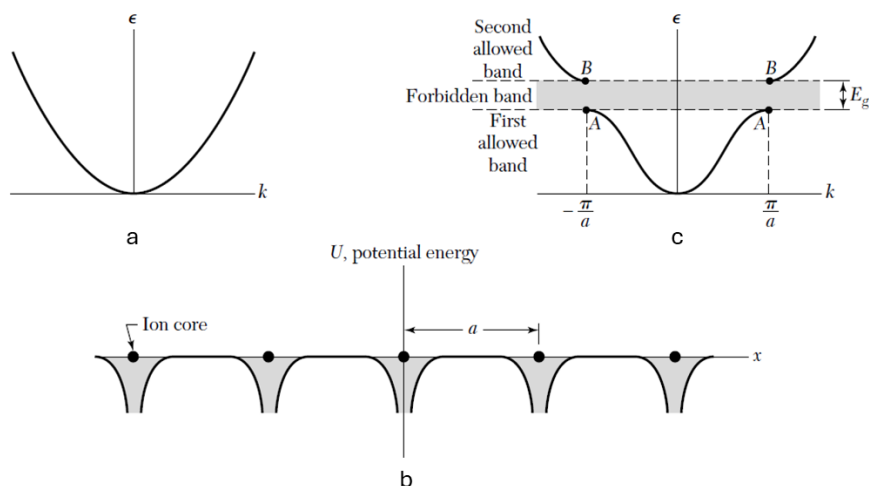


Figure 1.2 (a) Energy of an electron in function of its momentum k derived from the free electron model, then associated to the electron into a metal reticule; (b) representation of the potential periodicity into a semiconductor crystalline. This is generated by the charge of the ion cores displaced to a distance “a” each other and will influence the electron whose move in it; (c) energy of an electron in function of its momentum k into the semicrystalline lattice. The periodic potential of the crystal does not allow to have a continue function and, at the edge of the first Brillouin zone, a discontinuity point is formed. The amplitude of this discontinuity point, called also forbidden band, determining the bandgap of the material. Reproduced with the permission from ref.¹⁹ Copyright © 2018, John Wiley and Sons.

The type of bandgap in a semiconductor is determined by the relative positions of the VB maximum and the CB minimum in k -space, as illustrated in Figure 1.3.

In a *direct bandgap* semiconductor, the VB maximum and CB minimum occur at the same value of the wavevector (k). This alignment means that an electron can transit between the two bands simply by changing its energy, without any change in momentum. Consequently, the absorption of a photon with energy $\hbar\nu \geq E_g$ is sufficient to promote an electron directly from the VB to the CB. Such transitions are optically allowed and occur with high probability, making direct bandgap materials highly efficient for light emission and absorption processes, as in LEDs and laser diodes.^{16,17,19,21}

In contrast, an *indirect bandgap* semiconductor is characterized by a misalignment between the VB maximum and CB minimum in k -space. In this case, a photon-induced transition alone cannot simultaneously conserve energy and momentum, since the photon carries negligible momentum compared to that of the electron. In order to satisfy both energy and momentum conservation, a simultaneous change in the electron's momentum is required. Consequently, the vibronic motion of the crystal lattice is also involved in the transition. Therefore, an electronic transition in an indirect bandgap material necessitates the participation of both a photon and a phonon.^{16,17,19,21}

Thus, electronic transitions in indirect bandgap materials require the participation of both a photon (with energy $\geq E_g$) and a phonon (with energy $\hbar\Omega$, where Ω is the phonon frequency involved in the process). Because this mechanism involves three particles, the electron, photon, and phonon, the probability of such transitions is significantly lower than

in the direct case. As a result, materials with indirect bandgaps generally exhibit weaker optical absorption and lower radiative efficiency.

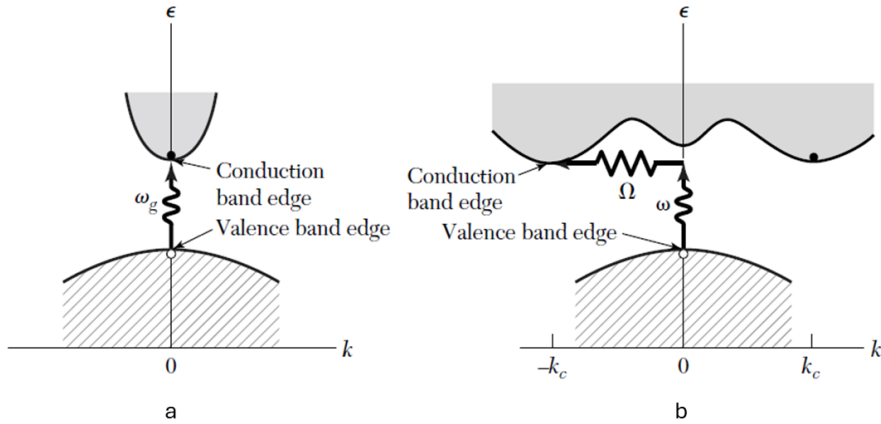


Figure 1.3 Representation of (a) direct and (b) indirect band gap. Notably how in the direct bandgap the excitation is given by the only changing of energy, and then by the absorbent of a photon, while into the indirect bandgap there is also a change of momentum of the electron, which requires the absorption of also a phonon. Reproduced with the permission from ref.¹⁹ Copyright © 2018, John Wiley and Sons. All rights reserved.

1.3 Properties of semiconductors

As previously discussed, the behaviour of semiconductors lies between that of conductors and insulators. Consequently, they can exhibit either conducting or insulating properties depending on the external conditions to which they are subjected. This versatility arises from the relatively small bandgap that characterizes this class of materials.

Under normal conditions, the valence electrons in a semiconductor are predominantly confined to the VB, leaving the CB essentially empty. In this state, the material behaves as an insulator, since there are no free charge carriers available to sustain an electric current. However, only a small amount of energy is required to excite some electrons across the bandgap into the conduction band, where they become free to move throughout the lattice and contribute to electrical conduction. In the conduction band, the available energy states are only partially filled, which allows electrons to move or “hop” between neighbouring orbitals. When an external potential difference is applied, these mobile electrons drift in response to the electric field, generating an electric current called “*drift current*”.¹⁶ This controlled transition between insulating and conducting states is the fundamental operating principle of semiconductor devices, such as transistors, which rely on the ability to modulate electrical conductivity with high precision.^{16,21}

For the semiconductors, a particular importance lies in their *optical properties*. Even in this case, these properties are strongly dependent on the bandgap energy, which governs the interaction between light and matter. As discussed in Paragraph 1.2, a photon with energy $\hbar\nu \geq E_g$ can induce the excitation or de-excitation of an electron between the VB and the CB. It is important to note that the promotion of an electron from the VB to the

CB does not occur exclusively through photon absorption; any external source of energy, such as thermal excitation or electrical bias, capable of overcoming the bandgap energy can produce the same effect.^{16,19,21}

The behaviour of excitons depends strongly on the type of bandgap. In direct bandgap semiconductors, excitons can move through the crystal as a single quasiparticle, transporting energy without carrying net charge. When the exciton energy approaches the absorption edge, the Coulombic interaction between the electron and the hole may become unstable, leading to *radiative recombination*. In this process, the electron recombines with the hole, emitting a photon with energy approximately equal to E_g (Figure 1.4a). Owing to the difference between the VB energy and the exciton level, the *Stokes shift* occurs. This meaning that the wavelength of the absorbed light is different from the emitted one (Figure 1.4b and c). Generally, the emitted light is influenced by a red shift. This emission process forms the basis for the operation of light-emitting devices.^{19,21,22}

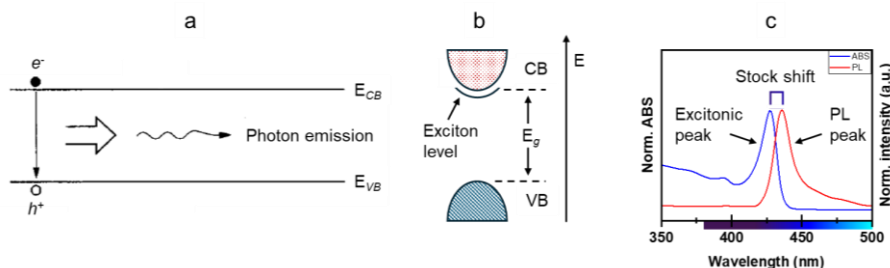


Figure 1.4 (a) representation of a radiative recombination between e^- and h^+ ; (b) illustration of valence band, conductive band and exciton level. Since the difference in energy between the CV edge and the exciton level, the bandgap and the photon emitted from the material should not have the same energy; (c) absorbance (blue line) and photoluminescence (red line) spectra of CsPbBr₃ nanoplatelets. The comparison between the position of the excitonic peak and the photoluminescence peaks highlights the Stokes shift. Figure 1.4a reproduced with the permission from ref.²³ Copyright © 2007 John Wiley & Sons, Inc. All rights reserved. Figure 1.4b adapted from ref.¹⁹

In contrast, indirect bandgap semiconductors exhibit a more complex recombination mechanism. Because the VB maximum and CB minimum occur at different points in k -space, both energy and momentum conservation must be satisfied during the transition. As a result, recombination requires not only the emission of a photon but also the participation of a phonon to accommodate the momentum change. This makes the process less efficient and results in significant non-radiative energy losses.^{19,21}

Excitons in indirect bandgap materials are generally unstable, decaying into free electrons and free holes. The hole can be treated as a quasiparticle equivalent to an electron with positive charge, an effective mass $m_h = -m_e$, and a wavevector $k_h = -k_e$. Consequently, after photon absorption, the total momentum of the electron–hole pair is $k_h + k_e = 0$.¹⁹ Like electrons, holes can move through the crystal lattice, but in the opposite direction, as illustrated in Figure 1.5.

The distinct behaviours arising from the bandgap type determine the practical applications of semiconductors. Indirect bandgap materials are primarily used in electronic devices such as transistors and microchips, where charge transport by free electrons and holes is essential. Conversely, direct bandgap semiconductors are ideal for optoelectronic

applications. Their efficient electron–hole recombination enables the fabrication of light-emitting diodes (LEDs), laser diodes and optical sensors. Finally, both material with direct or indirect bandgap can be employed in solar energy harvesting devices.^{14,16,17,21,24–26}

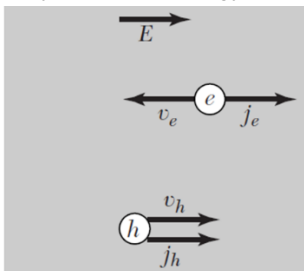


Figure 1.5 Motion of e^- in the conductive band and h^+ in the valence band under electric field E . e^- and h^+ present the same electron current vector, which is coherent with the E vector, but drift velocity opposite in direction. Reproduced with the permission from ref.¹⁹ Copyright © 2018, John Wiley and Sons. All rights reserved.

1.4 The luminescence

Among the various properties of semiconductors, luminescence is of particular importance in this work, as this thesis primarily focuses on materials exhibiting this phenomenon.

In simple terms, *luminescence* is the ability of a material to emit light, typically through radiative transitions of excited electrons.²⁷

Light is a form of *electromagnetic radiation*, a type of energy that propagates through space as oscillating electric and magnetic fields generated by the motion of electric charges.²⁸

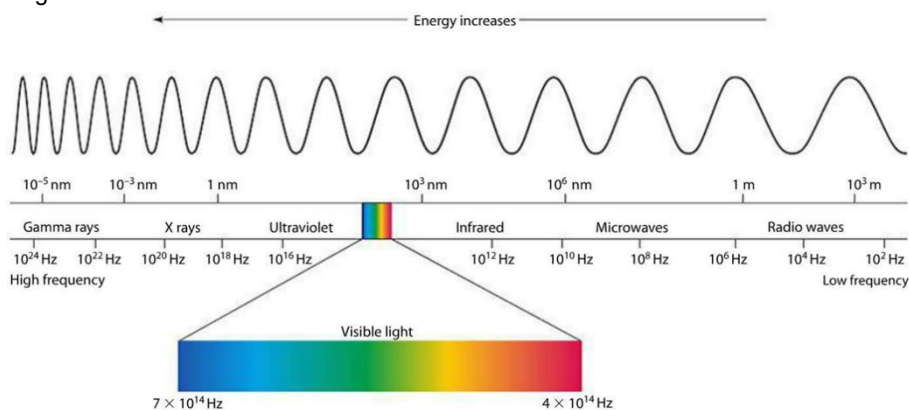


Figure 1.6 Representation of the electromagnetic spectra. The zone of the visible light, limited between 7×10^{14} Hz (380 nm) and 4×10^{14} Hz (750 nm), is highlighted by the colour spectrum visible from the human.³⁰

Electromagnetic radiation covers a wide range of frequencies and wavelengths, collectively known as the *electromagnetic spectrum* (Figure 1.6). This spectrum is divided into distinct regions according to wavelength (λ) and photon energy ($E = h\nu$). From the most energetic to the least energetic, it includes: γ -rays (< 0.01 nm), X-rays (0.01–10 nm),

ultraviolet (UV) light (10–400 nm), visible light (380–750 nm), infrared (IR) radiation (750 nm–1 mm), microwaves (1 mm–1 m), and radio waves (> 1 m).^{28,29}

In semiconductors, light emission typically occurs in the *near-ultraviolet* (300 nm) to *near-infrared* (1.5 μm) spectral range. The term “near” refers to the proximity of these regions to the visible spectrum.

The *visible light region* (400–700 nm) corresponds to the range detectable by the human eye and encompasses all perceived colours. Each colour is associated with a characteristic wavelength: violet (380–450 nm), blue (450–495 nm), cyan (495–520 nm), green (520–565 nm), yellow (565–590 nm), orange (590–620 nm), and red (620–750 nm).³¹

Human visual sensitivity is wavelength-dependent, with peak sensitivity around 555 nm under photopic (daylight) vision, whereas at the extremes of the visible spectrum is nearly to zero. This depending on the internal structure of the eye and the way of it to see the colour. When the light enters the eye, it is focalized on the retina. There, the photoreceptors are stimulated and allow the vision. In particular, this is mediated by two types of retinal photoreceptors: rods, responsible for scotopic (low-light) vision with maximum sensitivity at ~ 507 nm, and cones, which operate under photopic conditions and enable trichromatic colour vision through three subtypes (S, M, and L cones) with distinct spectral responses.³¹

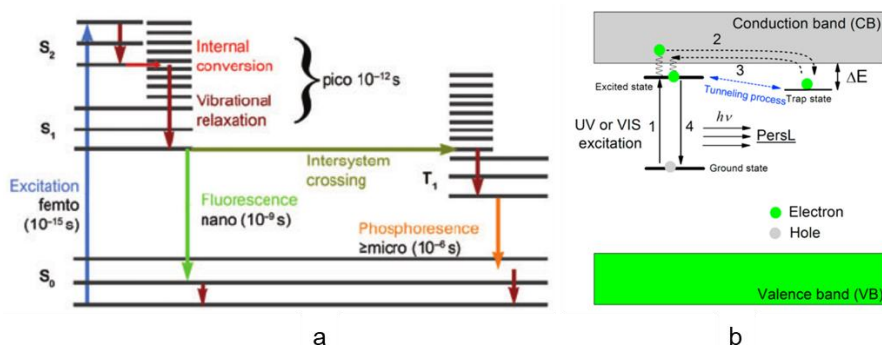


Figure 1.7 (a) Jablonsky diagram which represents the possible transition between ground and excited state of a molecule. The wavy lines indicate the non-radiative transitions, while the straight ones are used for the radiative transitions; (b) representation of persistent luminescence achieved by trap state internal to the bandgap. Figure 1.7a Reproduced with the permission from ref.³⁷ Copyright © 2005, Springer Nature America, Inc. Figure 1.7b Reproduced with the permission from ref.³⁸ 2018 Elsevier B.V. All rights reserved.

The radiative transitions are processes which involved the interaction between a quantum system, as the electron, and electromagnetic radiation. The primary mechanisms include: (i) *absorption* of the photon with excitement of the electron, (ii) *spontaneous emission* of a photon by the relaxing of an exited electron, (iii) *stimulated emission*. As cited in the Chapter 1.3, in the absorption an electron absorbs a photon with energy $\hbar\nu \geq E_g$ and is excited to a higher energy level. On the contrary, the spontaneous emission happens when an excited electron relaxes to a lower energy state, emitting a photon with energy corresponding to the energy gap between the two levels. More curious is the process of the stimulated emission. This occurs when an incoming photon of energy equal

to the energy difference between two electronic states induces an excited electron to relax, emitting a second photon that is coherent (same phase, frequency, and direction) with the first. This process underlies the operation of laser devices.^{21,32–36}

Radiative relaxation can follow several distinct pathways, giving different type of luminescence, as figure out in *Jablonski diagrams* (Figure 1.7a).³⁹

Fluorescence is the process in which the excited electron directly jumps to the ground state, emitting a photon with energy equal to the bandgap. This process is very fast and occurs within 10^{-9} - 10^{-7} s.²⁷

Phosphorescence is a delayed luminescence process that occurs when the electron undergoes intersystem crossing to a triplet state before returning to the ground state. The emission is characterized by a λ depending to the bandgap between the triplet state and ground one. The transition is spin-forbidden and therefore slower (10^{-3} - 10^2 s).^{27,40}

Persistent luminescence occurs in defect-rich crystals that contain trap states within the bandgap. Electrons captured in these traps can return to the excited state via different process (thermally or through tunnelling path) and subsequently recombine radiatively, releasing photons over long timescales, from seconds to days.^{13,38}

In addition to radiative transitions, electrons can lose energy through *non-radiative relaxation*, in which the excitation energy is dissipated as vibrational, rotational, or kinetic energy rather than light. Non-radiative pathways include internal conversion, intersystem crossing, and energy transfer (quenching) to nearby defects or impurities. These processes dominate in indirect bandgap semiconductors, where photon emission is less probable. To enhance radiative recombination in such systems, recombination centres or dopants are often introduced.²¹

Thus, the luminescence intensity of a semiconductor depends on its ability to favour radiative over non-radiative relaxation. Structural defects, particularly formed at the surface, act as quenching centres, reducing emission efficiency by facilitating non-radiative decay. Lastly, the luminescence intensity can be quenched by process of recombination internal to the crystal before the photon may be expelled.

The *photoluminescence quantum yield* (PLQY), or quantum efficiency (η), quantifies this behaviour.²² PLQY, expressed in the Equation 1.8, is defined as the ratio between the radiative recombination (γ_{rad}) and the total de-excitation processes (γ_{tot}), both radiative and non-radiative (γ_{nrad}). Therefore, PLQY depends not only on the intrinsic properties of the material but also on its structural quality and, then, on the synthesis conditions.

Equation 1.8 Quantum efficiency.

$$\eta = \frac{\gamma_{rad}}{\gamma_{tot}} = \frac{\gamma_{rad}}{\gamma_{rad} + \gamma_{nrad}}$$

To conclude the excursus on the luminescence, it could be further categorized based on the excitation source that promotes electrons to higher energy states. Then, the photoluminescence (PL) occurs when is used an optical radiation, cathodoluminescence (CL) in the case of excitation through an electron beam or cathode ray, radioluminescence (RL) for high-energy radiation or fast particles, electroluminescence (EL) if the energy derives from an electric field or current and chemiluminescence when the energy derives from a chemical reaction.^{21,40}

1.5 Nano-size and quantum confinement

Nanoparticles are generally defined as particles having at least one dimension in the nanoscale range (<100 nm). When these particles are crystalline, they are often referred to *nanocrystals*.^{41,42} The nanoscale dimension of these materials is particularly attractive and has been extensively studied since the early 1990s, as the properties of nanomaterials may strongly differ from those of their bulk counterparts.^{43–45}

A primary factor contributing to these differences is the *surface-to-volume ratio*.²² In bulk materials, the volume is much greater than the surface area, whereas in nanoparticles this ratio becomes strongly skewed toward the surface. As a result, surface effects exert a dominant influence on the overall physical and chemical properties of the material.⁴⁶

These systems have a generally enhanced reactivity, since a larger fraction of atoms are located on or near the surface, providing a greater number of active sites. Such a property is particularly advantageous for applications that rely on high surface area, including catalysis and energy storage processes.

In addition to reactivity, mechanical properties such as hardness, strength, and toughness can also be improved at the nanoscale. The yield strength (σ_y) diminishes in small particles because the grain boundaries act as a barrier to the dislocation motion. This phenomenon is described by the Hall-Petch law (Equation 1.9), where σ_y is compared to the intrinsic lattice resistance (σ_0), the Hall-Petch constant (k) and the average of the particles (d). This law is consistent with large nanoparticles (average >100 nm). When the length furtherer decrease, a trend inversion can occur, called inverse Hall-Petch. Generally, the thermodynamics and mechanicals properties are dramatically influenced by the nano-size, which can lead to a decreasing of the melting point, heat capacity, Debye temperature, Young's modulus depending on the material.^{47–49}

Equation 1.9 Hall-Petch law.

$$\sigma_y = \sigma_0 + k * d^{\frac{1}{2}}$$

The optical and electronic transport properties of materials are also profoundly influenced by nanoscale dimensions. First of all, since the exciton is confined in a little space, the wave functions of electron and hole can be overlapped easier, enhancing the probability of radiative recombination. When the exciton decays within a nanocrystal and emits photon can more easily escape without recombination inside the lattice because the crystal volume is small. Diversely, in the bulk material, since the volume is way high than the nanocrystal counterpart, the probability of recombination is high due to phonons, structural defects and impurities trapped in the crystal. Also the nanocrystal can suffer from defects, especially on the surface, which can reduce the intensity of luminescence. A good passivation of the surface overcomes this issue. Then, the overall of these effects ensures a general brighter luminescence for the nanocrystals than the bulk counterpart.^{50–54} Furthermore, metallic nanoparticles can exhibit plasmonic effects, in which the collective oscillation of conduction electrons interacts with incident light, thereby influencing the light absorption and scattering.^{52,55–61}

However, the large surface-to-volume ratio that enhances reactivity also poses a significant challenge to stability. The atoms or ions located on the surface are incompletely

coordinated and thus possess higher energy, making the material more prone to degradation.¹⁹ To mitigate this, surface passivation, which involves stabilizing surface atoms or saturating dangling bonds, plays a crucial role, as will be discussed in detail in Chapter II.

Although nanocrystals display a range of remarkable properties, perhaps the most fascinating is their ability to exhibit quantum mechanical effects that are absent in bulk materials. When the crystal dimensions decrease, the parameters governing the electronic states are altered, leading to the so-called *quantum confinement effect*. This phenomenon arises from the spatial restriction of the exciton formed in the material. While the exciton is a stable electron-hole pair, it can be described analogously to a hydrogenic system, with the difference of the positive mass particle. Then, it is possible to associate to the exciton a Bohr radius, called exciton Bohr radius (a_0), which define the distance between the electron and the hole. As expressed in Equation 1.10, a_0 is strongly depended on the effective masses of the electron (m_e^*) and the hole (m_h^*) which are themselves determined by the electronic bands of the semiconductor. Therefore, a_0 is an intrinsic property of each semiconductor material.

Equation 1.10 Expression for the effective Bohr radius of an exciton in a semiconductor.

$$a_0 = \frac{\hbar^2 \epsilon}{e^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

When the particle size becomes comparable to or smaller than a_0 , quantum confinement becomes significant. The Heisenberg uncertainty principle (Equation 1.11) states that the position (x) and momentum (k) of a particle cannot be simultaneously known with arbitrary precision. Thus, confining the exciton within a quantum “box” increases the spread of its wavefunction in k-space.⁶²

Equation 1.11 Heisenberg uncertainty principle.

$$\Delta x \Delta k \geq \frac{\hbar}{2}$$

Since the exciton is directly “touch” by in this effect, confinement causes a marked alteration of the electronic structure: the valence and conduction bands shift apart as the particle size decreases, resulting in an increase of the bandgap energy and in a releasing of discrete energy levels, as well (Figure 1.8). Consequently, the optoelectronics properties of the semiconductor are affected.²² For example, in the absorption spectra of smaller nanoparticles, the excitonic peak appears at higher energy.⁶³ The effect is even more detectable in luminescent semiconductors, where quantum confinement leads to the emission of more energetic photons. This results in a shift of the emission colour toward shorter wavelengths (higher energy), a phenomenon commonly known as the blue shift.^{55,59,61,64–71} Obviously, the exciton behaviour depends on its size, which in turn is determined by the Coulombic interaction between the e^- and h^+ . *Wannier-Mott exciton*, also known as free exciton, because it can move freely through the crystal, is characterized by a weak Coulombic binding and, consequently, a large a_0 that can extend across multiple

unit cells. This type of exciton, typical of materials such as CdSe and lead halide perovskites, is strongly influenced by quantum confinement effects.^{72–74} In contrast, trapped and self-trapped excitons are characterized by smaller Bohr radii and are therefore less sensitive to spatial confinement. *Trapped exciton* arises from the interaction of a free exciton with structural defects in the crystal, as can occur during crystal doping processes.⁷⁵ Differently, *self-trapped exciton* results from strong exciton-phonon coupling and are localized by a lattice distortion induced by the exciton itself. This type of exciton is commonly observed in double perovskites.^{76–79}

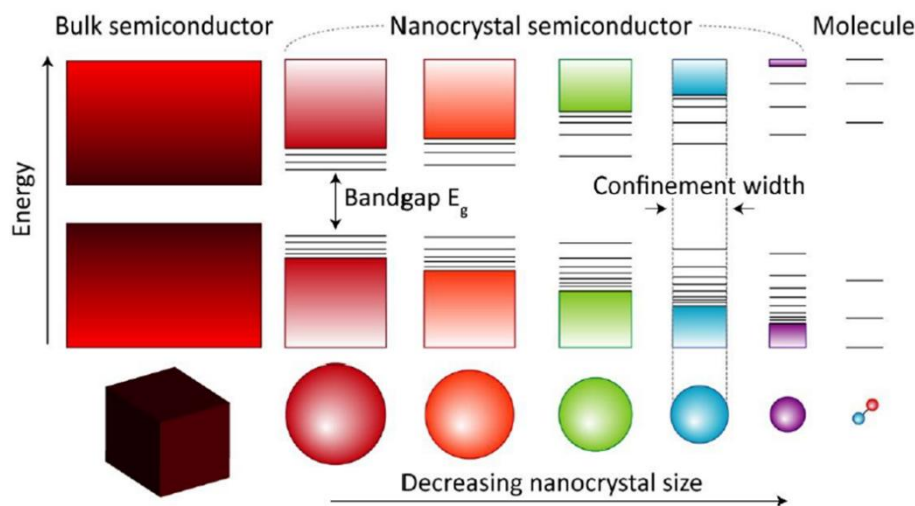


Figure 1.8 Illustration of quantum confinement effect on a nanoparticle bands. The size lowering leads to an increasing of the spacing between VB and CV, with a consecutively increasing of the B_g . Furthermore, discrete energy levels are released. Reproduced from ref.¹⁸

The spatial segregation to the nano-size defines particles having different *dimensionality*. Starting from a three-dimensional crystal (*bulk*) (Figure 1.9a), reducing only one dimension yields a structure extended in two dimensions, analogous to a thin sheet, known as *nanosheet* or *nanoplatelet* (Figure 1.9b). Continuing the shrinking along another edge, the resulting structure becomes elongated in a single direction, forming *nanorod* or *nanotube* (Figure 1.9c). Finally, when all three dimensions are confined to the nanoscale, *quantum dots* are obtained (Figure 1.9d). When the particle size reaches the appropriate range for quantum confinement, the dimensionality of the nanostructure directly affects the degree of confinement and, consequently, its electronic and optical properties.²²

A convenient way to visualize the effect of quantum confinement in nanostructures of different dimensionalities is through the *density of states* (DOS), which describes the number of states per given energy. The DOS provides a quantitative description of the electronic structure and is often evaluated computationally.

In the bulk semiconductors, the DOS is proportional to the square root of energy ($\epsilon^{1/2}$), as exciton can move freely in all three spatial dimensions (Figure 1.9a). In the 2D nanoparticles, the exciton is free to move within a plane but confined along one axis. The DOS slightly changes from the 3D model, since it has a constant dependency to the energy ($\epsilon = \text{constant}$), which leads to a stepwise graph (Figure 1.9b). Differently, in 1D nanoparticles the confinement occurs in two directions, then the exciton can move only along the length of the rod. Here, the DOS have an inverse square roots dependency to the energy ($\epsilon^{-1/2}$). This is translated in a quasi-discrete state of energy with a “sail-like” appearance (Figure 1.9c). Finally, in the quantum dots complete spatial confinement allows electronic states only at discrete energy levels (Figure 1.9d).¹⁸

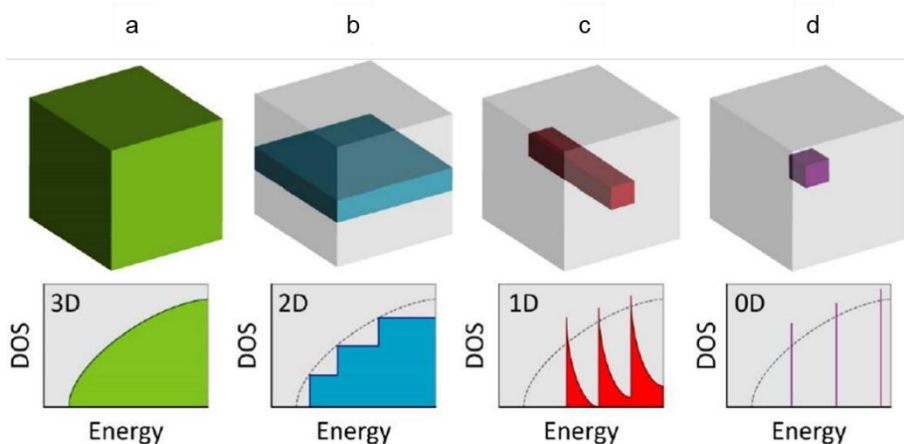


Figure 1.9 Spatial confinement of the nanoparticle and its effect on the density of state. It is possible to note how (a) the bulk particle is represented by a continuous DOS, (b) the nanoplatelets particle has a DOS similar to steps, (c) the nanorods leads to sail-like DOS and, finally, (d) the quantum dot determines a DOS with only discrete energy states available. Reproduced from ref.¹⁸

1.6 Nanoparticles across the human history

Despite nanocrystals were scientifically discovered only in the modern era, their use dates back to ancient times. In those early periods, the exploitation of nanoparticles occurred entirely by chance, or rather, unknowingly. Nevertheless, the properties imprinted by their usage had been researched.

Beginning from the *Bronze Age* in the Prehistory, the art of pottery often involved specific treatments of gold, silver, and/or copper to impart distinct colorations to the final products (Figure 1.10a).^{55,80} Advancing along the historical timeline, evidence has been found that the *ancient Egyptians* used lead sulphide (PbS) nanoparticles in the process of hair dyeing.⁸¹ Fragment of the history of the nanoparticles are implanted in the *Roman Age*. Indeed, the Romans were able to produce object with extraordinarily optical properties. The Lycurgus cup is one of the most representative manufactures (Figure 1.10b). This glass vessel exhibits a striking colour change depending on the light exposition. Indeed, it appears red or green when it is retro- or front-illuminated. The optical

behaviour of this cup arises from the presence of trace of gold nanoparticles as colloidal dispersion into the glass matrix.^{55,82}

During the *Middle Ages*, the unintentional use of nanoparticles continued in Europe. The vivid colours and iridescent effects of stained-glass windows in Gothic cathedrals (Figure 1.10c), as well as Italian medieval ceramics, are now known to result from metallic nanoparticles or nanostructured oxides formed during high-temperature firing and incorporated into the glass or glaze.^{83–86} At the same time, in the East, the legendary Damascus swords (Figure 1.10d), renowned for their exceptional strength and characteristic wavy surface patterns, were produced through complex metallurgical processes. These methods led to the spontaneous formation of aligned nanostructures composed of carbon and metallic carbides, which endowed the steel with extraordinary hardness, resilience, and sharpness.^{87–89}

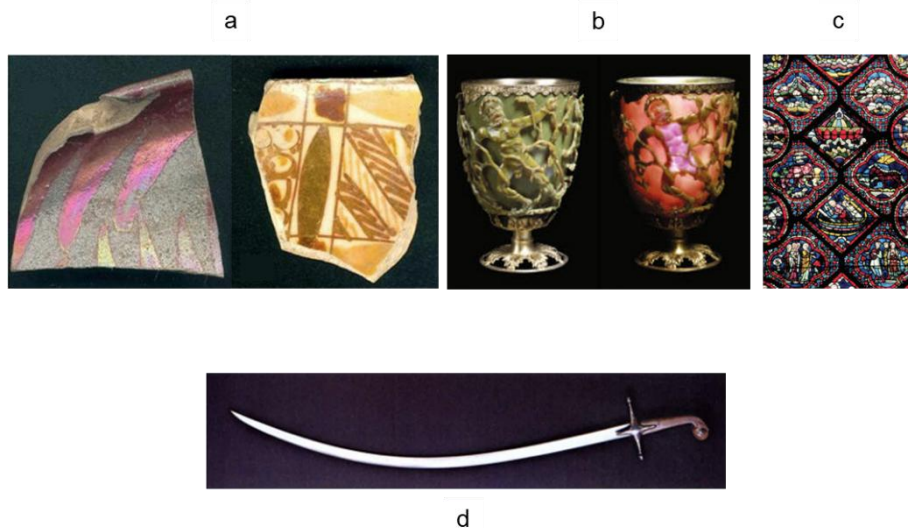


Figure 1.10 Pictures of: (a) Bronze Age pots' fragments;⁸⁰ (b) Lycurgus cup under front- (left picture) and retro-illumination (right picture);⁸² (c) stained glass window of the 13th century in the Chartres Cathedral, Chartres, France, represents Noah's Ark;⁹⁰ (d) Damascus swords. Figure 1.10d reproduced with the permission from ref.⁸⁹ Copyright Scientific American © 1985 Scientific American, Inc. All rights reserved.

Only in the *Modern Age*, these phenomena were scientifically attributed to the presence of nanoparticles. In 1857, *Michael Faraday* published one of the earliest scientific works directly related to nanoscience.⁹¹ He prepared colloidal suspensions of gold by chemically reducing gold chloride and observed that the resulting solutions exhibited deep red, purple, or blue colour, distinctly different from the metallic yellow of bulk gold. Faraday deduced that when metals are divided into extremely fine particles, they display entirely new properties, particularly in their interactions with light. He meticulously documented this effect, which is now understood as surface plasmon resonance. However, Faraday had no concept of "nanometers" or "nanoparticles," as atomic theory was still under debate, and instruments capable of observing such small structures did not yet exist. He simply described them as "very finely divided metals." Thus, although he was unaware of the

nanoscale nature of his gold colloids, his experiments were a visionary step that anticipated modern nanoscience.

Almost a century passed after Faraday's discovery before the nanoparticles "mania" exploded. Great progress had been done on the nanoparticle synthesis and the comprehension of their properties, especially about the optical ones,^{92,93} but incredibly advantages arose from the development of the *microscopy technique*, with the electronic microscopy from the 1930 and the atomic-force microscopy (AFM) in 1966,^{94–98} which opened the possibility for the first time to visualize and, crucially, measure the nanoparticles directly. These breakthroughs paved the way for the first theoretical models linking nanoscale dimensions to changes in the electronic band structure of semiconductors and metals, which in turn explained their novel optoelectronic properties.^{99–102} The success of semiconductor nanoparticles began with two nearly simultaneous discoveries. In 1979, *Yekimov and co-workers* studied the synthesis and characterization of CuCl nanoparticles embedded in a glass matrix. By varying the reaction temperature and heating time, they were able to control the particle size, which in turn altered the optical properties of the glass. Yekimov attributed these changes in absorption to the quantum size effect, or quantum confinement, affecting the exciton, and in particular, to the variation of the Coulombic attraction contribute between electron and hole in a confinement regime.^{103–105} Despite this discovery was remarkable, the nanoparticles were trapped in the glass matrix, limiting further processing. Meanwhile, in 1983, *Brus and co-workers* investigated colloidal nanoparticles and successfully synthesized monodisperse CdS nanoparticles dispersed in a copolymer matrix. They also correlated changes in the nanoparticles' optical properties to the variation of Coulombic interaction due to quantum confinement effects on the exciton.^{106,107} However, the as-synthesized nanoparticles were unstable, degrading within a day. The final piece for the success of colloidal nanocrystals came from the synthesis field in 1993 when *Murray, Norris, and Bawendi* developed the hot injection method to produce nearly monodisperse colloidal CdSe nanocrystals. This approach enabled precise size control and yielded nanoparticles with high optical quality. The colloidal suspensions were stable and easily handled, allowing these semiconductor nanocrystals to be incorporated into devices.^{43,44} These innovations revolutionized colloidal synthesis and their employment, ultimately led to Yekimov, Brus and Bawendi's *Nobel Prize in Chemistry* in 2023.¹⁰⁸

Today, nanocrystals represent one of the foundational elements of modern technology. Advanced synthetic protocols make it possible to produce nanoscale materials from a wide range of metals and semiconductors, not only with controlled composition and size but also with tunable dimensionality. Nanoparticles now find applications across an extraordinary variety of fields, from medicine and healthcare to electronics, energy technologies, materials science, and even aerospace engineering.^{109–115}

1.7 Lead Halide Perovskites

Lead halide perovskites (LHPs) are a class of semiconductor materials that have been widely studied since their first application as LEDs in the 1990s. Their exceptional optoelectronic properties have proven highly valuable across a broad range of applications, including displays, photodetectors, lasers, and, most notably, LEDs.^{16,17,21,109–111} However, despite the rapid expansion of LHP-based optoelectronic devices, it is the field of solar energy harvesting that has experienced the most profound

transformation following their introduction. Since 2009, when Kojima et al. achieved a power conversion efficiency (PCE) of 3.8% using a solar cell based on the organic–inorganic lead halide perovskite methylammonium lead iodide (MAPbI₃), research into perovskite-based photovoltaics has widely expanded.¹⁴ Today, single-junction solar cells employing MAPbI₃ has PCEs exceeds 25%, while hybrid tandem devices combining MAPbI₃ with silicon in triple-junction technologies have achieved record efficiencies exceeding 33%.^{116–119}

Equation 1.12 Expression of Goldschmidt tolerance factor.

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

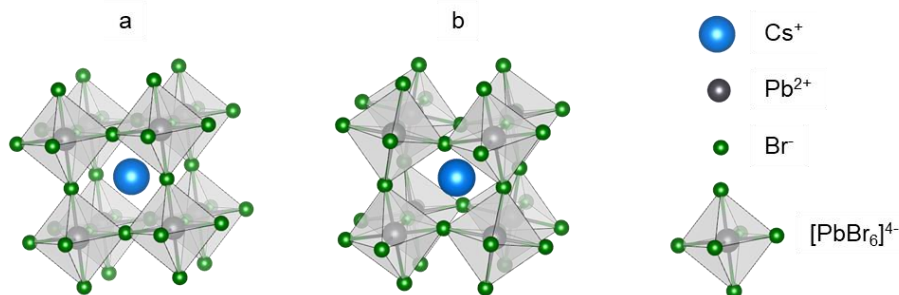


Figure 1.11 (a) Perovskite cubic cell (ICSD 204325) and perovskite orthorhombic cell (ICSD 14608) of CsPbBr₃. Perovskites have the ideal cubic phase when $t = 1$. On the other side, if the Goldschmidt tolerance factor is far from the 1, even in the range 0.9 - 1, the structure assumes a distorted phase, like the orthorhombic one.

Like other materials with a perovskite structure, the crystal lattice of LHPs consists of a three-dimensional network of corner-sharing octahedra. In this case, the framework is formed by [PbX₆]⁴⁻ complexes (X = Cl⁻, Br⁻, I⁻, or their mixtures) connected in all three dimensions. The resulting structure creates large cavities that accommodate monovalent A⁺ cations, ensuring overall charge neutrality. The nature of the A⁺ cation determines the classification of the LHPs: when A⁺ is caesium (Cs⁺) or rubidium (Rb⁺), the material is termed fully inorganic, while the organic–inorganic hybrid class incorporates small organic cations such as methylammonium (MA) or formamidinium (FA). To be incorporated into the crystalline lattice without causing structural destabilization, the cation A⁺ need to respect the *Goldschmidt tolerance factor* (t), expressed by Equation 1.12, where r_A , r_B and r_X are the ionic radii of the A-site cation, B-site cation (LHPs is Pb²⁺), and halide anion, respectively. A value of $t = 1$ corresponds to an ideal and stable cubic phase perovskite structure; for $0.9 \leq t < 1.0$, the crystal is slightly distorted but remains stable, while values of t minor of 0.9 or major of 1 indicate instability of the perovskite structure, in favour of other crystalline phases. Both fully inorganic and organic–inorganic LHPs fall into the slightly distorted range, with approximate $t \sim 0.9$ for Cs⁺, MA and 1.03 for FA as A⁺.^{120–123} Furthermore, the octahedra itself need to be stable. Its stability arises when the *octahedral factor* μ , which is defined as $\mu = r_B/r_X$, must be in the range between 0.442 and 0.895.¹²²

Depending on the degree of distortion, LHPs can crystallize in three polymorphs: the *cubic* and its tilted variants *tetragonal* and *orthorhombic* (Figure 1.11).^{109,122} For LHPs, the

orthorhombic phase is often the most stable at room temperature due to slight distortions induced by the A-site cation, which does not fit perfectly in the cubic lattice.

With the variation of the halide, it is found that the LHPs iodine base present an iodide-based LHPs have Goldschmidt tolerance factors further from ideality than the chloride- and bromide-based ones, resulting in more distorted and less stable structures that decompose more easily, particularly under environmental stress.¹⁰⁹

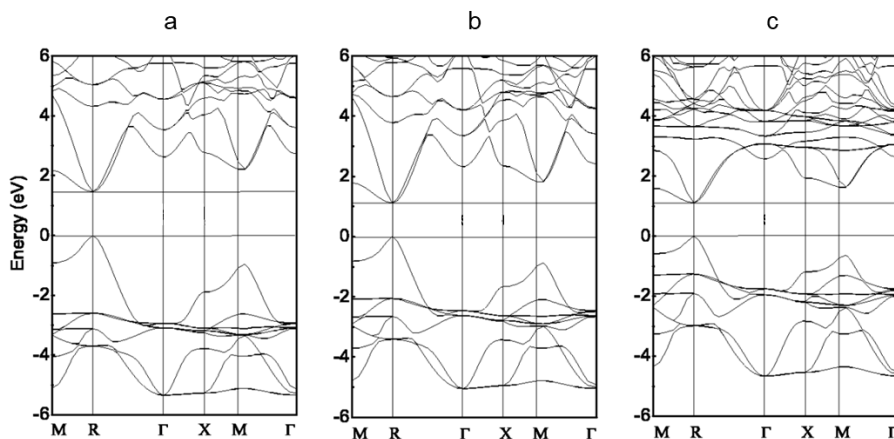


Figure 1.12 Electronic state of (a) CsPbCl₃, (b) CsPbBr₃ and (c) CsPbI₃. The figure displays the influence of the different halides on the electronic states, which slightly varying. Reproduced with the permission from ref.¹²⁶ Copyright © The Korean Physical Society. All rights reserved.

The outstanding optoelectronic properties of LHPs arise from high electron mobility, low trap density, tuneable and high optical absorption coefficient and high emission. These characteristics stem from the electron band structure of these materials (Figure 1.12), which features a direct band gap. The valence band is mainly derived from Pb²⁺ 6p orbital, where the conductive band arises from the overlap between Pb²⁺ 6s and X⁻ np orbital ($n = 3, 4$ or 5 respectively to Cl⁻, Br⁻ or I⁻), with the halide orbitals contributing predominantly. Hence, variations in halide composition leads to deep changes in band structure. The easy *tuneability* of LHPs arise from this behaviour of the electronic states. Therefore, the variation of halide leads to a dramatic change in the optical properties.^{109,124,125}

Among them, “looking” to the luminescence is the easiest way to perceive the tuneability of LHPs, since their emission spectrum lies within the visible region. The variation of the halide component directly determines the emission wavelength: chloride-based perovskites emit in the near-UV or violet region, bromide-based in the green region, and iodide-based in the red or near-IR (Figure 1.13a). Moreover, the ability to easily obtain mixed-halide LHPs, either by incorporating different halide precursors during synthesis or through post-synthetic halide-exchange treatments, particularly in nanocrystals, enables coverage of the entire visible spectrum. The luminescence of LHPs is further characterized by an exceptionally *narrow emission bandwidth*, resulting in highly pure colours, and by short radiative lifetimes, which are advantageous for fast optical response applications. In addition to photoluminescence, these materials also exhibit electroluminescence, produced under electrical excitation. This property explains their first successful

application as LEDs and the subsequent surge of research interest that has followed ever since.^{109,123,124}

Another crucial feature of LHPs is their *defect tolerance*. As discussed in Chapter 1.2, defects in the lattice or at the surface can introduce mid-gap states that usually deteriorate optoelectronic performance. Nevertheless, in LHPs, these defect-induced states tend to lie outside the band gap, either below the VB or above the CB, forming so-called “swallow” bands that do not interfere significantly with charge-carrier dynamics. The overall of the characteristics here described has made LHPs extremely fascinating, especially for the possibility to employ them in diverse field of applications.^{109,125}

Unfortunately, not all that glitters in LHPs is “gold”. Despite their outstanding properties, LHPs face two critical challenges: *environmental instability* and *lead toxicity*. Their high ionic character makes them highly sensitive to polar solvents, which can easily dissolve or degrade the lattice. Moisture accelerates photodegradation and oxidation processes, compromising long-term stability. Moreover, the ionic bonding leads to relatively low lattice energies and melting points compared to oxide perovskites, and this effect intensifies with larger halide ions. The second major issue concerns the intrinsic toxicity of lead. Structural instability exacerbates this problem, as lead is not stable strapped into the crystal can leach out from degraded devices, posing environmental and health risks.^{109,125}

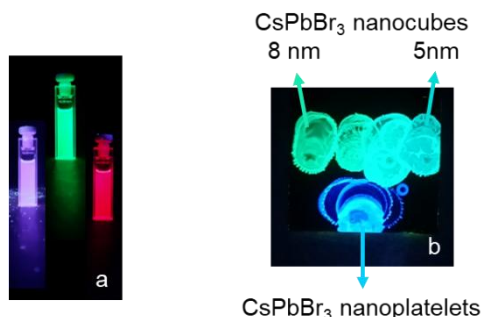


Figure 1.13 (a) Colloidal dispersion of CsPbX₃ (X = Cl, Br, I) nanocubes (NCs). The colour of the emission varying with the stoichiometry of the LHPs; CsPbCl₃ NCs emits in the violet region, the CsPbBr₃ NCs in green and CsPbI₃ NCs have a red emission. In this case, the different emission is given by the differences in the electronic states due to the different halide, as Figure 1.12 shows; (b) drop cast on silica wafer of colloidal dispersion of CsPbBr₃ nanocubes with different dimension, on top of the picture, and nanoplatelets, in the bottom. In this case, the different emission is given by the quantum confinement effect on the nanocrystals. In particular, larger NCs emits in the green region, while smaller ones in the light blue. The blue shift is given by the higher spacing between VB and CB for the quantum confinement effect, as Figure 1.8 shows. The reduction of dimensionality leads also to a changing of colour emission, even if the quantum confinement effect acts only for one side.

Even if the lonely optoelectronic properties would be enough to overcome the drawbacks, the possibility to reduce the LHPs as nanocrystals further improved the interest on them. *LHP nanocrystals* can be prepared with excellent control over shape, size, and dimensionality, especially via colloidal synthesis. Following the pioneering work of *Protesescu et al.* on the synthesis and characterization of LHPs nanocubes in colloidal suspension,¹²⁴ a wide array of different synthetic strategies based on the hot-injection

method (Hinj) have been developed to produce LHP nanocrystals of various compositions, sizes, and morphologies. Since its importance for nanocrystals fabrication, Hinj method will be extensively treated in Chapter 2.3.3.

The *nanoscale dimension* profoundly influences the photophysical behaviour of LHPs, particularly their luminescence. Reduced crystal volume diminishes the possibility of photon-lattice recombination processes, leading to enhanced PLQY. Although nanocrystals possess a high density of surface defects, the intrinsic defect tolerance of LHPs ensures minimal trap-mediated recombination, resulting in emission efficiencies comparable to those of bulk materials. Despite the defect tolerance, LHPs nanocrystals need to ligands which cover the surface and passivate the defect to achieve high values of PLQY.^{122,123} The overall of these characteristics leads to nanocrystals which present high luminescence, with PLQY of 65% for CsPbCl₃, 80% for CsPbI₃ and near 100% for CsPbBr₃.^{122,127–129}

Furthermore, achieving the nano-size enables size-dependent optical tunability through the quantum confinement effect (Figure 1.13b). For example, CsPbBr₃ enters the quantum confinement regime when the particle size is below 7 nm.^{130,131} Even before reaching this threshold, measurable shifts in emission occur. Bulk CsPbBr₃ presents emission as bright green light centered around 540 nm.^{132–134} Going into the nano regime, when the quantum confinement starting to take place, the nanocrystals are in the *weak quantum confinement region*. Thus, between 11 nm and 7 nm, the emission of the nanoparticles variate from 517 nm to 512 nm depending on the size, with higher λ for bigger size.^{64–67} However, the particles can be furtherer reduced, entering in the *strong quantum confinement region*, in which the bandgap increase rapidly with the lowering of the size, translating into a stronger blue shift effect.^{67–69}

A particularly intriguing feature of LHP nanocrystals is their ability to self-assemble into ordered *superlattices* (Figure 1.14) when their size distribution differs by less than 10%, a condition known as *monodispersity*. The LHPs nanocrystals superlattices structural and optical properties, especially of CsPbBr₃ in different morphologies, have been intensively investigated by Toso et al.^{135–139} The ordinate packaging of the nanocrystal is detectable by XRD studies and reveal characteristic distortions corresponding to the superlattice periodicity. Furthermore, superlattices formed by nanocrystals with different dimensionality leads to different XRD patterns. For instance, in nanoplatelets, superlattice peaks often dominate the diffraction pattern, overshadowing almost totally those of the perovskite crystal lattice. The altered XRD pattern gives information on both the distance between the packed nanoplatelets, and then the superlattice itself, by the spacing between these peaks and the thickness of the nanoparticles employed. In fact, superlattice of different nanoparticles lead to different XRD pattern due to a different interaction of the superstructure with the X-ray. Very explicative is the comparison between the patten of CsPbBr₃ as monolayer nanoplatelets against CsPbBr₃ nanocubes. In the first case, the XRD result completely altered and the peaks determined by the (001) and (002) crystallographic crystal plane, which characterizes the phase are quasi-totally overcome by the superlattice pattern. Comparatively, nanocubes exhibit the typical perovskite reflections with only minor superlattice-induced splitting. Increasing nanoplatelet thickness shifts the XRD features progressively toward the nanocubes pattern.^{135–138} Not only the XRD patten is influenced by the superlattice formation, but also the luminescence. Optical studies also reveal slight red shifts in emission upon these superstructures.¹³⁹

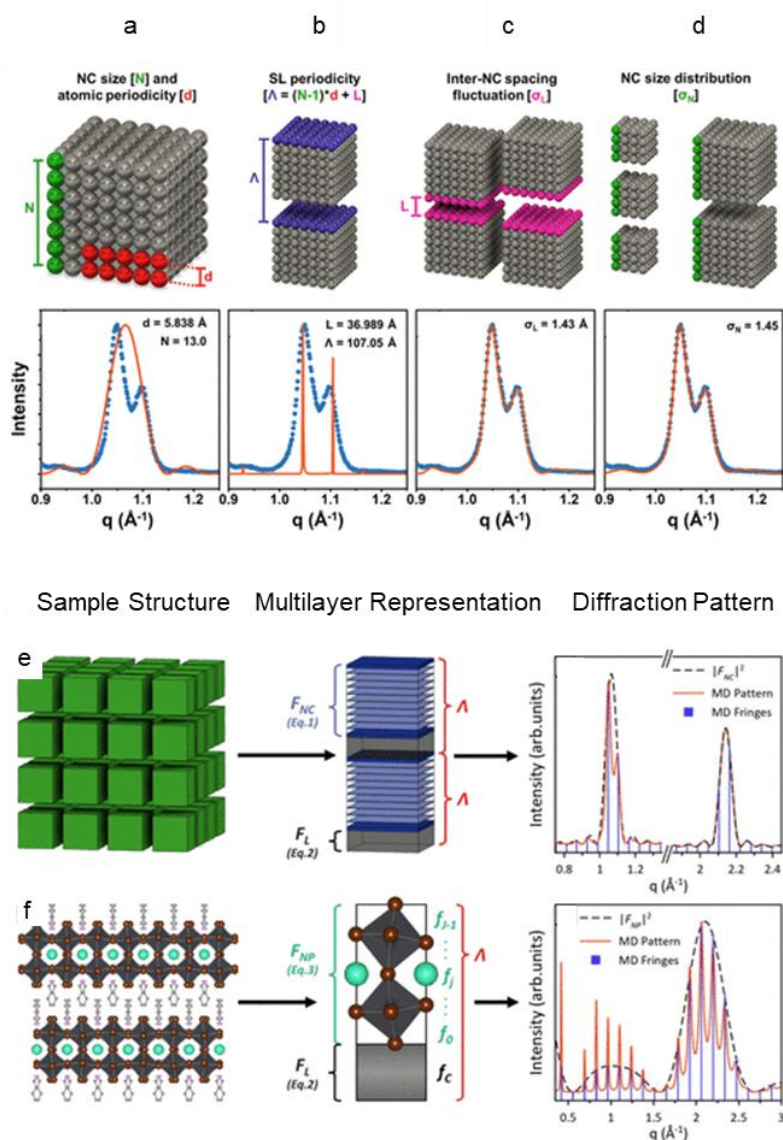


Figure 1.14 XRD pattern of nanocrystals arranged into a superlattice is highly influenced from this overstructure. Over the normal peaks given by (a) the distance d of the planes and their numeric amount N , which determine the position and the intensity, other parameters need to take in account. Owing the high ordering of the superlattice, every nanoparticle can act as repeated unit. Then, planes are formed by nanocrystals through a specific crystal direction and, consequently, their distance Λ can form new peaks. Moreover, (c) the distance between two nanoparticles σ_L , given by the ligand, and the nanocrystals' size distribution σ_N influence the final pattern. Finally, also the morphology has to take in account. In fact, where XRD pattern of thick nanostructure, as (e) nanocubes, is slightly influenced from the superlattice formation, for (f) layered nanoparticles it results highly influenced. Figure 1.14a, b, c, d are reproduced from ref.¹³⁷ under a CC-BY 4.0 license. Copyright © 2021 American Chemical Society. Figure 1.14e, f are reproduced from ref.¹³⁸ under a CC-BY 4.0 license. Copyright © 2022 The Authors. Published by American Chemical Society. All rights reserved.

However, downsizing also exacerbates the intrinsic instability of LHPs. In addition to their ionic internal bonding, the nanocrystal–ligand interactions are also highly ionic. This allows dynamic ligand exchange, leading to an equilibrium between bound and unbound ligands that can leave portions of the nanocrystal surface exposed and prone to degradation.^{42,122,123} The structural role of ligands and their stabilization effects will be discussed in detail in Chapter 2. It is also noteworthy that stability varies across morphologies: nanocubes are generally more robust, whereas nanoplatelets and nanorods tend to lose structural integrity more readily.

1.8 Alternatives to lead halide perovskite

Although lead halide perovskites (LHPs) exhibit marvellous optoelectronic properties, their intrinsic instability and the presence of toxic lead have motivated the search for alternative materials that can offer similar performance while being more stable and environmentally benign.^{140,141} A general strategy involves substituting Pb^{2+} with either homovalent cations, such as Sn^{2+} and Ge^{2+} , or heterovalent ones. The heterovalent category can be further subdivided into the ion splitting, which includes the category of double perovskite, and the ordered vacancies layered perovskite. In the double perovskite, lead is substituted by a pair of cations with valence one and three, resulting in a general stoichiometry of $\text{A}_2\text{B}(\text{I})\text{B}(\text{III})\text{X}_6$. Instead, the ordered vacancies perovskites implement a vacancy ($\square$) inside their lattice, leading to a general formula of $\text{A}_3\square\text{B}(\text{III})\text{X}_9$ or $\text{A}_2\square\text{B}(\text{IV})\text{X}_6$. Unfortunately, both approaches face challenges: homovalent substitution of Pb^{2+} with Sn^{2+} or Ge^{2+} tends to destabilize the crystal lattice, reducing structural integrity, while heterovalent substitutions enhance stability but often compromise desirable optoelectronic properties.¹²⁵

1.8.1 Halide double perovskites

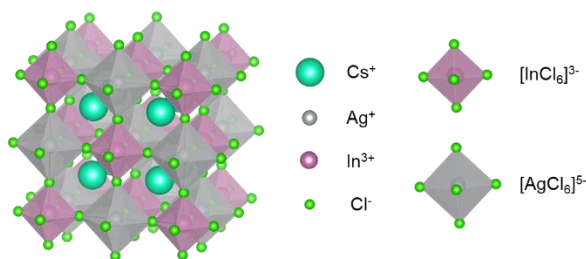


Figure 1.15 Illustration of double perovskite crystal. In particular, $\text{Cs}_2\text{AgInCl}_6$ cubic phase is represented (ICSD number 257115)

As already cited, *halide double perovskites*, also called *elpasolites*, overcome the lead issue of the lead halide perovskites by its replacing with a combination of monovalent B^+ and a trivalent cation B^{3+} . As a result, their general stoichiometry is $\text{A}_2\text{B}(\text{I})\text{B}(\text{III})\text{X}_6$. Similarly to lead halide perovskites, the double perovskite crystal structure is formed by the corner-sharing of $[\text{B}(\text{I})\text{X}_6]^{5-}$ and $[\text{B}(\text{III})\text{X}_6]^{3-}$ octahedra, which are alternately arranged. As in LHPs, A^+ cation occupies the cavities which are formed by conjunction of the octahedra (Figure 1.15). In addition to preserving the perovskite structure, the incorporation of multiple elements into the crystal lattice enables extensive compositional tunability in double

perovskites, while maintaining the Goldschmidt tolerance factor within the range required for perovskite structural stability.^{142–144}

Although halide double perovskites have only recently attracted significant attention, the first report of this crystal structure dates back to 1883, when K_2NaAlF_6 was identified by elemental analysis of rock samples collected in Colorado, USA.¹⁴⁵ On the other hand, the first synthetic double perovskite, $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, was reported in 1922.¹⁴⁶ Since then, a large number of double perovskites have been synthesized and structurally characterized,¹⁴⁷ although it was only between the 1970s and 1990s that interest in the physical properties of this class of materials began to grow, following the discovery of superconductivity in $(\text{Ba}_{1-x}\text{K}_x)_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ and the observation of luminescence in lanthanide-doped double perovskites.^{148–150} However, it is only within the last decade that double perovskite materials with optoelectronic properties have been discovered and promoted as potential substitutes for LHPs.^{151–154} Compared to LHPs, double perovskites generally exhibit superior stability under environmental conditions. Nevertheless, their optoelectronic performance typically remains inferior to that of LHPs. In this context, the vast chemical space accessible through compositional engineering of the double perovskite lattice offers significant opportunities for property optimization. For example, partial substitution of Ag^+ with Na^+ into the $\text{Cs}_2\text{AgInX}_6$ leads to the formation of $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InX}_6$ compositions, which display enhanced photoluminescence properties.¹⁵⁵ Another effective strategy to unlock optoelectronic functionality involves doping with optically active ions such as Cu^{2+} , Mn^{2+} or Bi^{3+} ions.^{155–158} Finally, the compositional versatility of double perovskites has enabled their synthesis in nanocrystalline form, allowing their processing as colloidal suspensions.¹⁵⁹

1.8.2 Chalcohalide semiconductors

Recently, a new class of semiconductors known as *chalcohalides*, materials that contain both halide and chalcogen anions, has attracted significant attention due to a great stability, similarly to the chalcogen perovskite, and similar properties than LHPs. Chalcohalides generally follow the formula MChX , where M represents one or more metal cations, Ch a chalcogen (S, Se, or Te), and X a halogen (Cl, Br, or I).¹⁶⁰

The unique properties of chalcohalides originate from the high dispersive character of the VB and CB due to their peculiar electronic structure given by a high-Z ns^2 levels of $\text{d}^{10}\text{s}^2\text{p}^0$, which lead to high carrier mobility and strong defect tolerance. A key factor underlying these features is the ns^2 electronic configuration of post-transition metal cations such as Bi^{3+} , Sb^{3+} , Sn^{2+} , and Pb^{2+} . This configuration leads to antibonding interactions between cation s and anion p orbitals, resulting in dispersive valence bands, shallow defect states, and enhanced dielectric screening. Consequently, structural and intrinsic point defects mainly induce slow recombination kinetics rather than deep trap formation, conferring remarkable defect-tolerant behaviour similar to that observed in Pb-halide perovskites. Although this concept is widely recognized for chalcohalides, its quantitative understanding remains limited and warrants further theoretical and experimental investigation. Furthermore, chalcohalide structure containing ns^2 cations with lone-pair s electrons exhibit favourable p–p transitions between the occupied anion p orbitals and the unoccupied cation p orbitals, resulting in strong optical absorption and emission. The ability to tune their composition, by varying the metal, chalcogen, and halogen components, enables control over their optical and electronic properties. In fact, the electronic structure depending on the elements which constitutes the final crystal and,

then, the final bandgap, which is typically spread between 0.75 eV and 3.0 eV. Furthermore, chalcogenide materials exhibit high absorption coefficient ($>1 \times 10^5 \text{ cm}^{-1}$) and, usually, an indirect bandgap. However, the difference between direct and indirect transitions is often very small (between 0.02 to 0.1 eV), making chalcogenides promising candidates for a wide optoelectronics and solar energy conversion devices.^{160–163}

Chalcogenide materials, usually characterized by their layered structures, strong anisotropy, and pronounced relativistic effects, have been shown through theoretical and experimental studies to exhibit nonlinear dielectric and piezoelectric properties. Many also display the ferroelectric photovoltaic (FE-PV) effect, where a steady photocurrent or photovoltage is generated along the spontaneous polarization direction without requiring a conventional p - n junction. Uniquely, the photocurrent direction in such materials can be reversed by switching the polarization with an external electric field.¹⁶⁰

As mentioned before, the chalcogenide materials share many properties with LHPs, but differ significantly in terms of stability. Whereas LHPs possess fully ionic lattices, the enhanced stability of chalcogenides arises primarily from the inclusion of chalcogen atoms. To understand this, it is helpful to consider chalcogenide materials with general composition ABCh_3 , where $\text{Ch} = \text{S}, \text{Se}, \text{or Te}$, and A and B are metals whose oxidation states sum to six. In contrast to LHPs, the B-Ch bond exhibits partial covalent character, which increases structural stability but with an increase in enthalpy formation. Similarly, in chalcogenides, the metal-chalcogen covalent interaction strengthens the crystal lattice. Specifically, the chalcogen form a covalent bond with the metal after it donates an electron to the halide. This metal-chalcogen interaction reduces the overall ionic character of the bond, which was the issue for the LHPs stability. Moreover, chalcogens help prevent the oxidation when sensitive cations such as Sn(II) and Ge(II) , further improving material robustness.^{160,162,164,165}

Chalcogenides can be broadly divided into subcategories based on the nature of the cations involved:

- I. Transition/post-transition metal chalcogenide, containing metal owing to the categories of transition or post-transition metal, such as silver (Ag), copper (Cu), tin (Sn), lead (Pb) and other.
- II. Heavy pnictogen chalcogenide, based on bismuth (Bi) or antimony (Sb). Generally, they present a Pnma orthorhombic crystal system and rod or needle-like structure.
- III. Mixed-metal chalcogenide, with general composition $\text{A(II)}_2\text{B(III)Ch}_2\text{X}_3$.
- IV. Hybrid organic-inorganic metal chalcogenides with general formula AB(Ch,X)_3 , where A is a small organic cation, such as methylammonium (MA) or formamidinium (FA), and B a trivalent metal.

A variety of synthetic strategies have been developed to prepare chalcogenide materials, including melt and vapor growth, self-flux, Bridgman, chemical and physical vapor transport, sonochemical, microwave-assisted, colloidal, and solvo-/hydrothermal methods (Figure 1.16). Traditionally, the Bridgman–Stockbarger and vapor growth techniques were the most commonly used. However, these approaches typically require prolonged high-temperature treatments and multiple grinding-annealing cycles. Due to the inefficient solid-state diffusion inherent in these methods, high temperatures and extended reaction times are necessary to obtain the thermodynamically stable phases. To address

these limitations, recent research has increasingly focused on solution-based crystal growth techniques, which offer milder conditions and better control over composition and morphology, as well as the possibility to synthesize them as nanocrystals.^{161,166–169}

Given their compositional diversity, chalcogenides cannot be confined to a single type of application. In fact, they become essential part of devices developed for optoelectronics applications, as well as photocatalysis, detectors, storage, piezoelectric and thermoelectric materials (Figure 1.16).¹⁶¹ Among these, one of the most actively studied areas is solar energy harvesting, owing to their suitable bandgaps, high absorption coefficients, and indirect bandgaps that lie very close to the direct transition. Some mixed-metal chalcogenides, such as $\text{Sn}_2\text{SbS}_2\text{I}_3$, even exhibit direct or quasi-direct bandgaps, making this class of materials particularly promising for next-generation photovoltaic applications.^{162,170,171}

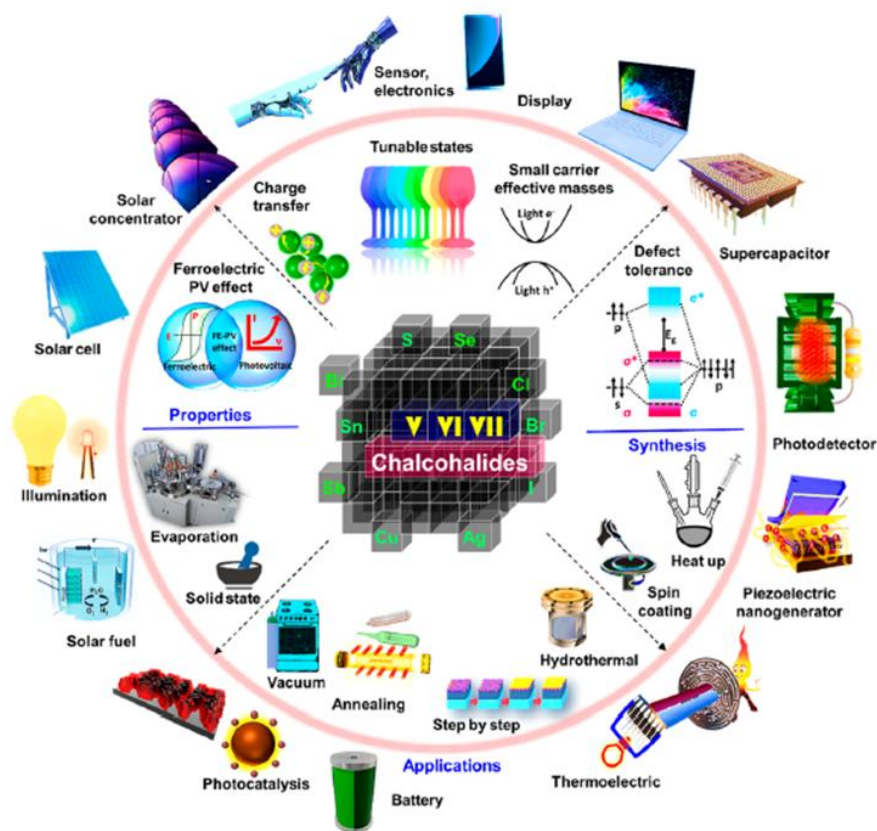


Figure 1.16 Résumé scheme of chalcogenide properties, synthesis and application fields. Reproduced from ref.¹⁶⁰ under a CC-BY-NC-ND 4.0 license. Copyright © 2022 The Authors. Published by American Chemical Society. All rights reserved.

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Chapter II

Colloidal synthesis: a route
to monodisperse
nanocrystals



Chapter II: Colloidal synthesis: a route to monodisperse nanocrystals

Abstract: Nanocrystals' synthesis is a fundamental part for the research on this field. In particular, obtaining monodisperse nanocrystals is crucial for a better comprehension about their properties. Among all the procedures, the colloidal synthesis approach, and in particular the hot-injection method, is the most versatile especially on control of size and morphology on the final nanocrystals. Chapter II brief introduces on the various techniques employed to obtain nanocrystal and then focuses, sequentially, on the colloidal synthesis of nanocrystals.

2.1 A brief overview about the nanoparticles' synthesis

The extensive interest in the properties of nanoparticles and their applications has led to an equally intensive search for techniques capable of producing them. Based on the approach used for nanoparticle production, synthesis techniques can be classified into two main categories: top-down and bottom-up methods (Figure 2.1).

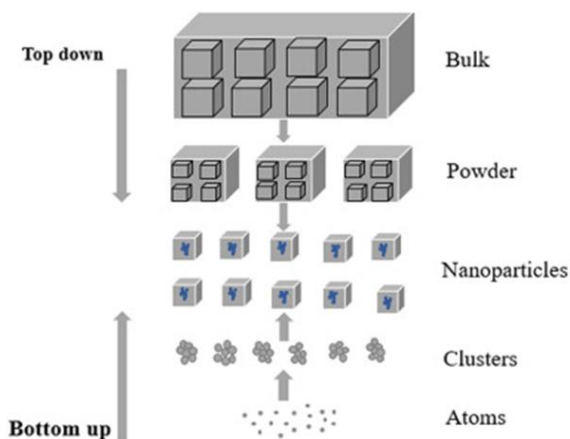


Figure 2.1 Illustration of top-down and bottom-up approach. Reproduced with the permission from ref.¹ Copyright © 2022 Elsevier B.V. All rights reserved.

The term top-down refers to an approach in which larger objects are progressively broken down into smaller ones. Specifically, the *top-down method* involves the fragmentation of bulk or micrometre-sized particles into nanoparticles through various physical techniques, such as ball milling, laser ablation, thermal evaporation, sputtering, and exfoliation (Figure 2.2). In general, this methodology is relatively simple, but control over particle shape and size is limited.

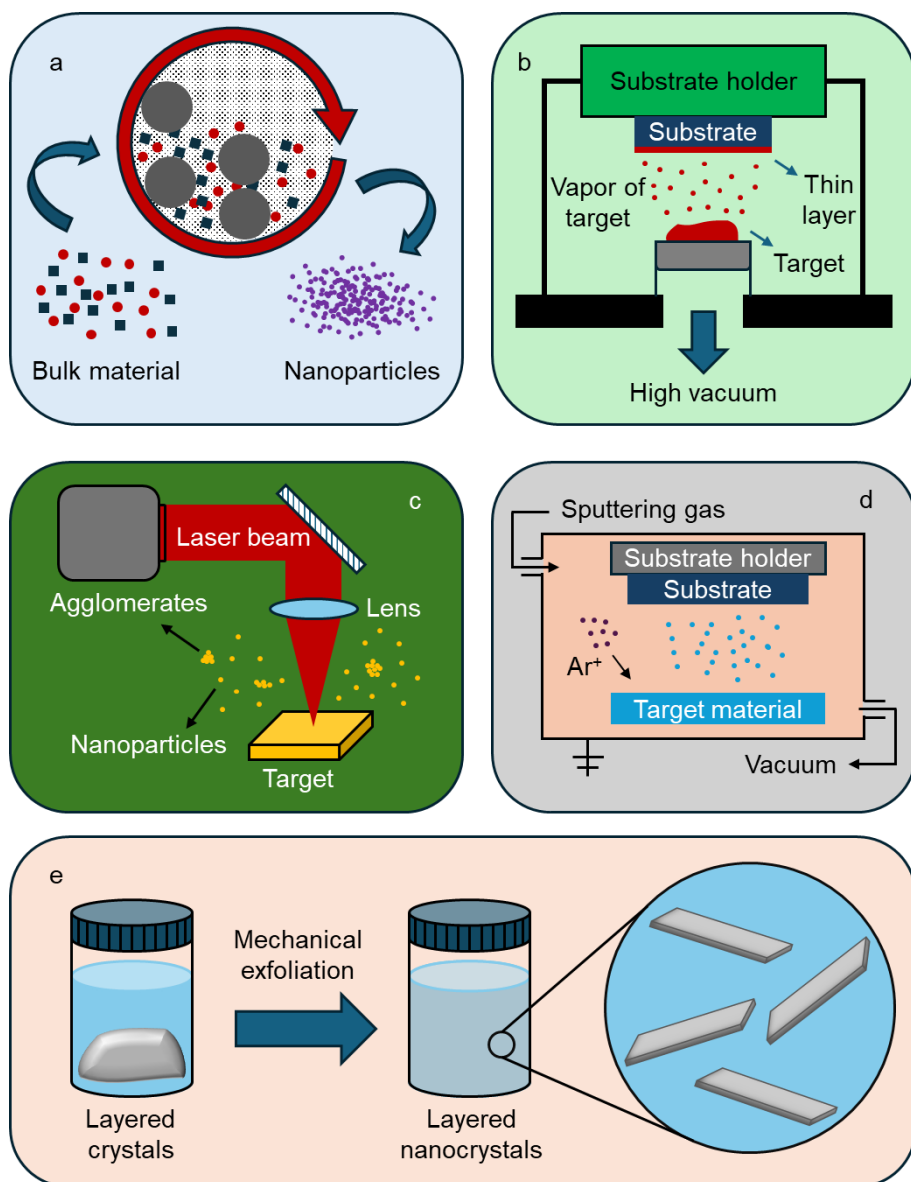


Figure 2.2 Schematization of top-down techniques: (a) ball milling, (b) thermal evaporation, (c) laser ablation, (d) sputtering and (e) liquid-based direct exfoliation. Figure 2.2a, b, c, d are adapted from ref.¹

The reduction of a material to the nanoscale by ball milling occurs through the grinding action of the milling media, typically steel or tungsten carbide balls, acting on the powder placed in the milling chamber (Figure 2.2a). Numerous parameters govern the formation of nanoparticles, including the type of mill used, the nature of the material to be reduced, the ball-to-powder ratio, the milling speed, the temperature, and the milling time. The amount of balls loaded is also critical: insufficient ball density results in a low collision

frequency, whereas excessive loading reduces the free path of ball motion. Due to friction inside the vessel, both temperature and pressure can become high, and ball milling may therefore induce phase transformations or chemical reactions between different powders. The advantages of this technique include its simplicity, versatility, reliability, and safety. However, ball milling can also damage the crystal structure of the powder, generate defects, and introduce impurities. Additionally, the process is energetically expensive.^{1,2}

The thermal evaporation method exploits the evaporation of a material to generate a supersaturated vapour, which subsequently enables the deposition of nanoparticles or, more commonly, a thin film on a substrate (Figure 2.2b). The process is influenced by several parameters, including the furnace temperature, the evaporation time, the source–substrate distance, and the vacuum efficiency of the chamber. The advantages of this technique stem from the high degree of control it provides over both the film or nanoparticle thickness and the deposition environment. However, materials with very high melting points are a significant limitation for this method. Furthermore, products with complex compositions are challenging to synthesize using this method.^{1,3}

The laser ablation technique consists of using a high-intensity pulsed beam of electromagnetic radiation to ablate nanoparticles from the surface of a target material. During the ablation process, the laser beam increases rapidly the temperature at the irradiated spot within an extremely short timescale (10^{-8} s) which leads to melt and vaporize the material. The process ended with the formation of the nanoparticles (Figure 2.2c). Because of the very high temperatures reached during the process, this technique is suitable for a wide range of materials, including metals, ceramics, glasses, and polymers. The characteristics of the nanoparticles produced by laser ablation depend not only on the nature of the target material but also on several operational parameters, such as the laser wavelength, frequency, pulse duration, and repetition rate. Despite its versatility, the technique has several drawbacks. It requires a large amount of energy, and the ablation efficiency decreases over time and as the laser spot size increases, which limits its compatibility with industrial-scale production.^{1,3,4}

The sputtering process involves the generation of gas cations, typically Ar^+ , in a low-pressure atmosphere by applying a high voltage, followed by their acceleration toward the target material, which acts as the cathode. The collision of these ionized gas particles with the target surface causes the ejection of atoms or clusters, which travel through the chamber and condense onto a substrate, forming nanoparticles or a thin film (Figure 2.2d). This technique is comparable to thermal evaporation, although the supersaturated vapour is produced through a different mechanism. For conductive target materials, a direct current (DC) is applied, whereas for insulating materials requires the radiofrequency (RF) voltage to eliminate the surface charge which is formed during the process. Numerous parameters influence the sputtering process, including annealing time, temperature, the relative orientation of the target and substrate, the mass of the bombarding particles, and the level of vacuum. Sputtering is an advantageous technique because it can be carried out at low temperatures and is compatible with a wide range of materials. However, it also exhibits several drawbacks: the purity of the resulting nanoparticles is often limited, a significant portion of the supplied energy is dissipated as heat, and the sputtering rate is generally lower than that achieved by thermal evaporation.^{1,3,4}

Liquid-based direct exfoliation is an effective technique for obtaining layered nanocrystals from a wide variety of materials (Figure 2.2e). The method consists of

removing the superficial layers of a bulk material using a mechanical energy source, such as stirring or ultrasonication, within a liquid medium, typically water, an organic solvent, or an ionic liquid. To facilitate exfoliation, intercalating agents are often employed; these species insert themselves between adjacent layers of the bulk material, weakening the interlayer forces. In addition, surfactants are commonly used to stabilize the resulting nanosheets within the solvent. This technique is highly versatile and scalable, enabling the production of nanosheets from many different materials and in significant quantities. However, it also presents several drawbacks, including limited control over nanosheet thickness and generally low conversion efficiency from the starting bulk material to exfoliated nanosheets.⁵

Bottom-up techniques follow a philosophy opposite to that of top-down methods. In these approaches, nanoparticles are formed through the assembly of atoms, molecules, or ions (Figure 2.3).

Supersaturated vapour synthesis is a method in which nanoparticles, and in particular 2D materials, are formed through the reaction of gaseous reagents with a heated substrate. After the precursors are introduced into the reactor, they may either diffuse directly to the surface of the heated substrate or undergo homogeneous gas-phase reactions, generating intermediate species and by-products that subsequently diffuse to the substrate surface (Figure 2.3a). The thickness of the resulting nanomaterial increases through the continuous deposition of new layers. Unlike exfoliation, the number of layers, their lateral size, and their morphology can be precisely controlled by adjusting the reaction parameters. It is also possible to employ a catalytic surface inside the reaction chamber to promote the formation of intermediate species, which then deposit onto the substrate. Typical temperatures used in this synthetic protocol range from 300 °C to 1000 °C. This method enables the production of high-purity nanoparticles or thin films with fine control over their crystalline properties and morphology. However, the process is limited by its high cost, the use of toxic, flammable, or explosive reagents, and the potential formation of hazardous gaseous by-products, which collectively reduce its practicality and availability.^{1,6,7}

Hydrothermal synthesis is a wet-chemical process in which solid precursors react in an aqueous medium to form nanoparticles (Figure 2.3b). The reaction takes place inside an autoclave under high temperature and pressure. The standard protocol consists of three main steps:

- i. preparation of the reaction mixture by dissolving or dispersing the precursor;
- ii. hydrothermal treatment in the autoclave;
- iii. purification by centrifugation and washing, followed by drying.

The morphology of the final material depends strongly on the hydrothermal conditions, particularly on the solvent used and on the reaction temperature and pressure, which influence both nucleation and crystal growth. By finely tuning these parameters, nanocrystals with high crystallinity and precise size control can be obtained. However, the technique has several drawbacks: the reaction cannot be monitored in real time, and the equipment required for hydrothermal synthesis is relatively expensive.^{1,8,9}

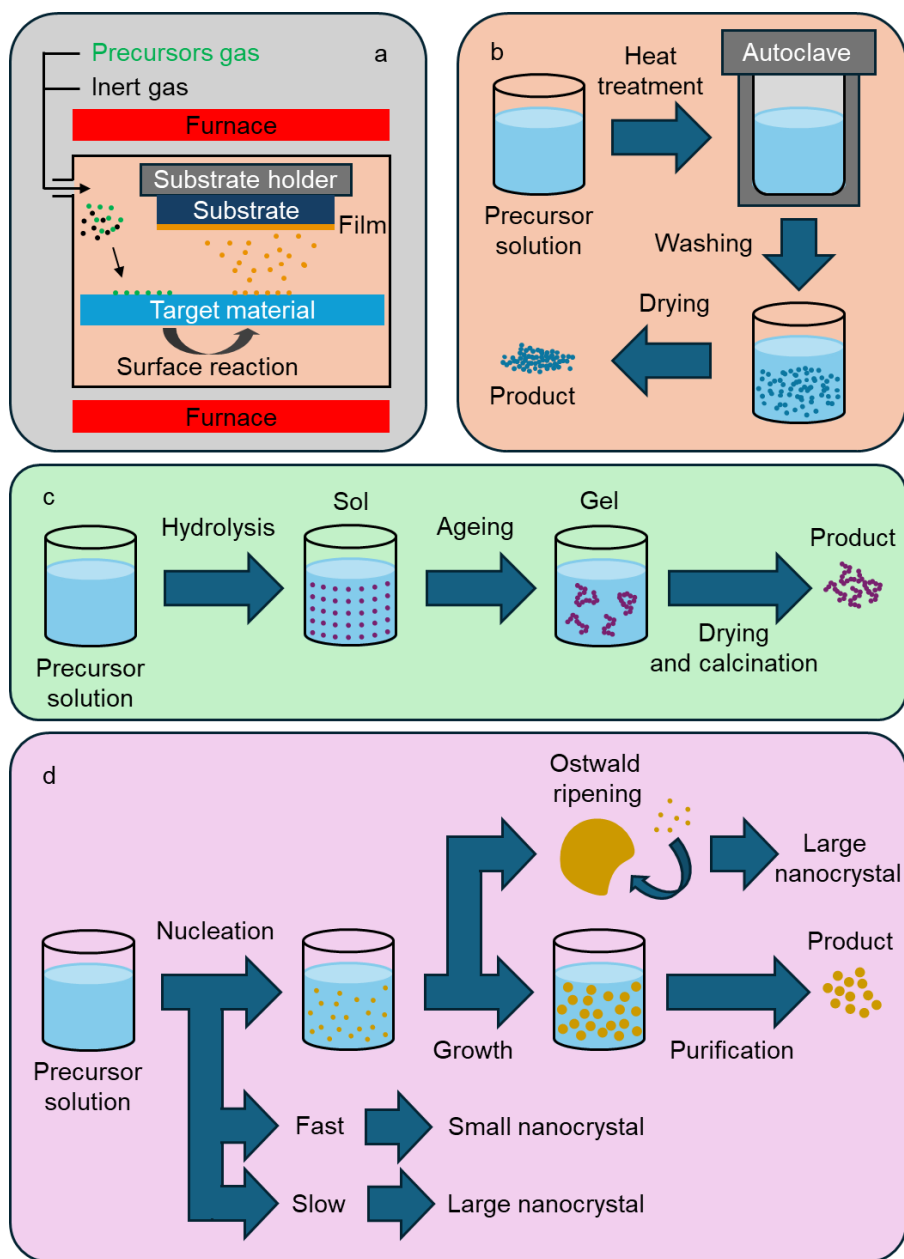


Figure 2.3 Schematization of bottom-up techniques: (a) supersaturated vapour synthesis, (b) hydrothermal synthesis, (c) sol-gel synthesis and (d) colloidal synthesis. Figure 2.2a, b, c, d are adapted from ref.¹

The sol-gel method is a simple and versatile approach for synthesizing nanoparticles and thin films (Figure 2.3c). The process begins with the formation of a sol, a colloidal suspension of reagent particles dispersed in a solvent, which subsequently transforms into a gel, a network of metal-oxide macromolecules. As polycondensation progresses, these

macromolecular species grow and eventually precipitate. The procedure continues with a drying step, which may be carried out by thermal-, supercritical- or freeze-drying methods. Finally, the nanoparticles are calcined to remove residual solvent and any remaining impurities. Each stage of the process, as well as several experimental parameters, significantly influences the properties of the final material. This technique is low-cost, highly tunable, requires relatively low temperatures, and generally yields products of high purity. However, it also presents limitations: reaction times are often long, purification steps are required, and organic compounds are commonly used, which may introduce health risks.¹

Finally, *colloidal synthesis* represents the main approach for producing colloidal nanoparticles (Figure 2.3d). This methodology will be described in detail in Chapter 2.3, as it constitutes the synthetic strategy underlying the entire PhD thesis.

2.2 Colloidal nanoparticles: between inorganic and organic chemistry

Colloidal nanoparticles represent a fascinating marriage between inorganic, physical and organic chemistry. Indeed, they consist of an *inorganic core* surrounded by an *organic shell*, which unlock *new properties* for the material (Figure 2.4). In this system, both components play a crucial role in determining the overall properties of the material.

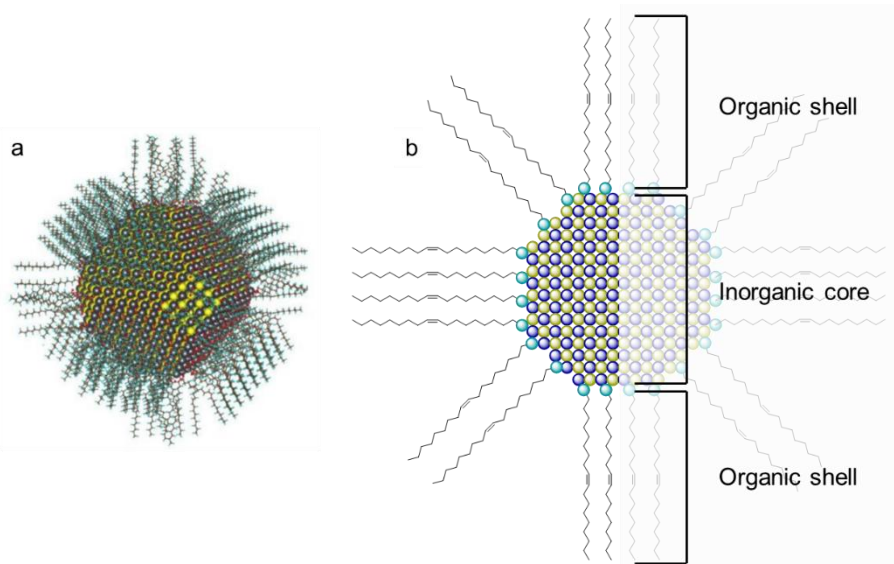


Figure 2.4 (a) Colloidal nanoparticles and (b) its trasversal section illustrations. Figure 2.4a reproduced with the permission from ref.¹⁰ Copyright © 2014, American Association for the Advancement of Science. All rights reserved. Figure 2.4b adapted from ref.¹¹

2.2.1 The inorganic core

The inorganic core constitutes the major part of the nanocrystal. Generally, it retains the stoichiometry of the corresponding bulk crystal, but at the nanoscale. Consequently, the properties of the resulting nanocrystals strongly depend on the electronic structure of the initial material, aside from quantum confinement effects.^{1,12–15} For example, colloidal

suspensions of CsPbCl_3 , CsPbBr_3 , and CsPbI_3 nanocubes emits violet, green and red light, respectively.¹⁶ Furthermore, in some cases, the stoichiometry can also change, as observed in layered nanoparticles.¹⁷ The composition of the nanocrystal core can be binary, ternary, or, in rare cases, quaternary.^{14–16,18–23} Additionally, alloying or doping can be employed to further tune the properties of the nanocrystals.^{24,25}

It is important to clarify the use of the term “inorganic.” In this chapter, “inorganic core” refers to the central part of the nanocrystal and is used to distinguish it clearly from the organic shell. Nevertheless, the core may also contain small organic cations, such as methylammonium (MA) or formamidinium (FA) in the case of LHP NCs.

2.2.2 The organic shell

The organic shell is formed by the binding of *organic ligands* to the surface of the nanocrystal. In general, ligands are organic molecules composed of a polar head group and an apolar tail. The alkyl portion of the tail is typically long, ranging from 8 to 18 carbon atoms. Common ligands include amines, carboxylic acids, phosphines, phosphine oxides, and thiols. Among these, *oleylamine* (OLAM) and *oleic acid* (OLAC) are the most frequently used in nanocrystal synthesis, but also trioctylphosphine (TOP), trioctylphosphine oxide (TOPO) and 1-dodecanethiol (1-DDT) are largely used. Other molecules can be attached to the nanocrystal surface, usually through post-synthesis treatments, in a process commonly referred to ligand-exchange.^{16,18–22,25–33}

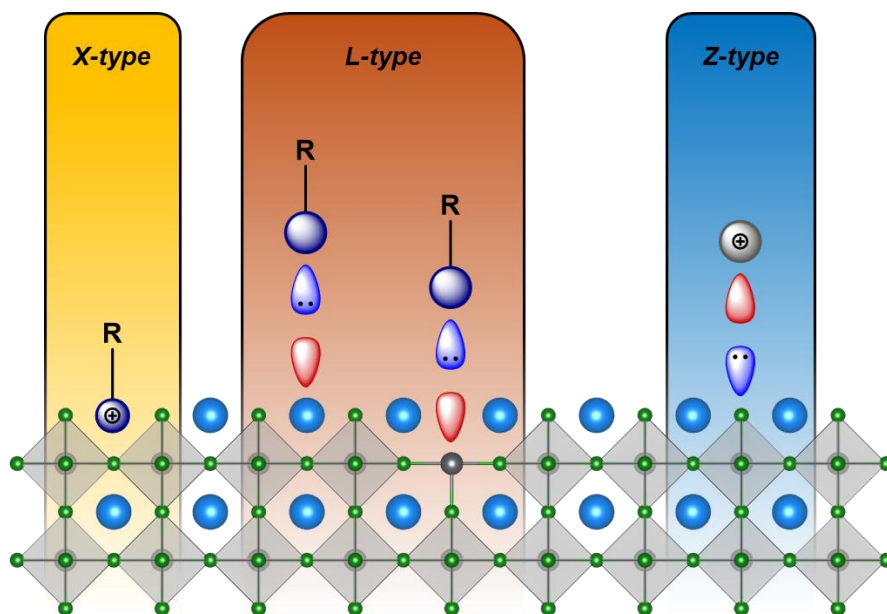


Figure 2.5 Illustration of ligands cataloguing on the basis of the surface-binding mode. In particular, it is explicit how the X-type ligands take the vacancies left, where both the other ligands interact using the lone pairs, given from the ligand in L-type ligands and from the ions of the crystal for Z-type ones.

Ligands can be classified into three groups based on the way they bind to the nanocrystal surface (Figure 2.5). L-type ligands are neutral molecules that act as Lewis

bases. They coordinate to surface metal atoms by donating a lone pair of electrons; common examples include amines and phosphines. *X-type* ligands are ionic species that bind to the surface as ion pairs, effectively replacing ionic species in the crystal structure. Examples of *X-type* ligands include ammonium carboxylates or ammonium halides, such as dodecyltrimethylammonium chloride (DDAC) or bromide (DDAB). *Z-type* ligands are neutral molecules that act as Lewis acids. They bind to the surface by accepting a lone pair of electrons from non-metal species on the nanocrystal. *Z-type* ligands are generally metallic or organometallic species, such as Na^+ , K^+ , $\text{Pb}(\text{RCOO})_2$.^{11,34}

The first function of the ligand is during the nanocrystal formation by bind the crystal surface during its growing. This event *restricts the expansion* of the crystal, thereby limiting further growth. After the nanocrystals' isolation, the organic shell contributes significantly to the *colloidal* and *structural stability* of the nanocrystals. However, the role of ligands extends beyond protection and stabilization, they are also crucial for enhancing nanocrystal properties by acting as *surface passivators*. As discussed in Chapter I, most defects in nanocrystals originate at the surface, often giving rise to electronic trap states. Given the high surface-to-volume ratio of nanocrystals, the abundance of surface defects can substantially degrade their functional properties. By binding to the surface, ligands fill these defects, mitigating trap states and thereby improving the quality of the final material. Complete passivation of a nanocrystal is challenging, as different facets may expose different atoms or ions. For this reason, a combination of ligands is often employed during synthesis. For example, in the synthesis of lead halide perovskite nanocrystals (LHP NCs), a mixture of OLAM and OLAC is commonly used. Moreover, due to the distinct chemistry of different facets, controlling ligand interactions during synthesis can also influence nanocrystal morphology.^{11,35,36} The topic of morphological control will be discussed in detail in Chapter 2.3.

Unfortunately, the ligands commonly used during synthesis often act as electrical insulators, which results in poor charge-carrier mobility and reduced performance, particularly in applications such as solar energy harvesting. To overcome this limitation, the native ligands are typically replaced with shorter ligands and/or ligands containing conjugated polyenes or aromatic groups. This process, known as *ligand exchange*, is generally performed by dispersing the synthesized nanoparticles in a solvent, such as hexane or toluene, in the presence of the new ligands. Exchange occurs in this medium, after which the nanoparticles are collected by adding an antisolvent and purified. This protocol has some critical challenges, including the risk of modifying or damaging the nanoparticles and the possibility of incomplete ligand substitution. Nevertheless, in many cases, the procedure leads to significant improvements in the functional properties of the nanocrystals.^{31,34} Furthermore, ligand exchange allows for the introduction of specialized functionalities; for example, chiral ligands, such as chiral amines or amino acids, can impart chiral properties to the nanocrystals.^{30,37,38} This topic will be discussed in detail in Chapter VI.

2.3 Colloidal synthesis

Colloidal synthesis is an effective approach for colloidal nanoparticles with a *good size distribution* and *morphology control*. The process begins with the dissolution of suitable precursors and ligands in a high-boiling, apolar organic solvent, which can be classified as either coordinating or non-coordinating depending on whether it can act as a ligand or

is chemically inert. Common solvents used in these reactions include TOPO, hexadecylamine (HDA), octadecene (ODE), dioctyl ether (DOE), and diphenyl ether (DPE).^{25,39–41} The reaction proceeds through the initial formation of monomers, which subsequently nucleate to form nanoparticle seeds. Growth continues as additional monomers are incorporated until the nanoparticles reach the desired size. The reaction is then quenched by lowering the temperature, followed by purification of the nanocrystals and their redispersion in an appropriate solvent, such as hexane or toluene.³⁶

The colloidal synthesis reaction can be divided into three main steps: (i) *formation of nuclei*, (ii) *nanoparticles growth* and (iii) *quenching* (Figure 2.6a). The first step occurs when the concentration of monomers reaches the *critical saturation concentration* (S_{crit}). At this stage, the nuclei can revert to monomers. However, when the monomer concentration reaches the *supersaturation level* (S_{sup}), the nuclei become unstable toward growth rather than disintegration. During the growth phase, nanoparticles initially increase in size through the incorporation of free monomers from the reaction mixture, which leads to a rapid decrease in monomer concentration. As the monomer concentration declines, growth continues via *Ostwald ripening*, also known as Lifshitz–Slyozov–Wagner (LSW) growth, where larger nanoparticles grow at the expense of smaller ones. This process becomes significant when the monomer concentration approaches the *minimal saturation concentration* (S_{min}). Throughout nucleation and growth, ligands act as capping agents. They dynamically bind and release from the nanocrystal surface, providing both chemical and colloidal stability to the nanoparticles. Finally, the reaction is terminated during the quenching step achieved by lowering the temperature to prevent further growth and purify the nanocrystals.³⁶

From a physicochemical perspective, the formation of nanocrystals can be described by *classical nucleation theory* (CNT). This theory states that the overall entropy of the system is lowered with the crystal formation and growth, leading to a decrease in Gibbs free energy (ΔG), as expressed in Equation 2.1. ΔG is composed by two contributions: the Gibbs free energy of the bulk (ΔG_v) and surface formation (ΔG_s). These two terms are in contraposition, where the ΔG_v diminishing the total ΔG , the ΔG_s have the opposite effect. In the Equation 2.1, r is the radius of the particle, ρ its density, $\Delta\mu$ the difference in chemical potential between monomers and nuclei, γ is the surface area energy. Since both ΔG_v and ΔG_s refer to the same particle, r is the same in both terms. Changes in r affect both ΔG_v and ΔG_s . Due to the higher magnitude of r into ΔG_v , the increasing of r causes a more rapid increase of the term which stabilize the system. Therefore, the threshold between nuclei dissolution and particle formation is determinate by a particular value of radius (Figure 2.6b), called *critical radius* (r_c), expressed in Equation 2.2 where k_b is the Boltzmann constant, T is the temperature and S is the entropy.^{11,36}

CNT explains how crystals form, but understanding why their size remains in the nanometre range requires a closer look at the synthesis process. In general, the final crystal size depends on the number of nuclei formed relative to the amount of monomers in the solution. If the number of nuclei is low compared to the monomer concentration at S_{sup} , each nucleus can incorporate a large number of monomers before the system reaches S_{min} , resulting in larger crystals. On the contrary, when the number of nuclei is high relative to the monomers, individual nuclei cannot grow excessively. Furthermore, S_{min} is reached quickly due to the rapid depletion of monomers. Therefore, achieving nanocrystal sizes requires the formation of a large number of nuclei at S_{sup} . Moreover, the

rapid decrease in monomer concentration also explains why colloidal synthesis produces a narrow size distribution. This is achieved if all the nuclei grow for approximately the same duration. To maintain this uniformity, multiple nucleation events must be avoided, which would otherwise occur if a high monomer concentration were sustained over an extended period.¹¹

Equation 2.1 Gibbs free energy for crystal formation

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

Equation 2.2 Critical radius equation

$$r_c = -\frac{2\gamma}{\rho k_b T \ln S}$$

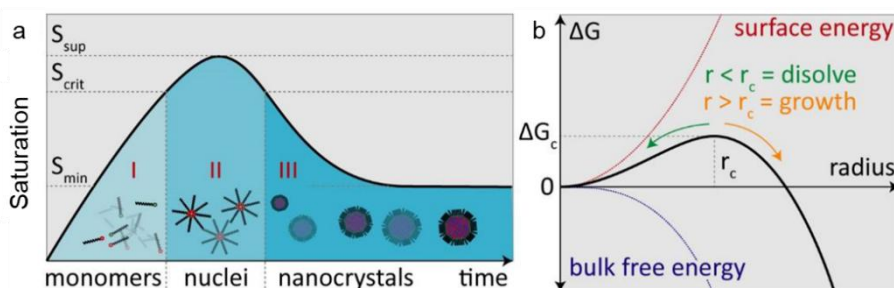


Figure 2.6 Graphs of (a) the colloidal synthesis stadium reported with time vs monomers concentration and (b) behaviour of the nuclei in function of the radius. Reproduced from ref.¹¹

A high number of nuclei can be achieved through two different approaches: by separating the nucleation and growth steps, as in the *ligand-assisted re-precipitation method* and the *heating-up method*, or by inducing a nucleation burst, as occurs in the *hot-injection method*. These synthetic strategies will be discussed in detail in Chapter 2.3.1, 2.3.2 and 2.3.3, respectively.

Finally, the quenching and subsequent purification steps also play an important role in determining the nanocrystal size. In particular, Ostwald ripening can lead to the growth of larger particles if the nanoparticles remain in the reaction mixture for too long. Therefore, separating the nanoparticles from the growth solution before the monomer concentration reaches S_{min} is crucial to maintain the nano-size and uniformity.¹¹

A key advantage of colloidal synthesis is the ability to *control crystal morphology* in addition to size. During growth, crystals develop specific facets to minimize the overall free energy, ultimately determining their final shape. This principle forms the basis of shape control in nanocrystals. The equilibrium shape of a crystal is typically achieved under conditions governed by thermodynamics. However, alternative shapes can be obtained by employing specific synthetic strategies that modify the growth kinetics.¹¹

The thermodynamically predicted shape of a material does not necessarily reflect the actual pathway of crystal growth, which is driven by the minimization of free energy at each growth step. This means that crystal growth can initiate on facets that are not dominant in the thermodynamic equilibrium shape. Consequently, the morphology of a crystal grown under kinetic control can be markedly different from the thermodynamic shape. Kinetic control is typically achieved by performing the synthesis under conditions that favour a high growth rate.

Since crystal facets are determined by the underlying crystal lattice, the lattice structure plays a crucial role in defining the final shape of the nanocrystals. For example, the wurtzite structure of CdSe enables the formation of rod-shaped and tetrapod-shaped nanocrystals. However, this parameter is material-specific and can therefore be applied only to the studied systems, as changing the material also alters the crystal lattice and, consequently, the facets along which the nanocrystal can grow.

The chemistry of ligands plays a crucial role in determining the shape of the final nanocrystal. As described in Chapter 2.2.3, different crystal facets exhibit varying affinities for ligands. This affinity depends both on the specific facet and on the nature of the ligand, including the functional group that binds to the nanocrystal surface, but also the length or structure of the carbon chain. The result is a differential stabilization of the crystal facets: facets that are more strongly stabilized by ligands grow more slowly, whereas less stabilized facets are freer to expand. Consequently, crystal growth preferentially occurs along these less stabilized facets, shaping the final morphology of the nanocrystal.

Morphology control can also be achieved through the use of templates that direct nanocrystal growth into a predetermined shape. These templates can be physically created using lithography techniques or formed by surfactants that assemble into micelles, creating nanoscale confined spaces where the reaction takes place.^{11,42–44}

Finally, the oriented attachment of small nanoparticles during synthesis can lead to the formation of nanocrystals with distinct shapes. This approach exploits the natural tendency of nanocrystals to minimize high-energy facets through auto-assembly, resulting in larger structures with controlled morphology.

2.3.1 Ligand-assisted re-precipitation (LARP) method

Supersaturated recrystallization is a well-established technique in which a crystallization solution is prepared by dissolving the desired ions in a solvent until saturation is reached. At this point, the equilibrium solution is destabilized to achieve supersaturation, thereby triggering the crystallization process, which continues until a new equilibrium is established. In general, destabilization can be achieved through various methods, such as lowering the temperature, evaporating the solvent, or altering the solution polarity by adding a so-called antisolvent. LARP technique (Figure 2.7) falls within this category. Its distinguishing feature is the addition of ligands to the ion solution, which bind to the surface of the forming nanocrystals and inhibit further growth. The typical LARP procedure involves dissolving the ions and ligands in an appropriate solvent, followed by solution dropping into an antisolvent. The rapid mixing generates instantaneous supersaturation followed by nucleation and growth step.^{34,35}



Figure 2.7 Illustration of LARP process. Reproduced with the permission from ref.³⁴ Copyright © 2021 Wiley-VCH GmbH. All rights reserved.

In LARP, control over nanocrystal size and morphology can be achieved by optimizing reaction conditions, such as the choice of antisolvent, the solvent–antisolvent mixing temperature, and the concentration and chemical structure of the ligands. For example, in the synthesis of LHP nanocrystals, it has been observed that using alkylammonium ligands with longer carbon chains provides stronger surface passivation due to enhanced electrostatic interactions, promoting preferential vertical growth of the nanocrystals.

Owing to its simplicity, reproducibility, and scalability, LARP is a highly useful technique for producing nanocrystals, particularly in industrial applications. However, the incomplete separation between nucleation and growth steps can result in a broader size distribution. The modified emulsion LARP method can help address this issue. In this approach, the ion and ligand solution is mixed with a non-miscible apolar solvent to form an emulsion. Nucleation occurs as a burst, and subsequent growth of the nuclei begins when a demulsifying solvent is added. Despite this improvement, residual polar solvents may remain after purification, leading to two potential issues: first, the structure of the nanocrystals may be destabilized, and second, the intrinsic toxicity of these solvents may pose safety concerns.

2.3.2 Heating-up method

The heating-up method (Figure 2.8), also known as the non-injection method, is based on heating a reaction mixture containing precursors and ligands in a high-boiling, apolar solvent. The key principle of this method is the temporal separation of nucleation and growth, which occurs at different temperatures. To ensure reproducibility, nucleation must not occur at room temperature. The course of the heating-up reaction can be divided into distinct stages over time.^{45,46}

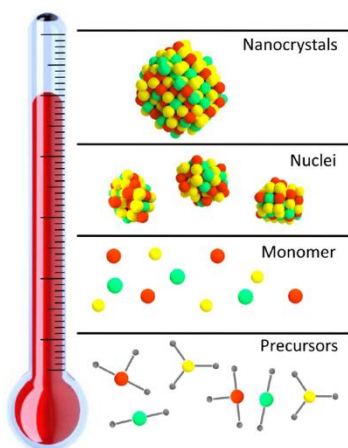


Figure 2.8 Illustration of heating-up process. Reproduced with the permission from ref.⁴⁵ Copyright © Published 2015 by the American Chemical Society. All rights reserved.

The first stage involves the formation of monomers from the precursor, either as free species or coordinated by ligands, during the heating of the reaction mixture up to the growth temperature.

The second stage is characterized by nucleation, which occurs as the temperature rises. During this stage, the concentration of nuclei increases until it reaches a maximum. The nucleation rate generally increases with temperature. Forming a large number of nuclei at this stage is crucial for obtaining nanoparticles of nanoscale dimensions. In addition to nucleation, moderate growth of the nuclei also occurs. As a result, this stage is typically associated with a relatively broad size distribution.

Once the growth temperature is reached, the growth stage begins. This stage is characterized by a decrease in the concentration of nuclei as they incorporate monomers diffusing onto their surfaces to form nanoparticles. During this stage, early time ripening occurs, in which the smallest clusters dissolve. As a result, the size distribution of the nanoparticles begins to narrow.

The equilibrium stage is characterized by the dissolution of the remaining small clusters, leading to stabilization of the nanocrystal concentration, size, and size distribution. During this stage, the reaction mixture is typically cooled to prevent further Ostwald ripening, followed by the purification and collection of the nanocrystals.

Because nucleation and growth steps are not perfectly separated, several experimental parameters must be carefully controlled to achieve a narrow size distribution. Among these, the heating rate and the selection of appropriate precursors are particularly critical.

The heating rate directly affects monomer formation. A slow heating rate results in gradual monomer formation, which can continue even during the growth stage. This overlap between nucleation and growth leads to a broader size distribution. Conversely, a rapid heating rate produces monomers quickly, which are then simultaneously converted into nuclei. These nuclei begin to grow at roughly the same time, causing a rapid depletion of monomers. Under these conditions, the resulting nanoparticles are smaller and exhibit a narrower size distribution.

The choice of precursors has a significant impact on monomer formation and, consequently, on the outcome of the reaction. Highly reactive precursors generate monomers too quickly, leading to immediate nucleation. As monomer production continues, new nuclei form while the previously formed nuclei are already growing. This results in a low concentration of small nanocrystals and a broad size distribution. On the other hand, poorly reactive precursors also present challenges. In this case, monomer formation begins at higher temperatures, delaying nucleation and prolonging its duration. Since the stability of the precursors, an equilibrium between monomers and precursors is instituted. This prolongs in the time the nuclei formation. Then, in the growth stage, few nuclei are survived in the solution, and monomers continued to form. This culminates with the formation of low large nanoparticles concentration with broad size distribution.

In contrast, moderately reactive precursors allow monomers to form at an optimal rate. This ensures a clear temporal separation between nucleation and growth, producing a high concentration of small nanocrystals with a narrow size distribution.

2.3.3 Hot-injection (Hinj) method

The first report of Hinj method was published in 1993 for the synthesis of CdCh (Ch = S, Se) nanocrystals.²⁰ The significance of this work lay in the ability to control nanocrystal size and achieve a narrow size distribution, marking a breakthrough in colloidal synthesis. This discovery sparked significant interest in the scientific community and enabled the preparation of *high-quality nanocrystals*, which facilitated a deeper understanding of their physical properties and transformations arising from quantum confinement. Furthermore, the technique resulted suitable for reducing at nano-size various materials, such as group IV, IV-VI and III-V semiconductors and metal-oxide. Among them, the reduction to nanocrystals of LHP by *Protesescu et al.*¹⁶ work with an excellent control on the size and its distribution had particularly importance due to the extraordinarily optoelectronic properties of this material. Additionally, a morphology control was discovered by the changing of the parameter, allowing systematic studies of how size and shape affect physical properties. Moreover, the possibility of obtaining materials with different size and shape had a great impact on the application. Nowadays, colloidal nanocrystals are principally employed in light emitting diodes (LEDs) and biological labelling, but varying applicative research fields are on these materials. Among them, the ones concern laser, detectors, solar cells and luminescent solar concentrator are very prosperous. The high interest toward colloidal nanocrystals, and then colloidal synthesis, with a particular mention on Hinj method, conducts Mounji G. Bawendi, Louis E. Brus and Aleksey Yekimov to be awarded with the *Nobel Prize in Chemistry 2023*.^{47,48}

Hinj method (Figure 2.9) holds particular importance in this thesis, as it is used for the synthesis of all the (nano)crystals discussed in the following Chapters. As the name suggests, the method involves the injection of one or more precursors into a reaction mixture at relatively high temperatures. The procedure begins with the dissolution of all precursors, except those intended for later injection, together with ligands in a high-boiling apolar solvent. The reaction mixture is heated to a well-defined temperature, typically between 90 °C and 300 °C. The maximum temperature of 300 °C is determined by the boiling point of the organic solvent typically used in this procedure. Once all the precursors are fully dissolved, the remaining precursor(s) are injected into the hot solution. Unlike the heating-up method, in which the reagents are mixed before the starting of the heating, in the hot-injection reaction the mixture is finalized by the injection of the precursor at the

target high temperature. The injection induces an instantaneous nucleation burst, generating a large number of nuclei within a few seconds. This rapid nucleation drastically reduces the monomer concentration, effectively terminating the nucleation step and initiating the growth of nanoparticles via monomer diffusion onto their surfaces. Subsequently, the reaction is quenched, and the nanocrystals are purified and resuspended to yield a stable colloidal solution.^{11,36}

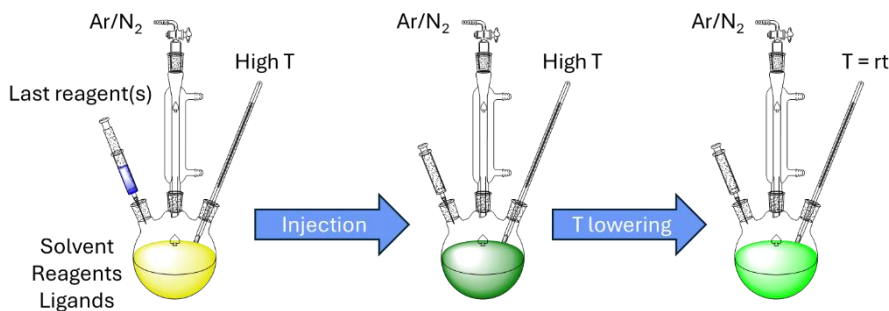


Figure 2.9 Illustration of Hinj process.

Generally, the Hinj produces nanocrystals with a narrow size distribution due to the clear temporal separation between nucleation and growth. The injection step is critical, as a non-perfect injection can result in multiple nucleation events. Additionally, it is essential to quench the reaction while it is still in the size-focusing regime, when the monomer concentration remains sufficiently high to promote uniform growth.^{34,35}

Equation 2.3 Equation of classical nucleation theory

$$\frac{dN}{dt} = Ae^{-\frac{\Delta G_N}{RT}}$$

Equation 2.4 Activation free energy of nucleation

$$\Delta G_N = \frac{16\pi\gamma^3 V_m^2}{3(RT \ln S)^2}$$

Equation 2.5 Explanation of supersaturation

$$S = \frac{[\text{Monomers}]}{C_{bulk}^0}$$

To describe the great nuclei generation, the CNT (Equation 2.3) can be considered. According to this theory, the nucleation rate (dN/dt) depends on the activation free energy of nucleation (ΔG_N) and the temperature (T). ΔG_N in Equation 2.4 is defined by the variable γ , the molar volume (V_m), T and the supersaturation (S), explicated in Equation 2.5, which is the ratio between the monomers concentration ($[\text{Monomers}]$) and the bulk material solubility (C_{bulk}^0). R is the universal gas constant. As a result, dN/dt is strongly correlated

to T and the quantity of monomers. Specifically, since the T and $[\text{Monomers}]$ appear in the denominator of the negative exponent of the nucleation rate expression, higher values of these parameters lead to a higher nucleation rate. Because the monomer concentration depends on the precursors, highly reactive precursors are generally preferred to achieve rapid and abundant nucleation.³⁶

The success of the hot-injection (Hinj) method is due to its high level of control over nanocrystal size, size distribution, and morphology. This control is achieved by carefully tuning almost all synthetic parameters, including the choice and quantity of precursors, the ligands and their concentration, the solvent, the injection temperature, the growth time, and the quenching method. Although the system is very complex due to the interconnection between the parameters, some simplifications can be made for practical considerations. Because different nanocrystal materials exhibit distinct behaviours, this dissertation focuses on LHP nanocrystals, since these stoichiometries are extensively studied throughout the thesis.

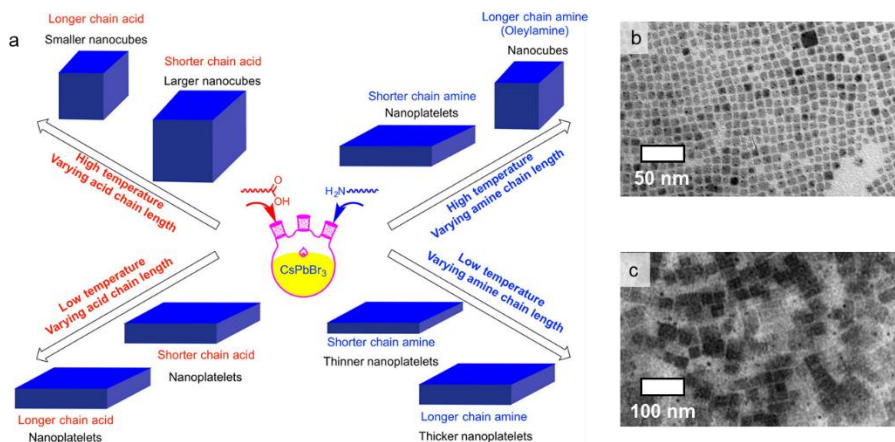


Figure 2.10 Illustration of temperature and ligand variation on the morphology control of CsPbBr_3 nanocrystals. Reproduced with the permission from ref.³⁵ Copyright © 2019 American Chemical Society. All rights reserved. TEM images of (b) nanocubes and (c) nanoplatelets.

Temperature and growth time strongly influence both the size of the nanoparticles and their size distribution (Figure 2.10), due to the increased likelihood of Ostwald ripening over time. Additionally, temperature affects the morphology of the nanocrystals: higher temperatures generally favour the formation of nanocubes, while lower temperatures, in the range of 90 - 130 °C, tend to produce more layered structures.

Due to their role in surface passivation, ligands play a central role in controlling nanocrystal properties (Figure 2.10a). In the synthesis of LHP nanocrystals, amines and carboxylic acids, particularly OLAM and OLAC, are commonly employed. At a constant temperature, increasing the chain length of the amine generally results in thicker nanoparticles, whereas increasing the chain length of the carboxylic acid has the opposite effect. Additionally, the ratio between amine and carboxylic acid is also important for shape control, as it influences the formation of ammonium cations. These ammonium cations compete with the A^+ cationic specie for incorporation into the crystal lattice. When A^+

cations are incorporated, crystal growth continues; when ammonium cations dominate, growth is arrested. The acid–base equilibrium can further be shifted by temperature changes, which helps explain the temperature-dependent morphological behaviour of the nanoparticles. Finally, the total quantity of ligands affects Ostwald ripening. Reducing the ligand concentration suppresses ripening, resulting in a narrower size distribution. Therefore, it is advisable to use the minimum amount of ligands necessary to maintain colloidal stability while minimizing ripening effects.^{35,49–53}

The main advantage of the hot-injection (Hinj) method lies in its precise control over all reaction parameters, allowing fine tuning of the properties of the final nanocrystals. Moreover, the method is suitable for synthesizing nanocrystals with various stoichiometries. Performing Hinj under inert conditions enables the use of highly reactive precursors that would otherwise degrade in the presence of oxygen and/or moisture. Additionally, the experimental setup relies on simple glassware, making the process relatively low-cost.

However, the Hinj method has some limitations. It can be operator-dependent, as the injection must be performed accurately to avoid multiple nucleation events. The method is also challenging to scale up because the reaction mixture must remain homogeneous immediately after injection to prevent concentration gradients, and rapid, uniform quenching of a large batch can be difficult to achieve. Finally, the process generates a significant amount of waste, primarily from the solvents used.^{34–36} A strategy to reduce it is reported in Chapter IV.

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Chapter III

Toward a sustainable
chemistry: an introduction on
the *green* solvent



Chapter III: Toward a sustainable chemistry: an introduction on the green solvent

Abstract: During the last decades, the attention on the impact of chemistry processes on the environment became a central point in the development of new synthetic strategies and, even more important, in the industry. This new branch of the chemistry, that studies the method to reduce the environmental footprint of chemical processes, is named “green chemistry”. Because of their extensive use, solvents represent one of the most critical factors in making reactions more environmentally sustainable. Chapter III provides an overview of the so-called green solvents, a class of solvents considered to be less hazardous for the environment.

3.1 The concept of green chemistry

Humanity has been interconnected with chemistry throughout its entire history, starting from the production of the earliest manufactured goods. Numerous chemical reactions were performed to obtain such objects, even though the underlying synthetic strategies were not yet understood. Beginning with the production of simple pottery,¹ the evolution of chemical processes gradually enabled the creation of increasingly sophisticated materials. However, it was only with the Second Industrial Revolution, at the end of the 1800s, that large-scale chemical production truly emerged. During this period, fine chemistry also experienced remarkable growth.^{2–4} Unfortunately, there was any care about hazards concern the new products as well as the new synthetic strategies. In many cases, problems related to a chemical substance or industrial process were discovered only after incidents that caused illness or death among exposed individuals. Numerous environmental and industrial disasters have been documented. Classical examples include the Bhopal disaster, ozone depletion, and global warming caused by greenhouse gases.^{5–9}

Only from the 1960s onward, the attention on the toxicity of chemicals strongly increased. Awareness regarding human health and environmental protection was formally introduced during the United Nations Commission on Environment and Development in 1987 (Brundtland Commission), which stated that development can be considered sustainable when it meets the needs of the present generation without compromising the ability of future generations to meet their own needs. In 1990, the Pollution Prevention Act emphasized the preventive elimination of hazards at the source. These approaches inspired Paul Anastas and John Warner to establish, in the 1990s, a new branch of chemistry devoted to developing safer alternatives to hazardous products and methods: the *Green Chemistry*.¹⁰

The pivots of the *green* chemistry are based on 12 principles:^{10–12}

- I. **Prevent waste:** it is better to prevent waste than to treat or clean up waste after it is formed.
- II. **Atom economy:** synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

- III. **Safe synthesis:** wherever practicable, synthetic methodologies should be designed to use and generate substance that possess little or no toxic to human health and environment.
- IV. **Safe products:** chemical products should be designed to preserve efficacy of function while reducing toxicity.
- V. **Lowering the auxiliary substance:** the use of auxiliary substance (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous where used.
- VI. **Energy efficiency:** energy requirements should be recognized for their environmental and economic impacts and should be minimize. Synthetic methods should be conducted at ambient temperature and pressure.
- VII. **Renewable feedstocks:** A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
- VIII. **Reduce derivatization:** Unnecessary derivation (blocking group, protection/deprotection, temporary modification of physical/chemical process) should be avoided whenever possible.
- IX. **Improve catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- X. **Safe dismissal of the products:** Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- XI. **Real-time analysis for pollution prevention:** Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- XII. **Safe chemicals:** Substances and form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Nowadays, Research and Development (R&D) sector of the industries must take these principles in account in order to minimize the health and environmental risk. Unfortunately, it is not always possible to apply all of them, either because they are incompatible with the production of a specific material, the required synthetic route, or economic constraints. Nevertheless, in most cases a balance is sought between the Green Chemistry principles and the practical realities of industrial manufacturing.¹⁰

3.2 Green solvent

Excluding particularly case, chemical reactions require a solvent, which not only provides the medium allowing reagents to interact, but also determines their concentration and can directly influence the reaction outcome; for example, by stabilizing specific excited states or by activating/inhibiting catalysts. In reactions that require a liquid medium, the solvent typically represents the majority of the total mass of the reaction mixture.¹³ Furthermore, once used, the “exhausted” solvent becomes part of the waste stream. For these reasons, the solvent question is taken greatly in account in optics of *green* chemistry. Therefore, conducting reactions under neat conditions is preferable, provided that comparable results can be obtained relative to their solution-phase counterparts.

However, many reactions, work up and purification steps require solvent.¹⁴ This is particularly evident in fine organic chemistry, such as pharmaceutical synthesis, where solvents are extensively employed. In particular, volatile organic compounds (VOCs) are frequently used due to their easy removal by evaporation. Nonetheless, VOCs pose several problems, including toxicity and flammability. In addition, they contribute to environmental issues such as ozone depletion and smog formation through free-radical air oxidation processes.^{15,16} Therefore, the substitution of classical organic solvent with more environmentally friendly alternatives, commonly referred to as *green solvent*, is desirable. The ideal *green* solvent should meet sustainability criteria across its entire life cycle (Figure 3.1). Its production should require minimal energy input, be economically viable, and exert no negative environmental impact. The solvent should also be easy to handle, versatile, and recoverable after use. At the end of its life cycle, it should be fully biodegradable, generating no harmful waste.¹³

Based on the concept of the ideal *green* solvent, Galuzska et al. proposed twelve desirable characteristics that these type of solvent should have: availability, low price, recyclability, possibility to use in technical grade to avoid purification step in the solvent production, easy synthesis, low toxicity, biodegradability, performance similar or superior to their classic counterpart, stability, non-flammability, safe storage and renewability. Although no currently available green solvent satisfies all these criteria, many of them meet a substantial portion of these requirements.^{17,18}

On the wave of *green* chemistry, old and new family of molecules are taken into account to be exploited as *green* solvent.

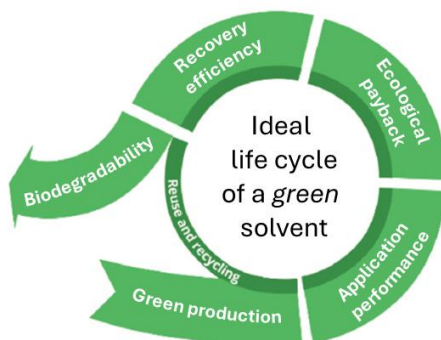


Figure 3.1 Schematization of the ideal *green* solvent life cycle, from its production, through its use and recovery, until its dismissal. Figure is adapted from ref.¹³

3.3 Supercritical solvents

A substance reaches the supercritical state when both its *critical temperature* (T_c) and *pressure* (P_c) are exceeded. A supercritical fluid (SCF) exhibits a density comparable to that of a liquid, while maintaining a viscosity close to that of a gas. These properties can be finely tuned by adjusting temperature and pressure. In general, solubility increases with pressure, whereas temperature has a less pronounced effect. Several compounds can be brought to a supercritical state, including ethane, propane, hexane, ethylene, and nitrous

oxide. However, the most efficient and environmentally friendly SCFs are carbon dioxide (CO₂) and water.¹⁴

3.3.1 Supercritical CO₂

CO₂ reaches its supercritical state when the temperature and pressure exceed 31.1 °C and 7.38 MPa, respectively. Supercritical CO₂ is *non-toxic* and *non-explosive*. In general, the properties of supercritical CO₂, such as diffusivity, viscosity, surface tension and solvent power, depend on its density. This typically ranges from 0.15 and 1.0 g/cm³ and could be modulated by adjusting temperature and pressure. Supercritical CO₂ is generally a good solvent for non-polar or slightly polar, low-weight molecules. Furthermore, it has a good affinity with the oxygenated organic compound with medium molecular weight due to its large quadrupole moment. Using polar modifiers, it is possible to modulate the solvating power of supercritical CO₂.

Supercritical CO₂ is stable until the conditions are above the critical temperature and pressure. This feature can be exploited for solute recovery. Indeed, CO₂ simply reverts to the vapour state, leaving behind the extracted solute without generating secondary contaminants.

The main use of supercritical CO₂ is in extractive processes, such as the decaffeination of coffee. Owing to its safety for human use, it is widely employed in the food, pharmaceutical, and cosmetic industries. In addition, supercritical CO₂ is used as solvent for chemical reactions, material processing and cleaning. CO₂ is readily available, nontoxic and its employment in industrial processes can contribute to reducing the overall amount of CO₂ in the atmosphere.^{13,14}

3.3.2 Supercritical and subcritical H₂O

From an ecological perspective, water is a non-impactful solvent. It is non-flammable, non-toxic, readily available and inexpensive. The major drawback is its immiscibility with apolar substances, which limits its applicability in several reactions, especially in organic chemistry.

However, water exhibits markedly different properties in its subcritical state, also referred to as pressurized water, when its temperature exceeds 200 °C. Under these conditions, the acid-base behaviour of water changes significantly. In particular, its pH decreases by about three units, meaning that reactions normally requiring acidic media can proceed with little or no added acid. At 250 °C at 50 bar, the dielectric constant (ϵ) decreases from 80 (room temperature) to about 27. When water reaches 300 °C, starting to behave similarly to acetone due to the hydrogen bonding reduction. By adjusting the temperature, it is therefore possible to obtain subcritical water with a polarity comparable to that of acetonitrile, methanol, ethanol, or acetone.^{14,15,17}

The main application of subcritical water is in the extraction of compounds from plant material. It is also possible its application as solvent for organic chemistry, thanks to the lowering of its polarity. In determinate cases, such as the Diels-Alder reaction between cyclopentadiene and butanone, the aqueous medium favours the reaction. Nevertheless, this application is limited for the few organic molecules that remain stable at the high temperatures and pressure required for subcritical conditions.

Subcritical water is both efficient and environmentally friendly, and it is generally cost-effective. The primary expense arises from the equipment, which must be able to withstand high temperatures and pressures.^{14,15}

Water can also be used as a green solvent in its supercritical state, which, even in this state, overcomes its limited solubility toward apolar substances. Water becomes supercritical when subjected to temperatures and pressures above 374.2 °C and 22.1 MPa, respectively. In this state, water exhibits $\epsilon = 12.16$, even lower than in the subcritical regime. As supercritical CO₂, its physicochemical properties can be tuned by adjusting temperature and pressure.

Supercritical water is applied to the synthesis of inorganic solid, as well as, in remediation and waste treatment applications. As with subcritical water, the main cost associated with its use lies in maintaining the required high temperature and pressure.^{14,15}

3.4 Ionic liquids

Ionic liquids (ILs) are organic salts with *melting points below 100 °C*, that results from the large size of the cation, the anion, or both involved in the ILs structure, which prevents efficient packing in the solid state. Bulky organic molecules with low symmetry and containing a positive charged functional group, such as ammonium or phosphonium group, are usually involved as cation. The complexity of the cation is depending on the organic moiety which may include simple alkyl chains or more elaborate functionalized and branched groups that can introduce chirality. On other side, the anion taking part of the ILs can be either inorganic or organic. The inorganic anions include halide, simple molecular anions such as nitrate or sulphate and anionic complex such as tetrafluoroborate and hexafluorophosphate. Organic anions include acetate, imide, and alkyl sulphates. As with the cation, the organic nature of the anion can greatly increase structural complexity.¹³

The combination of the cation and anion determined the complexity and the properties of the ILs. Besides their low melting points, common features of ILs include very low volatility, reduced sensitivity to air and moisture, higher viscosity than typical organic solvents, densities greater than water, and surface tensions lower than water but higher than n-alkanes. Their excellent solvation abilities arise from multiple interactions: *ionic interactions* between charged sites, as well as *hydrogen bonding*, *dipole–dipole forces* and *van der Waals interactions* contributed by the organic moieties. Indeed, even if the ILS have common properties, the final chemical-physical properties of the solvent can be tuned by the ions' organic chain. Consequently, ILs can be used as general-purpose solvents or designed for highly specific tasks.¹⁴

Most ILs are thermally stable up to approximately 150 °C. However, their thermal, chemical, and electrochemical stability strongly depend on the nature of the ions, both the ionic headgroup and the structural features of the cation and anion.¹³

Thanks to their *tuneability*, ILs can be employed as solvent in a wide range of applications. Owing to their ionic nature, ILs can be useful as solvent in electrochemistry, but they are also reported in other application fields such as fine organic chemistry, biochemistry, process technology and analytics. Very interesting is the possibility to use the ILs for homogeneous catalysis which usually are considered heterogeneous due to their good dissolution properties. This approach is particularly useful when the final product is insoluble in the ILs since are retained the advantages of the homogeneous catalysis, such as the high selectivity, catalytic activity and possibility of ligands tuning for the metalorganic complexes, while facilitating product separation and catalytic mixture

recycling. Conversely, reactions producing IL-soluble products are more challenging because, unlike VOCs, ILs cannot be removed by simple evaporation. In such cases, extraction with organic solvents is usually required, reducing overall eco-efficiency. Another interesting application involves the formation of ILs *in situ* to remove acidic reagents from reaction mixtures through the addition of a suitable cation.^{14,15}

Recovery strategies for ILs depend strongly on their structure, especially on the nature of the organic moieties. Methods of recovering include adsorption, centrifugation, nanofiltration, reverse osmosis and electrodialysis. Hydrophilic ILs can sometimes be recovered by thermal treatment, when they do not decompose under those conditions. Hydrophobic ILs employed in metal extraction process can be stripped by the addition of stripping agents such as HCl, H₂SO₄, NaOH, NH₃ or EDTA.

ILs are generally expensive due to the high cost of raw materials and the energy-intensive synthesis processes. However, this cost can be mitigated through solvent recycling. Additionally, depending on their structure, ILs may exhibit toxicity toward aquatic and terrestrial organisms, show poor biodegradability, and therefore pose persistence concerns. Nonetheless, the structural tunability of ILs offers a path to overcome these drawbacks. In particular, naturally derived, inexpensive, and biodegradable molecules can be employed as building blocks for the design of more sustainable ionic liquids.^{13,15}

3.5 Deep eutectic solvents

Deep eutectic solvents (DESs) are a new generation of solvents obtained by mixing two different components to form a *liquid mixture* at, or near, room temperature. The melting point of a DES is determined by *hydrogen-bond interactions* between a hydrogen-bond acceptor, typically a non-toxic quaternary ammonium salt, and a naturally derived, uncharged hydrogen-bond donor. The interaction between these two components leads to charge delocalization, which results in a significant depression of the melting point of the mixture. The molar ratio between the two components is also a crucial factor in achieving the eutectic composition. Because their melting-point depression originates from electrostatic and hydrogen-bonding interactions between the hydrogen donor and acceptor, DESs are often referred to as the “*fourth-generation*” of ILs, although not all components are ionic. The first deep eutectic solvent was reported from *Abbott et al.* in 2003 which consisted in the mixture of 2-hydroxyethyl-trimethylammonium chloride (choline chloride, melting point (T_m) = 302 °C) and urea (T_m = 133 °C) in a 1:2 molar ratio, which produces a liquid with a T_m of 12 °C.^{13,14,19}

Similarly to ILs, DESs are generally non-volatile, non-flammable, high viscose and exhibit good solvency power for a wide range of organic and inorganic compound. As with ILs, even the DESs are designer solvent due to the physicochemical properties of the final mixture depending on the structure of the two components.¹⁴

DESs exhibit thermal stability generally until 150 °C. However, they decompose before reaching the boiling point; therefore, their operating temperature range lies between the T_m and the degradation temperature (T_{deg}). In particular, hydrophobic DESs generally present a T_{deg} above 200 °C, whereas hydrophilic ones tend to decompose around 150 °C. Furthermore, the T_m of the hydrophilic DESs is influenced by water content, with a slight diminishing for small water amount and an increasing for high water contents.¹³

As the ILs, DESs have a wide range of applications owing to their structural tunability. In particular, DESs are employed as solvent in organic synthesis and (bio)catalysis, polymers production, biodiesel production, electrochemistry, electrodeposition, synthesis of nanoparticles, separation process and analysis. DESs can be used also for the treatment of water, enabling the removal of contaminants from aqueous phases. Furthermore, owing to their harmlessness, DESs have found applications in the medical field, such as drug delivery. Finally, DESs are employed into the extraction of biologically active compounds, since the dissolving power is often superior than both water and lipids.¹⁴

DESs can be recovered by simply addition of water, filtration and water evaporation. The recovered DESs can be directly reused with no or only minimal loss in performance.¹³

The production of DESs is very inexpensive since it requires only the mixing of readily available starting materials and the heating of the mixture. In most cases, any further purification is required. Their easy recovery further reduces overall cost. Generally, DESs are environmentally friendly due to the starting materials usually employed for the synthesis of this class of solvent are not toxic. Indeed, quaternary ammonium salts are, generally, low toxic and biodegradable.²⁰ The use of plant-derived primary metabolites for the preparation of DESs leads to the subclass known as natural deep eutectic solvents (NADESs), further enhancing the environmental sustainability of this solvent class.¹³

3.6 Glycerol

Glycerol has emerged as *green* solvent due to its non-volatility, non-toxicity, non-flammability, biodegradability and low cost. In fact, glycerol is part of the waste of the biodiesel generation, and its reuse contributes positively to circular-economy principles. Furthermore, glycerol has high polarity and ability to form hydrogen; thus, it becomes an attractive environmentally friendly solvent. Despite its similarities to water, glycerol is compatible with both hydrophobic and hydrophilic substances.

Owing to its high boiling point (290 °C) and its stability, glycerol can be used in processes requiring high temperature. Furthermore, its immiscibility with hydrophobic solvents allows liquid-liquid extraction. Thus, glycerol is employed as solvent in organic synthesis, biotransformation, separation and isolation procedure.

Nevertheless, glycerol has some intrinsic drawbacks. It can be used as solvent only for reactions conducted above 60 °C due to its high viscosity. Moreover, its hydroxyl may undergo undesired reactions in the presence of strong acids or bases. Its immiscibility with highly hydrophobic compounds and gases limits its employment. Lastly, because glycerol is obtained as a waste stream, purification is often required, which reduces the overall *greenness* of processes in which it is employed.¹⁴

3.7 Terpenes and terpenoids

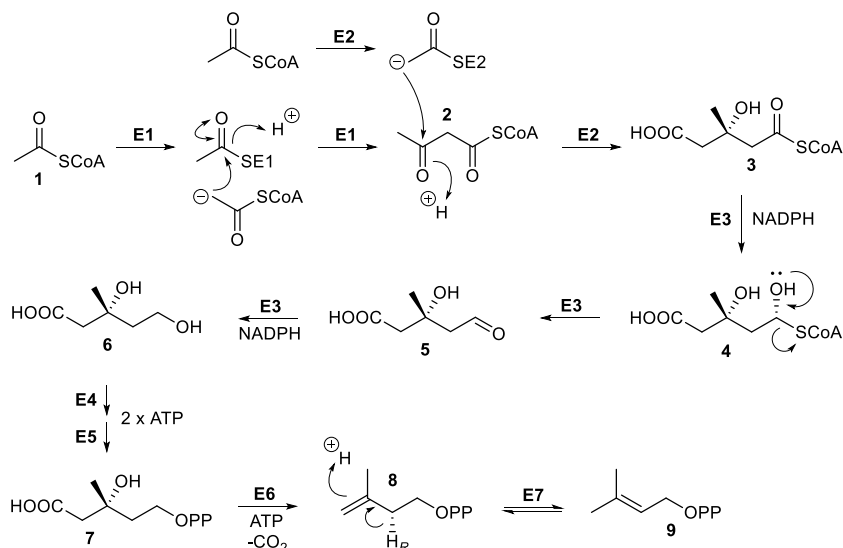
Terpenes and terpenoids are products of the *secondary metabolism*, generally produced by plants. For this reason, they can be extracted from biomass sources, including energy crops, forestry residues, and aquatic biomass. Additionally, the possibility of recovering these compounds from waste materials adds value to otherwise discarded resources.²¹

In plants, terpenes and terpenoids play fundamental roles in *biological functions* and *defence mechanisms*. From a human perspective, they are valuable in pharmaceutical,

food, perfume and cosmetics industry due to their medicinal properties, as they are often biologically active, and their characteristic strong aromas. Recently, this class of molecules, especially the monoterpenes and monoterpenoids, arise as *green* solvent in order to replace the classic apolar VOCs, as the hexane and toluene, especially in extraction process. Compared to n-hexane, terpenes and terpenoids exhibit similar solvent behaviour but are safer, owing to their higher flash points, lower flammability, and reduced toxicity. On the other hand, their recovery results more energetically expensive, since the general boiling point is higher than the n-hexane one.^{21–27}

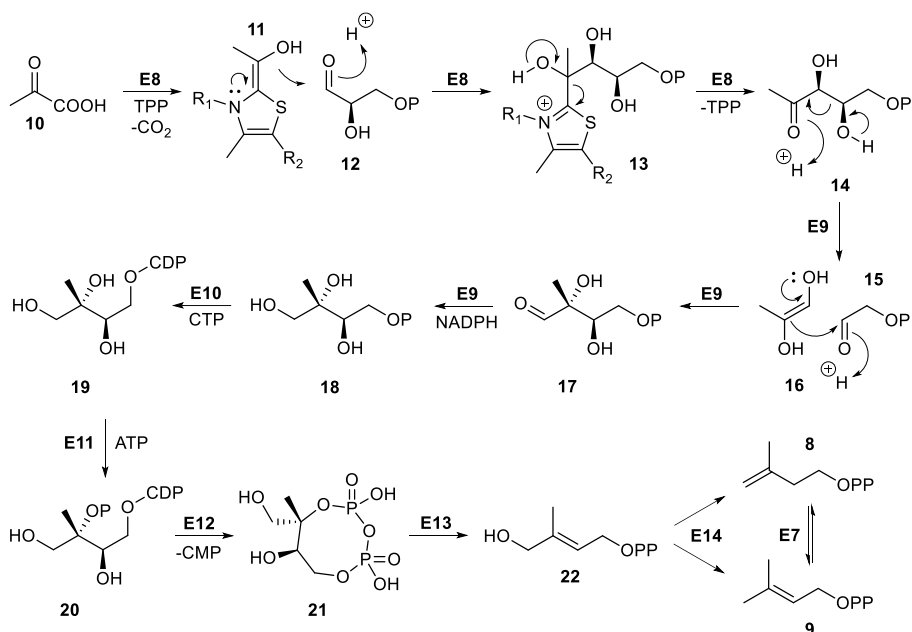
Terpenes are a class of unsaturated hydrocarbon composed of isoprene units C_5 . They are classified accordingly to the number of C_5 linked together: *hemiterpenes* (C_5), *monoterpenes* (C_{10}), *sesquiterpenes* (C_{15}), *diterpenes* (C_{20}), *sesterterpenes* (C_{25}), *triterpenes* (C_{30}) and *tetraterpenes* (C_{40}). Structures containing a higher number of isoprene units are classified as natural gum. The *terpenoids* are terpenes contain heteroatoms in their structure, such as nitrogen, oxygen or sulphur. Typically, the terpenes and terpenoids employed as *green* solvent are monoterpenes or monoterpenoids, which are present in the essential oils or oleoresins of plants. Despite the fundamental unit of terpenes is the *isoprene*, this is not produced naturally. Instead, it is incorporated into final terpene molecules via the precursors *isopentenyl diphosphate* **8** (IPP) and *dimethylallyl phosphate* **9** (DMAPP). The biosynthesis of these two precursors can proceed through two distinct biological pathways: the *mevalonate pathway* and the *methylerythritol phosphate pathway*.²⁸

The mevalonate pathway (Scheme 3.1) is named after the formation of *mevalonate acid* **6** (MVA) during the biosynthetic process. This involves three molecules of acetyl coenzyme A **1** (acetyl-CoA). The first acetyl-CoA is bound by acetyl-CoA synthetase **E1** which catalyses a Claisen reaction with another acetyl-CoA. The as-formed acetoacetyl-CoA **2** is involved into a stereospecific aldol reaction with the third acetyl-CoA bound to the 3-hydroxy-3-methylglutaryl-CoA synthetase **E2** (HMG-CoA synthetase) to form the (S)-3-hydroxy-3-methylglutaryl-CoA **3** (HMG-CoA). Notably, an umpolung occurs in the enzyme active site, in which the third acetyl-CoA acts as a nucleophile toward acetoacetyl-CoA. Next, HMG-CoA is stereospecifically reduced by HMG-CoA reductase **E3** (HMG-CoA reductase) at the thioester to form a hemiacetal intermediate **4**, which is subsequently hydrolysed to mevaldic acid **5** and finally reduced to MVA. The pathway continues by the sequential phosphorylation of the primary alcoholic group by the mevalonate kinase **E4** and phosphomevalonate kinase **E5**, each consuming one molecule of adenosine triphosphate (ATP). A third ATP is likely employed to phosphorylate the secondary alcohol, activating it for the elimination, which occurs by the final decarboxylation catalysed by the mevalonate 5-diphosphate decarboxylase **E6**. In this way, the IPP is formed and, successively, could be stereospecifically isomerized by the removal of the *pro-R* hydrogen (H_R) at C2 catalysed by the isopentenyl diphosphate isomerase **E7** (IPP isomerase) to form DMAPP.²⁸



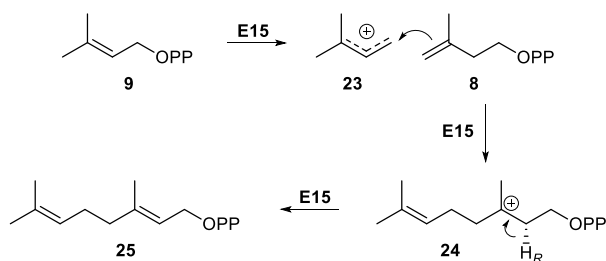
Scheme 3.1 Biosynthesis of IPP and DMAPP through mevalonate pathway. Scheme is adapted from ref.²⁸

The methylerythritol phosphate pathway (Scheme 3.2) is named after the formation of (2*R*,3*S*)-2,3,4-trihydroxy-3-methylbutyl dihydrogen phosphate **18**, also known as *methylerythritol phosphate* (MEP), during the biosynthetic process. The initial step of this pathway involves the reaction between pyruvic acid **10**, activated as enamine **11** by binding to thiamine pyrophosphate (TPP), and the glyceraldehyde 3-phosphate **12**. Both **10** and **12** are glycolysis intermediates. This reaction is catalysed by the 1-deoxy-D-xylulose 5-phosphate synthetase **E8** (DXP synthetase), producing 1-deoxy-D-xylulose 5-phosphate **13**. Next, 2-C-methyl-D-erytritol 4-phosphate synthetase **E9**, also called 1-deoxy-D-xylulose 5-phosphate reductoisomerase, catalyses a retro aldol reaction of **13**, followed by an aldol reaction and a reduction of the aldehyde **17** to yield MEP. The reaction between MEP and cytosine triphosphate lead to 4-(cytosine diphosphate)-MEP **19** (4-(CDP)-MEP), catalysed by the 4-diphosphocytidil-2-C-methyl-D-erytritol synthetase **E10** (IspD). **19** is subsequently phosphorylated using an ATP by the 4-diphosphocytidil-2-C-methyl-D-erytritol kinase **E11** (IspE). The product **20** is cyclized to the cyclic phosphoanhydride **21** by 2-C-methyl-D-erytritol-2,4-cyclodiphosphate synthetase **E12** (IspF). The followed steps remain not fully elucidated, but probably involves two enzymes: the 4-hydroxy-3methylbut-2-enyl diphosphate synthetase **E13** (IspG) and the 4-hydroxy-3methylbut-2-enyl diphosphate isomerase **E14** (IspH). The last enzyme seems to be involved in the formation of both IPP and DMAPP. Anyway, IPP can be isomerised into DMAPP by **E7**.²⁸



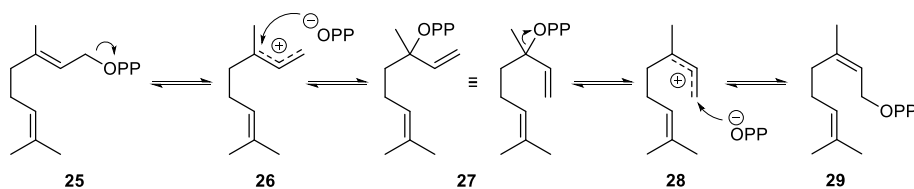
Scheme 3.2 Biosynthesis of IPP and DMAPP through methylerythritol phosphate pathway. Scheme is adapted from ref.²⁸

The monoterpenes are formed through the reaction between DMAPP and IPP catalysed by geranyl geraniol synthetase **E15** (Scheme 3.3). The reaction begins by the elimination of the diphosphate group from DMAPP to form the allylic cation **23** which is attacked to the double bond of the IPP. The carbocation formed **24** is quenched by the stereospecific elimination of the proton *pro-R* to form a new double bond in *E* configuration. The product of this reaction is the *geranyl diphosphate* **25** (GPP), which serves as the direct precursor to monoterpenes.



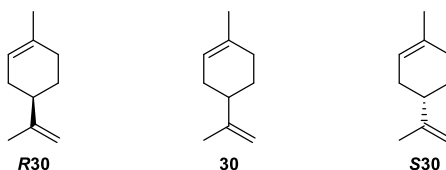
Scheme 3.3 Biosynthesis of geranyl diphosphate **25** from IPP and DMAPP. Scheme is adapted from ref.²⁸

The isomerisation of the GPP produce *linalyl diphosphate* **27** (LPP) and *neryl diphosphate* **29** (NPP) (Scheme 3.4). Subsequent rearrangement of these three molecules give rise to the diverse array of monoterpenes and monoterpenoids found in nature.²⁸



Scheme 3.4 Isomerisation of GPP into linalyl diphosphate **27** and neryl diphosphate **29**. Scheme is adapted from ref.²⁶

3.8 Limonene

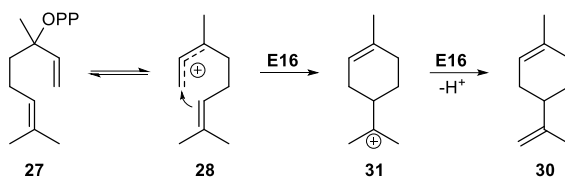


Scheme 3.5 General structure of limonene **30**. Structure of (*R*)-limonene **R30** and (*S*)-limonene **S30**.

Limonene **30**, reported in Scheme 3.5, is a terpene produced from the secondary metabolism of a wide variety of plant. Its structure contains an asymmetric carbon, giving rise to two enantiomers. Being a terpene, limonene is an apolar compound, with a dielectric constant (ϵ) at 20 °C of 2.44. It also has a relatively high boiling point, around 175 °C, and a characteristic aroma which depends on the specific enantiomer. Despite the presence of double bonds which are susceptible to oxidation, limonene is relatively stable under ambient conditions.^{26,29,30}

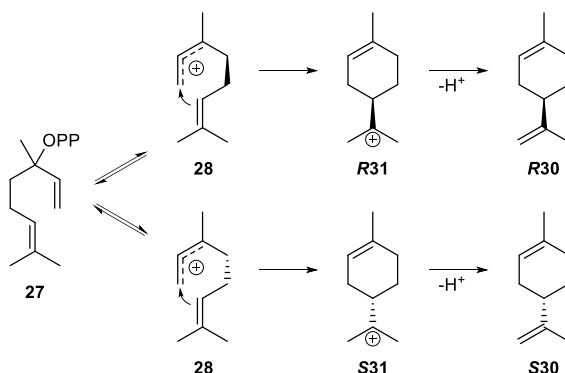
(*R*)-limonene **R30**, also known as *d*-limonene or (+)-limonene, is the major component of the citrus peels essential oil, contributing to its characteristic aroma bouquet. The highest concentration is found in lemon and orange peels (~95%), which are the major waste of the citrus processing industry. (*R*)-limonene can be extracted from these peels using methods such as steam distillation, high pressure-high temperature extraction, microwave assisted extraction, microwave accelerate distillation or dilute acid hydrolysis of these peels. These processes not only allow for the recovery of (*R*)-limonene but also add value to otherwise discarded industrial waste.²⁷

Diversly, (*S*)-limonene **S30**, also known as (*l*)-limonene or (-)-limonene, is part of the especial oil of the peppermint, spearmint, citronella and lemongrass. However, its concentration is much lower than that of its enantiomer in citrus peels, typically below 5%. Consequently, (*S*)-limonene is generally synthesized from α -pinene, another terpene derived from the pines which will be treated in the following subsection.^{31–33} The racemic mixture of limonene, known as *dipentene*, can be produced as by-product from the hydration of turpentine.³⁴



Scheme 3.6 Limonene synthesis from LPP. Scheme is adapted from ref.²⁸

The biosynthesis of limonene is schematized in Scheme 3.6. Limonene is synthesized from GPP or its isomer derivatives by the enzymes limonene synthetase **E16**. The pathway starts with the closing of the ring. Despite LPP and NPP should be major prone to form a ring, **E16** can work also on the GPP. Within the enzyme active site, an allylic cation is formed, similar to the reaction mechanism of DMAPP, followed by a nucleophilic attack of the double bond. The consequence is the closing of the ring and the formation of a tertiary carbocation, referred to as the menthyl or α -terpenyl cation **31**. Subsequent elimination of a proton from a methyl group yields the final limonene structure. The production of one enantiomer over the other depends on the distinct folding of the GPP or its isomers derivatives into two mirror-image conformations within the enzyme (Scheme 3.7).^{28,35}



Scheme 3.7 Synthetic pathway to (*R*)-limonene **R30** in the upper part of the scheme, and (*S*)-limonene **S30** in the bottom part of the scheme. Scheme is adapted from ref.²⁸

Limonene plays multiple roles in the plants which produce it. First of all, it acts as a *valuable scaffold* for the biosynthesis of other terpenoids. Both its double bonds and the allylic positions, particularly those within the ring, are chemically reactive. While biotransformations of the double bonds typically involve reduction or isomerization reactions, the allylic positions inside the ring are often oxidized. These transformations can yield compounds structurally related to limonene, such as carvone, piperitone, and menthol, and even more complex molecules like menthofuran. In addition to its role as a chemical precursor, limonene contributes to *plant defence*. It exhibits antifeedant activity by repelling certain insects, while also serving as an attractant for pollinators. In hot and dry climates, limonene can act as an allelopathic agent, inhibiting the growth of competing plants. Moreover, it possesses antifungal and antimicrobial properties, showing strong activity against yeasts and Gram-positive bacteria, but comparatively low effectiveness against Gram-negative bacteria.^{28,36,37}

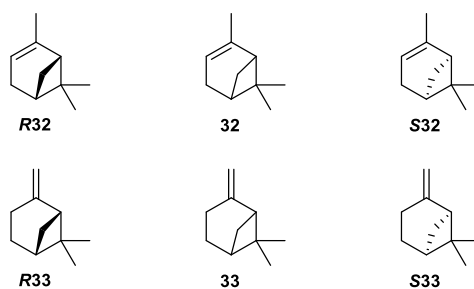
Limonene also exhibits various *biological activities* in the human body. Its double bonds contribute to antioxidant properties, while its small size and lipophilicity enable it to interact with and stabilize cell membranes, providing anti-inflammatory protection. Additionally, limonene may exert analgesic effects, likely through the inhibition of the synthesis and release of inflammatory mediators that trigger pain in nerve endings. Its lipophilic nature also makes it a potential candidate for transdermal drug delivery. Interestingly, limonene has been extensively studied for its chemopreventive and chemotherapeutic properties. It appears to induce cell cycle arrest at the G1 phase in tumour cells, promoting apoptosis and consequently contributing to tumour regression.³⁶

Owing to its biological activities, limonene finds applications in the *pharmaceutical industry*. Furthermore, the characteristic aroma, especially for the (*R*)- enantiomer, combining with its treasurable toxicity allowed limonene to be employed as *flavouring* in soft drinks, cosmetics, cleaning supplies and air freshener. Finally, limonene serves as a *valuable building block* in fine chemical synthesis, where its double bonds are often exploited in various transformations.^{34,36,38}

Limonene is well known as a *green* solvent capable of replacing apolar organic solvents in *extraction processes*, particularly for the extraction of fatty acids. However, relatively few studies have explored its use as a reaction solvent, despite the potential to provide not only a sustainable medium but also a chiral environment. Nagata et al. reported the synthesis of poly(quinoxaline-2,3-diyl)s (PQXs) in enantiomerically pure limonene. Their work highlights an asymmetric induction on the final helical structure of the polymers, which change depending on the enantiomers employed as solvent. This behaviour was attributed to the solvent interaction with the transition structure during the polymer formation.^{39,40}

Although limonene is generally considered a safe solvent, it can act as a potential allergen in humans. Additionally, it exhibits toxicity toward aquatic organisms, which should be taken into account in its environmental assessment.^{17,36,41}

3.9 Pinene

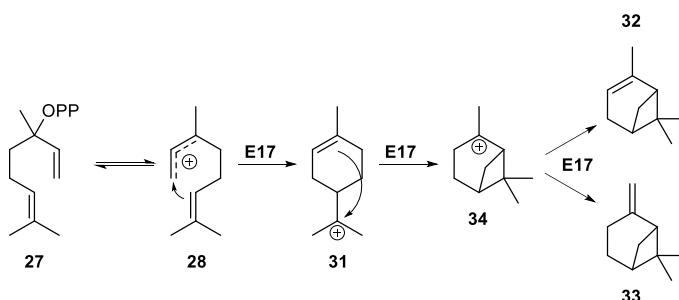


Scheme 3.8 General structure of α -pinene **32** and β -pinene **33**. Structure of (1*R*)- α -pinene **R32**, (1*S*)- α -pinene **S32**, (1*R*)- β -pinene **R33**, (1*S*)- β -pinene **S33**.

Pinene is a class of terpenes product from the secondary metabolism of a wide variety of plant, species of the *Pinaceae* family. Structurally, pinene is an unsaturated bicyclic hydrocarbon, consisting of a four- and a six-membered ring (Scheme 3.8). This framework allows for the existence of several isomers, although the most abundant are α -pinene **32**

and β -pinene **33**, which differ in the position of the double bond, endocyclic in α -pinene and exocyclic in β -pinene. As limonene, pinenes are apolar compound with relatively high boiling points. In particular, α -pinene has ϵ equal to 2.18 and boiling point of 155 °C, while for the β - isomer ϵ is 2.50 and the boiling point 165 °C. Despite their similar structure, the two isomers have slightly different aromas. Furthermore, each isomer exists as a pair of enantiomers with distinct olfactory properties.^{30,42}

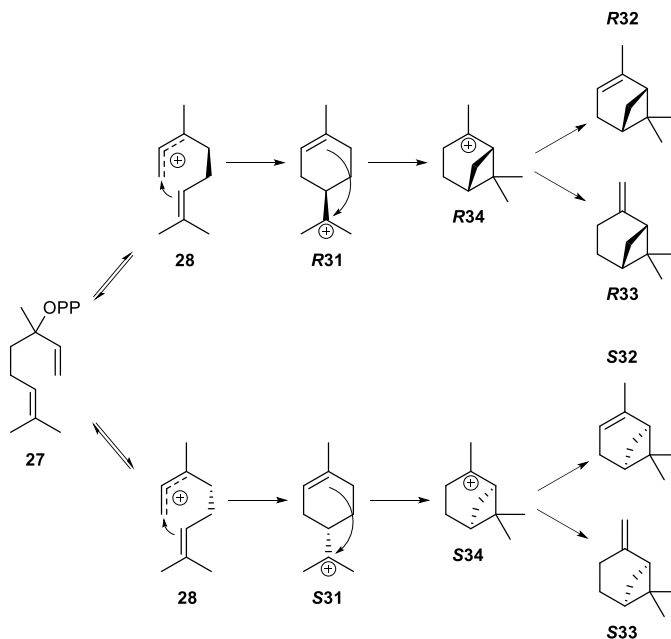
Pinenes are mainly obtained through extraction from tapping, turpentine and as by-product of paper pulping. In particular, α -pinene is the main monoterpene component of turpentine. High concentration of β -pinene is found into the essential oil of several species of the genera Cupressaceae and Artemisiae. However, α - and β -pinene can be produced via biotransformation using microorganisms capable of catalysing these conversions.^{30,42–44}



Scheme 3.9 α -pinene **32** and β -pinene **33** synthesis from LPP. Scheme is adapted from ref.²⁸

The biosynthesis of α -pinene **32** and β -pinene **33** is schematized in Scheme 3.9. Similar to limonene, the biosynthesis of both two isomers of pinene starting from the formation of the menthyl cation. However, in this case the cation is subjected to a folding to enable the electrophilic addition to the internal double bound of the cycle. This process generates the pinyll cation **34**, a bridged bicyclic intermediate consisting of a six- and a four-membered ring with a tertiary carbocation. The entire reaction is catalyzed by pinene cyclase **E17**, which facilitates the formation of the menthyl cation, its rearrangement to the pinyll cation, and the subsequent deprotonation of the methylene proton adjacent to the carbocation. This deprotonation yields either the endo- or exo-olefin, resulting in α -pinene **32** or β -pinene **33**, respectively. Analogous to limonene, the folding of GPP or its isomers produces two mirror-image conformations which in turn give rise to the different enantiomers: **R32** and **S32** for α -pinene and **R33** and **S33** for β -pinene (Scheme 3.10).^{28,45,46}

α - and β -pinene play important roles in *plant communication*. Both act as allelopathic agents: α -pinene has been shown to increase solute leakage in the *Cicer arietinum* roots and to inhibit seed germination, while β -pinene can inhibit root growth in certain plant species and reduce Cr(VI)-induced reactive oxygen species accumulation in maize. Additionally, these terpenes contribute to *plant defence* by functioning as repellents and exhibiting fungicidal, antiviral, and antimicrobial activities.^{42,45}



Scheme 3.10 Synthetic pathway to: (1*R*)-α-pinene **R32**, (1*R*)-β-pinene **R33** in the upper part of the scheme; (1*S*)-α-pinene **S32**, (1*S*)-β-pinene **S33** in the bottom part of the scheme. Scheme is adapted from ref.²⁸

There is significant interest in pinenes due to their *biological activities* in the human body. α-pinene acts as an anticoagulant, as it and its derivatives inhibit platelet aggregation by prolonging thrombin time. It also exhibits anxiolytic, analgesic, and anti-inflammatory effects. Both the pinenes demonstrate antitumor activity against various cancer cell lines, as well as gastroprotective, antimicrobial, and antimalarial effects. In particular, β-pinene shows higher activity than the α-isomer on both Gram-positive and negative bacteria. Furthermore, the enantiomers of each isomer display differing levels of antimicrobial activity.^{42,47,48}

Owing to their interesting biological activities, pinenes and their derivatives are employed in the *pharmaceutical industry*. Notably, some pinene derivatives, such as nopinone, are used as ligands in asymmetric syntheses catalysed by organometallic complexes. The ring strain of the bicyclic structure is exploited in *synthetic chemistry* to generate terpenes and terpenoids containing a single aliphatic or aromatic ring, such as (S)-limonene or *p*-cymene. Surely, the characteristic aroma of the pinenes, combined with their low toxicity, allows their use in the *food and cosmetic industries*.^{43,45} Currently, the use of pinene-based solvents as *green* alternatives is primarily limited to replacing n-hexane in *extraction processes*.^{25–27,49}

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Chapter IV

Limonene as *green* solvent
for LHP NCs synthesis



Chapter IV: Limonene as *green* solvent for LHP NCs synthesis

Abstract: Nowadays, the environmental impact of chemical processes has become a central focus in the development of new synthetic methods. This Chapter explores a sustainable approach for synthesizing lead halide perovskite nanocrystals (CsPbX_3 , $X = \text{Cl, Br, I}$) using limonene as green and reusable solvent. The nanocrystals produced exhibit structural and optical properties comparable to those obtained with conventional petroleum-derived solvents, while allowing solvent recovery and reuse. This method demonstrates a promising route toward environmentally friendly, low-waste production of perovskite nanomaterials.

4.1 Introduction

The big demand of nanocrystals during the last decades leads to the production of even more efficient nanomaterials^{1,2} even looked on the on the economy of the process and the environmental impact, as well. To follow this way, big effort was employed to obtain material which could compete with lead halide perovskites properties, obviating to their problem of stability and toxicity.^{3–10} Meanwhile, the synthetic strategy to obtain these environmentally friendly nanocrystals continued to exploit petroleum derived, such as 1-octadecene (ODE), dioctyl ether (DOE), diphenyl ether (DPE), and tri-n-octylphosphine oxide (TOPO)^{4,11–16} which is nearly the 80% of the reaction weight and takes part of the final waste.

In this chapter, the employment of *limonene* as alternative *green* solvent to ODE in the LHP NCs synthesis will be discussed. Limonene was chosen mainly for two reasons: (i) the similar polarity respect to the ODE^{17,18} and (ii) the relatively high boiling point (187 °C) which make it available as solvent for the synthesis of nanocrystals, by hot injection (Hinj) method.

Since limonene was employed for CsPbX_3 nanocubes (NCs) synthesis, with $X = \text{Cl, Br and I}$, the chapter will be start with the synthesis and the characterization of the three stoichiometries reported. For each stoichiometry, both (*R*)- and (*S*)-limonene were employed. A discussion on solvent recovery follows the CsPbX_3 NCs synthetic parts. The chapter ends though a discussion on the comparison of CO_2 footprint based on the life cycle assessment (LCA) of the process in which ODE or limonene is used as solvent. The LCA analysis was performed by Prof. Marco Vocciante.

4.2 Synthesis and characterization of CsPbX_3 nanocubes

CsPbX_3 NCs ($X=\text{Cl, Br, I}$) were synthesized using the hot-injection (Hinj) method. Although the synthetic approach is the same for all three stoichiometries, the specific

[†]**Based on:** Lead Halide Perovskites Nanocrystals Synthesized in a Green, Reusable Solvent. D. Pratolongo, M. Campolucci, M. Vocciante, L. Pugliesi, E. Di Giorgio, C. Lambruschini, L. Manna, F. Locardi. *Small* **2025**, 2500535.

conditions, such as injection temperature, injected reagents, and quenching procedure, vary slightly, as reported in Table 4.1. For this reason, a brief description of each synthesis is provided before the characterization section. Full experimental details are reported in the Experimental Section.

Table 4.1 Comparison of the size, PLQY, excitonic wavelength, emission wavelength and FWHM of the PL of the CsPbX₃ NCs synthesized in ODE, (R)- and (S)-limonene.

Stoichiometry	Solvent	T _{inj} (°C)	Size (nm)	PLQY	Excitonic peak wavelength	PL peak wavelength	FWHM of PL
CsPbCl₃	ODE	200	8.8 ± 1.2	34%	400 nm	408 nm	79 meV
	ODE	187	8.7 ± 1.0	20%	400 nm	408 nm	88 meV
	(R)- limonene	187	9.9 ± 2.5	2%	400 nm	408 nm	85 meV
	(S)- limonene	187	9.8 ± 2.5	5%	400 nm	408 nm	83 meV
CsPbBr₃	ODE	160	9.7 ± 1.0	64 %	502 nm	513 nm	72 meV
	(R)- limonene	160	9.2 ± 1.0	86%	502 nm	513 nm	75 meV
	(S)- limonene	160	9.1 ± 1.1	86%	502 nm	513 nm	74 meV
CsPbI₃	ODE	165	/	71%	665 nm	690 nm	86 meV
	(R)- limonene	165	17.0 ± 2.0	53 %	665 nm	692 nm	81 meV
	(S)- limonene	165	17.2 ± 1.8	66%	665 nm	692 nm	81 meV

CsPbCl₃ nanocubes were synthesized by modifying the method reported by Imran et al.¹⁹ The reaction was carried out by rapidly injection of benzoyl chloride (BzCl) under inert atmosphere in a solution of lead acetate trihydrate (Pb(OAc)₂·3H₂O), caesium carbonate (Cs₂CO₃), oleic acid (OLAC) and oleylamine (OLAM) 70%, employing limonene as solvent. The modification relative to the reported synthesis consists in lowering the injection temperature from 200 °C to 187 °C, at which the reaction mixture reaches the boiling point. The reaction was quenched after 20 s by lowering the temperature using an ice bath. After purification, the resulting colloidal dispersion was colourless and exhibited weak violet luminescence under 365 nm irradiation, as shown in the inset of Figure 4.2a.

CsPbBr₃ nanocubes were synthesized following the procedure described by Baranov et al.,²⁰ with slight modifications. The synthesis was carried out by rapidly injection of a caesium oleate (CsOLAC) stock solution at 160 °C into a solution of lead bromide (PbBr₂), OLAM 90% and OLAC in limonene under inert atmosphere. The reaction was cooled to room temperature in air immediately after the injection. After purification, the resulting colloidal dispersion was pale yellow and exhibited a bright green luminescence under 365 nm irradiation, as shown in the inset of Figure 4.2b.

Lastly, CsPbI₃ nanocubes were synthesized by adapting the procedure reported by Akkerman et al.²¹ The synthesis was carried out by a rapid injection of oleylamine iodine (OLAM-I) stock solution at 165 °C into a solution of Pb(OAc)₂·3H₂O, Cs₂CO₃ and OLAC in limonene under inert atmosphere. The reaction was quenched after 10 s through temperature lowering using a water bath. After purification, the resulting colloidal dispersions appeared red and exhibited bright red luminescence under 365 nm irradiation, as shown in the inset of Figure 4.2c.

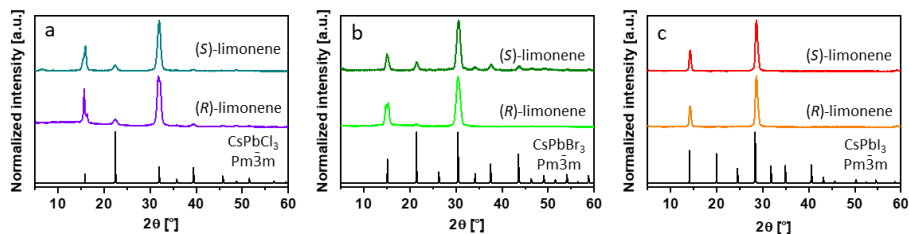


Figure 4.1 X-ray diffraction (XRD) patterns of CsPbX₃ NCs synthesized in limonene. In particular, (a) XRD pattern of CsPbCl₃ NCs synthesized in (*R*)-limonene (violet line) and (*S*)-limonene (cyan line), (b) XRD pattern of CsPbBr₃ NCs synthesized in (*R*)-limonene (light green line) and (*S*)-limonene (dark green line) and (c) XRD pattern of CsPbI₃ NCs synthesized in (*R*)-limonene (orange line) and (*S*)-limonene (red line). CsPbCl₃ Pm $\bar{3}$ m (ICSD number 23108), CsPbBr₃ Pm $\bar{3}$ m (ICSD number 204325) and CsPbI₃ Pm $\bar{3}$ m (ICSD number 161481) were reported as bulk reference (black line) in the bottom part of the corresponding graph.

The *structural properties* of the NCs were analyzed by X-ray diffraction (XRD). Figure 4.1 displays the X-ray diffraction (XRD) patterns of the samples, compared to the bulk cubic reference structure (Pm $\bar{3}$ m). The peaks position comparison of the reference with the samples confirms that the CsPbX₃ NCs synthesized in both (*R*)- and (*S*)-limonene adopted the cubic Pm $\bar{3}$ m structure for all the three stoichiometries presented. However, the samples' XRD patterns exhibit slight differences from the reference: the peaks are broader and the relative intensities are not preserved. These phenomena are well-documented in the literature.^{22,23}

Peak broadening arises from the finite size of the nanocrystals. The *Scherrer equation* (Equation 4.1) relates the crystallite size to parameters obtained from XRD analysis.²⁴ Specifically, the average crystallite size (*D*) is directly proportional to the shape factor (*K*, typically in the range 0.89–0.94) and the X-ray wavelength (λ) used for data acquisition. Conversely, *D* is inversely proportional to the Bragg angle (θ , in radians) and the full width at half maximum (β , in radians) of the diffraction peak. Therefore, the evaluation of peak broadening relative to the peak position provides information on the nanocrystal size: the broader the diffraction peak, the smaller the crystallites.

Equation 4.1 Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Variations in the relative peak intensities can be attributed to the *preferential orientation* of the nanocrystals on the sample holder, which enhances certain reflections

while suppressing others. In particular, all the samples display the enhancing of the (100) crystallographic plane family because the cube shape allows this plane to be perpendicular to the holder and have the stacking of the particles through ab plane, as is reported in Figure 4.3. The stacking could also lead to a *self-assembling phenomenon*, which is detectable on the nanocubes structure by a double peaking of the peak around 15° , given by the (100) plane.^{20,25–27} The XRD pattern of CsPbBr₃ NCs synthesized in (*R*)-limonene shows this feature. Even if nanocubes can be affected by self-assembling, different nanocrystal dimensionality, like nanoplatelets, displays XRD pattern stronger affected by the phenomenon, as it will be reported in Chapter 5.3 and 8.3.²⁸ Meanwhile, the other crystallographic planes are disfavoured to be detected, which lead to a decreasing of intensity, as for (110) plane, or their completely absence in the XRD pattern.

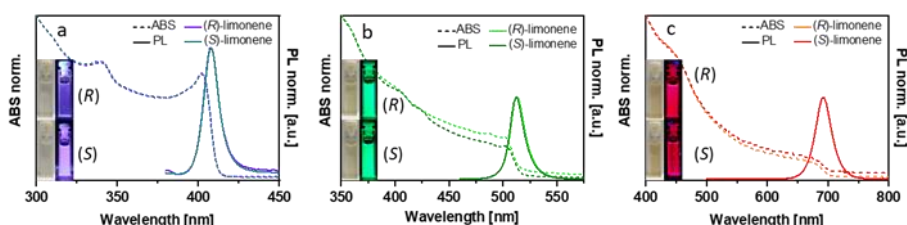


Figure 4.2 Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{\text{exc}} = 365$ nm) of (a) CsPbCl₃ NCs, (b) CsPbBr₃ NCs and (c) CsPbI₃ NCs (the reference colours were maintained from the ones in XRD pattern); insets show photographs of the colloidal dispersions under visible light and UV irradiation (365 nm).

The *optical properties* of the NCs were investigated by absorption (ABS) and photoluminescence (PL) spectroscopy (Figure 4.2). The absorption spectra (dashed line) exhibit features characteristic of CsPbX₃ nanocubes. In particular, they are characterized by a sharp increasing absorbance at higher wavelengths, given by the excitonic peak, followed by a constant absorption increasing toward lower wavelengths. The position of the excitonic peak is given by the stoichiometry of the material; for CsPbCl₃ it is observed at 400 nm, where for CsPbBr₃ at 502 nm and CsPbI₃ at 665 nm.

The PL spectra show a well-defined peak for all the samples, centred at 408 nm, 513 nm and 692 nm respectively for Cl-, Br- and I-based LHP NCs. Furthermore, the peak width gives insight on the size dispersion of the nanocrystals. Since the emission of a single LHP nanocrystal is very narrow and depends on its size, narrower is the sample emission, less disperse is the nanocrystals' size. For these systems, when the full width half maximum (FWHM) of the emission peak is around or below 80 meV is reflected to a monodisperse sample. The calculated FWHM on the emission peaks are 85 meV and 83 meV for CsPbCl₃ NCs, 75 meV and 74 meV for CsPbBr₃ NCs, 81 meV for CsPbI₃ NCs. For each stoichiometry, the first reported value is given by the sample synthesized in (*R*)-limonene where the second is for the (*S*)-limonene one, except for the CsPbI₃ NCs in which the same FWHM value was obtained from both the samples synthesized into the different enantiomers.

Finally, the emission intensity of the colloidal suspension of the different nanocubes were evaluated measuring the photoluminescence quantum yields (PLQY). CsPbCl₃ NCs achieve a PLQY of 2% and 5% for the samples synthesized in (*R*)- and (*S*)-limonene,

respectively. For this stoichiometry, the general value of this parameter results low due to defect on the nanocrystal surface which quench the photoluminescence. Unfortunately, these samples exhibited a PLQY value even lower than the typically one obtained by the employed of ODE as solvent. The reasons for this decrement are principally two. Firstly, the lower injection temperature has a detrimental influence on the final NCS, effect observed also using the ODE. Table 4.1 shows how decreasing the injection temperature from 200 °C to 187 °C, using ODE as solvent, resulting in PLQY decreased from 34% to 20%. The further reduction observed for NCs synthesized in limonene was likely due to the turbulence during the boiling state of the reaction mixture at the injection stage, which affected the final quality of the nanocrystals. This statement is strengthened by the fact that CsPbBr₃ and CsPbI₃ NCs which were not synthesized to the reaction mixture boiling point displayed similar, or even higher, PLQY than the ones synthesized in ODE. PLQY of CsPbI₃ NCs was determined to be 53% and 66% for the (*R*)-limonene and (*S*)-limonene sample, respectively. These values are comparable to those of NCs synthesized in ODE (Table 4.1). The best results were obtained with Br-based LHP NCs with the CsPbBr₃ NCs synthesized in both the limonene enantiomers that exhibited PLQY of approximately 85%. As expected,^{19,21,29} the PLQY of this stoichiometry results the highest. Notably, the values obtained from the samples synthesized with limonene exceed the one obtained for analogous NCs synthesized in ODE.

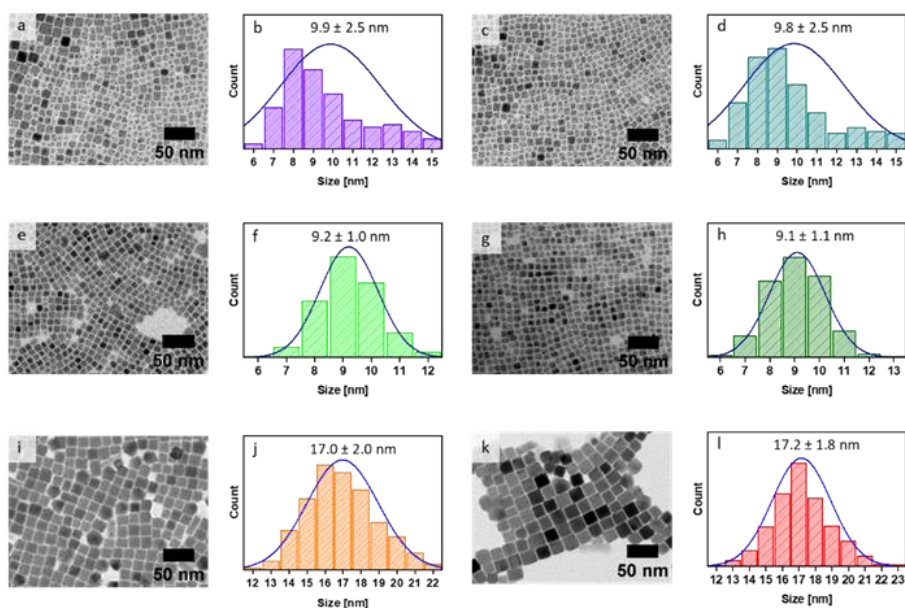


Figure 4.3 Low-resolution TEM images and corresponding size distributions of the CsPbX₃ NCs prepared in (*R*)-limonene and (*S*)-limonene. In particular, the first line refers to CsPbCl₃ NCs ((a, b) sample prepared in (*R*)-limonene, (c, d) sample prepared in (*S*)-limonene); the second line refers to CsPbBr₃ NCs ((e, f) sample prepared in (*R*)-limonene, (g, h) sample prepared in (*S*)-limonene) and the third refers to CsPbI₃ NCs ((i, j) sample prepared in (*R*)-limonene, (k, l) sample prepared in (*S*)-limonene).

Morphological analyses were evaluated by the technique of transmission electron microscopy (TEM) imaging. Figure 4.3 reports the morphology of the nanocrystals, and the size and size distribution, calculated measuring the edge length of the particles. Each sample shows nanocrystals with a *cubic shape*. The nanocubes size depends on the stoichiometry being 9.9 ± 2.5 nm and 9.8 ± 2.5 nm (Figure 4.3a-d) for CsPbCl₃ NCs, 9.2 ± 1.0 nm and 9.1 ± 1.1 nm for CsPbBr₃ NCs (Figure 4.3e-h), and 17.0 ± 2.0 nm and 17.2 ± 1.8 nm for CsPbI₃ NCs (Figure 4.3i-l). The values of each stoichiometry are referred to the samples synthesized in (*R*)-limonene and (*S*)-limonene, respectively. As expected, the different enantiomers of limonene do not affect the size and morphology of the crystals. Furthermore, the values obtained are comparable with the ones from the synthesis with the classical solvent (Table 4.1 and Figure A4.1).

The optical analysis and morphological analysis are consistent each other.^{30–32} The ABS spectra show a profile consistent with the cubic shape of the nanocrystal observed from the TEM image. The dimensions and the size distributions trend are consistent with the peak positions observed in the PL spectra, as well. Indeed, the peak position depends to the stoichiometry composition of the material by its intrinsically band gap, but also to the size of the material at the nanoscale which influences the valence and conductive band position.

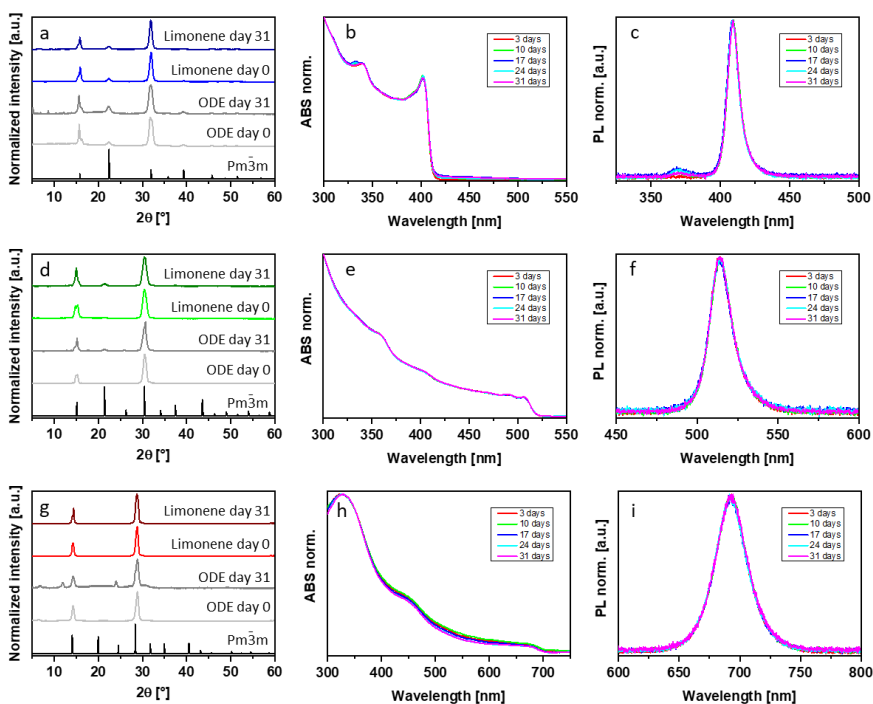


Figure 4.4 XRD, ABS and PL comparison between the fresh synthesized and after 31 days (a-c) CsPbCl₃ NCs, (d-f) CsPbBr₃ NCs, (g-i) CsPbI₃ NCs synthesized in limonene. The XRD graphs reported also the evolution of the sample fresh synthesized in ODE and after 31 days.

Table 4.2 Comparison of PLQY on fresh and aged (31 days) CsPbX₃ (X = Cl, Br, I) synthesized in ODE and limonene.

Stoichiometry	Solvent	T _{inj}	PLQY	PLQY after 31 days
CsPbCl₃	ODE	187 °C	34%	27%
	(<i>R</i>)-limonene	187 °C	2%	2%
CsPbBr₃	ODE	160 °C	64 %	53%
	(<i>R</i>)-limonene	160 °C	86%	42%
CsPbI₃	ODE	165 °C	71%	39%
	(<i>R</i>)-limonene	165 °C	53 %	38%

To evaluate the stability of the synthesized CsPbX₃ NCs, the pristine samples were stored at 4 °C for 31 days and subsequently analysed. All nanocrystals preserved their structural, morphological, and optical characteristics (Figure 4.4). Nevertheless, a reduction in the photoluminescence quantum yield (PLQY) was observed in both the samples synthesized in ODE and those prepared in limonene (Table 4.2). Thus, the decrease of the emission is induced by a intrinsic degradation not related to the solvent employed for the synthesis.

To conclude, the properties result similar to CsPbX₃ NCs synthesized in the classic solvent meaning that it is possible to substitute ODE with limonene. However, the PLQY of CsPbCl₃ NCs is affected by the lower maximum temperature reachable and the turbulence state of the reaction mixture at injection step, as already discussed. Lastly, the morphology of CsPbI₃ NCs results more defined when the limonene is employed as solvent, where the ODE employing lead to mixture of nanocubes and nanorods in the sample (Figure A4.1).

4.3 Solvent recovery

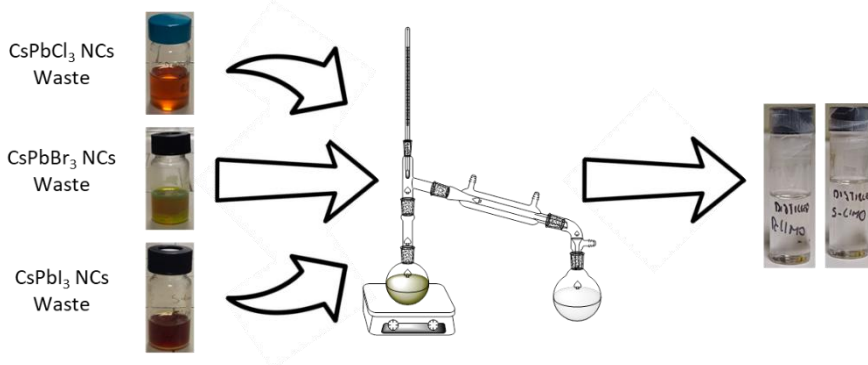


Figure 4.5 Under vacuum distillation process to recovery (*R*)/(*S*)-limonene from the synthesis waste

Limonene has a relatively low boiling point ($\sim 176^\circ\text{C}$). While this property restricts the available temperature range for the synthesis, it also offers the advantage of enabling solvent recycling and, in principle, its complete removal from the nanocrystals. The post-synthesis waste consisted of a coloured mixture containing the solvent, the ligands (OLAM and OLAC), and possible residual inorganic salts. Since OLAM and OLAC possess high boiling points and low vapor pressures, and metals and their derivatives are essentially non-volatile, we tested the feasibility of recovering pure limonene by *vacuum distillation* (Figure 4.5; see Experimental Section for details).

The recovered liquids appeared clear and colourless in the case of (*R*)-limonene and with a pale-yellow hue for (*S*)-limonene. The distillation yields were 70% and 90% for the (*R*)- and (*S*)-enantiomers, respectively. The purity of the recovered solvents was confirmed by ^1H NMR spectroscopy, which showed the absence of secondary organic products (Figure A4.2). Furthermore, ICP-AES analyses confirmed the absence of residual metal traces (Cs and Pb).

The recycled solvents were subsequently reused in the synthesis of CsPbBr_3 NCs. The nanocrystals obtained in this way exhibited the same characteristics as those synthesized in the original, pure solvents (Figure 4.6), demonstrating the feasibility of solvent recovery and reuse in this system.

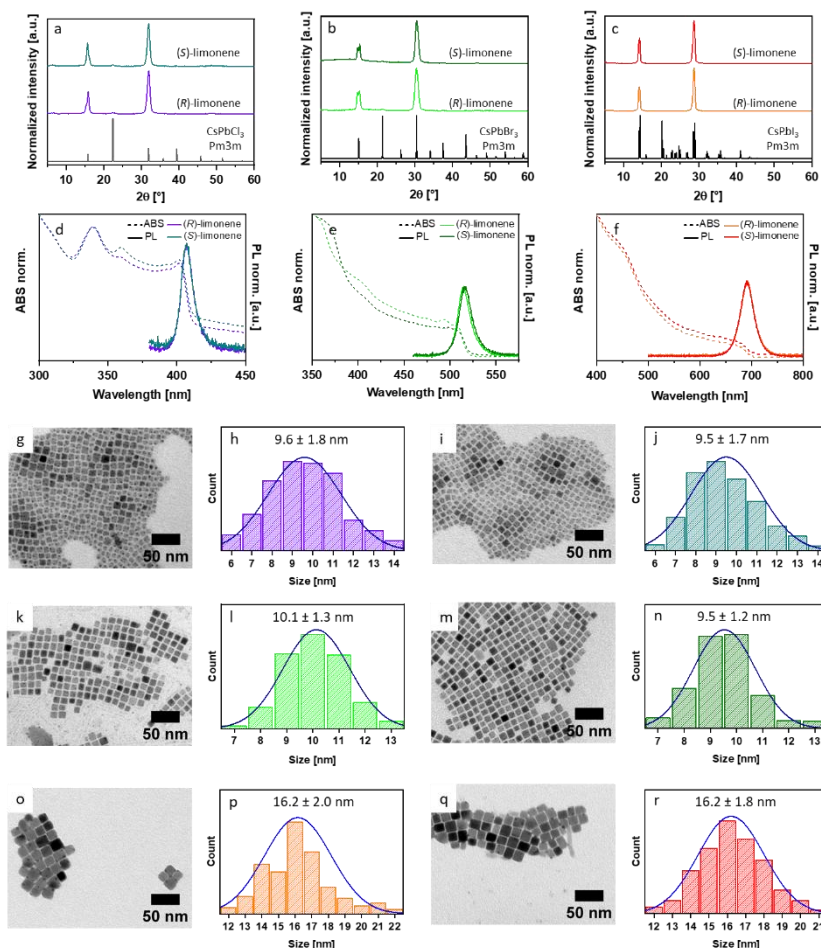


Figure 4.6 X-ray diffraction (XRD) patterns of CsPbX₃ NCs synthesized in the recycled solvents. In particular, (a) XRD pattern of CsPbCl₃ NCs synthesized in (R)-limonene (violet line) and (S)-limonene (cyan line), (b) XRD pattern of CsPbBr₃ NCs synthesized in (R)-limonene (light green line) and (S)-limonene (dark green line) and (c) XRD pattern of CsPbI₃ NCs synthesized in (R)-limonene (orange line) and (S)-limonene (red line). CsPbCl₃ Pm̄3m (ICSD number 23108), CsPbBr₃ Pm̄3m (ICSD number 204325) and CsPbI₃ Pm̄3m (ICSD number 161481) were reported as bulk reference (black line) in the bottom part of the corresponding graph. Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{exc} = 365$ nm) of as-synthesized (d) CsPbCl₃ NCs, (e) CsPbBr₃ NCs and (f) CsPbI₃ NCs (the reference colours were maintained from the ones in XRD pattern). Low-resolution TEM images and corresponding size distributions of the CsPbX₃ NCs as-synthesized. In particular, the first line refers to CsPbCl₃ NCs ((g, h) sample prepared in (R)-limonene, (i, j) sample prepared in (S)-limonene); the second line refers to CsPbBr₃ NCs ((k, l) sample prepared in (R)-limonene, (m, n) sample prepared in (S)-limonene) and the third line refers to CsPbI₃ NCs ((o, p) sample prepared in (R)-limonene, (q, r) sample prepared in (S)-limonene).

4.4 Solvent stripping

In conventional syntheses employing ODE, several studies have reported the problem of its incomplete removal from the nanocrystals, even after multiple washing cycles.^{33–35} Therefore, we verified that limonene can be quantitatively eliminated from the NCs simply by vacuum treatment. To demonstrate this, a portion of CsPbBr₃ NCs suspension in hexane was put under vacuum overnight; the NCs were then redispersed in tol-d₈ and analysed by ¹H NMR. The spectra confirmed the complete removal of limonene (Figure 4.7a, b).

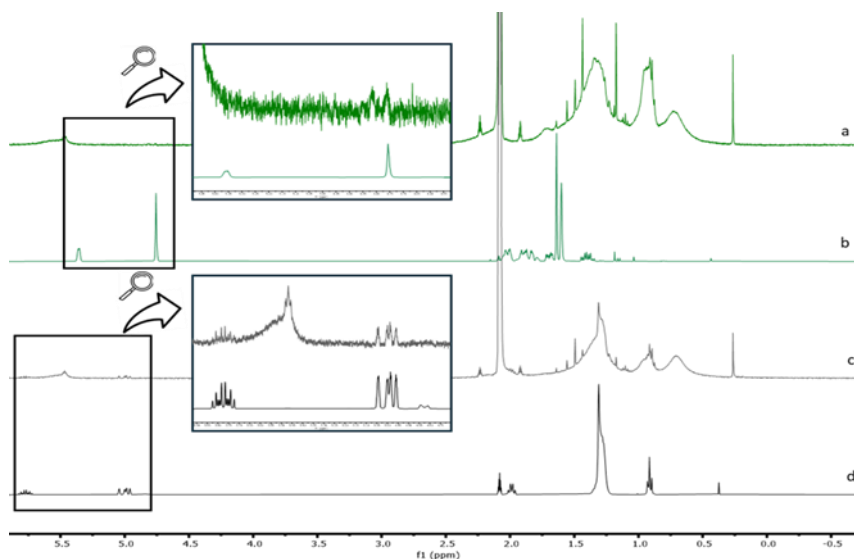


Figure 4.7 ¹H NMR spectra are shown for (a) CsPbBr₃ NCs produced in limonene and stored under vacuum overnight, (b) neat limonene, (c) CsPbBr₃ NCs synthesized in ODE and similarly degassed overnight, and (d) pure ODE. The samples were prepared by dispersing each material in toluene-d₈ (tol-d₈). A residual solvent peak is still visible for the NCs made in ODE (spectrum c), whereas limonene was fully removed in the corresponding sample (spectrum a). The sharp signal at 2.09 ppm arises from tol-d₈.

In contrast, nanocubes synthesized in ODE and subjected to the same vacuum treatment still exhibited residual solvent signals. As shown in Figure 4.7c and d, the multiplets at 5.77 and 5.00 ppm, as well as the peak at 1.31 ppm, attributed to the vinyl group and the aliphatic chain of ODE, respectively, were clearly visible. The quadruplet at 1.99 ppm, corresponding to the protons on the allylic carbon, was obscured by the residual solvent signal, while the triplet at 0.91 ppm derived from the methyl group appeared only faintly due to overlap with a peak originating from the nanocrystals.

4.5 LCA comparison between the different synthetic paths.

The results presented above demonstrate that limonene can be effectively employed as a solvent for the synthesis of LHP nanocrystals, particularly for Br- and I-based compositions. To further evaluate the sustainability of this approach, we performed LCA. Table 4.4 summarizes the environmental impacts in terms of global warming potential

(GWP), expressed as kilograms of CO₂ equivalent released during the synthesis of 100 g of NCs. Replacing ODE with limonene significantly reduces CO₂ emissions, with reductions ranging from 58% to 83% (for CsPbBr₃, Table 4.4). The benefit is even more pronounced for CsPbBr₃ NCs when limonene is recovered by distillation, resulting in a reduction of up to 95% (42.4 GWP for ODE versus 2.14 GWP for limonene; Table 4.4 and Figure 4.8).

When limonene is considered as a raw material, the advantage obtained through its recovery is partially offset by the additional environmental burden associated with the distillation process, leading to an overall comparable impact.

Table 4.3. GWP values associated with producing 100 g of NCs. The numbers in parentheses correspond to the distilled limonene.

Phase	Material/ Operation	GWP (kgCO ₂ eq / 100g CsPbCl ₃)		GWP (kgCO ₂ eq / 100g CsPbBr ₃)		GWP (kgCO ₂ eq / 100g CsPbI ₃)	
		ODE	Limonene	ODE	Limonene	ODE	Limonene
Reaction	Solvent	4.52	1.91 (0.57)	42.4	7.12 (2.14)	9.39	2.83 (0.85)
	Pb source	0.07	0.18	*	**	0.15	0.28
	Cs source	0.03	0.08	3.84	4.05	0.06	0.12
	X source	0.34	0.89	1.17	1.23	1.11	2.10
	Oleic compound	0.35	0.93	1.27	1.34	0.12	0.23
	Sub total	5.31	3.99 (2.65)	48.7	13.8 (8.8)	10.83	5.56 (3.58)
AUX	Distillation	---	---	---	---	---	---
	Disposal	5.46	14.48 (9.10)	98.19	103.5 (83.5)	14.69	27.83 (19.84)
Total		10.77	18.47 (13.09)	146.89	117.7 (97.28)	25.52	33.39 (25.4)

Since limonene is industrially produced by distillation, its environmental impact is essentially equivalent to that of a production process starting from scratch. Therefore, the main benefit of using this solvent lies in the substantial reduction of waste volume requiring disposal.

A comparison of the three syntheses (reaction phase) for the three syntheses highlights that the use of limonene as a solvent lead to a measurable reduction in the carbon footprint, by approximately 25%, 70%, and 50% for CsPbCl₃, CsPbBr₃, and CsPbI₃, respectively (Figure 4.8). However, based on the yield of CsPbI₃ obtained, the use of limonene is less efficient for the nanocrystal production, as reflected in the larger amounts of reagents required, despite the fact that the NCs synthesized in limonene exhibit superior

properties compared to those prepared in ODE. The loss of efficiency in the solvent replacement is significantly more pronounced in the case of CsPbCl₃.

This reduced efficiency, stemming from the higher consumption of other reagents caused by the lower synthetic yield, explains why, when considering the disposal step and thus the total environmental impact of the process, limonene is advantageous for CsPbBr₃, has an impact comparable to ODE for CsPbI₃, and is actually less favourable for CsPbCl₃ (Figure 4.8).

The analysis also revealed significant differences in the overall impact of the three syntheses, irrespective of the solvent used, with CsPbBr₃ synthesis emerging as the most impactful process. Notably, a substantial contribution arises from the dispersing/stabilizing agents, with ethyl acetate (AcOEt) appearing particularly detrimental to the overall sustainability (Table A4.1). Consequently, reconsidering the synthetic routes with the replacement of AcOEt by less impactful alternatives should be regarded as a priority in the development of *greener* procedures.

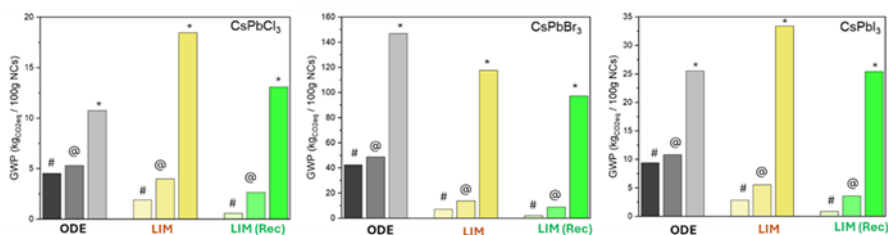


Figure 4.8 GWP values for the production of 100 g of CsPbX₃ (X = Cl, Br, I), calculated by considering (#) the solvent contribution alone, (@) the combined impact of solvent and reagents, and (*) the overall contribution including solvent, reagents, distillation, and waste disposal.

4.6 Conclusion

In this work, we successfully synthesized CsPbX₃ (X = Cl, Br, I) nanocrystals (NCs) employing the green and sustainable solvents (*R*)- and (*S*)-limonene. The resulting NCs exhibited cubic morphology, with crystal structures and optical properties comparable to those of their counterparts obtained using the conventional solvent ODE. Taking advantage of the relatively low boiling point of limonene, we demonstrated both its facile removal from the as-synthesized NCs and its recovery from the reaction waste as a pure solvent suitable for reuse in subsequent syntheses.

Furthermore, life cycle assessment (LCA) confirmed the environmental benefits of substituting ODE with limonene, particularly in terms of reduced greenhouse gas emissions. Beyond the specific case of lead halide perovskites, limonene holds promise as a green solvent for the synthesis of other metal halide NCs and potentially for nanocrystals of different compositions. Overall, this study highlights how the use of green solvents can substantially reduce waste generation and lower both the economic and environmental footprint associated with nanomaterial synthesis.

4.7 Experimental section

Materials. Benzoyl chloride (BzCl, Acros Organic, 99%), caesium carbonate (Cs_2CO_3 , Alfa Aesar, 99.9%), deuterated chloroform (chloroform-d, CDCl_3 , Eurisotop, 99.8 atom % D, +0.03% TMS v/v), ethyl acetate (AcOEt, Sigma-Aldrich, >99.5%), hexane (Sigma-Aldrich, 99%), iodine (I_2 , Fluka, >99.8%), lead(II) acetate trihydrate ($\text{Pb}(\text{OAc})_2 \times 3\text{H}_2\text{O}$, ThermoFisher Scientific, 99.995%), lead(II) bromide (PbBr_2 , Sigma-Aldrich, 99%), (*R*)-limonene (ThermoFisher Scientific, 96%), (*S*)-limonene (Sigma-Aldrich, 96%), oleic acid (OLAC, Alfa Aesar, tech. 90%), oleyl amine (OLAM, ThermoFisher Scientific, 80-90%), oleyl amine (OLAM, Sigma-Aldrich, 70%), toluene (Alfa Aesar, 99%), deuterated toluene (tol-d_8 , Sigma-Aldrich, 99.6 atom % D). All the chemicals were employed without any further purification.

CsOLAC synthesis. 400 mg of Cs_2CO_3 and 1.75 mL of oleic acid (OLAC) are loaded in a 40 mL vial with 15 mL of either (*R*)- or (*S*)-limonene, and the system is placed under a nitrogen atmosphere.²⁰ The mixture is heated at 100 °C under vigorous stirring until the solution becomes fully transparent. The final transparent yellow solution (0.15 M) is used for the synthesis of CsPbBr_3 NCs.

Synthesis of OLAM-I. 0.75 g of I_2 , 4.5 mL of OLAM (80-90%) and 10.5 mL of either (*R*)- or (*S*)-limonene are loaded into a 25 mL three-neck flask and the system is placed under nitrogen.²¹ Then, the mixture is heated at 100 °C, leading to a red solution. The so obtained OLAM-I solution (0.4 M I_2) is transferred, when still hot, into a vial, without any further purification and is then stored under nitrogen.

Synthesis of CsPbCl_3 NCs. 76.0 mg of $\text{Pb}(\text{OAc})_2 \times 3\text{H}_2\text{O}$, 16.0 mg of Cs_2CO_3 , 0.3 mL of OLAC, 1 mL of OLAM (70%) and 5 mL of either (*R*)- or (*S*)-limonene are loaded into a 25 mL three-neck flask.¹⁹ The solution is put under vigorous stirring and left under vacuum for 1 hour. Then, the atmosphere is switched to nitrogen, the reaction temperature is raised until reflux (187 °C) and 210 μL of BzCl are swiftly injected, triggering the nucleation and growth of the NCs. After 20 s, the flask is cooled in an ice bath. The final suspension is orange and cloudy, and is centrifugated at 4000 rpm for 10 min. The precipitate is centrifuged again for 1 min to remove additional solvent, gently washed twice using 300 μL of toluene and then dispersed in 2 mL of hexane. The final colloidal suspension is clear and colourless.

Synthesis of CsPbBr_3 NCs. 72.4 mg of PbBr_2 , 410.2 mg (500 μL) of OLAM (80-90%), 44.5 mg (50 μL) of OLAC and 5 mL of either (*R*)- or (*S*)-limonene are loaded into a 20 mL vial.²⁰ The reaction mixture is put under nitrogen under vigorous stirring and heated at 165 °C to dissolve all of the precursors. Then, at 160 °C, 500 μL of a CsOLAC solution (0.15 M) are swiftly injected and the flask is cooled to room temperature in air (Table S2). The reaction mixture is centrifugated at 4000 rpm for 5 min, and the precipitate is discharged. A solution of AcOEt with 5% in volume of the ligands (in 10:1 OLAM:OLAC ratio) is dropped into the supernatant until it turns cloudy. Then, the resulting mixture is centrifuged at 4000 rpm for 5 min, the precipitate is collected and dispersed in 1.5 mL of hexane. The washing process is performed twice, leading to a green, transparent colloidal suspension.

Synthesis of CsPbI_3 NCs. 75.9 mg of $\text{Pb}(\text{OAc})_2 \times 3\text{H}_2\text{O}$, 16.3 mg of Cs_2CO_3 , 183.4 mg (200 μL) of OLAC and 5 mL of the chosen solvent ((*R*)- or (*S*)-limonene) are loaded into a 20 mL vial and pumped to vacuum for 1 hour.²¹ Then, the temperature is quickly raised up at 165 °C and 2 mL of pre-heated OLAM-I (0.4 M I_2) solution are swiftly injected. After 10s the reaction is quenched using a water bath, leading to a cloudy and red

suspension. The latter mixture is centrifugated at 6000 rpm for 5 min and the precipitate is washed as described for the synthesis of CsPbCl₃ NCs. The final NCs are then dispersed in 5 mL of hexane.

Vacuum distillation. The waste from the initial centrifugation step of each synthesis is placed in a flask fitted with a Vigreux column and subjected to vacuum (5 mmHg). The flask is heated to 140 °C, causing the limonene to vaporize (boiling point 55 °C). The distilled limonene is clear and colourless, with a recovery yield of at least 70% and 90% for (*R*)- and (*S*)-limonene, respectively.

Optical Absorbance measurements. These were carried out on a Shimadzu UV–2600i spectrophotometer. The samples were diluted in 3 mL of hexane in a quartz cell (optical path 10 mm) to obtain an absorption of ~ 0.3 at the bandgap. The spectra were acquired in the 300 – 700 nm range for the CsPbCl₃ and CsPbBr₃ NCs, and 300 – 900 nm range for the CsPbI₃ NCs.

Photoluminescence (PL) and Photoluminescence Quantum Yield (PLQY) measurements. The photoluminescence spectra were recorded using an Edinburgh FS5 Spectrofluorometer, equipped with a continuous Xe lamp as an excitation source. The PL spectra were measured at λ_{exc} = 365 nm, 357 nm and 350 nm for CsPbCl₃, CsPbBr₃, and CsPbI₃, respectively (excitation slit width 3 nm, emission slit width 2 nm). The PLE spectra were measured at the PL maximum (excitation slit width 2 nm, emission slit width 3 nm). The PLQY was estimated using an integrating sphere (0.8 nm excitation slit width and 0.8 nm detection slit width). The analyses were carried out on diluted NC solutions dispersed in hexane in quartz cuvettes (path length of 1 cm).

X-ray Diffraction (XRD) analysis. The XRD patterns were collected by a Rigaku MiniFlex 600 diffractometer. The samples were prepared by drop casting the final colloidal solution obtained from the synthesis on a zero background Silica wafer. The diffractogram were acquired using the Cu K α irradiation, in the range 5°-60°, step 0.02° and speed 2.5°/min.

Transmission Electron Microscopy (TEM). TEM images were acquired using a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. The samples were prepared by dropping dilute suspensions of NCs onto carbon-coated 200 mesh copper grids. The images elaboration was performed using the software ImageJ.

Nuclear Magnetic Resonance (NMR) spectrometry. NMR spectra were measured on a JEOL JNM-ECZ400R at 400 MHz (1H) at 20 °C. The chemical shifts (δ) were expressed in parts per million relatives to tetramethylsilane (TMS) as internal standard (0.00 ppm) when CDCl₃ was used as solvent or to the solvent peak of deuterated toluene (Ph-CH₃: 2.09 ppm). The data treatment was performed using the MestReNova 14 software.

Inductive Coupled Plasma (ICP-OES) elemental analysis. Lead concentrations in the distilled solvents were estimated by (ICP-OES) using an iCAP 6300 DUO ICP-OES spectrometer (ThermoScientific). 30 μ L of each distilled solvent was mixed with 1 mL of aqua regia (HCl:HNO₃ 3:1, final concentration 10% v/v). After 8 h, the solution was added to 10 mL of ultrapure water. Thus, the final solution was filtered by 0.45 μ m filter and analysed.

Life Cycle Analysis (LCA). The assessment of the environmental consequences of an activity can be achieved through an LCA, which generally includes the following four different steps (ISO 14040 (2006) and ISO 14044 (2006)): i) identification of objectives and scope (definition of system boundaries, functional units and required data); ii) Life Cycle Inventory (LCI): collection of data, with analysis of related balances (energy and mass) according to the objective and scope; iii) Life Cycle Impact Assessment (LCIA): conversion of the LCI into environmental impacts, including consumption of natural resources and possible health impacts; iv) Interpretation: detailed analysis of the results obtained and identification of possible improvements to mitigate environmental impacts. Although originally developed to assess the life cycle of a product, the LCA methodology is also finding increasing application in assessing the impact of processes.³⁶ In a similar vein, it can also be used to assess the sustainability of different synthesis pathways and thus identify the most environmentally acceptable option. All analyses were performed using the Ecoinvent 2.3 database; all results were expressed in terms of Global Warming Potential over a 100-year period (GWP-100), according to the CML2001 - January 2016 method.³⁷ GWP is a relative measure based on the quantification of greenhouse gas emissions; other parameters could have been used,³⁸ but GWP was considered the most interesting in relation to the current situation of global warming and climate change.

To obtain an easily interpretable and sufficiently meaningful evaluation, 100 g of each final product was considered as a functional unit for each synthetic route. Therefore, all amounts of reagents used were rescaled according to the yield of each synthesis. For compounds for which no footprint data were available, such data were conveniently derived from the data of the precursors by looking at their production process. The analyses were carried out considering the entire life cycle of the different processes (from the cradle to the grave). Since limonene can be easily recovered by distillation from the reagent solution, with an experimentally verified efficiency of not less than 70%, this alternative scenario of partial limonene recovery was also considered.

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Appendices

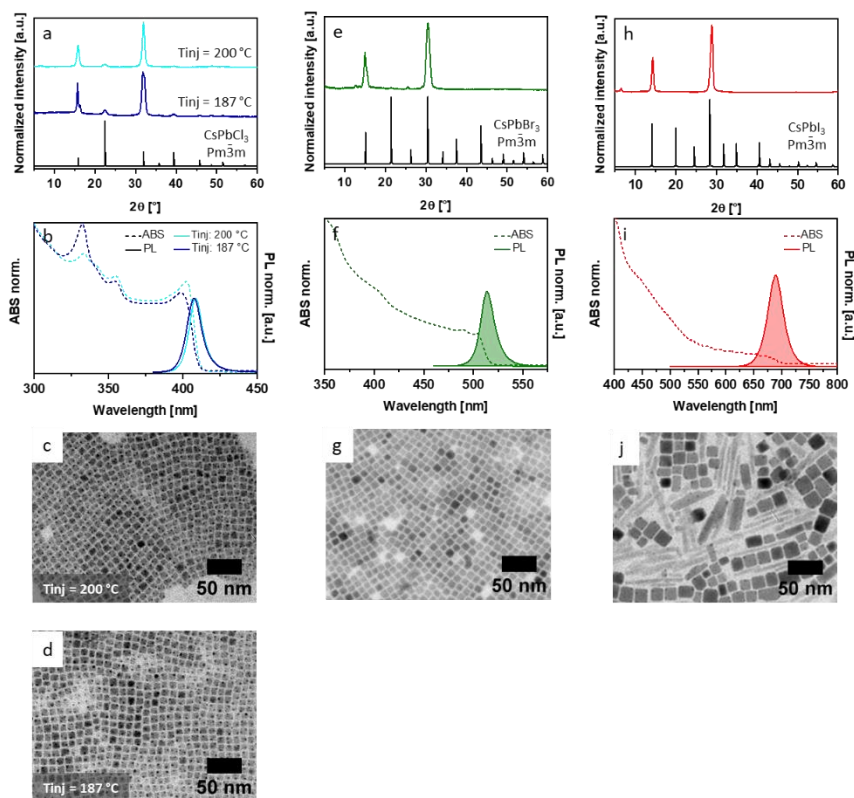


Figure A 4.1 XRD patterns, optical analysis (ABS: dashed line, PL, solid line) and Low-resolution TEM images of (a-d) CsPbCl₃ NCs, (e-g) CsPbBr₃ NCs and (h-j) CsPbI₃ NCs synthesized in ODE. Except for the CsPbI₃ NCs, where two temperatures were reported for the synthesis, the other stoichiometry followed the same procedure employ for the synthesis in limonene.

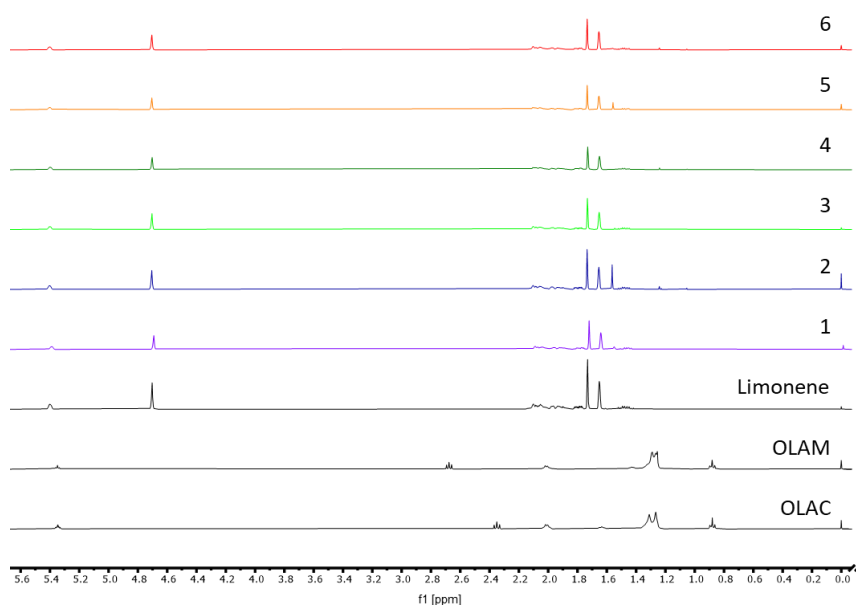


Figure A 4.2 ^1H NMR spectra of the distilled limonene from reaction waste. The analysis confirmed the structure and the absence of organic impurities in the recovered limonene obtained from CsPbCl_3 NCs synthesis used (*R*)- (spectrum 1) and (*S*)-limonene (spectrum 2), CsPbBr_3 NCs synthesis with (*R*)- (spectrum 3) and (*S*)-limonene (spectrum 4) and CsPbI_3 NCs synthesis used (*R*)- (spectrum 5) and (*S*)-limonene (spectrum 6). In spectra 2 and 5, the peak at 1.56 derived from the water.

Table A 4.1 GWP values for the dispersing/stabilizing agents (see Experimental section), calculated for 100 g of NCs.

Material/ Operation	GWP ($\text{kgCO}_2\text{eq} / 100\text{g}$ CsPbCl_3)		GWP ($\text{kgCO}_2\text{eq} / 100\text{g}$ CsPbBr_3)		GWP ($\text{kgCO}_2\text{eq} / 100\text{g}$ CsPbI_3)	
	ODE	LIM	ODE	LIM	ODE	LIM
Dispersing/ stabilizing agents	1.38	3.66	172.3	181.7	3.27	6.20

Chapter III

Pinene as alternative solvent
in colloidal nanocrystals
synthesis



Chapter V: Pinene as alternative solvent in colloidal nanocrystals synthesis

Abstract: Encourage from the results obtained with the employment of limonene as solvent for the colloidal synthesis of CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) nanocubes, the family of pinene molecules was also explored. This Chapter illustrates the use of this solvent for the CsPbX_3 ($X = \text{Br}, \text{I}$) nanocubes synthesis, enlarging the procedure to different morphology (nanoplates and nanorods) and to lead-free perovskites.

5.1 Introduction

Nowadays, nanocrystals are very exploited in new technologies, such as microelectronics, optoelectronics, photocatalysis and renewable energy.^{1–10} On this purpose, colloidal synthesis represents a highly effective strategy for producing nanocrystals, with the hot-injection (Hinj) method being among the most powerful and versatile approaches.¹¹ Despite the high efficiency of the method, the amount of waste generated during the reaction remains disproportionately large relative to the mass of the final product. As reported in Chapter 4.1, the waste primarily consists of the employed solvent, which usually is a petroleum-derivate.^{12–16} After the excellent results obtained employing the limonene¹⁷ in the hot-injection synthesis (exposed in Chapter IV), the class of pinene molecules was also explored as possible solvent.

In this Chapter, the use of (1*R*)- α -pinene, (1*S*)- α -pinene and (1*S*)- β -pinene as renewable and environmentally friendly solvents for nanocrystal synthesis via the hot-injection method is presented. Nanocrystals with different morphologies and stoichiometries were successfully synthesised, including lead halide perovskites and lead-free double perovskites. Differently from what was observed for the limonene, the solvent influenced the outcome of the synthesis: nanocrystals with identical stoichiometry displayed distinct features when prepared in different diastereomeric pinenes. This work highlights the potential of pinenes as *green* solvents, expanding the sustainable alternatives for nanocrystal synthesis while simultaneously revealing the critical role of solvent structure in determining nanocrystal properties.

5.2 Synthesis and characterization of CsPbBr_3 nanocubes

CsPbBr_3 nanocubes (NCs) were synthesized following the method proposed by Baranov et al.¹⁸ under an argon atmosphere. Briefly, the synthesis involved a hot-injection method, where a stock solution of CsOLAC was swiftly injected into a reaction mixture containing PbBr_2 and ligands dissolved in pinene at 160 °C (see Experimental Section for details). The resulting colloidal solutions appeared yellow and exhibited bright photoluminescence under 365 nm UV light (Table A5.1). For the α -pinene, which has a boiling point of 155 °C, we observed a slight increase of the reaction mixture boiling point to approximately 160 °C, similarly to what observed for limonene in our previous work.¹⁹

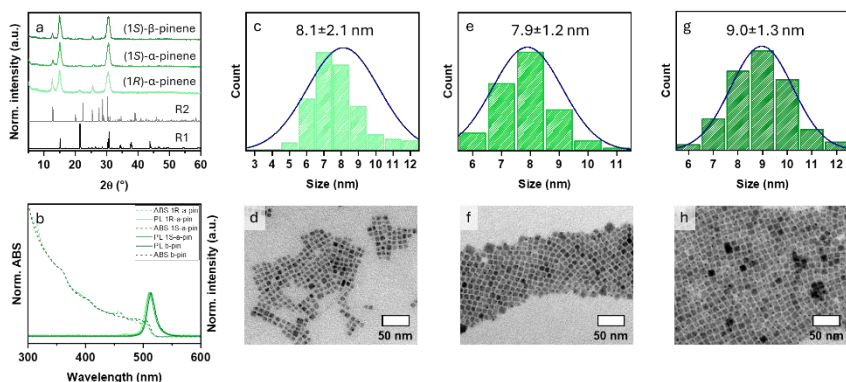


Figure 5.1 (a) XRD patterns of CsPbBr₃ NCs synthesized in (1R)-α-pinene (light green), (1S)-α-pinene (green), and (1S)-β-pinene (dark green). The black line (R1) represents the CsPbBr₃ Pnma reference (ICSD No. 231025), while the grey line (R2) is Cs₄PbBr₆ 0D trigonal R-3c (ICSD No. 23646). (b) ABS (dashed line) and PL spectra (solid lines, $\lambda_{\text{exc}} = 365$ nm) of CsPbBr₃ NCs (the reference colours were maintained from the ones in XRD pattern). Size distribution histograms and low-resolution TEM images and of the CsPbBr₃ NCs synthesized in (1R)-α-pinene (c, d), (1S)-α-pinene (e, f) and (1S)-β-pinene (g, h).

XRD analysis (Figure 5.1a) indicates that the samples consist of a mixture of phases. The peaks at 15.1° and 30.5°, associated with the (002) and (004) diffraction planes respectively, confirm the presence of the desired CsPbBr₃ in Pbnm orthorhombic structure. Additionally, the small peak at 21.5°, corresponding to the (020) plane, further supports this hypothesis. However, a secondary phase was identified; the peaks at 12.7° and 25.5° can be attributed to (012) and (024) crystallographic plane of the 0D Cs₄PbBr₆ structure, e.g. the trigonal R-3c phase.

As commonly reported in the literature for nanostructures, two main differences are observed when compared with the reference bulk pattern.^{20,21} First, the diffraction peaks exhibit noticeable *broadening*, which is attributed to the nanocrystalline nature of the material. Second, variations in the relative peak intensities are evident, arising from the *preferential orientation* of the nanocubes on the substrate. For the principal phase, this effect results in diffractograms dominated by the reflections corresponding to the (002) and (004) planes in all three samples. For the Cs₄PbBr₆ 0D phase, enhanced intensities are observed for the (012) and (024) reflections. This phenomenon also causes a reduction in the intensity of other peaks, which explains why only a limited number of reflections are visible in the XRD patterns. The reason of the formation of the 0D phase is still not clear and further experiments are planned. Yet, this indicates a possible influence of the solvent on the final compounds, being all of the experimental parameters equal to the synthesis in limonene and ODE.

Figure 5.1b shows the ABS and PL spectra. The ABS spectra display the characteristic features of LHP nanocubes, consisting of an initial strong absorption given by the excitonic peak followed by a continuous increase in absorption toward higher energies. For all three samples, the excitonic peak is located at 504 nm. The PL spectra exhibit well-defined emission peaks at 509 nm, 511 nm, and 513 nm, with corresponding full width at half maximum (FWHM) values of 85 meV, 79 meV, and 76 meV for (1R)-α-pinene, (1S)-α-pinene, and (1S)-β-pinene, respectively. Unfortunately, the ABS and PL analyses cannot

provide any evidence of the presence of the 0D phase, that has similar absorption and usually emits in the same region. Indeed, the green luminescence of the Cs_4PbBr_6 is still debated especially at the nanoscale.^{22–24}

Figure 5.1c-h reported the TEM images and the size distribution of the nanocubes as-synthesized. TEM images reveal a population of well-defined *nanocubes*. The nanocrystal size, determined from the edge length of the nanocubes, varies depending on the solvent employed. Samples synthesized in (1*R*)- α -pinene and (1*S*)- α -pinene exhibit an average edge length of 8.1 ± 2.1 nm and 7.9 ± 1.2 nm, whereas those obtained using (1*S*)- β -pinene display a slightly larger average size of 9.0 ± 1.3 nm. Indeed, this variation is reflected by the PL analyses.

The differences in emission wavelength and particle size observed for the α - and β -stereoisomers of pinene can be attributed to the distinct physicochemical characteristics of the two solvents. Specifically, the injection in α -pinene occurred at the boiling point of the reaction mixture, whereas this was not the case for the synthesis carried out in β -pinene. The influence of conducting the injection at the solvent's boiling point on the resulting nanoparticle properties has also been reported in our previous work, where CsPbCl_3 nanocubes synthesized at the boiling point of limonene displayed different characteristics compared to those obtained in the conventional solvent.¹⁹

5.3 Synthesis and characterization of CsPbBr_3 nanoplatelets

CsPbBr_3 nanoplatelets (NPs) were synthesized following the method reported by Toso et al.²⁵ Briefly, the synthesis involved the hot injection of benzoyl bromide (BzBr) into a solution containing CsOLAC , Pb(OLAC)_2 , and ligands dissolved in (1*R*)-, (1*S*)- α -pinene, or (1*S*)- β -pinene, at 95 °C (see Experimental Section for details). The resulting colloidal suspensions exhibited bright blue photoluminescence under 365 nm UV light (Table A5.1).

XRD patterns of the samples exhibit the characteristic features of self-assembled nanoplates, with repeated peaks appearing at regular $\Delta 2\theta$ intervals in the 5°–20° and 25°–30° regions (Figure 5.2a).^{25–27} Comparative analysis indicates that samples synthesized using (1*R*)- and (1*S*)- α -pinene exhibit more defined and structured diffraction patterns, suggestive of better nanoplatelet self-assembly, compared with those obtained using (1*S*)- β -pinene. Overall, the XRD patterns are consistent with those reported by Toso et al. for monolayer nanoplatelets (Figure A5.1).²⁵

The TEM investigation confirmed the XRD analyses; all the samples are formed by well-defined *rectangular nanoplatelets* (Figure 5.2b-d). The particles exhibit non-uniform contrast, which is attributed to differences in their vertical position (Z-axis), caused by stacking induced through self-assembly. The self-assembly process was intentionally promoted during sample preparation, as isolated nanoplatelets deposited on carbon-coated 200 mesh copper grids were too fragile to withstand the environmental conditions or the vacuum inside the TEM. The ability to observe overlapping nanoplatelets, due to their transparency, further confirms their low thickness.

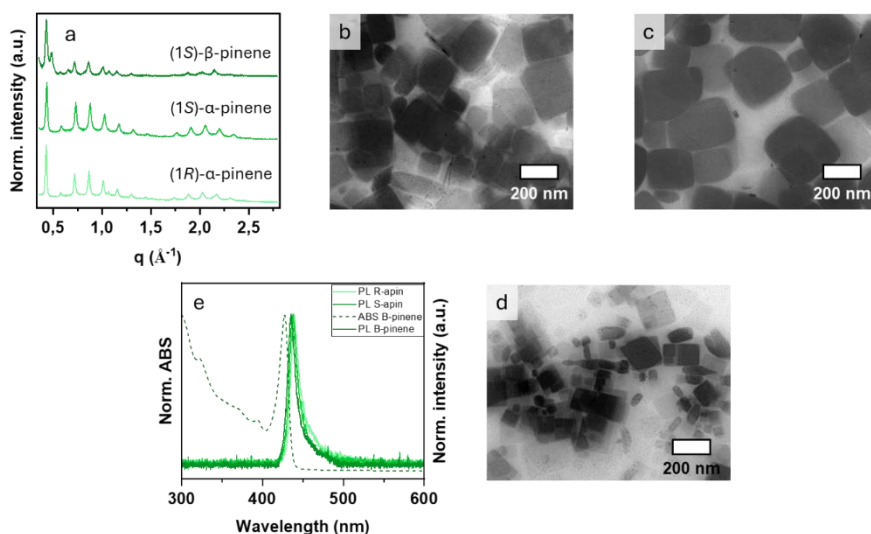


Figure 5.2 (a) XRD patterns of CsPbBr₃ NPs synthesized in CsPbBr₃ NCs synthesized in (1*R*)-α-pinene (light green), (1*S*)-α-pinene (green), and (1*S*)-β-pinene (dark green). Low-resolution TEM images of the CsPbBr₃ NPs synthesized in (1*R*)-α-pinene (b), (1*S*)-α-pinene (c) and (1*S*)-β-pinene (d). (e) Absorbance (dashed line) and PL spectra (solid lines, $\lambda_{\text{exc}} = 365$ nm) of CsPbBr₃ NPs (the reference colours were maintained from the ones in XRD pattern).

Figure 5.2e reports the ABS and PL spectra of the samples. The ABS spectra display the characteristic features of LHP nanoplatelets, with a well-defined excitonic peak observed at 428 nm for all samples. The PL spectra exhibit well-defined emission peaks at 440 nm, 438 nm, and 436 nm, with corresponding full width at half maximum (FWHM) values of 104 meV, 99 meV, and 98 meV for samples synthesized in (1*R*)-α-pinene, (1*S*)-α-pinene, and (1*S*)-β-pinene, respectively. The PL peaks are not perfectly symmetric, showing a slight asymmetry with a tail on the high-energy side of the maximum (higher wavelengths).

5.4 Synthesis and characterization of CsPbI₃ nanoparticles

CsPbI₃ nanoparticles were synthesized following the procedure reported by Akkerman et al.²⁸ Briefly, the synthesis involved the hot injection of oleylamine iodide (OLAM-I) into a reaction mixture containing caesium carbonate (Cs₂CO₃), lead acetate trihydrate (Pb(OAc)₂·3H₂O), and oleic acid (OLAC) in (1*R*)-α-pinene, (1*S*)-α-pinene, or (1*S*)-β-pinene, at 160 °C. The mixture was maintained at this temperature for 10 seconds before being quenched to room temperature using a water bath. The resulting colloidal dispersions appeared dark red and exhibited bright red photoluminescence under 365 nm UV illumination (Table A5.1).

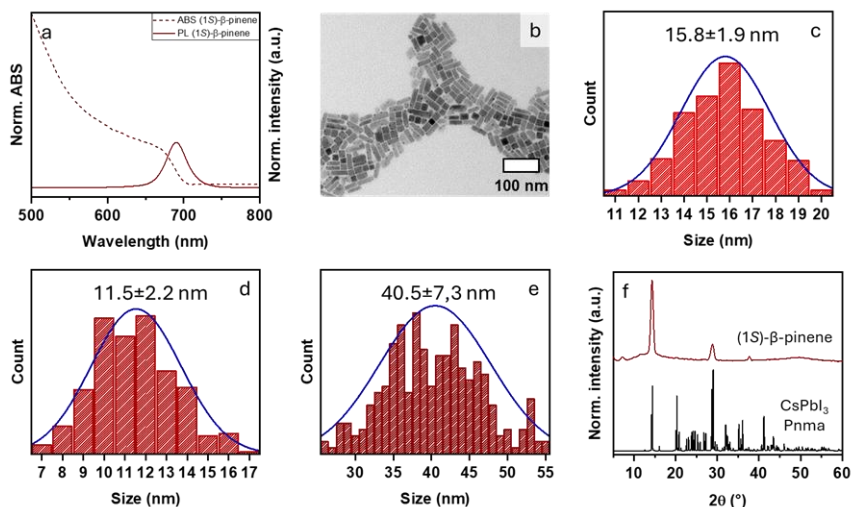


Figure 5.3 (a) Optical absorption spectrum (dashed line) and photoluminescence (PL) spectrum (solid line, $\lambda_{\text{exc}} = 365$ nm), (b) low-resolution TEM images, (c) size distribution of nanocubes, (d) width and (e) length distribution of nanorods, present in the same sample (f) XRD patterns of CsPbI₃ nanoparticles synthesized in (1S)-β-pinene. The black line corresponds to the CsPbI₃ Pnma reference (ICSD no. 32302).

The optical properties of the samples are shown in Figure 5.3a and A5.2a. The sample synthesized in (1S)-β-pinene exhibits an ABS spectrum featuring an excitonic peak at 672 nm, and a PL spectrum characterized by a well-defined emission peak at 690 nm with a FWHM of 96 meV. In contrast, optical properties of CsPbI₃ nanoparticles synthesized in (1R)- and (1S)-α-pinene display an emission characterized by a double peak, more evident for the sample prepared in (1S)-α-pinene. Therefore, for the latter materials we expected nanocrystals formed of different size and morphology. Indeed, TEM images reveal a *non-uniform nanocrystal population* formed by rods (Figure A5.2b-g) with variable lengths. A coexistence of two populations is evident also for the nanocrystals synthesized in 1S-β-pinene. TEM analysis reveals the coexistence of cube and rod morphologies (Figure 5.3b-e). The nanocubes have an average edge length of 15.8 ± 1.9 nm, while the nanorods are characterized by a length of 40.8 ± 7.5 nm and a width of 13.9 ± 3.0 nm. These values explain why in this case we observe a single peak in the PL spectrum. Indeed, the width of the rods are similar to the cubes, and both the morphologies have a same contrast in the images indicating a similar thickness. Thus, we did not observe any quantum confinement effect, differently for the samples synthesized in α-pinene.

XRD patterns confirmed that all of the nanocrystals crystallize in the Pnma phase (Figure 5.3f and A5.2h). As described for the previous compounds, the experimental patterns differ from the reference bulk pattern for the relative peak intensity. The most pronounced peaks were observed at 2θ of 14.3°, 28.8° and 37.7° related to (101), (202) and (312) crystallographic plane, respectively.

Additionally, samples synthesized using the α-pinene enantiomers display supplementary low-angle peaks, which can attribute to self-assembly phenomenon confirmed the obtainment of crystals with a small thickness.

5.5 Synthesis and characterization of $\text{Cs}_2\text{NaInCl}_6$ nanoparticles

Having demonstrate the possibility to employ the pinene molecules in the preparation of lead-based perovskites, we attempted the preparation of *lead-free double perovskites nanocrystals*. $\text{Cs}_2\text{NaInCl}_6$ nanoparticles, both undoped ($\text{Cs}_2\text{NaInCl}_6$) and Mn^{2+} -doped ($\text{Cs}_2\text{NaInCl}_6:\text{Mn}$), were synthesized by a modified version reported in Locardi et al. work.²⁹ The synthesis involved the injection of benzoyl chloride (BzCl) into a reaction mixture at 145 °C containing CsOLAC, sodium acetate (NaOAc), indium acetate ($\text{In}(\text{OAc})_3$), OLAM, and OLAC in (1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene, followed by immediate quenching to room temperature using a water bath. For the doped nanoparticles, manganese acetate ($\text{Mn}(\text{OAc})_2$) was also added to the initial reaction mixture. The resulting colloidal solutions were white, with only the Mn^{2+} -doped samples exhibiting orange photoluminescence under 254 nm UV irradiation (Table A5.1).

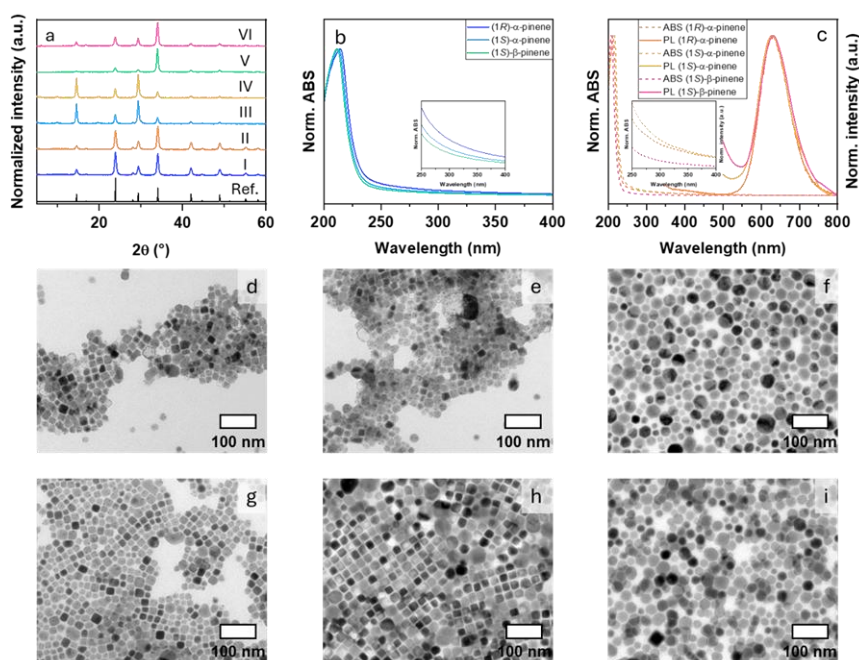


Figure 5.4 (a) XRD patterns of $\text{Cs}_2\text{NaInCl}_6$ nanoparticles synthesized in different pinene isomers: (I) undoped in (1*R*)- α -pinene (blue), (II) Mn^{2+} -doped in (1*R*)- α -pinene (orange), (III) undoped in (1*S*)- α -pinene (light blue), (IV) Mn^{2+} -doped in (1*S*)- α -pinene (light orange), (V) undoped in (1*S*)- β -pinene (aqua green), and (VI) Mn^{2+} -doped in (1*S*)- β -pinene (pink). The black line corresponds to the $\text{Cs}_2\text{NaInCl}_6$ Fm-3m reference (ICSD no. 161152). (b) Optical absorption spectra of undoped $\text{Cs}_2\text{NaInCl}_6$ nanoparticles. (c) Optical absorption (dashed line) and photoluminescence (PL) spectra (solid line, $\lambda_{\text{exc}} = 230$ nm) of Mn^{2+} -doped $\text{Cs}_2\text{NaInCl}_6$ nanoparticles. The reference colours were maintained from the ones in XRD pattern. The insets show the expansion of the ABS between 250 – 400 nm. Low-resolution TEM images of undoped $\text{Cs}_2\text{NaInCl}_6$ nanoparticles synthesized in (d) (1*R*)- α -pinene, (e) (1*S*)- α -pinene and (f) (1*S*)- β -pinene. Low-resolution TEM images of undoped Mn^{2+} -doped nanoparticles synthesized in (g) (1*R*)- α -pinene, (h) (1*S*)- α -pinene and (i) (1*S*)- β -pinene.

According to the XRD patterns shown in Figure 5.4a, all the samples crystallized in the cubic Fm-3m phase characterized the double perovskites. Peak broadening is observed throughout the patterns, reflecting the nanocrystalline nature of the samples and no significant peak shifts are observed in the $\text{Cs}_2\text{NaInCl}_6\text{:Mn}$ samples, suggesting that Mn^{2+} doping does not induce any detectable crystal distortion. Samples synthesized in the same solvent display similar diffraction patterns. Undoped and Mn-doped $\text{Cs}_2\text{NaInCl}_6$ nanocrystals synthesized in (1*R*)- α -pinene (Figure 5.4a I and II) show patterns in which the intensity ratios reflected the reference. In contrast, the samples synthesized in (1*S*)- α -pinene (Figure 5.4a III and IV) display enhanced peaks at 14.5° and 29.3° , corresponding to the (111) and (222) crystallographic planes. Finally, the patterns of the particles synthesized in (1*S*)- β -pinene (Figure 5.4a V and VI) are dominated by a peak at 33.9° , corresponding to the (400) plane. These observations, together with the results obtained in the previous work suggest a possible influence of the solvent on the formation and growth of the crystals. Whereas a variation may be expected between β -pinene and α -pinene, the enantiomers of the latter molecule should have the same behaviour since the other reagents employed in the synthesis are not chiral. Differences between samples synthesized in (1*R*)- and (1*S*)- α -pinene may be attributed to variations in solvent impurities.

Figure 5.4b and c show the optical properties of undoped and Mn – doped $\text{Cs}_2\text{NaInCl}_6$, respectively. The peak of ABS spectra originates from the absorbance of the solvent (hexane) partially masks the nanoparticle absorption peak that start to absorb approximately in the range of 250 - 300 nm.³⁰ The presence of Mn^{2+} dopants does not significantly affect the absorption characteristics. In contrast, only the doped samples display photoluminescence under UV excitation. PL spectra were recorded using 230 nm excitation, revealing a symmetric emission peak cantered at 631 nm with a FWHM of 274 meV. This emission is consistent with the Mn^{2+} emission in the double perovskite matrix.^{31–35}

Figure 5.4d-i reports the TEM images of all the samples synthesized in the three solvents. In the α -pinenes, the nanocrystals assumes a *cubic shape* with an average edge length around 18.8 nm for the undoped samples (Figure 5.4d, e and Figure A5.3a, c), and an average edge lengths of 17.4 ± 2.8 nm and 16.4 ± 2.9 nm for samples prepared using (1*R*)- and (1*S*)- α -pinene, respectively (Figure 5.4g, h and Figure A5.3b, d). In contrast, synthesis in (1*S*)- β -pinene produces nanoparticles with a *hexagonal morphology* (Figure Xf, i and Figure Xe, f), similarly with the work published by Locardi et al. where dioctyl ether was employed as solvent.²⁹ In this case, the particle length, measured as the distance between two parallel opposite sides of the hexagon, was 21.6 ± 5.6 nm and 23.2 ± 4.4 nm for undoped and doped nanoparticles, respectively.

5.6 Conclusion

In conclusion, we demonstrated that (1*R*)- and (1*S*)- α -pinene, as well as (1*S*)- β -pinene, can serve as effective *green* alternatives to the tradition solvent for perovskite nanocrystal syntheses below 160 °C. Using these bio-derived solvents, we successfully synthesized CsPbBr_3 nanocubes and nanoplatelets, CsPbI_3 nanocrystals, together with lead - free undoped and Mn^{2+} -doped $\text{Cs}_2\text{NaInCl}_6$ nanoparticles. Interestingly, the results highlight that the diastereomeric form of pinene may influence the outcome of synthesis, with effects on structural, morphological, and optical features of the nanocrystals. These

findings underscore the potential of pinene-based solvents as sustainable media for colloidal nanocrystal synthesis while also revealing the need for careful consideration of solvent stereochemistry in achieving desired material properties.

5.7 Experimental section

Materials. (1*R*)- α -pinene (Sigma-Aldrich, 97%), (1*S*)- α -pinene (Sigma-Aldrich, >97%), (1*S*)- β -pinene (Sigma-Aldrich, 99%), benzoyl bromide (BzBr, Across Organic, 99%), benzoyl chloride (BzCl, Across Organic, 99%), caesium acetate (CsOAc, Sigma-Aldrich, 99.9%), caesium carbonate (Cs₂CO₃, Alfa Aesar, 99.9%), ethyl acetate (EtOAc, Sigma-Aldrich, >99.5%), hexane (Hex, Sigma-Aldrich, 99%), indium(III) acetate (In(OAc)₃, Alfa Aesar, 99.99%), iodine (I₂, Fluka, >99.8%), lead(II) acetate trihydrate (Pb(OAc)₂·3H₂O, ThermoFisher Scientific, 99.995%), lead(II) bromide (PbBr₂, Sigma-Aldrich, 99%), manganese(II) acetate (Mn(OAc)₂, Alfa Aesar, anhydrous, 98+%), methyl acetate (MeOAc, ThermoFisher Scientific, 99%), oleic acid (OLAC, Alfa Aesar, tech. 90%), oleyl amine (OLAM, ThermoFisher Scientific, 80-90%), sodium acetate (NaOAc, Alfa Aesar, 99%), toluene (Alfa Aesar, 99%). All the chemicals were employed without any further purification.

CsOLAC synthesis. CsOLAC (0.15M)¹⁸ was prepared loading Cs₂CO₃ (400 mg) and OLAC (1.75 mL) into a 40 mL glass vial containing 15 mL of the chosen solvent ((1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene) under an argon atmosphere. The mixture was heated to 100 °C under vigorous stirring until a fully transparent yellow solution was obtained. The resulting stock solution was stored under air at room temperature. CsOLAC (1M)²⁵ was prepared following the same procedure but employing 192 mg of CsOAc and 1 mL of OLAC loaded into a 4 mL vial.

Pb(OLAC)₂ (0.67 M) synthesis.²⁵ Pb(OAc)₂·3H₂O (379 mg) and OLAC (1.5 mL) were loaded into a 4 mL glass vial. The mixture was heated to 100 °C under vacuum for 1 h till the complete dissolution of the precursors. The resulting stock solution, that solidifies at room temperature, was stored under air at room temperature.

Synthesis of OLAM-I (0.4 M).²⁸ I₂ (0.75 g), OLAM (4.5 mL) and 10 mL of solvent ((1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene) were loaded into a 25 mL three-neck flask under an argon atmosphere. The mixture was heated to 100 °C, undergoing a colour change from red to brown and finally to a red, clear solution. The resulting OLAM-I solution (0.4 M I₂) was transferred while still hot into a vial and used directly without further purification.

Synthesis of CsPbBr₃ NCs. PbBr₂ (72.4 mg), OLAM (500 μ L, 80–90%), OLAC (50 μ L), and 5 mL of solvent ((1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene) were loaded into a 20 mL glass vial. The mixture was stirred vigorously in an argon atmosphere and heated to 160 °C to dissolve all the precursors. Then, CsOLAC solution 0.15 M (500 μ L), prepared in the same solvent employed for the reaction, was swiftly injected, and the vial was allowed to cool to room temperature under air. The crude mixture was centrifuged at 4000 rpm for 5 min, and the precipitate was discarded. AcOMe was added dropwise to the supernatant until turbidity appeared. The resulting mixture was centrifuged at 4000 rpm for 5 min, gently washed twice with 300 μ L of toluene (added slowly to avoid forming a colloidal suspension), and finally dispersed in 1.5 mL of Hex, yielding a green, transparent colloidal suspension of CsPbBr₃ NCs.

Synthesis of CsPbI₃ NCs. Pb(OAc)₂·3H₂O (75.9 mg), Cs₂CO₃ (16.3 mg), OLAC (200 μ L) and 5 mL of solvent ((1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene) were loaded into a 20 mL glass vial and pumped to vacuum at room temperature for 1 h. The mixture was then placed under argon, and the temperature was rapidly raised to the target value (165 °C for (1*S*)- β -pinene and 160 °C for (1*R*)- or (1*S*)- α -pinene). Pre-heated OLAM-I

solution (0.4 M I_2 , 2 mL) was swiftly injected, and after 10 s the reaction was quenched in a water bath, yielding a cloudy red suspension. The mixture was centrifuged at 6000 rpm for 5 min, and the precipitate was washed following the same procedure as described for $CsPbBr_3$ NCs. The resulting $CsPbI_3$ nanocrystals were suspended in 1 mL of Hex.

Synthesis of $CsPbBr_3$ nanoplates. OLAM (114 μ L), OLAC (160 μ L), and 2 mL of the solvent ((1*R*)- α -pinene, (1*S*)- α -pinene or (1*S*)- β -pinene) were loaded into a 4 mL vial and heated to 95 °C under vigorous stirring. Then 20 μ L and 60 μ L of pre-heated $CsOLAC$ (1 M) and $Pb(OLAC)_2$ (0.67 M), respectively, were added to the ligand solution using micropipettes, with dipping and flushing to ensure quantitative transfer. Finally, 20 μ L of $BzBr$ was injected into the reaction mixture. The reaction proceeded at 95 °C for 1 min and was quenched by lowering the temperature in a water bath without stirring. The crude mixture was purified by adding $EtOAc$ until turbidity appeared. The resulting suspension was centrifuged at 4000 rpm for 2 min, and the precipitate was resuspended in 1.2 mL of Hex to yield the purified $CsPbBr_3$ nanoplates.

Synthesis of $Cs_2NaInCl_6$ nanocrystals. Cs_2CO_3 (81.5 mg), $NaOAc$ (20.5 mg), $In(OAc)_3$ (73.0 mg), OLAC (1200 μ L), OLAM (600 μ L), and 4 mL of solvent ((1*R*)- α -pinene, (1*S*)- α -pinene, or (1*S*)- β -pinene) were loaded into a 25 mL three-neck flask and stirred vigorously. The mixture was degassed under vacuum at room temperature for 15 min and then placed under argon. The temperature was firstly increased to 115 °C and maintained for 5 min to dissolve the salts, and then to 140 °C; at this temperature, $BzCl$ (200 μ L) diluted in 600 μ L of the same degassed solvent employed for the reaction was swiftly injected. The reaction was immediately quenched by temperature lowering in a water bath. The product was purified by centrifugation at 4500 rpm for 5 min, the supernatant discarded, and the precipitate resuspended in 3 mL of Hex. Further purification was performed by adding $EtOAc$ until turbidity appeared, followed by centrifugation at 6000 rpm for 3 min. The final product was suspended in 3 mL of Hex. Mn^{2+} -doped $Cs_2NaInCl_6$ nanocrystals were prepared following the same procedure but also adding 8.6 mg of $Mn(OAc)_2$ together with the other precursors salts.

Absorbance (ABS) measurement. ABS spectra were measured by a Shimadzu UV–2600i spectrophotometer. The samples were diluted in 3 mL of hexane in a quartz cell (optical path 10 mm) to obtain an absorption of ~ 0.3 at the bandgap. Scan step size 1.0 nm, time for one scan: program slow (speed for one scan of $CsPbBr_3$ NCs and NPs 3 min, speed for one scan of $CsPbI_3$ nanocrystals, $CsNaInCl_6$ nanocrystals and $Cs_2NaInCl_6:Mn$ nanocrystals 4.5 min, calculated scan speed 2.22 nm/s).

Photoluminescence (PL). The photoluminescence spectra were recorded using an Edinburgh FLS1000 Spectrofluorometer, equipped with a continuous Xe lamp as an excitation source. The PL spectra were measured at $\lambda_{exc} = 365$ nm for $CsPbBr_3$ NCs, NPs and $CsPbI_3$ nanocrystals and 230 nm for $Cs_2NaInCl_6:Mn$ (excitation slit width 3 nm, emission slit width 2 nm). The PLE spectra were measured at the PL maximum (excitation slit width 2 nm, emission slit width 3 nm). The analyses were carried out on diluted NC solutions dispersed in hexane in quartz cuvettes (path length of 10 mm).

X-ray Diffraction (XRD) analysis. The XRD patterns were collected by a Rigaku MiniFlex 600 diffractometer. The samples were prepared by drop casting the final colloidal solution obtained from the synthesis on a zero background Silica wafer. The diffractogram are acquired using the $Cu K_\alpha$ irradiation, in the range 5° - 60°, step 0.02° and speed 2.5°/min.

Transmission Electron Microscopy (TEM). TEM images were acquired using a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. The samples were prepared by dropping dilute suspensions of nanocrystals onto carbon-coated 200 mesh copper grids. The images elaboration was performed using the software ImageJ.³⁶

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Appendices

Table A 5.1 Photographs of the luminescence of colloidal suspensions of nanoparticles (3 mL in hexane) under UV lamp excitation (excitation wavelengths reported in the accompanying table). The synthesis solvent is indicated in the table header, while the nanoparticle type (stoichiometry and morphology) is listed in the first column.

	Excitonic wavelength	(1 <i>R</i>)- α -pinene	(1 <i>S</i>)- α -pinene	(1 <i>S</i>)- β -pinene
CsPbBr ₃ nanocubes	365 nm			
CsPbBr ₃ nanoplatelets	365 nm			
CsPbI ₃ nanoparticles	365 nm			
CsNaInCl ₆ :Mn nanoparticles	254 nm			

Table A 5.2 Comparison of the size, emission wavelength, and PL FWHM of nanoparticles synthesized in (1*R*)- α -pinene, (1*S*)- α -pinene, and (1*S*)- β -pinene. The first column reports the stoichiometry of the nanoparticles, the second their morphology, and the third the solvent employed. For nanorods, both width (W) and length (L) are reported; for nanocubes, the size corresponds to the edge length; for hexagonal nanoparticles, the size is given by the distance between two opposite parallel sides. The size of CsPbBr₃ nanoplatelets was not determined, as their optical properties are governed by the platelet thickness (quantum confinement) rather than surface dimensions. The PL FWHM of CsPbI₃ nanorods synthesized in α -pinene could not be extracted due to overlapping peaks. PL data for Cs₆NaInCl₆ are not included, as these nanoparticles do not exhibit photoluminescence.

Stoichiometry	Morphology	Employed solvent	Size (nm)	PL wavelength (nm)	FWHM of PL (meV)
CsPbBr ₃	Nanocubes	(1 <i>R</i>)- α -pinene	8.1±2.1	509	85
		(1 <i>S</i>)- α -pinene	7.9±1.2	511	79
		(1 <i>S</i>)- β -pinene	9.0±1.3	513	76
	Nanoplatelets	(1 <i>R</i>)- α -pinene	/	440	104
		(1 <i>S</i>)- α -pinene	/	438	99
		(1 <i>S</i>)- β -pinene	/	436	98
CsPbI ₃	Nanorods	(1 <i>R</i>)- α -pinene	W: 13.9±3.0	684	/
			L: 50.8±11.4	686	/
	Nanorods	(1 <i>S</i>)- α -pinene	W: 13.9±3.0	624	/
			L: 50.8±11.4	686	/
	Mixed	(1 <i>S</i>)- β -pinene	Nanocubes 15.8 ± 1.9	690	96
			Nanorods W: 13.9±3.0 L: 40.8±7.5		
Cs ₂ NaInCl ₆	Nanocubes	(1 <i>R</i>)- α -pinene	18.7±3.1	/	/
	Nanocubes	(1 <i>S</i>)- α -pinene	18.8±3.2	/	/
	Hexagonal shape	(1 <i>S</i>)- β -pinene	21.6±5.2	/	/

Cs ₂ NaInCl ₆ :Mn	Nanocubes	(1 <i>R</i>)- α -pinene	17.4 $\pm$ 2.8	631	274
	Nanocubes	(1 <i>S</i>)- α -pinene	16.4 $\pm$ 2.9	631	274
	Hexagonal shape	(1 <i>S</i>)- β -pinene	23.2 $\pm$ 4.4	631	274

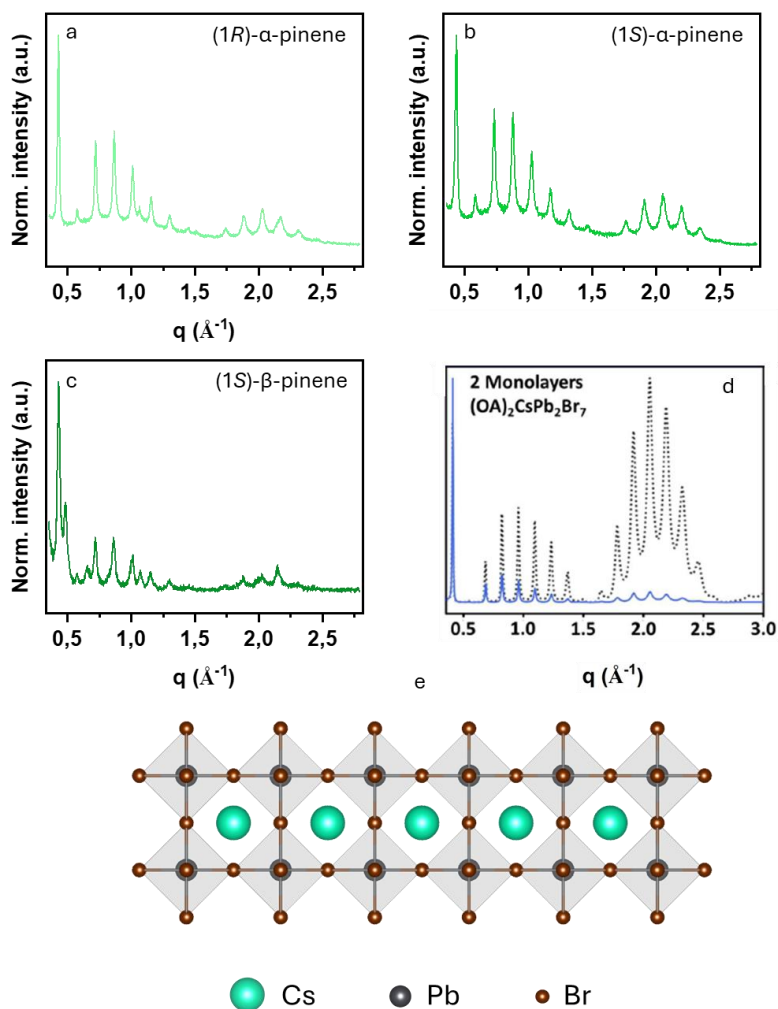


Figure A 5.1 XRD pattern reported in function of the scattering vector (q) of CsPbBr₃ NPs synthesized in (a) (1*R*)- α -pinene (light green), (b) (1*S*)- α -pinene (green), and (c) (1*S*)- β -pinene (dark green). (d) theoretical XRD pattern of 2 monolayer CsPbBr₃ NPs reported by Toso et al. Reproduced from ref.²⁵ under a CC-BY 4.0 license. Copyright © 2021 The Authors. Published by American Chemical Society. All rights reserved. (e) Representation of 2 monolayers nanosheetlets.

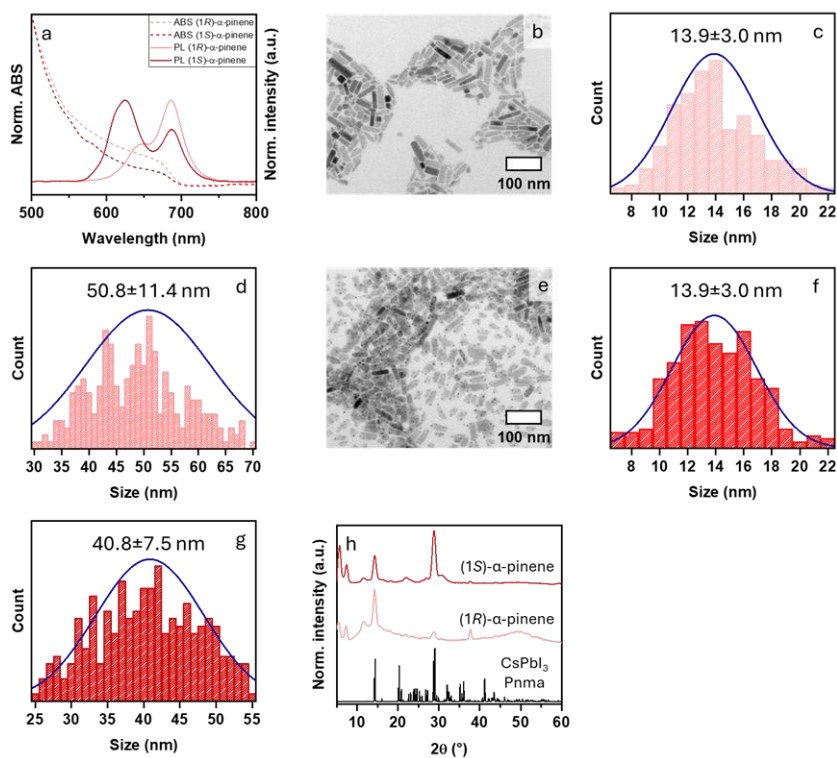


Figure A 5.2 (a) Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{\text{exc}} = 365$ nm) of the same samples. TEM image, width distribution, and length distribution of CsPbI₃ nanorods synthesized in (b-d) (1R)-α-pinene and (e-g) (1S)-α-pinene. (h) XRD patterns of CsPbI₃ nanoparticles synthesized in (1R)-α-pinene (rose) and (1S)-α-pinene (red). The black line corresponds to the CsPbI₃ Pnma reference (ICSD no. 32302).

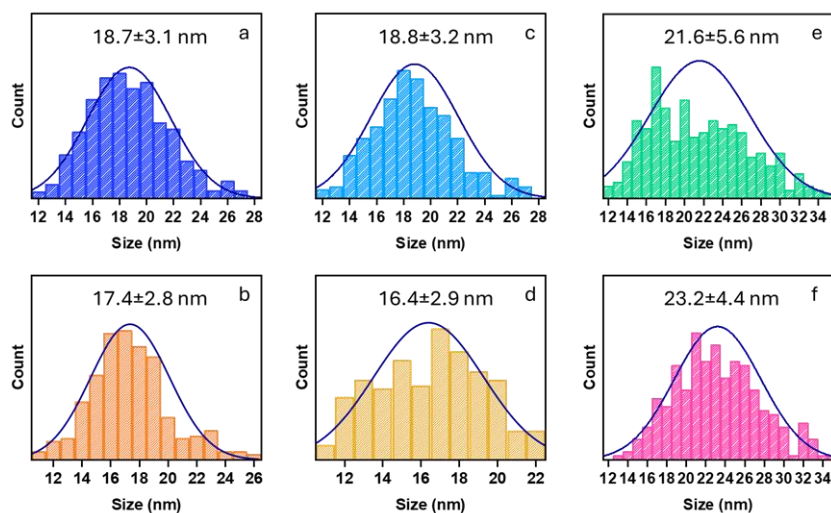


Figure A 5.3 Size distribution and low-resolution TEM images of undoped and Mn^{2+} -doped $\text{Cs}_2\text{NaInCl}_6$ nanoparticles synthesized in (a, b) (1*R*)- α -pinene, (c, d) (1*S*)- α -pinene and (e, f) (1*S*)- β -pinene. In the round bracket, the first letter refers for the synthesis of the undoped nanoparticles, while the second stands for the doped ones. The reference colours were maintained from the ones in XRD pattern in Figure 5.4.

Chapter VI

Chiral ligand to chiroptical
properties



Chapter VI: Chiral ligand to chiroptical properties

Abstract: Chiroptical properties are among the most intriguing features of luminescent materials that exhibit structural chirality. Circular dichroism and, in particular, circularly polarized luminescence can be exploited in advanced analytical techniques and next-generation optical devices. Chapter VI introduces these two phenomena and explains how centrosymmetric luminescent materials, especially lead halide perovskites, can be engineered to obtain chiroptical properties despite their intrinsically achiral crystal structure.

6.1 Introduction on chiroptical properties

Luminescent materials that exhibit chirality can transfer this feature to their optical properties through differential interactions with the two components of circularly polarized light. Consequently, the observed phenomena arise from *chiroptical effects*, which originate from the fact that light consists of chiral components that interact in opposite ways with the two enantiomers.^{1–3}

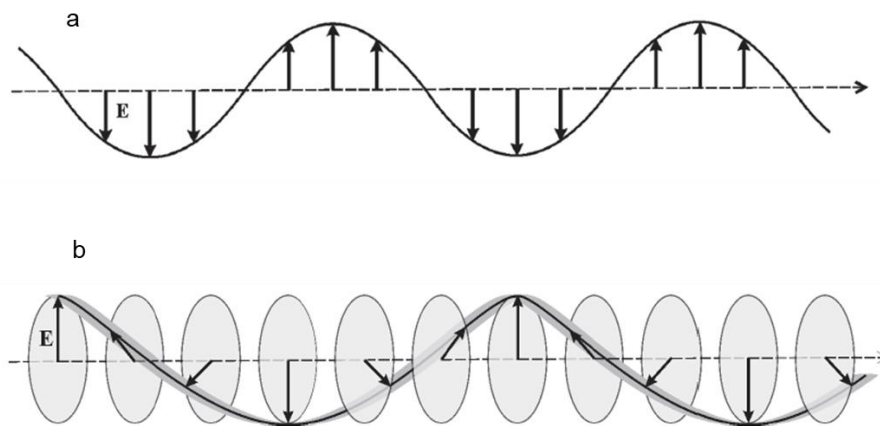


Figure 6.1 Oscillation of the electric field vector for (a) linear and (b) circularly polarized light along the propagation axis. In this example, right-circularly polarized light is represented. Reproduced with the permission from ref.¹

As described in Chapter 1.4, light consists of electromagnetic radiation that propagates through space by means of oscillations of the electric and magnetic fields, which are perpendicular to each other. Owing to this perpendicularity, the properties of an electromagnetic wave can be fully described by considering only one of these two components. The plane in which the chosen field vector oscillates is referred to the *plane*

of *polarization*. When electromagnetic waves are constrained to oscillate within a single plane, the resulting light is termed *polarized light*. (Figure 6.1a).^{1,4}

Linearly polarized light can be described as the racemic combination of two orthogonal circularly polarized waves of equal amplitude that rotate in opposite directions. Each of these components propagates through the rotation of its electric field vector around the direction of propagation. Therefore, it is referred to them as *circularly polarized light* (Figure 6.1b). Depending on whether the rotation is clockwise or counterclockwise, the circularly polarized light is defined as *right-* or *left-circularly polarized*, respectively. These two components are mirror images of each other and can therefore be considered enantiomeric. As shown in Figure 6.2, the resultant vector (E_s) obtained by summing the vectors of the left- (E_l) and right-circularly polarized (E_r) components oscillates along a single plane, generating linearly polarized light. When the two components are aligned, E_s reaches its maximum or minimum magnitude. As the rotation proceeds, the magnitude of E_s decreases until the two vectors point in opposite directions. At this point, the magnitude of E_s becomes zero. Because the two circular components have identical amplitudes, the resultant vector E_s always oscillates along the same axis.^{1,2,4}

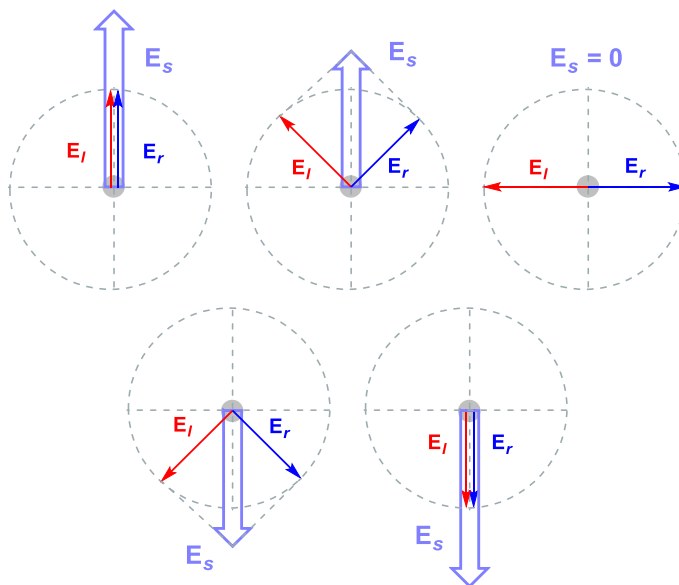


Figure 6.2 Variation of the electric field vector (violet vector) of the linear polarized light given by the vectorial sum of the electric field vectors of left- (red vector) and right-circularly polarized light (blue vector).

It is well known that enantiomeric objects exhibit identical physicochemical properties only in an achiral environment, whereas a chiral surround confers different features. Since light is composed of chiral components, it can therefore interact differently with chiral objects.

The first way in which this interaction was exploited fell into the *polarimetry technique*. In this analysis the rotation of the polarized light is quantified across a chiral solution (Figure 6.3). This phenomenon is known as *circular birefringence* and occurs because the left-

and right-circularly polarized components of the light propagate at different velocities within a chiral medium. As there is no differential absorption between the two components, the magnitudes of their vectors, and consequently that of E_s , remain unchanged. However, the direction of E_s rotates by an angle α , which is detected by the polarimetric measurement.^{1,5}

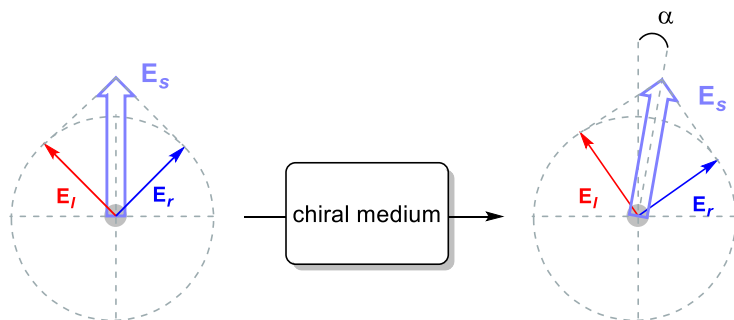


Figure 6.3 Explanation of the circular birefringence phenomenon. When the linear polarized light passes through a chiral medium without absorbance effect, the velocity of electric field vectors of left- (red vector) and right-circularly polarized light (blue vector) changes due to the different refraction index of this light into the chiral solution. Their vectorial sum allows the electric field vector (violet vector) to oscillate onto a different polarization plane. The difference between the initial and final polarization plane position determine the optical rotation α , which will be measured by polarimetry analysis.

Nevertheless, additional types of radiation–matter interactions can be observed in the context of circularly polarized light. Among these, the differential absorption or emission of one of the two circular components is particularly relevant for luminescent materials.

6.1.1 Circular dichroism (CD)

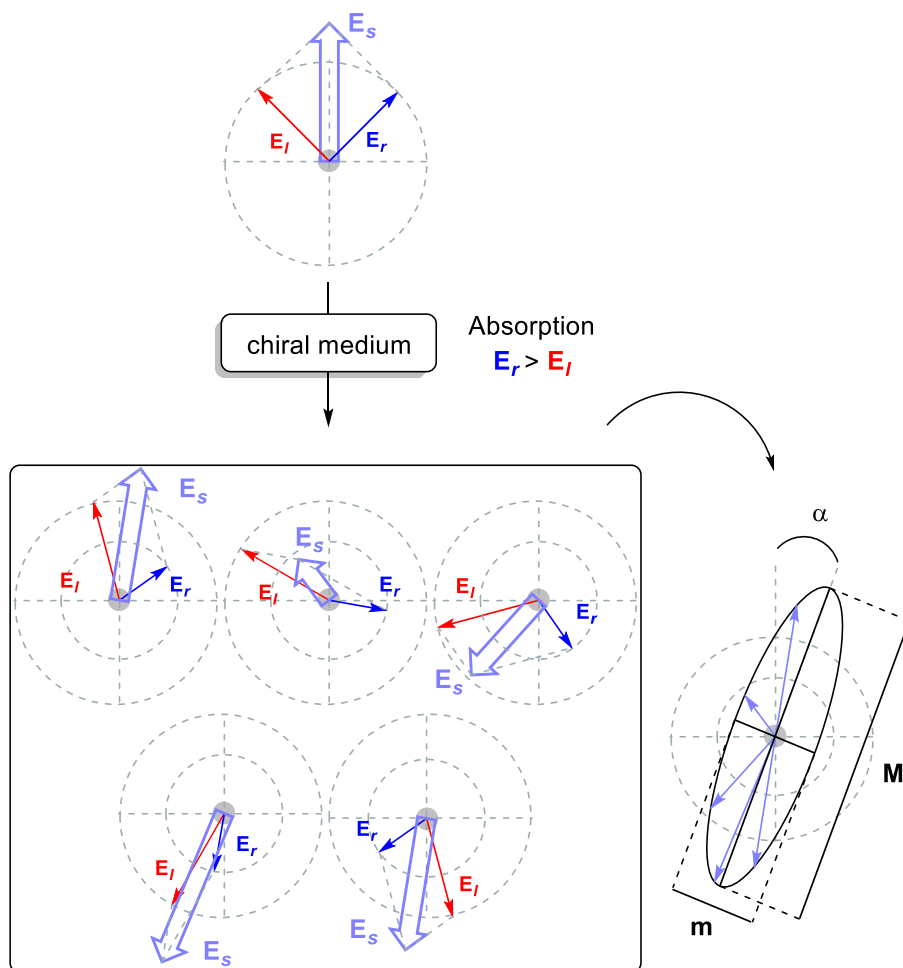


Figure 6.4 Explanation of the circular dichroism phenomenon. When the linear polarized light passes through a chiral medium with absorbance effect, not only the velocity of electric field vectors of left- (red vector) and right-circularly polarized light (blue vector) changes, but they are absorbed in a different way. In particular, with this representation, the right-circularly polarized light is absorbed more than the left- one. Since these two vectors are not more identical in magnitude, the electric field vector sum vector (violet vector) does not more oscillate along a polarization plane, but describes an ellipse. This ellipse is described by a major (M) and a minor (m) axis. As for the birefringence phenomenon, the variation of velocity of the left- and right-component leads to a rotation of the principal ellipse axis than the polarization plane, giving a value of the optical rotation α .

Circular dichroism refers to the ability of a chiral object to absorb left- and right-circularly polarized light to different extents. After passing through the sample, the transmitted light becomes enriched in the less-absorbed component and therefore acquires a degree of circular polarization. In this case, E_s no longer oscillates along a

straight line, as in linearly polarized light, but instead traces an *ellipse* due to the unequal magnitudes of E_r and E_i (Figure 6.4). As in the case of circular birefringence, the two circular components experience different refractive indices, causing the major axis of the ellipse to be rotated relative to the original polarization direction by an angle α .^{1,3,6–8}

As discussed in Chapter 1.3, a wavelength is absorbed when its energy matches that required for a transition between electronic states. A transition from an initial state i to a final state f occurs if it possesses sufficient transition strength, which arises from changes in the electric ($\vec{\mu}$) and/or magnetic ($\vec{m}$) dipole moments. Since, $\vec{\mu}$ is typically much higher than $\vec{m}$, electronic transitions are generally classified as allowed or forbidden solely on the basis of the changes in $\vec{\mu}$. For transitions that do not involve circularly polarized light, the transition strength is expressed as the oscillator strength ($f_{i \rightarrow f}$). Conversely, when the transition involves circularly polarized light, both dipole moments must be considered, because the light is described by an elliptical trajectory. In this case, the transition strength is defined as the *rotational strength* ($R_{i \rightarrow f}$), which corresponds to the scalar product between the imaginary component of $\vec{\mu}$ and $\vec{m}$ (Equation 6.1). $R_{i \rightarrow f}$ is depending on the wavelength (λ). This leads to observe CD only at specific λ . The sum of all the $R_{i \rightarrow f}$, and then the CD, across the entire electromagnetic spectrum equals zero. Finally, for a pair of enantiomers, the $R_{i \rightarrow f}$ at a given λ has the same absolute value but opposite sign.^{1,9}

Equation 6.1 Rotational strength

$$R_{i \rightarrow f} = \text{Im}(\langle i | \vec{\mu} | f \rangle \cdot \langle i | \vec{m} | f \rangle)$$

The output of CD analysis is the difference ($\Delta A_{CD}(\lambda)$) between the absorbance of left-circularly polarized light ($A_l(\lambda)$) and right-circularly polarized light ($A_r(\lambda)$) at a given λ (Equation 6.2). $\Delta A_{CD}(\lambda)$ is related to the *ellipticity* θ of the ellipse traced by the resultant vector, as illustrated in Figure 6.4. Ellipticity is defined as arctangent of the ratio between its minor and major axes of the ellipse (Equation 6.3).¹

Equation 6.2 Difference in absorbance of the left and right circularly polarized light and its correlation with ellipticity

$$\Delta A_{CD}(\lambda) = A_l(\lambda) - A_r(\lambda) = \frac{\theta}{\left(\frac{180}{4\pi} \ln 10\right)} = \frac{\theta}{32.98}$$

Equation 6.3 Definition of ellipticity

$$\theta = \tan^{-1} \frac{m}{M}$$

Since there is a difference in absorbance, it is possible to define a molar extinction coefficient for left-circularly polarized light ($\epsilon_l(\lambda)$) and right-circularly polarized light ($\epsilon_r(\lambda)$), at given λ . Consequently, a form of the *Beer–Lambert law* can be applied to $\Delta A_{CD}(\lambda)$ (Equation 6.4), where $\Delta \epsilon(\lambda)$ is the difference between the two molar extinction coefficients (Equation 6.5), C is the concentration of the sample and l is the optical path length.⁹

Equation 6.4 Lambert-Beer law applied to CD

$$\Delta A_{CD}(\lambda) = \Delta \varepsilon * C * l$$

Equation 6.5 Difference of molar extinction coefficient

$$\Delta \varepsilon(\lambda) = \varepsilon_l(\lambda) - \varepsilon_r(\lambda)$$

Finally, the *g-factor*, or *Kuhn's dissymmetry factor*, for CD (g_{abs}) provides a normalized measure of the optical activity of an electronic transition. It is expressed in Equation 6.6 as the ratio between $\Delta \varepsilon(\lambda)$ and the molar extinction coefficient $\varepsilon(\lambda)$. g_{abs} is dependent to the λ observed and is extremely important because it is independent from C and l , making it an intrinsic property of the substance under study.^{1,9}

Equation 6.6 Practical calculation of *g-factor* for CD

$$g_{abs} = \frac{\Delta \varepsilon(\lambda)}{\varepsilon(\lambda)}$$

CD analyses are valuable for the study of chiral objects, particularly for probing electronic transitions that involve circularly polarized light. In organic molecules, CD can also be used to investigate the relative orientation and distance between chromophores, and ultimately to assign the stereochemistry of enantiomers.^{1,9}

6.1.2 Circularly polarized luminescence (CPL)

Circularly polarized luminescence (CPL) is the phenomenon in which the emission of a material exhibits an intensity ratio between left- and right-circularly polarized light that differs from unity. Because the two components are not equal, the emitted light possesses a certain ellipticity and therefore appears circularly polarized.¹

CPL can be generated in different ways. The earliest method was purely physical: linearly polarized light is divided into its left- and right-circularly polarized components by passing through a quarter-wave plate placed at 45° with respect to the polarization direction. Since this approach relies on a "racemic resolution" of linearly polarized light, at least 50% of the optical power is lost.^{10,11} Alternatively, CPL can be produced using emitters that intrinsically generate circularly polarized light. In this case, the effect arises from the combination of a *luminescent chromophore* and a *chiral environment*. This means that CPL can originate not only from chiral luminophores, whose molecular structure contains inherent chirality, but also from achiral emitters placed in chiral surroundings.^{1,11–13}

For the same reasons as in CD, the electronic transitions that give rise to CPL are also governed by $R_{f \rightarrow i}$. In particular, $R_{f \rightarrow i}$ determines the *luminescence dissymmetry factor* (g_{lum}) according to Equation 6.7, where $D_{f \rightarrow i}$ is the transition dipole strength. This quantity can be approximated as the sum of the squares of the electric ($\overrightarrow{\mu_{f \rightarrow i}}$) and magnetic ($\overrightarrow{m_{f \rightarrow i}}$) transition dipole moments. Since the magnitude of $\overrightarrow{\mu_{f \rightarrow i}}$ is usually much higher than that of $\overrightarrow{m_{f \rightarrow i}}$, the governing equation can be simplified to its final approximate form. Based on this, maximizing g_{lum} can be achieved by increasing $\overrightarrow{m_{f \rightarrow i}}$, decreasing $\overrightarrow{\mu_{f \rightarrow i}}$ or aligning the two vectors. Generally, increasing $\overrightarrow{m_{f \rightarrow i}}$ is a more practical strategy. Since decreasing

$\overrightarrow{\mu_{f \rightarrow i}}$ generally leads to an improvement of the g_{lum} , but also to a reduction of other properties of the luminescence materials, such as the intensity of luminescence, increasing $\overrightarrow{m_{f \rightarrow i}}$ is a more practical strategy. This is, for example, the case in lanthanide complexes, which exhibit high g_{lum} .^{13–17}

Equation 6.7 Theoretical expression and common approximation used for calculating the CPL dissymmetry factor from electric and magnetic transition dipole moments

$$g_{lum} = \frac{4R_{f \rightarrow i}}{D_{f \rightarrow i}} \approx \frac{4\overrightarrow{\mu_{f \rightarrow i}} \cdot \overrightarrow{m_{f \rightarrow i}}}{|\overrightarrow{\mu_{f \rightarrow i}}|^2 + |\overrightarrow{m_{f \rightarrow i}}|^2} = \frac{4|\overrightarrow{\mu_{f \rightarrow i}}||\overrightarrow{m_{f \rightarrow i}}|\cos\theta}{|\overrightarrow{\mu_{f \rightarrow i}}|^2 + |\overrightarrow{m_{f \rightarrow i}}|^2} \approx \frac{|\overrightarrow{m_{f \rightarrow i}}|\cos\theta}{|\overrightarrow{\mu_{f \rightarrow i}}|}$$

Through CPL spectroscopy, which measures the difference in intensity between the left- (I_l) and right- (I_r) circularly polarized light emitted by the sample, g_{lum} can be calculated using the Equation 6.8. The value of this g_{lum} ranges from -2 to $+2$: the extrema correspond to the exclusive emission of left- or right-circularly polarized light, whereas a value of zero indicates the absence of CPL. Values of $|g_{lum}|$ in the order of 10^{-5} – 10^{-3} are considered low, whereas values in the range of 10^{-1} – 10^{-2} , as observed for certain metal complexes, are regarded as high.^{11,18} Similarly to g_{abs} , g_{lum} is both material- and wavelength-dependent, and it exhibits opposite signs for a pair of enantiomeric emitters at a given λ .

Equation 6.8 Practical expression for the calculation of the CPL dissymmetry factor from left- and right-circularly polarized emission intensities

$$g_{lum} = \frac{2(I_l - I_r)}{I_l + I_r}$$

As with achiral emitters, chiral luminescent materials can be characterized by their brightness. In the context of circularly polarized emission, this property is referred to as *CPL brightness* (B_{CPL}). B_{CPL} is calculated as the product of the molar extinction coefficient (ϵ_λ), the emission quantum yield (Φ) and the absolute value of g_{lum} (Equation 6.9).^{18–20}

Equation 6.9 Definition of CPL brightness, which quantifies the efficiency of circularly polarized emission by combining molar absorption, photoluminescence quantum yield, and the magnitude of the luminescence dissymmetry factor

$$B_{CPL} = \frac{1}{2}\epsilon_\lambda\Phi|g_{lum}|$$

CPL properties have attracted considerable interest due to their wide range of potential applications. Displays that employ this technology can achieve high image contrast, as the use of circularly polarized light reduces reflections from the surrounding environment.^{21,22} Furthermore, materials exhibiting CPL activity can be used in the fabrication of optical sensors, which work by the perturbation of CPL signal given by external stimuli. Such perturbations may induce variations in CPL intensity or even trigger the activation or suppression of the CPL response.^{23–26} In addition, materials with intrinsic CPL activity enable higher-density information storage compared to conventional luminescent materials, and they offer promising opportunities in the field of optical encryption.^{27–31} CPL-

based devices are also highly relevant for bioimaging, where the suppression of background noise afforded by circular polarization significantly enhances signal clarity.^{32–34} Furthermore, comparing CPL and CD provides insights into the geometrical differences between the ground and excited states of a chiral luminescent material.^{11,13} Although rare, CPL is also exploited in nature. Certain stomatopods, benthic marine crustaceans, possess a highly complex retinal structure and a specialized organization of photoreceptors that allow them to detect not only linearly polarized light (LPL) but also CPL. It has been hypothesized that this ability provides these species with a private communication channel invisible to most other organisms, and may also play a role in improving visual contrast and reducing haze in their natural environment.^{35–38}

6.2 Chiral Engineering of LHP (nano)crystals

Despite their exceptional properties, LHP are largely limited in terms of intrinsic chiroptical activity due to their centrosymmetric crystal structure, which prevents the emergence of structural chirality. Leaving aside this “little” particular, LHPs exhibit strong spin–orbit coupling in their electronic states, spin-dependent optical selection rules, and large Rashba splitting, providing a solid foundation for the potential incorporation of chiroptical properties alongside their well-known optoelectronic features.^{39–41} A widely adopted strategy to induce chirality in LHPs is the *incorporation of chiral molecules*, such as ammonium cations, into the crystal lattice.^{10,39,42–44} Billing and Lemmerer provided the first report about the inclusion of a chiral ammonium cation, namely bis[(S)- β -phenylethylammonium], into organic–inorganic hybrid lead halide perovskites (OIHPs) in 2003.⁴⁵ In this approach, the chiral ammonium cation replaces the A⁺ site in the perovskite structure, enabling the synthesis of chiral 0D, 1D, and 2D OIHP structures.^{46–52} In contrast, 3D OIHPs are more challenging to synthesize due to the bulkiness of the chiral ammonium cation. At the nanoscale, a common strategy involves the use of chiral amines as surface ligands to passivate perovskite nanocrystals. This can be achieved either by incorporating chiral ligands during the colloidal synthesis, typically in combination with oleylamine, or, more commonly, through post-synthesis ligand exchange.^{53–58} Moon et al. first reported LHP nanocrystals decorated with 1,2-diaminocyclohexane (DACH) in 2017.⁴³ Finally, embedding nanocrystals into chiral supramolecular structures, such as polymeric matrices or superlattices, can further enable the development of chiroptical properties.^{12,42,59–63} Figure 6.5 depicts the various techniques described to break the centrosymmetric crystal structure of LHPs.

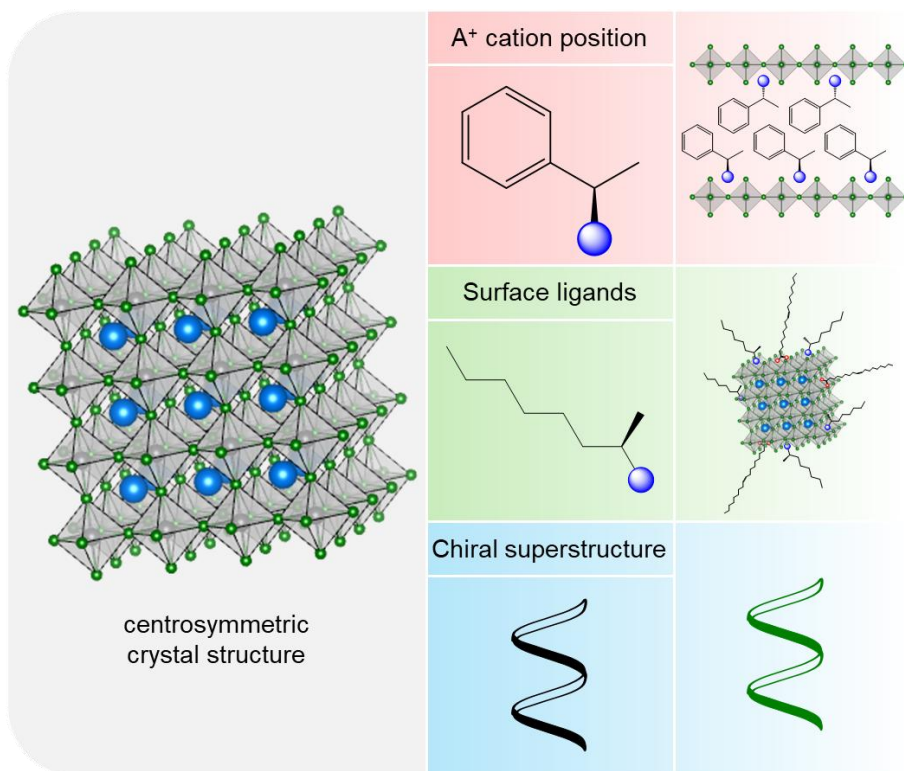


Figure 6.5 Illustration of the strategies employed to break the centrosymmetry of LHPs crystals and how the final material appears.

Although it is now well established that the chirality of the ligand is a key factor in inducing chiroptical properties, the precise mechanism by which these properties arise remains a topic of debate. Clearly, the chiral ligand serves as the starting point, but it is not fully understood whether it imparts chirality through electronic interactions or by inducing distortions in the crystal lattice, although the latter hypothesis appears to be more widely supported.^{64–69} *Georgieva et al.* proposed that chirality is transferred through *electronic coupling* between the ligand and the synthesized nanoparticles; in their study, nanoplatelets affect the exciton and leading to observable chiroptical properties.⁶⁴ In contrast, *Chen et al.* described a model in which the chiral transfer occurs via *surface distortions*, often referred to as a "*chiral footprint*".^{68,69} This surface-distortion model was further supported by *Kim et al.*,⁷⁰ who studied variations in the Pb–Br–Pb bond angles in the crystal lattice of CsPbBr₃ upon binding of a (S)-MBA⁺ chiral ammonium ligand using DFT calculations. In their model, the ligand occupies the position of surface Cs⁺ ions (Figure 6.6a). The uncovered crystal displayed a Pb–Br–Pb bond angle of 154°. After addition of the chiral ligand, the bond angles in the first layer were significantly altered, but rapidly returned to their normal values moving away from the surface. Starting from the second layer, the bond angles exhibited smaller deviations, with the effect persisting up to the fifth layer. By the sixth layer, no variation was observed (Figure 6.6b and c). These results indicate that the nanocrystal surface is strongly influenced by the chiral ligand,

generating a non-centrosymmetric structure, although the effect diminishes rapidly into the bulk of the crystal (Figure 6.6d).

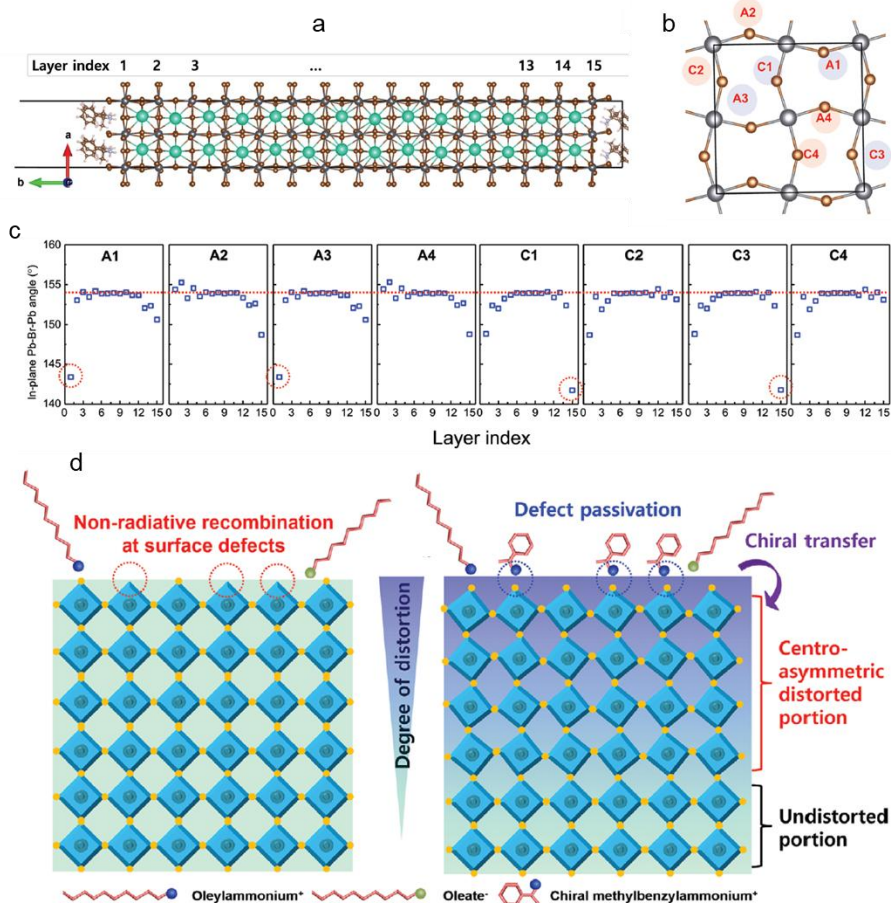


Figure 6.6 (a) representation of the fifteen-layers CsPbBr₃ slab employed to the DFT-calculation. The first and last layer are terminated with (S)-MBA⁺ which takes the place of the Cs⁺ cation, (b) Labelling scheme for the Pb-Br-Pb bond angles within the orthorhombic CsPbBr₃ crystal cell, (c) variation of labelled Pb-Br-Pb bond angles in function of the crystal layer. This figure highlighted the strong changing in Pb-Br-Pb bond angles of the layer which is bound by the ligand and its fast recovering to the bulk value of 154° going in deep into the crystal, (d) illustration of the chiral transfer mechanism through the surface distortion of the nanocrystal. Reproduced from ref.⁷⁰ under a CC-BY 4.0 license. Copyright © 2022 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH. All rights reserved.

The chiroptical properties of nanocrystals are not determined solely by the presence and structure of the chiral ligand; other parameters, such as morphology and chiral ligand concentration, also play a fundamental role.¹⁰ Because lattice distortions primarily affect the first layer, nanoplatelets, particularly monolayered ones, tend to exhibit the highest g_{lum} value.^{10,54,71,72} In contrast, multilayered nanocrystals generally display weaker chiroptical responses. Kim *et al.* further demonstrated that optimal CPL is achieved at relatively low

concentrations of chiral ligands on the nanocrystal surface.⁵³ This behaviour is analogous to the "*Sergeant–Soldier*" effect reported for chiral OIHs, where the addition of a small achiral cation, such as formamidine (FA), reduces lattice distortion and enhances g_{lum} .^{53,73} Temperature also plays a crucial role in the chiral transfer process. Increasing temperature causes thermal expansion of the crystal lattice, reducing the lattice distortion. Additionally, at higher temperatures, spin-flip processes occur more readily, further suppressing spin-polarized emission. Consequently, improved chiroptical properties are typically observed at low temperatures. One strategy to mitigate thermal effects is to apply an external magnetic field, which can help preserve the spin-polarized emission and maintain CPL performance.^{10,40,74,75}

Despite the novel properties imparted by the use of chiral ligands, chiral LHPs suffer from significant stability issues. It is well known that short carbon-chain ligands with steric hindrance on the amine head, which are most commonly employed as chiral ligands, negatively affect the stability of the nanocrystals.^{76,77} Additional instability arises from lattice distortions, which, although essential for inducing chiroptical properties, make the nanocrystals more fragile. Consequently, the inherent instability of chiral LHPs renders them difficult to handle and complicates their incorporation into devices.¹⁰

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Chapter VII

Synthetic approach to new
chiral oleylamine-based
ligand



Chapter VII: Synthetic approach to new chiral oleylamine-based ligand

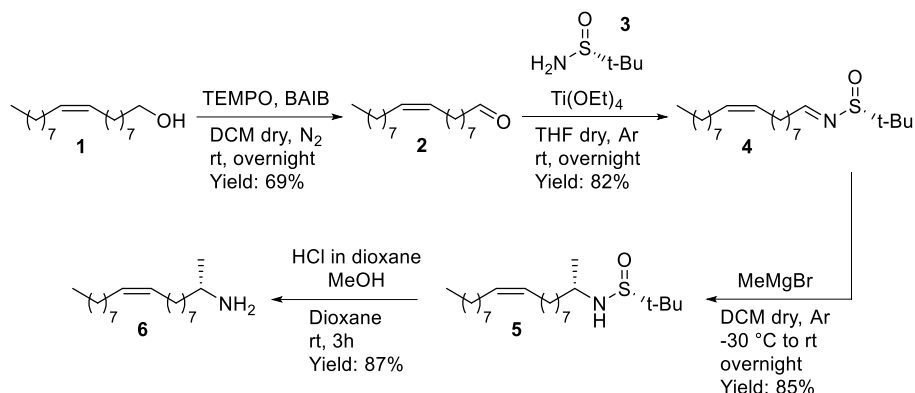
Abstract: Frontier research on luminescent nanocrystals increasingly focuses on uncovering new optoelectronic properties, such as circular dichroism (CD) and circularly polarized luminescence (CPL). Despite the strong appeal of this emerging field, progress is often hindered by the limited commercial availability of enantiomerically pure chiral molecules, particularly chiral amines. Moreover, the structural and electronic characteristics of the commercially available ligands are not always optimal for achieving the desired properties in the resulting nanocrystals. For these reasons, integrating organic-synthesis methodologies to design and prepare new custom ligands can be essential for advancing research in this area. In this context, Chapter VII describes the synthesis of (S,Z)-nonadec-10-en-2-amine, a tailored chiral amine featuring a stereogenic centre embedded within the oleyl backbone of oleylamine (OLAM).

7.1 Synthetic strategy

The presence of a chiral ligand on the surface of a nanocrystal can strongly influence its final material properties. Numerous studies have reported such effects, particularly regarding the optoelectronic behaviour of LHP NCs. Indeed, the chiral environment introduced by these ligands can induce CD as well as CPL.

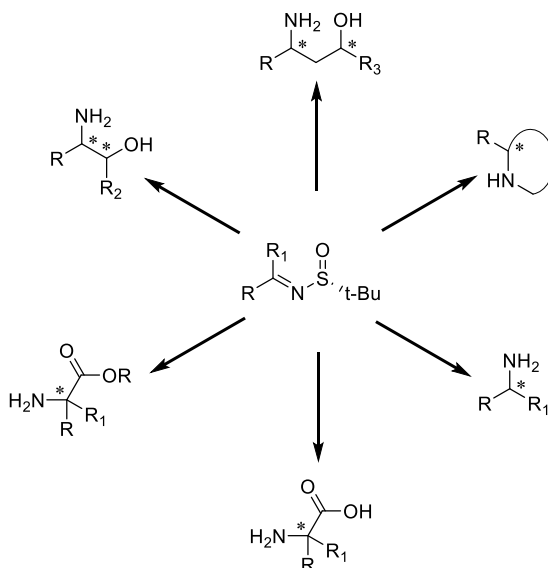
Two general strategies are typically employed to introduce chiral ligands onto LHP nanocrystal surfaces. The first involves *in-situ synthesis*, usually using a mixture of enantiopure 2-octylamine/OLAM to obtain quantum dots. The second relies on *post-synthetic ligand-exchange procedures* in which short-chain chiral amines replace oleylamine on the nanocrystal surface.¹⁻⁴ The most commonly used chiral amines include (R)/(S)-2-octylamine, (R)/(S)-methylbenzylamine ((R)/(S)-MBA), (R)/(S)-methylphenethylamine ((R)/(S)-MPEA), (R)/(S)-1-(2-naphthyl)ethylamine ((R)/(S)-NEA).⁴⁻⁸ Although these approaches generally produce nanocrystals exhibiting CD and CPL, their structural stability is often inferior to that of LHP nanocrystals capped with OLAM. This observation highlights the stabilizing role of long-chain amines in enhancing nanocrystal robustness.¹ However, chiral amines combining both enantiomeric purity and a long oleyl-like hydrocarbon chain are neither commercially available nor reported in the literature. For this reason, a synthetic route was designed to obtain such ligands.

The synthetic pathway leading to (S,Z)-nonadec-10-en-2-amine **6** is illustrated in Scheme 7.1. This newly designed aminic ligand features the characteristic oleyl backbone, modified by the introduction of a methyl group on the α -carbon. This substituent was deliberately chosen to introduce low steric hindrance and thereby generate a “chiral oleylamine” without excessively altering the structural features that make OLAM an effective ligand. Positioning a small substituent close to the amine headgroup ensures that the ligand remains functionally similar to standard OLAM. Conversely, introducing the substituent, and thus the stereocentre, farther from the anchoring amine functionality might fail to transmit chirality to the nanocrystal surface.



Scheme 7.1 Synthetic pathway to obtain the “chiral oleyl amine” (*S,Z*)-nonadec-10-en-2-amine from the oleyl alcohol

Briefly, the synthesis of **6** begins with the oxidation of the oleyl alcohol **1** to the corresponding olealdehyde **2**. The aldehyde is then subjected to a condensation reaction with a chiral auxiliary, yielding imine **4**. The electrophilic carbon of this imine is subsequently attacked by a Grignard reagent, introducing the desired substituent. Finally, cleavage of the chiral auxiliary releases the free amine **6**.

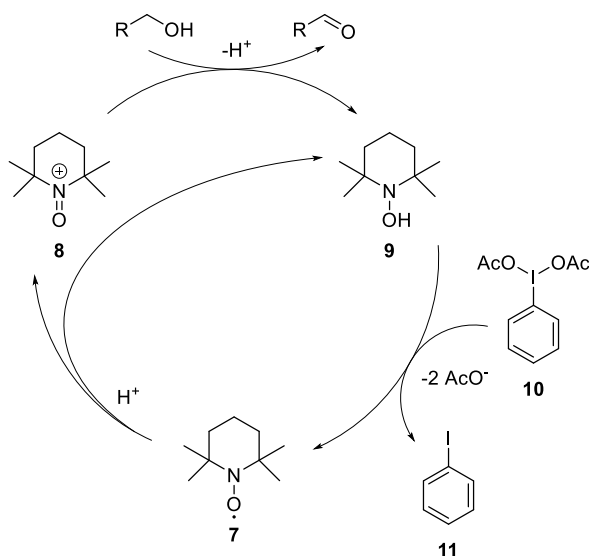


Scheme 7.2 Chiral building block derived from the employment of Ellman sulfinamide in their synthesis.

From the Scheme 7.1 is evident that the employment of the chiral auxiliary is crucial to obtain **6** in a high amount and enantiomeric excess. For this purpose, *Ellman sulfinamides* were employed.

This class of compounds was first introduced by Ellman in 1997 as chiral ammonia equivalents.⁹ Since then, they have become widely used as chiral auxiliaries in asymmetric synthesis involving imines as electrophiles. The resulting *N*-sulfinyl imines can serve as versatile intermediates for the preparation of various chiral building blocks, including α - or β -amino acid or ester, 1,2 or 1,3-amino alcohols, nitrogenous heterocycles or, more simply, amines (Scheme 7.2).^{10–15} As a chiral auxiliary, the sulfonamide introduces a stereogenic centre with a defined configuration near to the carbonyl-derived carbon. The subsequent nucleophilic attack on the imine typically affords two possible diastereoisomers, often with high levels of diastereoselectivity. An additional advantage of Ellman-based methodology is the mild and efficient cleavage of the auxiliary, which cleanly releases the free amine.¹⁴

7.2 Oxidation of oleyl alcohol



Scheme 7.3 Catalytic cycle of TEMPO/BAIB oxidation

The oxidation of **1** to **2** was performed using the Piancatelli–Margarita oxidation,^{16,17} also known as *TEMPO/BAIB oxidation* (Scheme 7.1), whose mechanism is illustrated in Scheme 7.3. In this approach, the active oxidant originates from the stable the 2,2,6,6-tetramethylpiperidine 1-oxyl free radical **7** (TEMPO) added to the reactive mixture in catalytic amount. The reaction begins with the acid-catalyzed dismutation of TEMPO into the oxoammonium **8** (TEMPO⁺), which serves as the actual oxidizing agent, and the hydroxylammonium **9** (TEMPO-H). Here, TEMPO⁺ selectively abstracts a hydride from the α -carbon of the primary alcohol, yielding **2** and the hydroxylammonium **9** (TEMPO-H). To sustain the catalytic cycle, TEMPO-H must be reoxidized to TEMPO.^{16,17} Therefore, (diacetoxyiodo)benzene (BAIB) must be used in stoichiometric amounts, or in slight excess, relative to oleyl alcohol. Among the various oxidation protocols capable of converting primary alcohols into aldehydes, TEMPO/BAIB strategy is particularly

advantageous due to its mild reaction conditions, operational simplicity, and the safe, easy-to-handle nature of the reagents.^{16–18}

7.3 N-sulfinyl imine formation

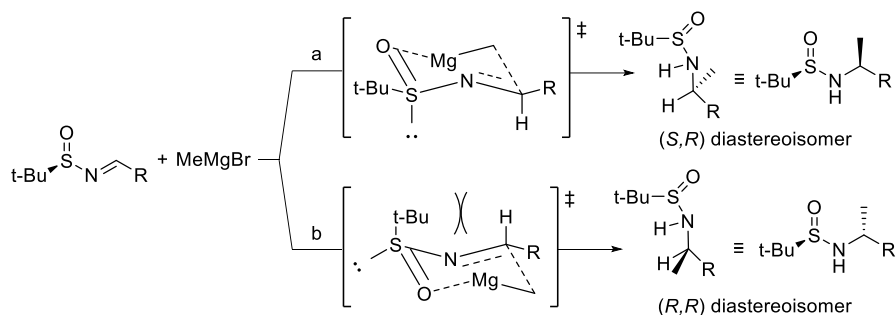
The second step of the synthetic route focuses on the introduction of a chiral centre onto the aldehyde using the Ellman sulfinamides.

The *N*-sulfinyl aldimine **4** was obtained through the condensation of **2** and the Ellmann sulfinamide (*R*)-(+)-2-metil-2-propanesulfinamide **3** (Scheme 7.1). The imine formation was promoted by $\text{Ti}(\text{OEt})_4$ which acts both as a Lewis acid and as a dehydrating agent. The employment of $\text{Ti}(\text{OEt})_4$ allowed mild condition reaction, thereby suppressing any potential epimerization of **3**. Although several $\text{Ti}(\text{IV})$ complexes are commercially available, the more sterically hindered species, such as $\text{Ti}(\text{iPrO})_4$, require higher temperatures (around 60 °C) and are generally less effective for this transformation, whereas more powerful Lewis acid, like TiCl_4 , promotes also the undesired aldol condensation. The employment of $\text{Ti}(\text{IV})$ species takes advantage also in the work up step, since readily form inorganic salts that can be removed by straightforward filtration.¹⁵ The new C=N bond had been considered with *E* configuration from the literature reports.¹⁹

7.4 Formation of the asymmetric centre

Undoubtedly, the *crucial step* of the entire synthetic strategy is the nucleophilic attack of the Grignard reagent on the imine carbon of **4** (Scheme 7.1), as this transformation introduces the new substituent onto the oleyl carbon chain. The presence of the chiral auxiliary directs the addition and results in the formation of two diastereoisomers, which were successfully separated by chromatography. This separation is essential, as isolating a single diastereoisomer directly contributes to increasing the enantiomeric excess (e.e.) of the final amine obtained after auxiliary cleavage.

The use of the Ellman auxiliary typically affords high diastereoselectivity, especially when the reaction is carried out in a non-coordinating solvent. Because the reaction proceeds under kinetic control, understanding the origin of the diastereoselectivity requires analysis of the relevant transition state. In such systems, *Zimmermann-Traxler transition state* must be used to describe this Grignard addition (Scheme 7.4). In this model, a six-membered cyclic transition state is formed through coordination of the Mg to the sulfinyl oxygen. When represented as a chair-like conformation, preferred due to its lower energy relative to the boat form, the bulky *tert*-butyl group (t-Bu) prefers to occupy an equatorial position to minimize steric interactions. Within this transition-state geometry, Grignard reagent approaches from the *Si* face of the imine carbon, leading to the newly formed stereocentre adopting (*S*) configuration (Scheme 7.4a). On the contrary, the attack on the *Re* face (Scheme 7.4b) would require the t-Bu group to adopt an axial orientation in the transition state, significantly increasing steric strain. This destabilized transition state is therefore higher in energy and disfavoured, resulting in minor formation of the corresponding (*R*)-configured product.^{20–23} Generally, high diastereoisomeric ratio (d.r.) are reported in favour of (*S,R*) diastereoisomer.^{24–28}



Scheme 7.4 The scheme shows the two Zimmerman-Traxler transition states which lead to the two different configuration of the final product. (a) The upper way shows the attack of MeMgBr on the *Re* face of the imine. The Zimmerman-Traxler transition state foresees the $t\text{-Bu}$ moiety in equatorial position. Assuming that R has higher priority than Me , this transition state lead to the formation of a new stereocentre with (*S*) configuration. On the contrary, (b) the lower way shows the attack on the *Si* face. In this case, $t\text{-Bu}$ takes the axial position in the transition state, giving sterically issue. This transition state leads to the formation of a new stereocentre with (*R*) configuration.

(*R*)-2-methyl-*N*-((*S,Z*)-nonadec-10-en-2-yl)propane-2-sulfonamide **5** was obtained in good yield and with a high diastereomeric ratio (d.r.) of 95:5 in favour of the (*S,R*) configuration over the (*R,R*) diastereoisomer **5-m**. This ratio was determined from the ^1H NMR spectrum of the crude mixture (Figure 7.1a). Because both diastereoisomers share the same oleyl backbone, their proton spectra are largely similar. However, the signals corresponding to the newly introduced methyl group, the proton at the α -carbon and the amide proton have different chemical shifts depending on the diastereoisomer (Figure A 7.2). Unfortunately, only one of these signals is suitable for determining the d.r. The doublet associated with the methyl group of the major diastereoisomer overlaps with the alkyl-region signals and then is not integrable, while the heptuplet arising from the proton on the α -carbon of the two diastereoisomers have a similar chemical shift; therefore, the integration of these signals cannot be selective (Figure A 7.1c). The only clean, well-resolved signal that can be used to calculate the d.r. is the N-H doublet, which appears at 2.85 ppm and 3.04 ppm for **5** and **5-m**, respectively (Figure 7.1b and A 7.1c).

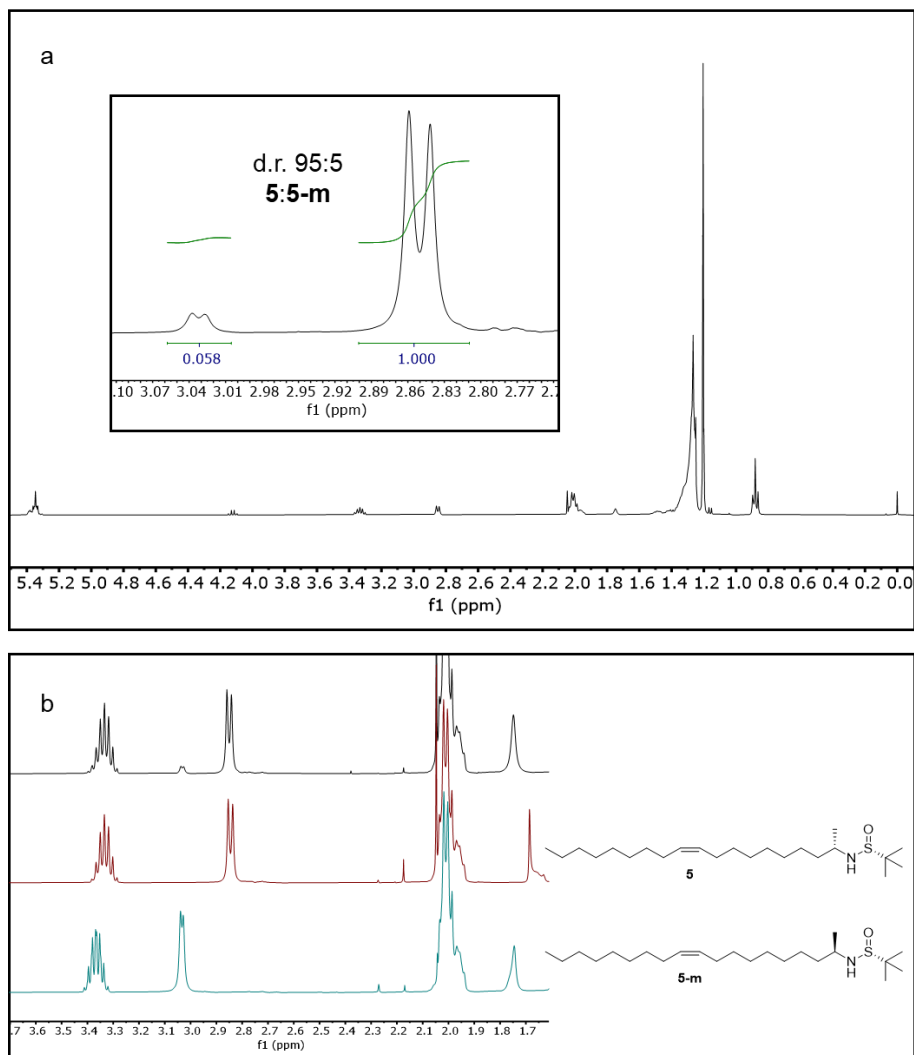
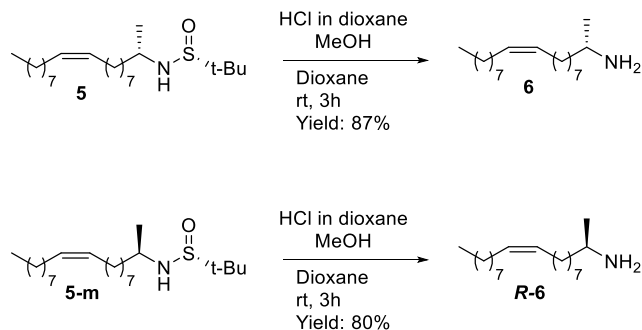


Figure 7.1 (a) ^1H NMR spectrum of the crude used to calculate the d.r. The insert shows the expansion between 2.76 ppm and 3.10 ppm to have a better look on the peaks on which the d.r. was calculated; (b) ^1H NMR spectra stacking of the minor diastereoisomer **5-m** (blue spectrum), major diastereoisomer **5** (red spectrum) and crude (black spectrum) to explicit the origin of the peaks at 2.85 ppm and 3.03 ppm. The spectra were cropped to show only the part interested in the d.r. calculation.

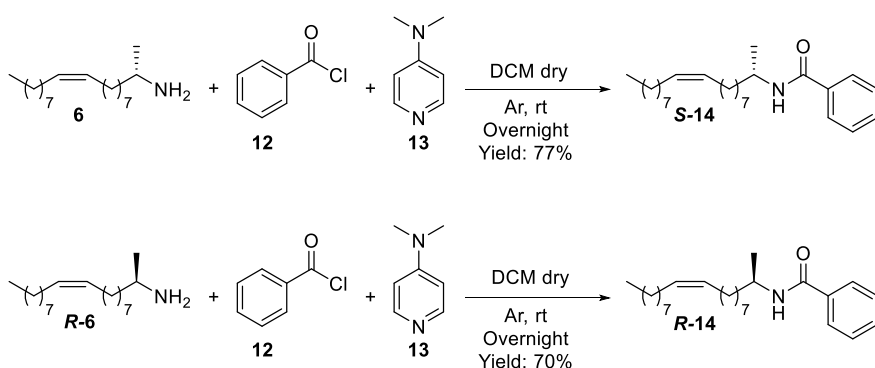
7.5 Free chiral amine



Scheme 7.5 Formation of (*S,Z*)-nonadec-10-en-2-amine **6** and (*R,Z*)-nonadec-10-en-2-amine **R-6**

As reported in literature, the deprotection of the amine group from the N-sulfinyl group occurs by acidic cleavage.¹⁴ This reaction afforded the final product (*Z*)-nonadec-10-en-2-amine in high yield. Both purified diastereoisomers from the previous step were successfully converted into the corresponding amines. It is assumed that the stereochemistry at the α -carbon is retained during this transformation. Hence, (*S,R*) diastereoisomer yielded (*S,Z*)-nonadec-10-en-2-amine **6**, whereas (*R,R*) one produced (*R,Z*)-nonadec-10-en-2-amine **R-6** (Scheme 7.5). Due to limitations in material quantity, only the product derived from the major diastereoisomer was employed as the aminic ligand in the synthesis of CsPbBr₃ nanocrystals synthesis, as reported in Chapter VIII. However, **5-m** was converted into **R-6** in order to obtain its reference peak in the chromatogram (Figure A7.2) and, then, calculate the e.e. of **6**.

7.5.1 Enantiomeric excess (e.e.) calculation



Scheme 7.6 Benzoylation of **6** and **R-6**. The reactions undergo through the employment of benzoyl chloride **12** and the 4-(dimethylamino)pyridine **13** (DMAP) as base.

The e.e. of the amine could not be determined directly, as its intrinsic properties were not compatible with the analytical methodology. Indeed, the separation of enantiomers

was performed by HPLC using a chiral stationary-phase column, with analyte detection via UV absorbance at 266 nm. Since the as-synthesized amine exhibits weak UV absorbance, derivatization prior to analysis was required. Specifically, the amine was converted into the corresponding benzoyl amide through reaction with benzoyl chloride **12** (Scheme 7.6). The resulting benzoyl derivatives were purified and then analysed by chiral HPLC. Detailed procedures are provided in the Experimental Section, and representative chromatograms are shown in Figure A7.2 – 7.4. The e.e. were determined to be 95% and 99% for **S-14** and **R-14**, respectively, indicating that compound **6** possesses an e.e. of 95%, while **R-6** has an e.e. of 99%.

7.6 Reactions procedure and possible scale up

The synthetic way to obtain **6** starts with the oxidation of oleyl alcohol using TEMPO/BAIB strategy to the corresponding aldehyde. The reaction was quenched with an aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, worked up by liquid–liquid extraction, and purified by column chromatography.

The aldehyde was subsequently converted into imine **4** via reaction with compound **3** in the presence of $\text{Ti}(\text{OEt})_4$. This step is very important for the synthetical strategy due to the insertion of the chiral auxiliary into the structure of the imine. To remove unreacted $\text{Ti}(\text{OEt})_4$, the reaction was quenched with brine, filtered, extracted, and purified by column chromatography.

Subsequently, nucleophilic addition of the Grignard reagent to the imine was carried out. Typically, Grignard reactions are performed at temperatures between $-50\text{ }^\circ\text{C}$ and $-30\text{ }^\circ\text{C}$, and in some cases even lower temperatures are required. In contrast, the addition of MeMgBr to the electrophilic imine **4** proceeded at relatively high temperatures. Indeed, the Grignard reagent was added at $-30\text{ }^\circ\text{C}$, after which the reaction mixture was allowed to slowly warm to room temperature. Upon completion, excess MeMgBr was quenched by the slow addition of an aqueous NH_4Cl solution. The mixture was then extracted. The proton spectrum of the crude was acquired to calculate the d.r. Then, the crude was purified by column chromatography. This purification step is particularly important, as it allows the separation of the two diastereoisomers, **5** and **5-min**.

The final step involved liberation of the amine group via acidic cleavage in the presence of MeOH . The reaction was subsequently worked up, and the crude product was purified by column chromatography. To calculate the e.e. of the final product, a little part of the compound was derivatized by benzylation, purified and then analysed by chiral HPLC.

Further details on the synthetic procedures are available in the Experimental section.

Considering that the amount of amine employed for LHP nanocrystal synthesis in Chapter VIII ranges from approximately 100 mg to 400 mg, depending on the desired CsPbBr_3 nanocrystal morphology, a relatively large quantity of (*S,Z*)-nonadec-10-en-2-ol was required. A target of approximately 10 g was therefore set. Performing the synthesis on such a large scale is highly solvent- and time-consuming, particularly due to the multiple purification steps. Analysis of the synthetic sequence suggested that by-products remaining after work-up in the first two steps would not interfere with subsequent reactions. Consequently, purification after the first and second steps was omitted. In contrast,

purification after the third and fourth steps was deemed crucial to the purity and to enhance the e.e. of the final product and therefore could not be eliminated.

Unfortunately, due to time constraints, this strategy was not fully completed and was interrupted before the first purification following the Grignard addition. Nevertheless, the approach appeared promising, as the proton NMR of the crude after methyl group insertion showed only the two diastereoisomers and benzyl iodide, the by-product of the first reaction (Figure 7.2). Furthermore, the d.r. calculated on the crude results slightly enhance in comparison than the reaction on the purified imine (Table 7.1).

Completion of this synthetic strategy will be essential to fully assess the effectiveness of reducing purification steps and to determine whether this synthetic route is suitable for large-scale production.

Table 7.1 d.r. comparison between the reaction conducted on the purified and unpurified imine.

	Purified imine	Unpurified imine
d.r. (5:5-m)	95:5	98:2

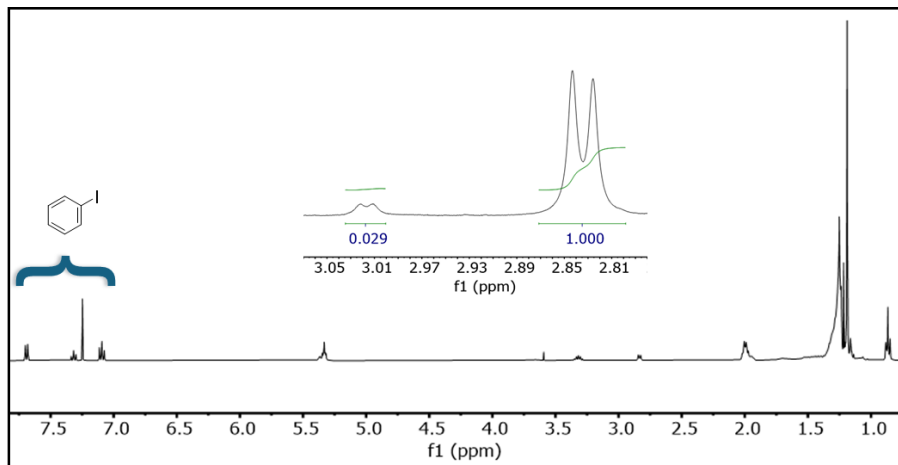


Figure 7.2 ¹H NMR spectrum of the crude obtained from the Grignard attack on the unpurified imine used to calculate the d.r. No impurities result from the NMR spectra, except for the peaks derived from the iodobenzene around 7.0 – 7.75 ppm. The inset shows the two peaks used for the d.r. calculation and their respective integrals.

7.7 Conclusions

In conclusion, the synthetic route described proved to be an efficient method for the preparation of the (S,Z)-nonadec-10-en-2-amine, which could be employed as a ligand in the production of colloidal nanocrystals. The synthesis of this amine was never reported before. (S,Z)-nonadec-10-en-2-amine was obtained in sufficient amount, around 2 grams, for the preliminary synthesis and characterization of nanocrystals. The use of this chiral amine is expected to impart new optoelectronic properties to the nanocrystals while retaining the structural stability provided by the oleyl backbone. The possibility of developing a synthetic route that requires less solvent and is less time-consuming could make this strategy suitable for large-scale synthesis; therefore, further studies are needed. Moreover, the

straightforward strategy outlined in this chapter can be extended to the synthesis of other amines bearing the oleyl scaffold with various substituents by employing Grignard reagents with R groups different from methyl. In this way, it becomes possible to systematically study the effect of oleylamine-based ligands with different substituents on the properties of nanocrystals, opening avenues for the rational design of functional nanomaterials.

7.8 Experimental section

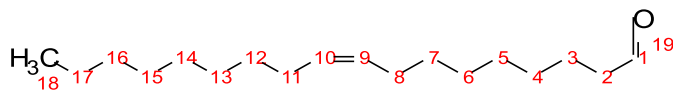
Materials. (diacetoxyiodo)benzene (**10**, BAIB, ThermoFisher Scientific, 98%), (*R*)-(+)-2-metil-2-propanesulfinamide (**3**, VWR, 98%), 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (**7**, TEMPO, TLC, 98%), 4-dimethylaminopyridine (**13**, DMAP, Sigma-Aldrich, ≥99%), ammonium chloride (NH₄Cl, Carlo Erba), benzoyl chloride (**12**, BzCl, Acros Organic, 99%), chloroform (CHCl₃, Sigma-Aldrich, ≥99.8%), deuterated chloroform (chloroform-d, CDCl₃, Eurisotop, 99.8 atom % D, +0.03% TMS v/v), dry dichloromethane (DCM dry, ThermoFisher Scientific, 99.8%), diethyl ether (Et₂O, Honeywell, ≥99.8%), ethyl acetate (EtOAc, Honeywell, ≥99.5%), hydrochloric acid (HCl/dioxane, TCI, 4M in dioxane), methanol (MeOH, Sigma-Aldrich, ≥99.9%), methyl magnesium bromide (MeMgBr, ThermoFisher Scientific, 4M in Et₂O), oleyl alcohol (**1**, Sigma-Aldrich, 85% technical grade), petroleum ether (ETP, Honeywell, ≥90%), sodium hydroxide (NaOH, Carlo Erba), dry sodium sulphate (Na₂SO₄ dry, Carlo Erba), sodium thiosulfate (Na₂S₂O₃, Carlo Erba), dry tetrahydrofuran (THF dry, ThermoFisher Scientific, 99.85%), Titanium(IV) ethoxide (Ti(OEt)₄, TCI, 65%), triethylamine (Et₃N, Apollo Scientific).

Olealdehyde 2. Into a 100 mL flask, oleyl alcohol **1** (5.05 g, 18.8 mmol, 1 eq), BAIB (6.71 g, 20.8 mmol, 1.1 eq), TEMPO (885.0 mg, 5.66 mmol, 0.3 eq) were dissolved in DCM dry under N₂ atmosphere. A red solution was formed. The flask was covered with alumina foil. The reaction was left under stirring, N₂ and rt overnight. The reaction was controlled by TLC (ETP:Et₂O 7:3). The reaction was quenched adding 20 mL of Na₂S₂O₃ 0.7 M. The mixture was left for 15 min. then extracted. The aqueous layer was washed 2 times with DCM. The organic layers were united, dried over Na₂SO₄ dry, filtered and the solvent removed under reduced pressure. The crude was purified through flash chromatography on silica gel (ETP:Et₂O 20:1). The product was obtained as pale-yellow oil (yield: 69%).

Mw: 266.47 g/mol

R_r: 0.41 (ETP:Et₂O 20:1, molybdic acid)

IR: ν (cm⁻¹): 3002.5, 2922.82, 2853.3, 2712.56, 1727.69, 1464.45, 1377.6, 967.23, 722.21.



¹H NMR: (400 MHz, Chloroform-d) δ 9.76 (t, *J* = 1.9 Hz, 1H, **1**), 5.41 – 5.30 (m, 2H, **9**, **10**), 2.42 (td, *J* = 7.4, 1.9 Hz, 2H, **2**), 2.06 – 1.93 (m, 4H, **8**, **11**), 1.68 – 1.56 (m, 2H, **3**), 1.38 – 1.21 (m, 20H, **4** – **7**, **12** – **17**), 0.87 (t, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-d) δ 203.071 (**1**), 130.185 (**9** or **10**), 129.835 (**9** or **10**), 44.047 (**2**), 32.039 (**8** or **11**), 29.894 (**4** – **7**, **12** – **17**), 29.795 (**4** – **7**, **12** – **17**), 29.657 (**4** – **7**, **12** – **17**), 29.457 (**4** – **7**, **12** – **17**), 29.386 (**4** – **7**, **12** – **17**), 29.269 (**4** – **7**, **12** – **17**), 29.185 (**4** – **7**, **12** – **17**), 27.348 (**8** or **11** or **4** – **7**, **12** – **17**), 27.276 (**8** or **11** or **4** – **7**, **12** – **17**), 22.816 (**4** – **7**, **12** – **17**), 22.204 (**3**), 14.247 (**18**).

(*R*)-2-methyl-N-((1*E*,9*Z*)-octadec-9-en-1-ylidene)propane-2-sulfinamide 4. Into a 250 mL 3-neck flask, **2** (3.45 g, 12.9 mmol, 1 eq), **3** (1.73 g, 14.2 mmol, 1.1 eq) were solubilized in 52 mL of THF dry under Ar atmosphere. Ti(OEt)₄ (5.50 mL, 25.8 mmol, 2 eq) were slow injected by a syringe into the reaction mixture. The reaction was left under

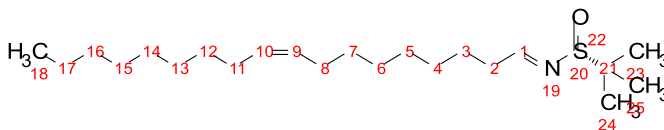
stirring, Ar and rt overnight. The reaction was controlled by TLC (ETP:DCM 7:3). The reaction was quenched adding 180 mL of brine. The reaction was filtered and, then, extracted by AcOEt/Brine. The aqueous layer was washed 2 times with AcOEt. The organic layers were united, dried over Na₂SO₄ dry, filtered and the solvent removed under reduced pressure. The crude was purified through flash chromatography on silica gel (ETP:AcOEt 10:1). The product was obtained as pale-yellow oil (yield: 83%).

Mw: 369.65 g/mol

R_f: 0.33 (ETP:AcOEt 10:1, UV light: 254 nm, molybdc acid)

IR: ν (cm⁻¹): 3004.05, 2922.98, 2853.46, 1621.99, 1457, 1362.73, 1185.09, 1086.31, 966.97, 722.6, 676.28.

[α]_D²²: -154.07 (C = 0.935 cg/mL, CHCl₃)



¹H NMR: (400 MHz, Chloroform-*d*) δ 8.07 (t, *J* = 4.8 Hz, 1H, **1**), 5.41 – 5.29 (m, 2H, **9**, **10**), 2.51 (td, 2H, **2**), 2.07 – 1.93 (m, 4H, **8**, **11**), 1.68 – 1.58 (m, 2H, **3**), 1.41 – 1.24 (m, 20H, **4** – **7**, **12** – **17**), 1.20 (s, 9H, **23** – **25**), 0.87 (t, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-*d*) δ 169.933 (**1**), 130.179 (**9** or **10**), 129.847 (**9** or **10**), 56.631 (**21**), 36.259 (**2**), 32.039 (**8** or **11**), 29.897 (**4** – **7**, **12** – **17**), 29.812 (**4** – **7**, **12** – **17**), 29.656 (**4** – **7**, **12** – **17**), 29.455 (**4** – **7**, **12** – **17**), 29.383 (**4** – **7**, **12** – **17**), 29.355 (**4** – **7**, **12** – **17**), 29.241 (**4** – **7**, **12** – **17**), 27.356 (**8** or **11** or **4** – **7**, **12** – **17**), 27.284 (**8** or **11** or **4** – **7**, **12** – **17**), 25.637 (**4** – **7**, **12** – **17**), 22.815 (**4** – **7**, **12** – **17**), 22.484 (**23** – **25**), 14.248 (**18**).

(*R*)-2-methyl-*N*-((*S,Z*)-nonadec-10-en-2-yl)propane-2-sulfinamide 5. Into a 500 mL 3-neck flask, **4** (3.98g, 10.5 mmol, 1 eq) was diluted in 70 mL of DCM dry under Ar atmosphere. The mixture temperature was lowered until -30 °C. MeMgBr 3M (15 mL, 45 mmol, 4 eq) were slowly dropped into the reaction mixture within 30 min by dropping funnel. During this stage the T were between -32 and -28 °C. The reaction mixture was maintained at -30 °C for 30 min, then the temperature was slowly increased until r.t. The reaction was left under stirring and Ar overnight. The reaction was controlled by TLC after a microquenching in NH₄Cl_{sat}/Et₂O (ETP:AcOEt 10:1). The reaction mixture was cooled to -5 °C, then 210 mL of saturated NH₄Cl was slowly added. The addition led to the CH₄ release. The reaction was filtered and, then, extracted. The aqueous layer was washed 2 times with AcOEt. The organic layers were united, dried over Na₂SO₄ dry, filtered and the solvent removed under reduced pressure. The crude was analysed by ¹H NMR to calculate the d.r. The crude was purified through flash chromatography on silica gel (ETP:AcOEt 3:2). **5** was obtained as pale-yellow oil (yield: 80%). (*R*)-2-methyl-*N*-((*S,Z*)-nonadec-10-en-2-yl)propane-2-sulfinamide **5-min** was obtained as pale-yellow oil (yield: 6%).

Mw: 385.70 g/mol

R_f 5: 0.37 (ETP:AcOEt 3:2, UV, molybdc acid)

R_f 5-min: 0.5 (ETP:AcOEt 3:2, UV, molybdc acid)

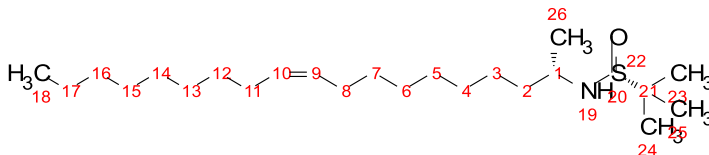
D.r.: 95:5 (**5:5-min**)

IR 5: ν (cm⁻¹): 3211.89, 3002.45, 2922.7, 2853.27, 1457.01, 1362.49, 1140.33, 1052.92, 965.94, 883.7, 795.78, 721.95.

IR 5-m: ν (cm⁻¹): 3212.01, 3006.23, 2922.76, 2853.36, 1457.22, 1362.36, 1054.4, 966.36, 877.08, 795.36, 722.07.

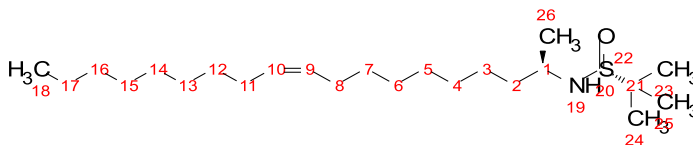
[α]_D²³ 5: -29.56 (C = 0.940 cg/mL, CHCl₃)

[α]_D²³ 5-min: -52.99 (C = 0.870 cg/mL, CHCl₃)



¹H NMR: (400 MHz, Chloroform-*d*) δ 5.41 – 5.29 (m, 2H, **9**, **10**), 3.33 (hept, *J* = 6.5 Hz, 1H, **1**), 2.85 (d, *J* = 7.0 Hz, 1H, **19**), 2.00 (dq, *J* = 11.9, 5.9, 5.2 Hz, 4H, **8**, **11**), 1.56 – 1.24 (m, 27H, **2** – **7**, **12** – **17**, **26**), 1.20 (s, 9H, **23** – **25**), 0.88 (t, *J* = 6.8 Hz, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-*d*) δ 130.125 (**9** or **10**), 129.933 (**9** or **10**), 55.732 (**21**), 52.688 (**1**), 38.292 (**2**), 32.741 (**3** – **7**, **12** – **17**), 32.043 (**8** or **11**), 29.903 (**3** – **7**, **12** – **17**), 29.863 (**3** – **7**, **12** – **17**), 29.659 (**3** – **7**, **12** – **17**), 29.613 (**3** – **7**, **12** – **17**), 29.582 (**3** – **7**, **12** – **17**), 29.459 (**3** – **7**, **12** – **17**), 29.361 (**3** – **7**, **12** – **17**), 27.353 (**8** or **11**), 27.320 (**3** – **7**, **12** – **17**), 25.898 (**3** – **7**, **12** – **17**), 23.365 (**26**), 22.764 (**23** – **24**), 14.253 (**18**).



¹H NMR: (400 MHz, Chloroform-*d*) δ 5.48 – 5.21 (m, 2H, **9**, **10**), 3.37 (hept, 1H, **1**), 3.04 (d, *J* = 4.5 Hz, 1H, **19**), 1.99 (qd, *J* = 11.8, 11.2, 5.3 Hz, 4H, **8**, **11**), 1.61 – 1.50 (m, 1H, **2**), 1.50 – 1.39 (m, 1H, **2**), 1.38 – 1.23 (m, 22H, **3** – **7**, **12** – **17**), 1.20 (s, 9H, **23** – **25**), 1.16 (d, *J* = 6.4 Hz, 3H, **26**), 0.88 (t, *J* = 6.7 Hz, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-*d*) δ 130.098 (**9** or **10**), 129.941 (**9** or **10**), 55.336 (**21**), 51.359 (**1**), 38.638 (**2**), 32.738 (**3** – **7**, **12** – **17**), 32.037 (**8** or **11**), 29.902 (**3** – **7**, **12** – **17**), 29.861 (**3** – **7**, **12** – **17**), 29.786 (**3** – **7**, **12** – **17**), 29.655 (**3** – **7**, **12** – **17**), 29.558 (**3** – **7**, **12** – **17**), 29.453 (**3** – **7**, **12** – **17**), 29.361 (**3** – **7**, **12** – **17**), 27.345 (**8** or **11**), 27.317 (**3** – **7**, **12** – **17**), 25.964 (**3** – **7**, **12** – **17**), 22.813 (**3** – **7**, **12** – **17**), 22.673 (**23** – **24**), 21.554 (**26**), 14.250 (**18**).

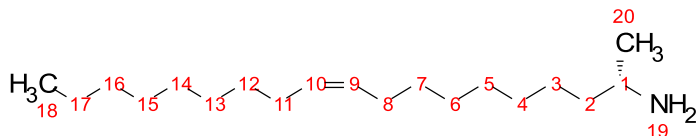
(S,Z)-nonadec-10-en-2-amine 6. Into a 100 mL flask, **5** (3.22 g, 8.81 mmol, 1 eq), MeOH (7.35 mL, 176.9 mmol, 20 eq), HCl/dioxane 4M (8.81 mL, 35.24 mmol, 4 eq) are diluted in 44 mL of dioxane. The reaction was left at r.t. under stirring for 3h. The reaction was controlled by TLC (ETP:AcOEt 3:2). The reaction was solvent removed under reduced pressure and, then, extracted by Et₂O/NaOH 0.25 M. The aqueous layer was washed 2 times with Et₂O. The organic layers were united, dried over Na₂SO₄ dry, filtered and the solvent removed under reduced pressure. The crude was purified through flash chromatography on silica gel (AcOEt + 10% MeOH + 2% Et₃N). The product was obtained as pale-yellow oil (yield: 87%).

Mw: 281.53 g/mol

R_f: 0.28 (AcOEt + 10% MeOH + 2% Et₃N, molybdc acid)

IR: ν (cm⁻¹): 3007.82, 2921.83, 2852.62, 1583.1, 1463.8, 1376.66, 966.44, 800.31, 721.81.

[α]_D²⁴: 1.00 (C = 0.985 cg/mL, CHCl₃)



¹H NMR: (400 MHz, Chloroform-*d*) δ 5.44 – 5.30 (m, 2H, **9**, **10**), 2.86 (h, J = 5.8 Hz, 1H, **1**), 2.07 – 1.92 (m, 4H, **8**, **11**), 1.43 – 1.21 (m, 24H, **2** – **7**, **12** – **17**), 1.05 (d, J = 6.3 Hz, 3H, **20**), 0.87 (t, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-*d*) δ 130.093 (**9** or **10**), 129.991 (**9** or **10**), 47.094 (**1**), 40.401 (**2** – **7**, **12** – **17**), 32.747 (**8** or **11**), 32.049 (**2** – **7**, **12** – **17**), 29.907 (**2** – **7**, **12** – **17**), 29.877 (**2** – **7**, **12** – **17**), 29.840 (**2** – **7**, **12** – **17**), 29.793 (**2** – **7**, **12** – **17**), 29.687 (**2** – **7**, **12** – **17**), 29.666 (**2** – **7**, **12** – **17**), 29.467 (**2** – **7**, **12** – **17**), 29.408 (**2** – **7**, **12** – **17**), 27.349 (**8** or **11**), 26.603 (**2** – **7**, **12** – **17**), 24.153 (**2** – **7**, **12** – **17**), 22.828 (**19**), 14.263 (**18**).

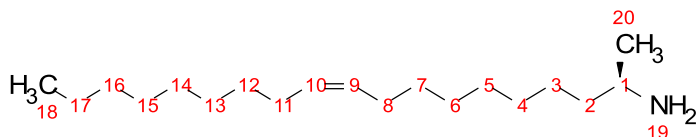
(*R,Z*)-nonadec-10-en-2-amine R-6. Into a 100 mL flask, **5-min** (232.2 mg, 0.635 mmol, 1 eq), MeOH (527 μ L, 12.7 mmol, 20 eq), HCl/dioxane 4M (640 μ L, 2.56 mmol, 4 eq) are diluted in 3.2 mL of dioxane. The reaction was left at r.t. under stirring for 3h. The reaction was controlled by TLC (ETP:AcOEt 3:2). The reaction was solvent removed under reduced pressure and, then, extracted by Et₂O/NaOH 0.25 M. The aqueous layer was washed 2 times with Et₂O. The organic layers were united, dried over Na₂SO₄ dry, filtered and the solvent removed under reduced pressure. The crude was purified through flash chromatography on silica gel (AcOEt + 10% MeOH + 2% Et₃N). The product was obtained as pale-yellow oil (yield: 80%).

Mw: 281.53 g/mol

R_f: 0.28 (AcOEt + 10% MeOH + 2% Et₃N, molybdc acid)

IR: ν (cm⁻¹): 3005.28, 2921.86, 2852.64, 1580.48, 1463.82, 1376.66, 966.46, 800.33, 721.79.

[α]_D²⁴: -1.56 (C = 0.935 cg/mL, CHCl₃)



¹H NMR: (400 MHz, Chloroform-*d*) δ 5.41 – 5.29 (m, 2H, **9**, **10**), 2.86 (q, J = 5.9 Hz, 1H, **1**), 2.07 – 1.92 (m, 4H, **8**, **11**), 1.41 – 1.21 (m, 24H, **2** – **7**, **12** – **17**), 1.05 (d, J = 6.3 Hz, 3H, **20**), 0.87 (t, 3H, **18**).

¹³C NMR: (101 MHz, Chloroform-*d*) δ 130.085 (**9** or **10**), 129.983 (**9** or **10**), 47.087 (**1**), 40.378 (**2** – **7**, **12** – **17**), 32.745 (**8** or **11**), 32.045 (**2** – **7**, **12** – **17**), 29.901 (**2** – **7**, **12** – **17**), 29.867 (**2** – **7**, **12** – **17**), 29.826 (**2** – **7**, **12** – **17**), 29.796 (**2** – **7**, **12** – **17**), 29.684 (**2** – **7**, **12** – **17**).

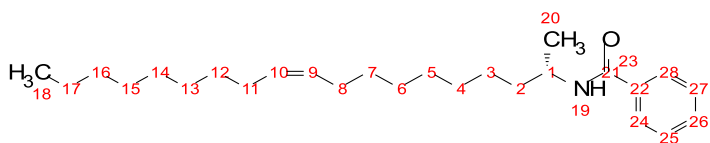
– 17), 29.663 (2 – 7, 12 – 17), 29.461 (2 – 7, 12 – 17), 29.402 (2 – 7, 12 – 17), 27.344 (8 or 11), 26.596 (2 – 7, 12 – 17), 24.132 (2 – 7, 12 – 17), 22.825 (19), 14.259 (18).

(S,Z)-N-(nonadec-10-en-2-yl)benzamide S-14. Into a 4 mL vial, **6** (30.4 mg, 0.11 mmol, 1 eq) and DMAP (26.9 mg, 0.22 mmol, 2 eq) were solubilized in 140 μ L of DCM dry under Ar atmosphere. BzCl (19.2 μ L, 0.17 mmol, 1.5 eq) was added to the reaction mixture at 0 °C. The reaction was left under stirring and Ar overnight. The reaction was controlled by TLC (AcOEt + 10% MeOH + 2% Et₃N). The reaction was solvent removed under reduced pressure. The crude was purified by preparative TLC (ETP:AcOEt 9:1). The product was obtained as white solid (yield: 77%).

Mw: 385.64 g/mol

R_f: 0.42 (ETP:AcOEt 9:1, UV light: 254 nm)

e.e.: 95%



¹H NMR: (400 MHz, Chloroform-*d*) δ 7.75 (dd, 2H, 24, 28), 7.48 (tt, 1H, 26), 7.46 – 7.39 (m, 2H, 25, 27), 5.87 (d, *J* = 8.4 Hz, 1H, 19), 5.42 – 5.28 (m, 2H, 9, 10), 4.19 (hept, *J* = 8.4, 6.5 Hz, 1H, 1), 2.06 – 1.92 (m, 4H, 8, 11), 1.58 – 1.50 (m, 2H, 2), 1.43 – 1.20 (m, 25H, 3 – 7, 12 – 17, 20), 0.88 (t, *J* = 6.8 Hz, 3H, 18).

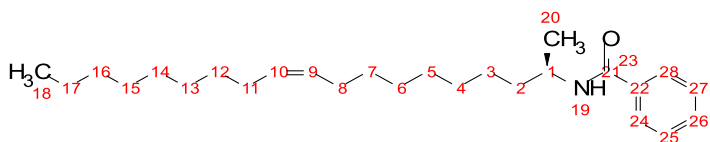
¹³C NMR: (101 MHz, Chloroform-*d*) 166.946 (21), 135.246 (22), 131.389 (26), 130.105 (9 or 10), 129.952 (9 or 10), 128.673 (25, 27), 126.930 (24, 28), 45.917 (1), 37.248 (2), 32.738 (8 or 11), 32.043 (3 – 7, 12 – 17), 29.908 (3 – 7, 12 – 17), 29.875 (3 – 7, 12 – 17), 29.794 (3 – 7, 12 – 17), 29.660 (3 – 7, 12 – 17), 29.604 (3 – 7, 12 – 17), 29.458 (3 – 7, 12 – 17), 29.373 (3 – 7, 12 – 17), 27.355 (8 or 11 or 3 – 7, 12 – 17), 27.327 (8 or 11 or 3 – 7, 12 – 17), 26.237 (3 – 7, 12 – 17), 22.821 (3 – 7, 12 – 17), 21.204 (20), 14.251 (18).

(R,Z)-N-(nonadec-10-en-2-yl)benzamide R-14. Into a 4 mL vial, **R-6** (30.5 mg, 0.11 mmol, 1 eq) and DMAP (26.9 mg, 0.22 mmol, 2 eq) were solubilized in 140 μ L of DCM dry under Ar atmosphere. BzCl (19.2 μ L, 0.17 mmol, 1.5 eq) was added to the reaction mixture at 0 °C. The reaction was left under stirring and Ar overnight. The reaction was controlled by TLC (AcOEt + 10% MeOH + 2% Et₃N). The reaction was solvent removed under reduced pressure. The crude was purified by preparative TLC (ETP:AcOEt 9:1). The product was obtained as white solid (yield: 70%).

Mw: 385.64 g/mol

R_f: 0.42 (ETP:AcOEt 9:1, UV light: 254 nm)

e.e.: 99%



¹H NMR: (400 MHz, Chloroform-*d*) δ 7.75 (dd, 2H, 24, 28), 7.48 (tt, 1H, 26), 7.46 – 7.39 (m, 2H, 25, 27), 5.88 (d, *J* = 8.4 Hz, 1H, 19), 5.43 – 5.29 (m, 2H, 9, 10), 4.19 (hept, *J*

= 8.4, 6.6 Hz, 1H, **1**), 2.07 – 1.91 (m, 4H, **8**, **11**), 1.58 – 1.49 (m, 2H, **2**), 1.41 – 1.20 (m, 25H, **3** – **7**, **12** – **17**, **20**), 0.88 (t, J = 6.8 Hz, 3H, **18**).

^{13}C NMR: (101 MHz, Chloroform- d) δ 166.962 (**21**), 135.242 (**22**), 131.392 (**26**), 130.105 (**9** or **10**), 129.952 (**9** or **10**), 128.671 (**25**, **27**), 126.935 (**24**, **28**), 45.925 (**1**), 37.246 (**2**), 32.740 (**8** or **11**), 32.042 (**3** – **7**, **12** – **17**), 29.907 (**3** – **7**, **12** – **17**), 29.873 (**3** – **7**, **12** – **17**), 29.659 (**3** – **7**, **12** – **17**), 29.603 (**3** – **7**, **12** – **17**), 29.456 (**3** – **7**, **12** – **17**), 29.373 (**3** – **7**, **12** – **17**), 29.259 (**3** – **7**, **12** – **17**), 27.352 (**8** or **11** or **3** – **7**, **12** – **17**), 27.325 (**8** or **11** or **3** – **7**, **12** – **17**), 26.236 (**3** – **7**, **12** – **17**), 22.818 (**3** – **7**, **12** – **17**), 21.200 (**20**), 14.248 (**18**).

Nuclear Magnetic Resonance (NMR) spectrometry. NMR spectra were measured on a JEOL JNM-ECZ400R at 400 MHz (^1H) at 20 °C. The samples were prepared diluting ~ 10 mg of substance in 600 μL CDCl_3 . The chemical shifts (δ) were expressed in parts per million relatives to tetramethylsilane (TMS) as internal standard (0.00 ppm). The data treatment was performed using the MestReNova 14 software.

Gas chromatography - mass spectrometry (GC-MS) analysis. Mass spectra were acquired on Shimadzu GC-2010 Plus, flow-controlled mode: linear velocity, column flow: 1.00 mL/min, split ratio: 10.0, oven temperature program: starting temperature 100.0 °C maintained for 3.00 min, increasing rate: 25.0 °C/min, final temperature 300.0 °C maintained for 4 min. The samples were prepared diluting the substance in AcOEt until a concentration of 0.1 g/L.

Polarimetry analysis. To calculate the specific rotational power (α_d) of the samples, the intensity of the polarized light rotation was acquired by JASCO P-2000 digital polarimeter. The samples were prepared diluting the substance in CHCl_3 until a concentration of ~ 1 cg/mL. 2 mL of the solution were used to fill the quartz sample cell with a optical path of 1 dm. The analysis was performed with 589 nm light. α_d was calculated using equation 7.1, where α is the observed rotation angle, c is the concentration of the solution, expressed in cg/mL, and l is the optical path, expressed in dm.

Equation 7.1 α_d calculation.

$$\alpha_d = \frac{\alpha}{c * l}$$

High performance liquid chromatography (HPLC) equipped with chiral stationary phase analysis. To calculate the enantiomeric excess (e.e.) of the **S-14** and **R-14**, the separation between the two enantiomers was done employing Agilent HP 1100 equipped with chiral column Phenomenex LUX Amylose-1 (250×4,6 mm without pre-column). The detection was done by a detector DAD (266 nm). The sample was prepared diluting the substance in hexane until a concentration of 300 $\mu\text{g/mL}$. The chromatographic run was performed using hexane/isopropanol 97:3 as eluent. The e.e. was calculated using Equation 7.2, where E is the area of the peak determined by the major enantiomer and e is the area of the peak determined by the minor enantiomer in the sample.

$$e.e. = \frac{E - e}{E + e} * 100$$

Infrared (IR) spectroscopy. IR spectra were acquired by FT Perkin Elmer Spectrum 65 spectrophotometer in attenuated total reflectance (ATR) mode. number of sample scans 32, collection length 95.44 s, resolution 4000 cm^{-1} , number of scan points 12 415, wavelength range 500–4000 cm^{-1} . The response was expressed as % transmittance.

Powder and liquid samples were deposited directly onto the diamond crystal prior to spectral acquisition.

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Appendices

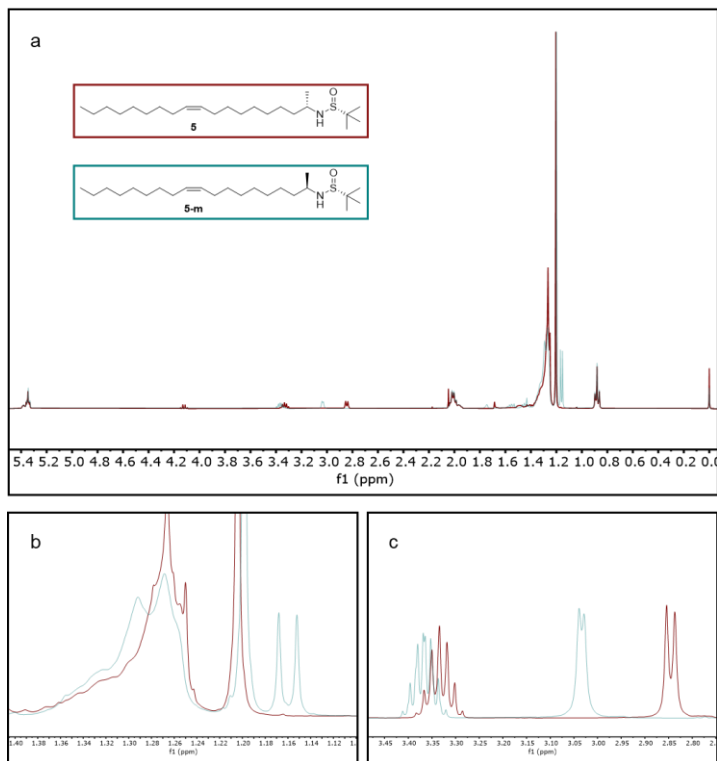


Figure A 7.1 (a) Overlap of ^1H NMR spectra of **5** (red spectrum) and **5-m** (blue spectrum); Spectra expansions between (b) 1.11– 1.40 ppm and (c) 2.75 – 3.50 ppm. The two expansions explicit the differences in the spectra of **5** and **5-m**. Figure A7.2b shows the position of the doublet derived from the methyl group inserted through the Grignard attack. This is visible for **5-m** (1.16 ppm), while the signal of the same CH_3 **5** (probably at 1.25 ppm) of fall under the large peak of the alkyl chain; Figure A7.2c shows the peaks derived from the N-H (the red and blue signals on the right) and the $\alpha\text{C-H}$ (the red and blue signals on the left) of two diastereoisomers. The right signals are well separated, while the right ones suffer of partial overlapping.

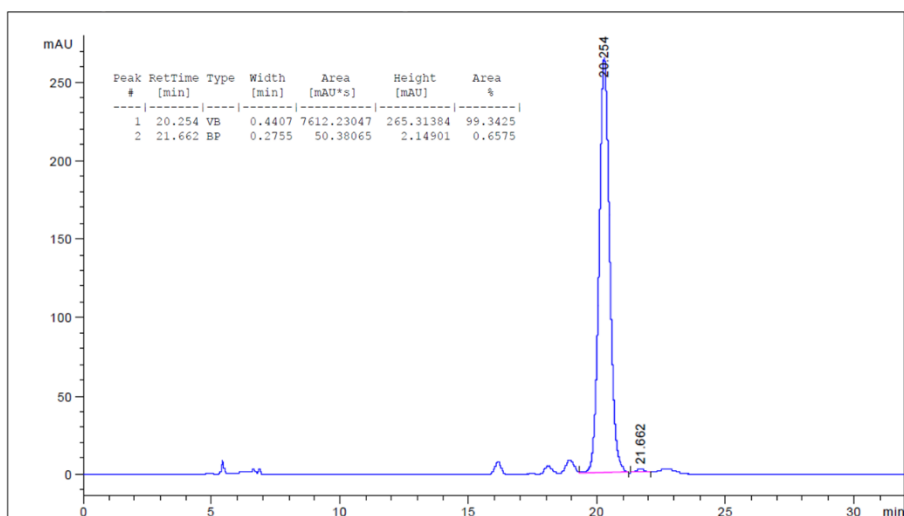


Figure A 7.2 Chromatogram of the purified product derived from the benzoylation of **R-6**. The calculated e.e. is 99%.

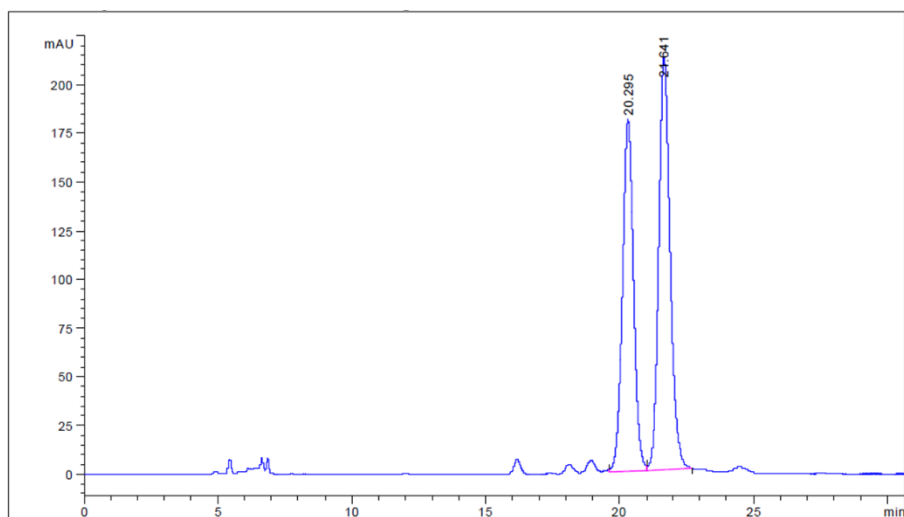


Figure A 7.3 Chromatogram of the quasi-racemic mixture of **S-14** and **R-14**. The peaks are well-defined. The retention time is ~20.3 min and ~21.6 min.

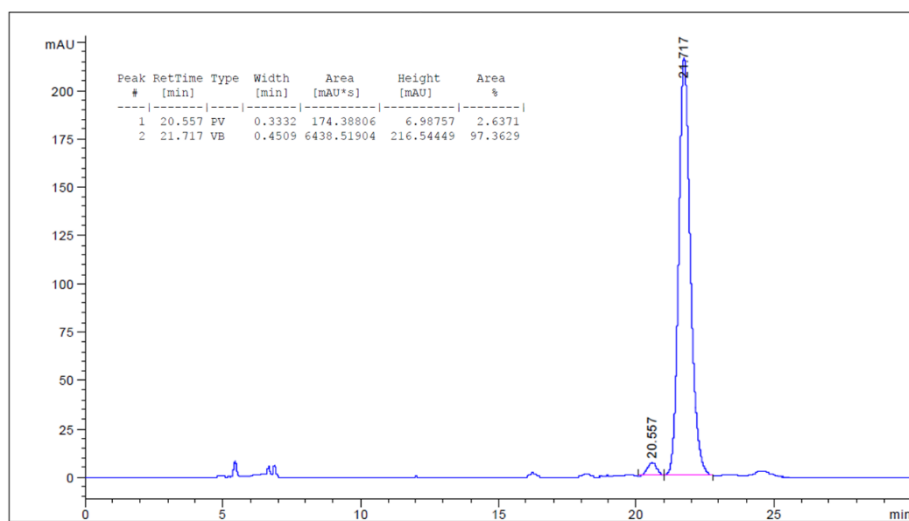


Figure A 7.4 Chromatogram of the purified product derived from the benzylation of **6**. The calculated e.e. is 95%.

Chapter VIII

Chiral oleylamine as new
ligand for CsPbBr_3
nanocrystal synthesis



Chapter VIII: Chiral oleylamine as new ligand for CsPbBr₃ nanocrystal synthesis

Abstract: The possibility of breaking the centrosymmetric structure of lead halide perovskites further poses this class of materials into the centre of the studies and application of luminescence materials. Indeed, these strategies unlock the latent chiroptical properties of these materials, enlarging the possible application. Among the various strategies to obtain chiral colloidal nanocrystals, the employment of chiral amine is one of the most popular. Therefore, this Chapter will focus on the employment of (S,Z)-nonadec-10-en-2-amine, which synthesis was described into the previously Chapter, as new ligand. Hence, CsPbBr₃ nanocrystals in various morphologies were obtained and characterized. Moreover, the chiral oleyl amine was combined with a chiral synthetic environment. Furthermore, an insight into the role of the ammonium formation into the nanoplatelet synthesis was carried out through NMR study. Finally, the CD spectra of the as synthesized nanoparticles was acquired.

8.1 Introduction

Recently, interest in chiroptical materials has increased significantly due to their potential applications in emerging technologies such as 3D displays, agriculture, bioencoding, bioimaging, photoelectric devices, information storage, and optical encryption.^{1–12} The development of these new technologies requires materials with strong optical and chiroptical responses.¹³

Since chiroptical activity often originates from intrinsic molecular chirality, chiral luminescent organic compounds have played a central role in this research field. These molecules typically exhibit high photoluminescence quantum yields (PLQY), but their CPL dissymmetry factors (g_{lum}) are generally low due to negligible magnetic transition dipole moments. The g_{lum} can be enhanced through the formation of chiral supramolecular aggregates; however, this often leads to reduced PLQY due to an increased scattering. Moreover, organic chiral emitters frequently feature broad emission spectra.^{14–17} Lanthanide complexes, on the other hand, are remarkable for their exceptionally high g_{lum} , approaching unity. Unfortunately, they lack in terms of PLQY and in general material stability.^{14,18–22}

As described in Chapter 6.2, lead halide perovskites are a promising class of materials even in this application field due to strong spin–orbit coupling in their electronic states, spin-dependent optical selection rules, and large Rashba splitting, all of which can give rise to notable chiroptical responses.^{23–25} Combined with their high PLQY, especially in colloidal nanocrystal form, LHPs have naturally attracted interest also for their application in chiroptical devices.¹³ Yet, they have achiral structure, so that strategies to break the symmetric structures are required to unlock the chiroptical properties. A widely adopted approach employs chiral ligands that bind to the nanocrystal surface. Typical chiral amines include (R)/(S)-methylbenzylamine ((R)/(S)-MBA) or (R)/(S)-2-octylamine.^{23,26,27} Although the resulting nanocrystals exhibit clear chiroptical activity, replacing oleylamine (OLAM) with shorter-chain chiral amines often compromises material stability.²⁸

To overcome this issue, a new ligand bearing an oleyl-like carbon chain was designed. The synthesis pathway was thoroughly described in the previous chapter. Here, the as-synthesized (*S,Z*)-nonadec-10-en-2-amine (OLAM*) was successfully employed as ligand for the synthesis of CsPbBr₃ nanocrystals with different morphologies. Furthermore, the synthesis of the CsPbBr₃ nanoplatelets was extended with the employment of (*R*)/(*S*)-limonene as solvents, in order to investigate possible synergistic effects between OLAM* and chiral environment. Furthermore, an NMR study on the (*S,Z*)-nonadec-10-en-2-ammonium formation was performed to rationalize the formation of nanoplatelets when this new ligand is used.

8.2 Synthesis and characterization of CsPbBr₃ nanocubes

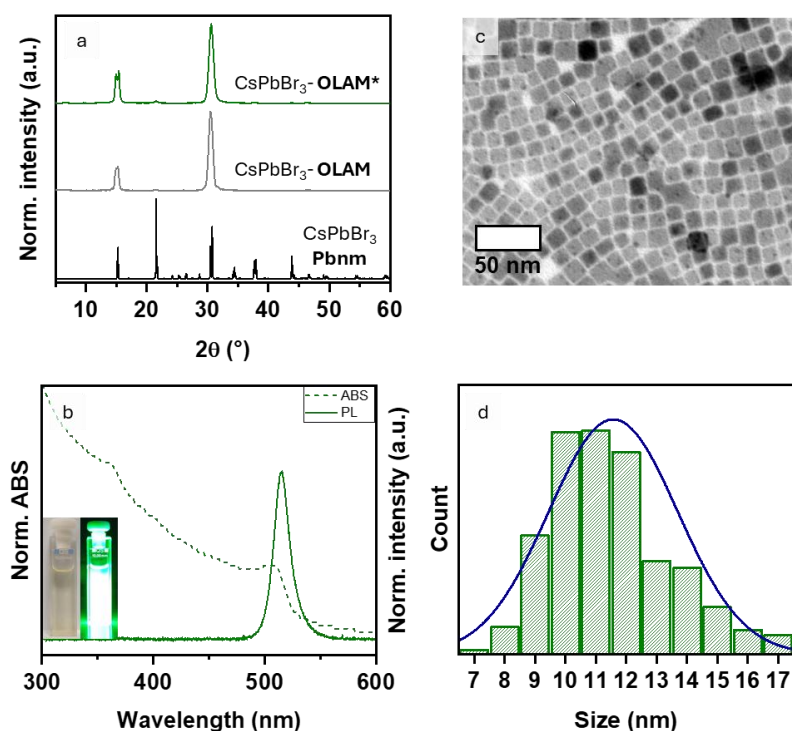


Figure 8.1 (a) Comparison of X-ray diffraction (XRD) patterns of CsPbBr₃ NCs synthesized using OLAM* (green line), OLAM (grey line) and the CsPbBr₃ Pbnm reference (ICSD number 14608). (b) Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{exc} = 365$ nm) of the same sample; insets show photographs of the colloidal dispersions under visible light and UV irradiation (365 nm). (c) Low-resolution TEM images and corresponding (d) size distributions of the CsPbBr₃ NCs prepared using OLAM*.

CsPbBr₃ nanocubes (NCs) were synthesized following the procedure reported by Baranov et al.,²⁹ with slight modifications. The synthesis was carried out by rapidly injection of a caesium oleate (CsOLAC) stock solution at 160 °C into a solution of lead bromide (PbBr₂), OLAM* and OLAC in 1-octadecene (ODE) under inert atmosphere. The reaction

was cooled to room temperature in air immediately after the injection. After purification, the resulting colloidal dispersion was pale yellow and exhibited a bright green luminescence under 365 nm irradiation, as shown in the inset of Figure 8.1b. Because the amine headgroup of OLAM* is sterically more hindered than OLAM, the dissolution of PbBr₂ was more difficult. For this reason, a total of 300 μ L of OLAC were employed to facilitate the salt solubilization.

The structural properties of the NCs were analysed by X-ray diffraction (XRD). Figure 8.1a shows the X-ray diffraction (XRD) patterns of the sample, compared to the CsPbBr₃ NCs synthesized using OLAM and to the bulk Pbnm orthorhombic reference structure. The comparison between the reference pattern and the experimental data confirms that the as-synthesized nanocrystals crystallize in the *orthorhombic phase*. As reported in Chapter 4.2, the deviations between the bulk and the nanocrystal patterns arise from *size-dependent effects*, which cause peak broadening, and from preferential orientation on the sample holder, which leads to an enhancement of the (002) and (004) reflection planes at approximately 15° and 30°, respectively. The diffraction patterns of CsPbBr₃ NCs synthesized using OLAM* and those obtained with OLAM are completely superimposable, indicating that the ligand exchange does not induce any change in the crystal structure.

The optical properties of the NCs were investigated by absorption (ABS) and photoluminescence (PL) spectroscopy (Figure 8.1b). Moving from longer to shorter wavelengths, the absorption spectrum (dashed line) shows a sharp increasing at 508 nm, giving by the excitonic peak, and followed by a constant absorption increasing. This feature is characteristics of CsPbBr₃ nanocubes. The colloidal suspension exhibited a sharp emission peak (solid line) centered at 515 nm, with a full width half maximum (FWHM) of 80 meV.

The morphology of the as-synthesized nanocubes was evaluated by TEM imaging. Figure 8.1c confirms the formation of well-defined *cubic nanoparticles* with an average edge length of 11.6 ± 2.1 nm. This value is in line with the position of the emission peak and its slight broad width. This size is consistent with both the position and the moderate broadening of the PL peak. The average dimension, as the FWHM, is slightly larger than that reported for NCs synthesized using OLAM (Table A8.1). This behaviour can be attributed to the higher steric bulk of OLAM*, which reduces its ability to effectively bind and passivate the surface, thus allowing the nanocrystals to grow more extensively under identical reaction conditions. Finally, the broader size distribution can be ascribed to an enhanced Ostwald ripening, which becomes more pronounced at higher ligand concentrations.^{30,31}

The presence of the OLAM* on the nanocrystals was confirmed by the acquisition of the ¹H NMR spectra (Figure 8.2). In the first experiment, the dried nanoparticles were dispersed in tol-d₈. As expected, the proton spectrum exhibits broadened signals at 0.95, 1.37 and 5.55 ppm, assigned to the oleic chain of OLAC and OLAM*, corresponding respectively to the terminal methyl group, the alkyl chain, and the vinylic protons of the double bond. A broad resonance at 2.15 ppm, partially overlapped with the signal of the solvent -CH₃, is attributed to the allylic -CH₂ group. In addition, a small shoulder at 1.02 ppm, adjacent to the main methyl signal, likely arises from the -CH₃ on the α -carbon of OLAM*.^{32–34}

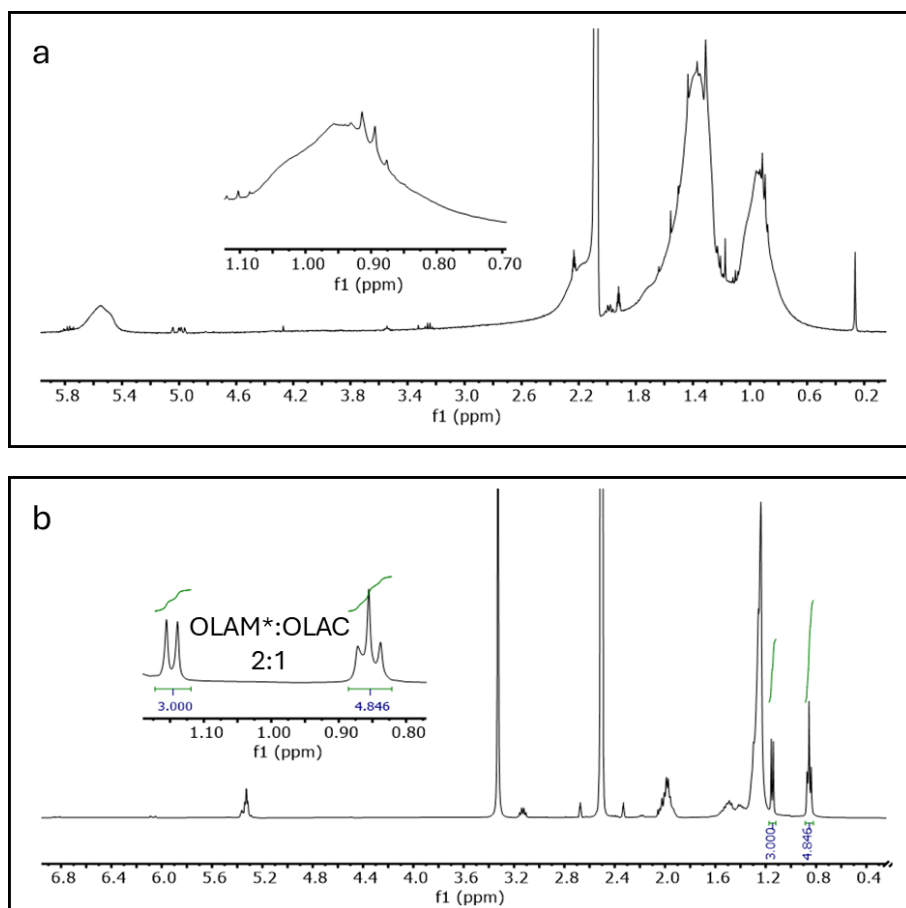


Figure 8.2 (a) ¹H NMR spectra of CsPbBr₃ NCs synthesized using OLAM* dispersed in tol-d₈; the inset shows the broad peak at 0.95 ppm that has a shoulder, probably given by the -CH₃ substituent on the α-carbon. (b) ¹H NMR spectra of the same sample solubilized in DMSO-d₆; the inset highlights the peaks derived from the methyl group of the oleic chain (0.85 ppm) and the other methyl group bound to the α-carbon (1.14 ppm). The comparison of their integrals permits to calculate the ratio between OLAM* and OLAC.

Afterwards, the sample was dried again, redissolved in DMSO-d₆ and a second ¹H NMR spectrum was acquired. The solubilization of the nanoparticles led to the releasing of the ligands. Therefore, the proton resonances appear sharp and with clearly distinguishable multiplicities. Of particular relevance is the doublet at 1.14 ppm, which originates from the α-methyl group of OLAM*, providing direct evidence of its presence among the surface ligands.

A quantitative comparison between the integrated area of this doublet ($A_{\alpha\text{CH}_3}$) and the area of the triplet at 0.85 (A_{CH_3}), assigned to the terminal -CH₃ of the oleic chain coming from both ligands, enables an estimation of the *relative ligand ratio*. Using Equation 8.1, the OLAM*/OLAM ratio is calculated to be approximately 2:1 in favour of OLAM*.

Equation 8.1 OLAM*:OLAM ratio calculation

$$OLAM^*:OLAC = \frac{A_{\alpha CH_3}}{A_{CH_3} - A_{\alpha CH_3}}$$

8.3 Synthesis and characterization of CsPbBr₃ nanoplatelets

CsPbBr₃ nanoplatelets (NCs) were synthesized following the procedure described by Toso et al.,³⁵ with slight modifications. The synthesis was carried out by the rapid injection of benzoyl bromide (BzBr) into a solution at 95 °C of lead oleate (PbOLAC₂), CsOLAC, OLAM* and OLAC in decane. After the injection, the reaction mixture was kept at 95 °C for 1 min and subsequently cooled to room temperature using a water bath. After purification, the resulting colloidal dispersion was pale yellow and exhibited a bright blue luminescence under 365 nm irradiation, as shown in the inset of Figure 8.3b. Compared to the standard procedure, this synthesis was performed using half of the typical amount of CsOLAC.

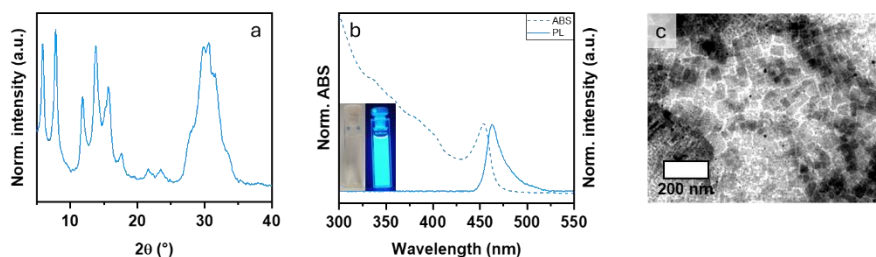


Figure 8.3 (a) X-ray diffraction (XRD) patterns of CsPbBr₃ NPs synthesized using OLAM* (b) Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{exc} = 365$ nm) of the same sample; insets show photographs of the colloidal dispersions under visible light and UV irradiation (365 nm). (c) Low-resolution TEM images distributions of the CsPbBr₃ NPs prepared using OLAM*.

Figure 8.3a shows the XRD pattern of the as-synthesized sample. Differently from CsPbBr₃ NCs, the diffractogram is strongly influenced by the *self-assembling phenomenon*, similarly to the behaviour observed for the CsPbBr₃ NPs capped with OLAM (CsPbBr₃ NPs-OLAM) shown in Chapter 5.3. However, high differences arise when comparing the two patterns (Figure A8.1). While CsPbBr₃ NPs-OLAM exhibit well-defined peaks in the 5°–20° and 25°–35° regions, the corresponding features of CsPbBr₃ NPs-OLAM* are less pronounced. In particular, the signal around 30° appears as a single broadened peak. Toso et al.³⁵ reported the evolution of the XRD pattern as a function of CsPbBr₃ nanoplatelets thickness (Figure A8.2). Their theoretical study revealed that, by increasing the number of layers, the diffractogram becomes progressively less affected by self-assembly, eventually resembling the typical pattern of CsPbBr₃ nanocubes. Furthermore, the ligand employed can modify the self-assembling behaviour of the nanoplatelets, yielding differences in the resulting XRD response. The pattern of CsPbBr₃ NPs-OLAM* closely matches the one reported for the nanoplatelets formed by *four monolayers*, where each layer consists of sheets of corner-sharing [PbBr₆]⁴⁻ octahedra (Figure 8.4). The slight discrepancies between the two patterns might be attributed to minor differences in the ligand structure as suggest in the literature.³⁶

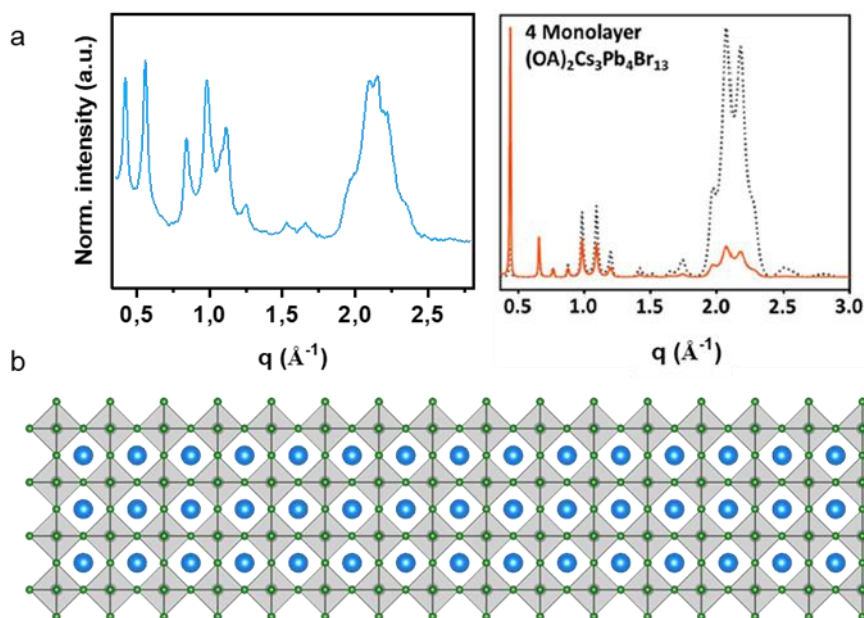


Figure 8.4 (a) comparison between the XRD pattern of CsPbBr₃ NPs as synthesized with the theoretical one reported by Toso et al. for a 4 monolayers nanoplatelets. Reproduced from ref.³⁵ under a CC-BY 4.0 license. Copyright © 2021 The Authors. Published by American Chemical Society. All rights reserved. (b) Representation of 4 monolayers nanoplatelets.

Figure 8.3b shows the optical analysis of the sample in colloidal suspension. ABS (dashed line) displays a well-defined excitonic peak at 454 nm, where the PL (solid line) exhibits a relatively sharp emission peak at 463 nm, with a FWHM of 111 meV. Compared to the optical analysis reported for CsPbBr₃ NPs-OLAM, the sample synthesized using OLAM* has a less pronounced excitonic peak. In addition, both the excitonic and emissive peaks are red-shifted (Table A8.1). Generally, smaller nanoparticles exhibit more prominent excitonic features.^{37,38} Furthermore, as discussed in Chapter I, stronger quantum confinement results in an increased separation between the valence and conduction bands, which manifests as a more significant blue-shift of the optical transitions. Therefore, the observed spectral differences in both the ABS and PL measurements are consistent with a thicker structure for the CsPbBr₃ NPs-OLAM*.

Figure 8.3c reports the TEM images. The pictures reveal a population of well-defined *rectangular nanoplatelets*. The particles display non-uniform contrast, which can be attributed to variations in stacking along the Z-axis arising from self-assembly. As in the earlier case, these layered structures are intrinsically fragile; thus, the vacuum conditions required for TEM imaging can induce partial degradation of the nanoplatelets. To mitigate this effect, the deposition on the carbon-coated 200 mesh copper grids is performed cautiously by forming a drop on the grid.

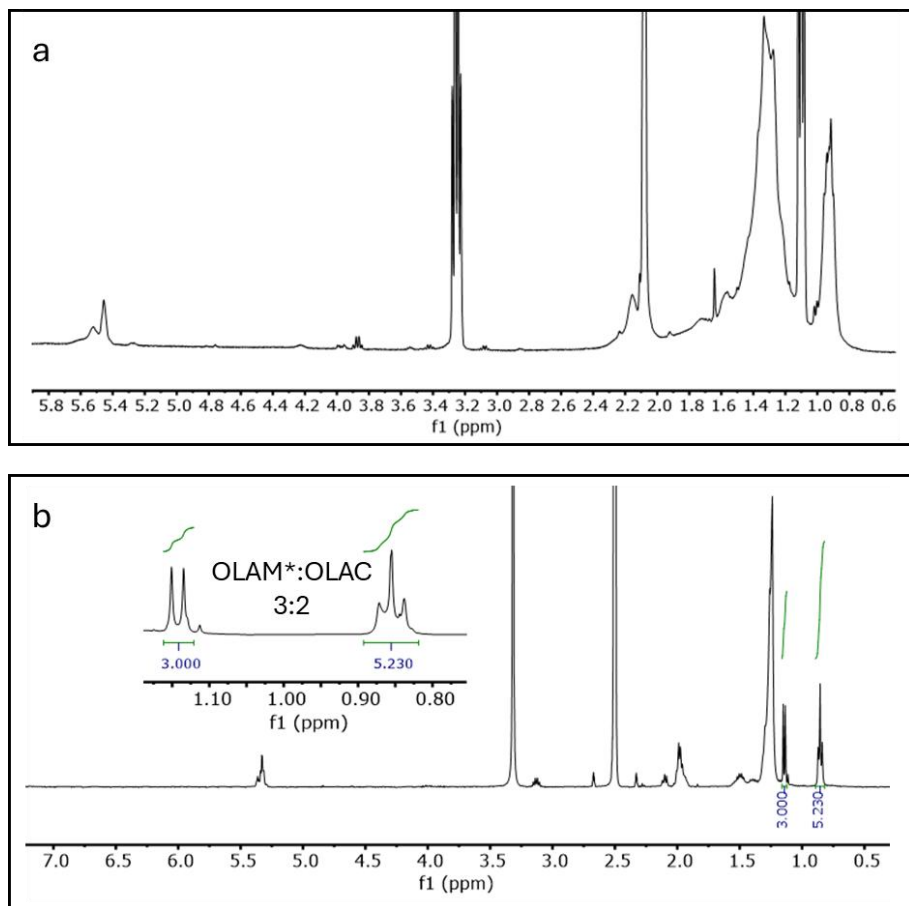


Figure 8.5 (a) ^1H NMR spectra of CsPbBr_3 NPs synthesized using OLA* dispersed in $\text{tol}-d_8$. (b) ^1H NMR spectra of the same sample solubilized in $\text{DMSO}-d_6$; the inset highlight the peaks derived from the methyl group of the oleic chain (0.85 ppm) and the other methyl group bound to the α -carbon (1.14 ppm). The comparison of their integrals permits to calculate the ratio between OLA* and OLAC.

As for CsPbBr_3 NCs, the ligand bound on the nanoplatelets surface were investigated through the acquisition of proton spectra in $\text{tol}-d_8$ and $\text{DMSO}-d_6$ (Figure 8.5). The spectrum of the nanoplatelets suspension exhibits broadened peaks at 0.93, 1.30, 2.15, and around 5.50 ppm, confirming the presence of organic ligands on the nanoparticle surface. The assignment of these peaks has been previously discussed in Chapter 8.2. A comparison between the nanocubes and nanoplatelets spectra reveals a notable difference in the peak associated with the $-\text{CH}=\text{CH}-$ group around 5.50 ppm (Figure 8.6). In the nanocubes spectrum, a single broadened peak centered at 5.55 ppm is observed, whereas the nanoplatelets display a more complex feature composed of multiple broadened peaks: the highest intensity peak at 5.45 ppm, followed by a peak at 5.52 ppm, and a shoulder at 5.60 ppm. Hens' group has extensively studied the behaviour of ligands bound to nanocrystal surfaces.^{32,39,40} The broadening of these peaks arises from two main phenomena. First, the *slow rotation of ligands* bound to the nanocrystal surface induces rapid transverse

relaxation, governed by the transverse relaxation time T₂. T₂ is inversely proportioned to the FWHM of the NMR peak, as expressed in Equation 8.2; therefore, a fast transverse relaxation leads to *homogeneous peak broadening*.³²

Equation 8.2 Correlation between transversal relaxation time (spin-spin) and FWHM of the peak

$$T_2 = \frac{1}{FWHM_{peak}}$$

The second factor influencing the broadening of the NMR peaks is the *inability of the ligands to rapidly rotate* to all the possible molecular conformations during the measurement. As a result, protons in the same molecular position are “frozen” in slightly different conformations, experiencing different magnetic environments. Consequently, these protons are no longer magnetically equivalent, producing multiple peaks at very similar chemical shifts that collectively contribute to *heterogeneous broadening*. (Figure A8.3).³² Hens' group further reported an increase in the peak at 5.45 ppm upon adding OLAC to the nanocrystal colloidal suspension, suggesting that this peak arises from the free OLAC fraction. In our case, the signal at this position likely originates from both free OLAM* and OLAC remaining in solution after purification, displayed also in the Figure 8.3c. Conversely, the differences of the signal around 5.55 ppm may result from variations in ligand solvation and packing density. Ligands bound to the nanocrystal surface produce signals at higher chemical shifts compared to those at the edges.^{39,41} Accordingly, the nanocubes spectrum (green line) exhibits the expected peak shape, while the nanoplatelet spectrum (blue line) is more complex. Detailed inspection of the main nanoplatelet peak, figured in inset of the Figure 8.6, reveals a small shoulder at upfield due to the large surface area of the nanoplatelets, the number of ligands at the edges is lower than on the basal surfaces, making the corresponding signal less intense. For the same reason, the edge-related signal is less visible for the nanoplatelets compared to the nanocubes. The shoulder at 5.60 ppm may reflect differences in ligand solvation or denser ligand packing. Therefore, the peaks at 5.52 ppm and 5.60 ppm are indicative of *variations in ligand packing* on the nanoplatelet surface. Additionally, the lower chemical shift of the nanoplatelet surface ligand peak compared to the nanocubes suggests higher solvation and, consequently, lower surface ligand density.

The spectrum of the sample dissolved from DMSO-d₆ (Figure 8.5b) allows to recognise the nature of the bound ligands. Indeed, this analysis confirms the presence of both OLAM* and OLAC. Following the procedure described in Chapter 8.2, integration of the doublet at 1.14 ppm and the triplet at 0.85 ppm yields an OLAM*:OLAC ratio of 3:2. This confirms the stronger binding affinity of the amine than the oleic acid for the CsPbBr₃ nanoparticle surface, even when the initial ligand mixture favours oleic acid. Obviously, the differences in amount of acid and amine ligands in the synthetic procedure for CsPbBr₃ nanocubes and nanoplatelets resulted in a higher amount of OLAC bound on the nanoplatelet surface.

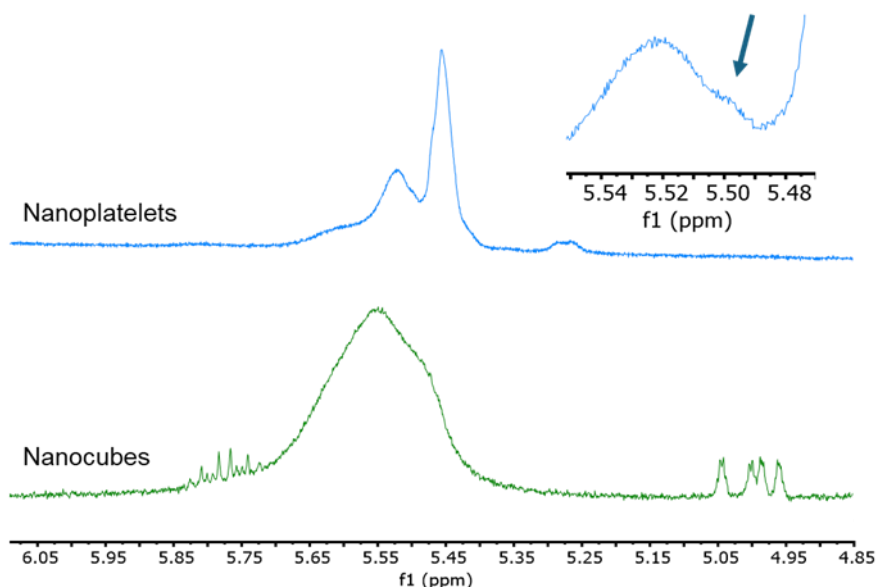


Figure 8.6 Comparison between proton signal of the $-\text{CH}=\text{CH}-$ derived from the ligands bound to the surface of CsPbBr_3 NCs (green line) and CsPbBr_3 NPs (blue line). The spectra were acquired suspended the sample in $\text{tol}-d_8$ for seeing the signal $-\text{CH}=\text{CH}-$ derived from the ligand yet bound on the nanocrystals surface. The inset shows an expansion of the peak derived from the ligand on the nanoplatelets to highlights the little shoulder. This derived from the ligands bound on the edge, while the principal body is compound from the signal of the ligand positioned on the nanoplatelets surface. It is possible to notice the same behaviour for the peak related to the nanocubes.

8.3.1 Nanoplatelets synthesis in chiral solvent

Exploiting the aforementioned procedure, nanoparticles were synthesized replacing the solvent (decane) with (*R*)- and (*S*)-limonene. As discussed in Chapter IV, these natural derivatives can replace classical non-coordinating solvents due to their apolarity and relatively high boiling points. Beyond their *green* character, the introduction of these solvents adds complexity to the system because chirality is inherently present in their molecular structure. Indeed, the interaction of each enantiomer with another chiral component, in this case, the chiral amine, can result in different outcomes, as summarized in Table 8.1.

The syntheses were conducted following the same procedure as for the nanoplatelets described previously, allowing a direct comparison between the two limonene-based samples and the reference prepared in decane. After purification, the samples exhibited slightly different emission colours under 365 nm irradiation. The sample synthesized in (*S*)-limonene showed bright blue luminescence, similar to the decane sample, whereas the (*R*)-limonene sample displayed a lighter blue emission, as illustrated in the insets of Figure 8.7c and d.

Table 8.1 Comparative table of the excitonic peak, PL peak and its width, ratio between the ligand on the surface and circular dichroism of the CsPbBr₃ NPs synthesized in decane, (*R*)-limonene and (*S*)-limonene.

Solvent	Excitonic peak wavelength	PL peak wavelength	FWHM of PL	OLAM*:OLAC ratio	Circularly dichroism	
					Wavelength	Intensity
Decane	454 nm	463 nm	111 meV	3:2	416	- 8.0 mdeg
(<i>R</i>)-limonene	452 nm	476 nm	314 meV	54:46	418	- 2.45 mdeg
(<i>S</i>)-limonene	451 nm	463 nm	177 meV	3:2	416	- 8.0 mdeg

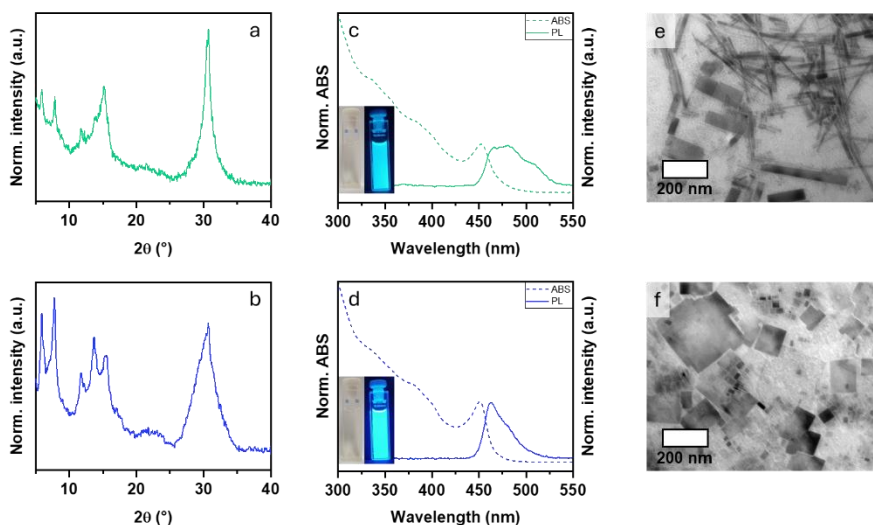


Figure 8.7 X-ray diffraction (XRD) patterns of CsPbBr₃ NPs synthesized using OLAM* in (a) (*R*)-limonene and (b) (*S*)-limonene. Optical absorption spectra (dashed lines) and photoluminescence (PL) spectra (solid lines, $\lambda_{exc} = 365$ nm) of the sample synthesized in (c) (*R*)-limonene and (d) (*S*)-limonene; insets show photographs of the colloidal dispersions under visible light and UV irradiation (365 nm). (e) Low-resolution TEM images distributions of the CsPbBr₃ NPs prepared in (e) (*R*)-limonene and (f) (*S*)-limonene.

The XRD pattern of CsPbBr₃ NPs-OLAM* synthesized in (*S*)-limonene (Figure 8.7b) presents features similar to those observed for the decane sample (Figure A8.4, blue and light blue line, respectively). In particular, the peaks in the 5°–20° range indicate the formation of nanoplates self-assembled on the sample holder. In contrast, the sample prepared in (*R*)-limonene (Figure 8.7a and A8.4, aquamarine line) exhibits an XRD pattern dominated by two broad peaks around 15° and 30.5°.

The optical analysis reported in Figure 8.7c and d and Table 8.1 confirms differences between the two samples. The ABS spectra show an excitonic peak at a slightly higher wavelength for the (*R*)-limonene (Figure 8.7c, dashed aquamarine line) compared to the one obtained from (*S*)-limonene (Figure 8.7d, dashed blue line). However, the most pronounced differences appear in the PL spectra. (*S*)-limonene sample (Figure 8.7d, solid line) displays a well-defined emission peak centred at 463 nm, similar to the nanoplatelets obtained in the achiral solvent, whereas the (*R*)-limonene sample (Figure 8.7c, solid line)

exhibits a broader peak centered at 476 nm. In both of the samples, the PL spectra highlight the presence of at least two populations.

Indeed, the TEM images confirmed that (Figure 8.7e and f). Synthesis in (*S*)-limonene effectively produced nanoplatelets, whereas the (*R*)-limonene sample contained a mixture of nanoplatelets and nanorods, in line with the broader PL emission. The presence of this mixed population also explains the differences in the XRD patterns: the coexistence of multiple morphologies hinders uniform self-assembly, leading to broader and less-defined diffraction features.

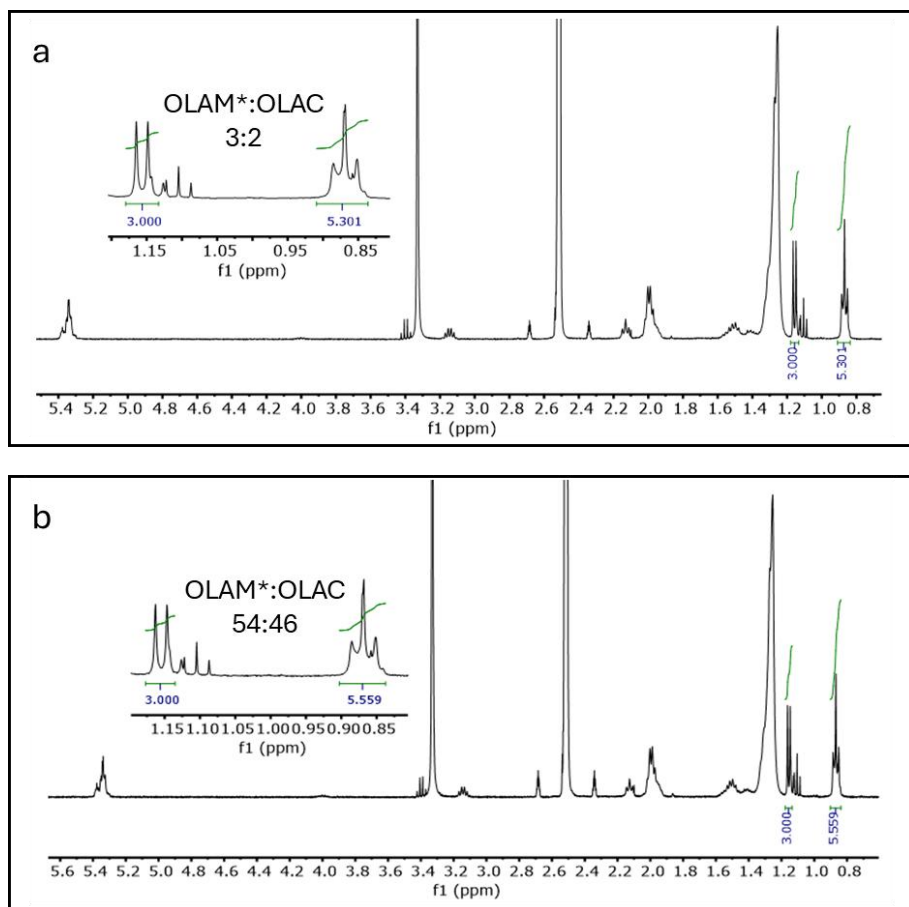


Figure 8.8 (a) ^1H NMR spectra of CsPbBr_3 NPs synthesized using OLAM* in (*S*)-limonene solubilized in DMSO-d_6 ; the inset highlight the peaks derived from the methyl group of the oleic chain (0.85 ppm) and the other methyl group bound to the α -carbon (1.14 ppm). (b) ^1H NMR spectra of CsPbBr_3 NPs synthesized using OLAM* in (*R*)-limonene solubilized in DMSO-d_6 ; the inset highlight the peaks derived from the methyl group of the oleic chain (0.85 ppm) and the other methyl group bound to the α -carbon (1.14 ppm). The comparison of the integrals in the same inset permits to calculate the ratio between OLAM* and OLAC of the sample.

Finally, the organic fractions were analysed by the acquisition of the proton spectra of the dissolved nanoparticles into DMSO-d₆ (Figure 8.8). Both samples display the presence of OLAM* and OLAC, albeit in different ratios. Indeed, in line with the other analysis, the (*S*)-limonene sample had a similar ratio than the decane sample (Figure 8.8a and Table 8.1). Instead, the calculate OLAM*:OLAC ratio of the (*R*)-limonene sample is approximately 1:1. This difference in surface-bound ligand might be attributed to the distinct interactions between OLAM* and the two solvent enantiomers. The results suggest that the interaction of OLAM* with (*S*)-limonene-OLAM* resembles that in decane, despite the solvents' different chemical nature. Conversely, sample synthesized in (*R*)-limonene present differences respects to the other two, probably given by the different interaction OLAM*-solvent.

8.4 Insight into the CsPbBr₃ nanoplatelets synthesis

The formation of nanoplatelets requires rapid passivation of the surface to prevent excessive growth in thickness. This is achieved by the *preferential insertion* of the ligand in place of Cs⁺.^{30,31} Consequently, the affinity of the amine for the nanocrystal surface plays a crucial role. This affinity is strongly influenced by the *ligand's structure*, which affects both the formation of the ammonium species, responsible for competing with Cs⁺, and the steric hindrance of the amine head. Indeed, a more sterically hindered amine faces greater difficulty in incorporating onto the nanocrystal surface, potentially altering the passivation efficiency and, therefore, the final morphology (Figure 8.9).

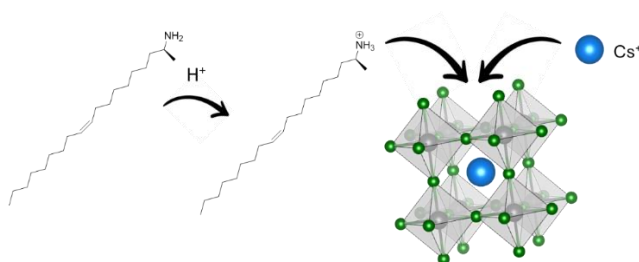


Figure 8.9 Illustration of (*S,Z*)-nonadec-10-en-2-ammonium formation and its competition with Cs⁺ to enter in the crystal structure.

Since the amount of ammonium in the solution directly influences nanocrystal growth, understanding how this cation forms is crucial for a better control on the syntheses, especially when new amines are used. Several factors affect ammonium formation. Firstly, the acid–base reaction is influenced by the acidity and basicity of the species involved: strong acids and bases lead to complete protonation, whereas weak species allow the establishment of a dynamic equilibrium, as is the case of OLAC and OLAM. Each amine has its own base dissociation constant (K_b), which is influenced by steric hindrance on the amine head; greater steric hindrance makes protonation more difficult.⁴² Thus, the amount of acid added directly influence the dissociation equilibrium, and an excess of acid drives the reaction toward ammonium formation by mass action.³¹ Furthermore, the solvent may also influence the reaction outcome,⁴³ while an increase of the temperature hinders the

protonation (since this reaction is exothermic, on the basis of Le Chatelier's principle, higher temperatures reduce the extent of protonation).³¹

To gain insight into ammonium formation from OLAM*, a 0.1 M solution in tol-d_8 was allowed to react with OLAC and monitored by ^1H NMR analysis. The concentration was chosen to minimize molecular interactions that could influence chemical shifts at higher acid equivalents. Deuterated toluene was used to approximate the apolar environment of the nanoplatelet synthesis in decane.

Initially, spectra of pure OLAM* were acquired, followed by spectra of solutions with stepwise addition of ~ 0.4 equivalents of OLAC. For each solution, the spectrum at 25 °C, 50 °C, 75 °C and 90 °C was acquired (Figure 8.10a-d). The progression of the reaction was followed by the shifting to downfield of the peak derived from the proton bound to the α -carbon of the amine. Protonation progress was monitored via the downfield shift of the α -carbon proton of the amine, plotted against the amount of OLAC added (Figure 8.10e). As expected, lower temperatures produced steeper slopes due to stronger acid–base interactions. Increasing the temperature led to upfield shifts, indicating reduced protonation (Figure A8.5).³¹ The same experiment was reproduced using OLAM as amine (Figure A8.6). To compare the two amines trend, OLAC amounts were converted to equivalents, and chemical shifts were normalized to the percentage reaction progress. Since the molecular interactions also influence the chemical shift after the reaction completion, the “knee points” were extrapolated from deviations at high acid equivalents, serving as reference end points (Figure A8.7). After this point, it was considered that the chemical shift was given principally from the molecular interactions. Hence, the progression of the reactions was calculated compared with this “knee point”. More details are reported in Experimental section.

As expected, protonation of OLAM* is more difficult than OLAM due to its steric hindrance. Figure A8.8 shows that, with the same OLAC equivalent, OLAM is more extensively protonated than OLAM*. This difference increases with temperature. Under conditions similar to those used for the nanoplatelet synthesis described in the Experimental section (acid equivalents = 1.39), close to the reaction temperature, OLAM protonation reaches $\sim 60\%$, whereas OLAM* only reaches $\sim 54\%$. At ambient temperature, these values are 89% and 88%, respectively. Thus, to achieve the same degree of protonation as OLAM at 25 °C, ~ 1.43 equivalents of OLAC would be required, but this value increases to ~ 1.6 equivalents at 90 °C. Therefore, studies of acid–amine interactions cannot be approximated at T_{amb} and must be extended to the actual reaction temperature. Unfortunately, this is limited by the boiling point of the deuterated solvent, making it impossible to fully probe the acid–base interactions occurring at higher temperature than 90 - 100 °C using tol-d_8 . Furthermore, the presence of other species into the reaction environment further increases the complexity of the system.

However, the moderate decrease in OLAM* protonation under the same equivalents of OLAC does not explain the formation of small nanocubes (Figure A8.9) under these similar reaction conditions used for obtaining nanoplatelets reported in Chapter 5. Therefore, the capability of the OLAM* to bind to the nanocrystal surface is probably strongly affected by its steric hindrance. Therefore, to favour binding of OLAM* over Cs^+ incorporation, the Cs^+ concentration in the solution was reduced.

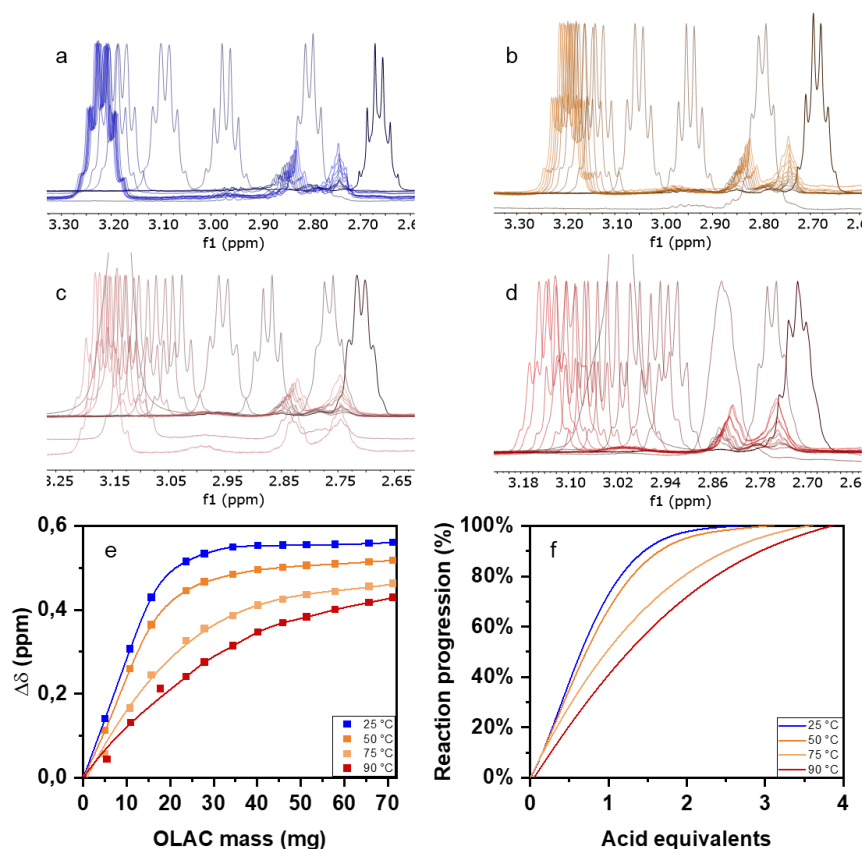


Figure 8.10 Shift of the peak derived from the proton bound to the α -carbon of (S,Z)-nonadec-10-en-2-ammonium by the progressively addition of OLAC at (a) 20 °C (blue line), (b) 50 °C (orange line), (c) 75 °C (pink line) and (d) 90 °C (red line). The reaction was carried out in tol-*d*₈. (e) Plot of the variation of chemical shift ($\Delta\delta$) giving by different protonation of the ammine produced by a progressive higher quantity of OLAC at 20 °C (blue line), 50 °C (orange line), 75 °C (pink line) and 90 °C (red line). (f) Plot of the percentage of reaction progression against the equivalents of acid added to the solution at the same temperature reported for plot (e). Further information of the manipulation of plot (e) to obtain plot (f) are reported in Experimental section.

8.5 Chiroptical properties

Thanks to the OLAM* on the surface of the nanocrystals, the centrosymmetry of the lead halide perovskites was broken. Consequently, chiroptical properties might be observed.

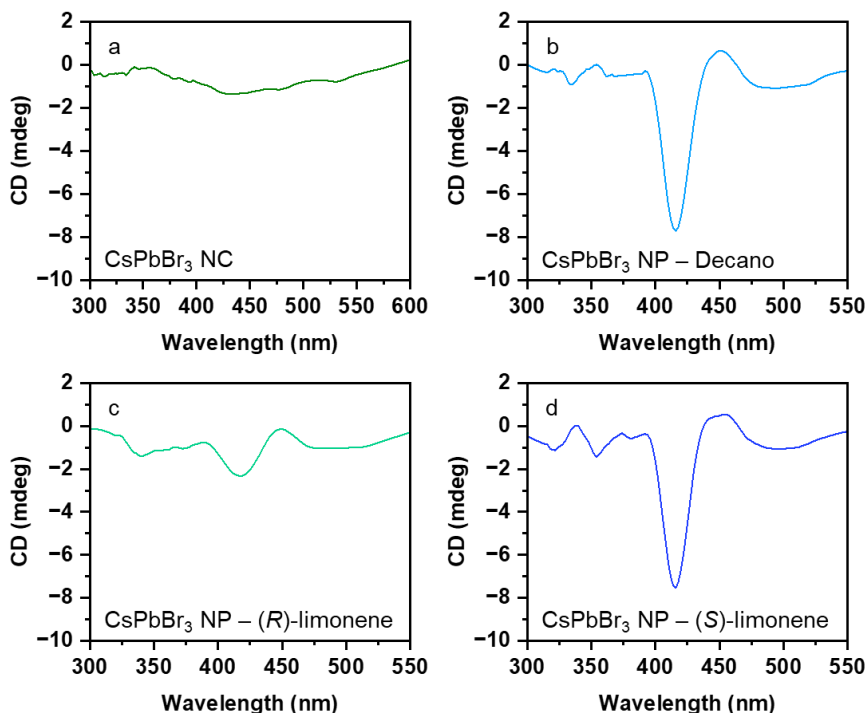


Figure 8.11 Circular dichroism spectra of (a) CsPbBr₃ NCs and CsPbBr₃ NPs synthesized in (b) decane, (c) (*R*)-limonene and (d) (*S*)-limonene.

Figure 8.11 shows the circular dichroism (CD) spectra of the samples. In particular, CsPbBr₃ NCs do not exhibit any difference in absorption of right- and left-circularly polarized light (Figure 8.11a). In contrast, the nanoplatelets (Figure 8.11b, c and d) present CD. The nanoplatelets synthesized in decane -exhibit a peak at 416 nm with a magnitude of -8 mdeg. Similarly, the nanoplatelets prepared in (*R*)-limonene and (*S*)-limonene (Figure 8.11c and d, respectively, and Table 8.1) also show CD, although with different intensities: the (*R*)-limonene sample has a very low CD signal, whereas the (*S*)-limonene sample shows a CD magnitude comparable to the decane sample.

The observed CD can be attributed to the distortion of the nanocrystal surface induced by the binding of the chiral ligands. Since this distortion rapidly decreases toward the interior of the nanocrystals,⁴⁴ the absence of CD in the larger nanocubes is consistent, whereas layered structures such as nanoplatelets can easily exhibit CD. The measured CD values are consistent with literature reports for CsPbBr₃ nanoparticles, in particular for nanocubes bearing 2-octylamine and nanoplatelets functionalized with methylbenzylamine or methylphenethylamine.^{14,27,45}

However, even if the CD values are relatively low, the study of the chiroptical properties of these structures results only into a preliminary phase. A future perspective

should be the implementation of “Sergeant–Soldier” effect described for similar systems,²⁶ and, thus, employing a mixture of OLAM and OLAM* during nanoplatelet synthesis.

8.6 Conclusion

In conclusion, the syntheses employing OLAM* successfully led to the formation of the targeted CsPbBr₃ nanocrystals, including both nanocubes and nanoplatelets. The structural and optical properties of these nanocrystals were consistent with those obtained using conventional OLAM. ¹H NMR analysis provided insights into the ligand arrangement on the nanocrystal surfaces and allowed the determination of the OLAM*:OLAM ratio.

The synthesis of CsPbBr₃ NPs also highlighted the influence of enantiomeric solvents, namely the (*R*)- and (*S*)-limonene, on the reaction outcome, likely due to differences in the solubility of OLAM* in the two enantiomers.

Additionally, NMR studies clarified the role of OLAM* in controlling the formation of nanoplatelets, highlighting the importance of the ammonium structure for the competition with Cs⁺ in the surface binding.

Circular dichroism measurements revealed that the nanocubes did not exhibit any chiroptical activity, likely due to their greater thickness, whereas the layered nanoplatelets displayed CD. These properties might potentially be further enhanced using a “Sergeant–Soldier” strategy, combining OLAM and OLAM* during synthesis.

8.7 Experimental section

Materials. Benzoyl bromide (BzBr, Acros Organic, 97%), caesium carbonate (Cs_2CO_3 , Alfa Aesar, 99.9%), deuterated dimethyl sulfoxide (DMSO-d_6 , Thermo Fisher Scientific, 99.8 atom % D), ethyl acetate (AcOEt, Sigma-Aldrich, >99.5%), hexane (Sigma-Aldrich, 99%), lead(II) acetate trihydrate ($\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, ThermoFisher Scientific, 99.995%), lead(II) bromide (PbBr_2 , Sigma-Aldrich, 99%), (R)-limonene (ThermoFisher Scientific, 96%), (S)-limonene (Sigma-Aldrich, 96%), oleic acid (OLAC, Alfa Aesar, tech. 90%), oleyl amine (OLAM, ThermoFisher Scientific, 80-90%), 1-octadecene (ODE, Alfa Aesar, 90%), deuterated toluene (tol-d_8 , Sigma-Aldrich, 99.6 atom % D). All the chemicals were employed without any further purification.

CsOLAC synthesis. CsOLAC (0.15M) was prepared loading Cs_2CO_3 (400 mg) and OLAC (1.75 mL) into a 40 mL glass vial containing 15 mL of 1-octadecene (ODE) under an argon atmosphere. The mixture was heated to 100 °C under vigorous stirring until a fully transparent yellow solution was obtained. The resulting stock solution was stored under air at room temperature. CsOLAC (1M) was prepared following the same procedure but employing 192 mg of CsOAc and 1 ml of OLAC loaded into a 4 mL vial.

Pb(OLAC)₂ (0.67 M) synthesis. $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ (379 mg) and OLAC (1.5 mL) were loaded into a 4 mL glass vial. The mixture was heated to 100 °C under vacuum for 1 h till the complete dissolution of the precursors. The resulting stock solution, that solidifies at room temperature, was stored under air at room temperature.

Synthesis of CsPbBr₃ NCs. 72.4 mg of PbBr_2 , 425.1 mg of (S,Z)-nonadec-10-en-2-amine, 300 μL of OLAC and 5 mL of ODE are loaded into a 20 mL vial. The reaction mixture is put under nitrogen under vigorous stirring and heated at 165 °C to dissolve all of the precursors. Then, at 160 °C, 500 μL of a CsOLAC solution (0.15 M) are swiftly injected and the flask is cooled to room temperature in air. The reaction mixture is centrifuged at 4000 rpm for 5 min, the precipitate is collected and dispersed in 1 mL of hexane, leading to a green, transparent colloidal suspension.

Synthesis of CsPbBr₃ NPs. (S,Z)-nonadec-10-en-2-amine (98.5 mg), OLAC (160 μL), and 2 mL of the solvent (decane, (R)-limonene or (S)-limonene) were loaded into a 4 mL vial and heated to 95 °C under vigorous stirring. Then 10 μL and 60 μL of pre-heated CsOLAC (1 M) and $\text{Pb}(\text{OLAC})_2$ (0.67 M), respectively, were added to the ligand solution using micropipettes, with dipping and flushing to ensure quantitative transfer. Finally, 20 μL of BzBr was injected into the reaction mixture. The reaction proceeded at 95 °C for 1 min and was quenched by lowering the temperature in a water stopping the stirring. The crude mixture was centrifuged to discard a non-emissive by-product. Then, the supernatant was destabilized adding EtOAc until turbidity appeared. The resulting suspension was centrifuged at 4000 rpm for 2 min, and the precipitate was resuspended in 1.2 mL of Hex to yield the purified CsPbBr₃ nanoplates.

Amine-OLAC reaction. A 0.1 M solution of the desired amine (either OLAM or (S,Z)-nonadec-10-en-2-amine) was prepared in tol-d_8 , and 500 μL of this solution was transferred into an NMR tube. A first proton spectra was acquired. Subsequently, OLAC (~ 0.4 equivalents) was added, and after thorough mixing, a new proton spectrum was acquired. This procedure was repeated until a total of 70 mg of OLAC was added for (S,Z)-nonadec-10-en-2-amine and 60 mg for OLAM. For each addition, ^1H NMR spectra were recorded at 25 °C, 50 °C, 75 °C, and 90 °C. The reactions were followed by the peak shifting relatively to the protons bound on the α -carbon. The value of the variations in

chemical shift ($\Delta\delta$) from the initial position were graphic against the OLAC mass added. Subsequently, OLAC mass was converted into equivalents of acid added, and $\Delta\delta$ was transformed into the percentage of reaction progression, calculated according to Equation 8.3, using $\Delta\delta_{knee}$ as the reference point, which corresponds to the onset of linearity at high OLAC concentrations (Figure A8.7). Due to progressively stronger molecular interactions between the amine and OLAC at higher acid concentrations, the curves did not reach a clear plateau. The NMR spectra were elaborated using MestReNova 14 software, the graphs elaboration were performed using OriginPro software.

Equation 8.3

$$Reaction\ progress\ (\%) = \frac{\Delta\delta}{\Delta\delta_{knee}} * 100$$

Optical Absorbance (ABS) measurements. These were carried out on a Shimadzu UV–2600i spectrophotometer. The samples were diluted in 3 mL of hexane in a quartz cell (optical path 10 mm) to obtain an absorption of ~ 0.3 at the bandgap. The spectra were acquired in the 300 – 700 nm range.

Photoluminescence (PL) measurements. The photoluminescence spectra were recorded using an Edinburgh FLS1000 Spectrofluorometer, equipped with a continuous Xe lamp as an excitation source. The PL spectra were measured at $\lambda_{exc} = 365$ nm (excitation slit width 3 nm, emission slit width 2 nm). The analyses were carried out on diluted NC solutions dispersed in hexane in quartz cuvettes (path length of 1 cm).

X-ray Diffraction (XRD) analysis. The XRD patterns were collected by a Rigaku MiniFlex 600 diffractometer. The samples were prepared by drop casting the final colloidal solution obtained from the synthesis on a zero background Silica wafer. The diffractogram were acquired using the Cu K α irradiation, in the range 5° - 60°, step 0.02° and speed 2.5°/min.

Transmission Electron Microscopy (TEM) imaging. TEM images were acquired using a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. The samples were prepared by dropping dilute suspensions of NCs onto carbon-coated 200 mesh copper grids. The images elaboration was performed using the software ImageJ.

Nuclear Magnetic Resonance (NMR) spectrometry. NMR spectra of nanoparticles were measured on a JEOL JNM-ECZ400R at 400 MHz (1H) at 20 °C. The chemical shifts (δ) were expressed in parts per million relatives to the solvent peak (tol-d₈ at 7.09 ppm and DMSO-d₆ at 3.33 ppm). The samples were prepared suspended the nanoparticles in tol-d₈. After the first analysis, the samples were dried and solubilized in DMSO-d₆. The spectra for following of the amine-acid reactions progress were acquired using the same instrument at 20 °C, 50 °C, 75 °C and 90 °C. The data treatment was performed using the MestReNova 14 software.

Circular dichroism (CD) measurements. The CD spectra were acquired on a nanocrystal suspension in hexane using a Jasco J-815 CD spectrometer.

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Appendices

Table A 8.1 Comparative table of the excitonic peak, PL peak and its width, size of CsPbBr₃ NCs and NPs synthesized using different amine. Both the syntheses of NCs were conducted in ODE, whereas the NPs were synthesized in decane. (*) The data for the NCs synthesized with OLAM were taken from Table 4.1 reported in the Chapter VI. (**) The data for NPs synthesized with OLAM were taken from Table A5.2 reported in the Chapter V.

Morphology	Amine ligand	Excitonic peak wavelength	PL peak wavelength	FWHM of PL	Size (nm)
Nanocubes	Oleyl amine (*)	502 nm	513 nm	72 meV	9.7 ± 1.0
	(S,Z)-nonadec-10-en-2-ammonium	508 nm	515 nm	80 meV	11.6 ± 2.1
Nanoplatelets	Oleyl amine (**)	428 nm	438 nm	86 meV	/
	(S,Z)-nonadec-10-en-2-ammonium	454 nm	463 nm	111 meV	/

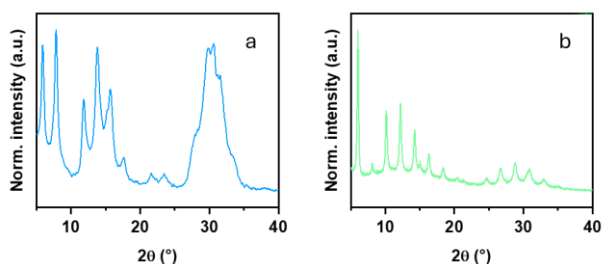


Figure A 8.1 XRD pattern comparison between nanoplatelets obtained using (a) OLAM* and (b) OLAM.

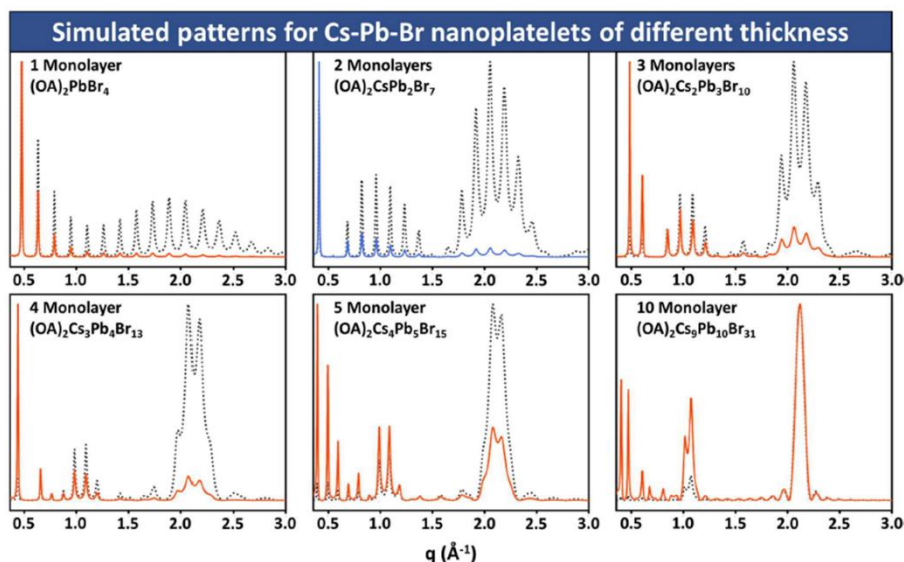


Figure A 8.2 Theoretical XRD pattern of CsPbBr₃ nanoplatelets with different thickness. Reproduced from ref.³⁵ under a CC-BY 4.0 license. Copyright © 2021 The Authors. Published by American Chemical Society. All rights reserved.

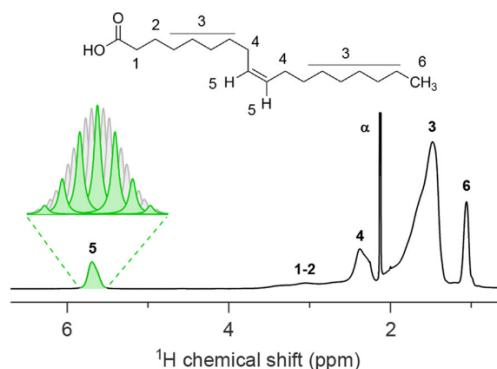


Figure A 8.3 Assignment of the peak to the oleic acid bound to a nanoparticle. The deconvolution of the peak at 5.55 ppm highlights the composition of the final peak as a overlapping of multiples peaks. They are derived from protons 5 which are immersed in different chemical environment due to the slowly rotation of the molecule for the binding of the nanocrystal surface. Reproduced with the permission from ref.³² Copyright © 2018 American Chemical Society. All rights reserved.

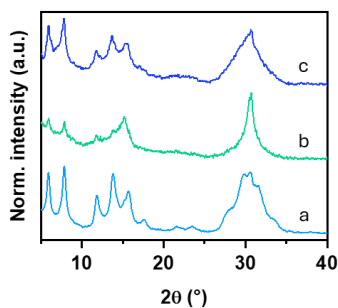


Figure A 8.4 XRD pattern comparison of CsPbBr₃ NPs synthesized with OLAM* in (a) decane, (b) (*R*)-limonene and (c) (*S*)-limonene.

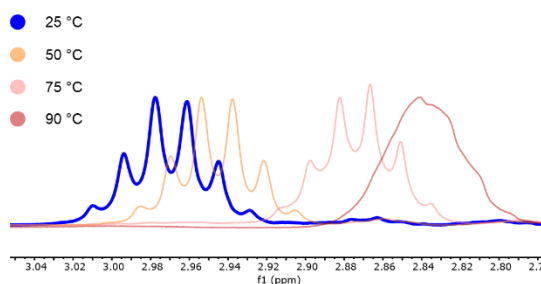


Figure A 8.5 Shifting of the signal derived from the proton bound to the α-carbon of the (*S,Z*)-nonadec-10-en-2-amine after the addition of 10.8 mg of OLAC. The shifting is caused from the enhancement of the T which lead to a lower percentage of amine protonation. The same effect was already reported for the OLAM – OLAC reaction by Almeida et al.³¹

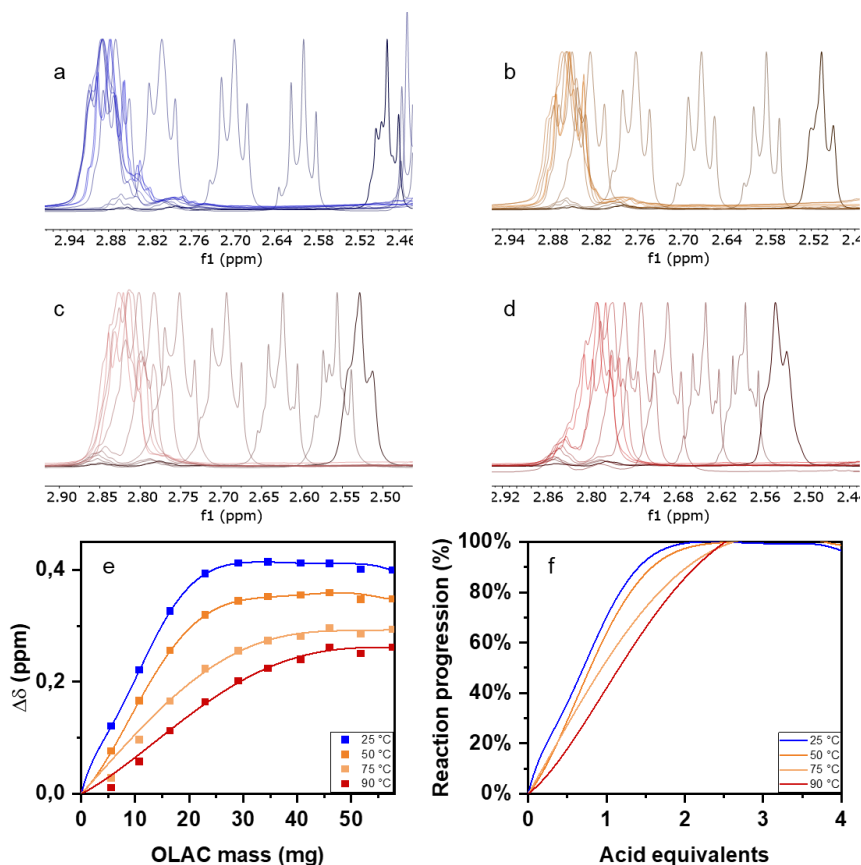


Figure A 8.6 Shift of the peak derived from the proton bound to the α -carbon of oleyl ammonium by the progressively addition of OLAC at (a) 20 °C (blue line), (b) 50 °C (orange line), (c) 75 °C (pink line) and (d) 90 °C (red line). The reaction was carried out in tol-*d*₈. (e) Plot of the variation of chemical shift ($\Delta\delta$) giving by different protonation of the ammine produced by a progressive higher quantity of OLAC at 20 °C (blue line), 50 °C (orange line), 75 °C (pink line) and 90 °C (red line). (f) Plot of the percentage of reaction progression against the equivalents of acid added to the solution at the same temperature reported for plot (e). Further information of the manipulation of plot (e) to obtain plot (f) are reported in Experimental section.

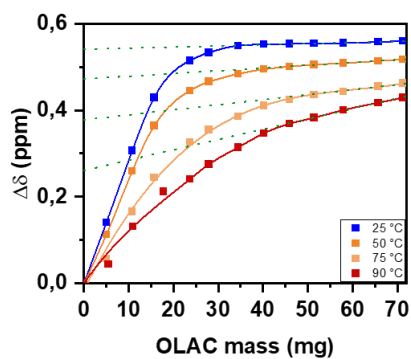


Figure A 8.7 Representation of the knee point of the curves given by the $\Delta\delta$ in function of the amount of OLAC added to the reaction. The knee point was taken where the linearity of the curves is interrupted. For a better visualization, the dot line follows the linearity of the last part of the curves.

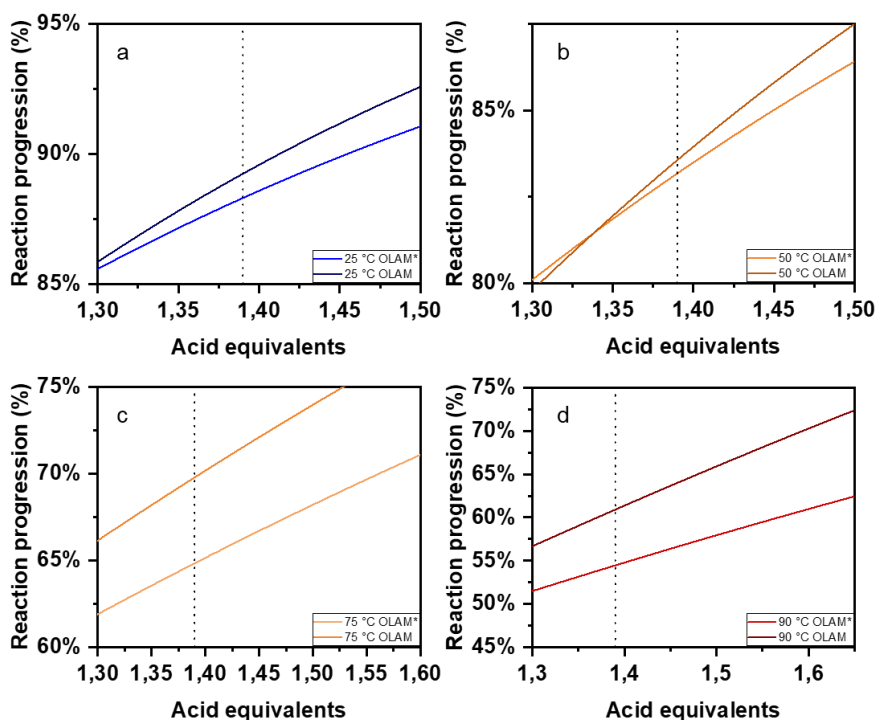


Figure A 8.8 Comparison between the graphs obtained from the OLAM or OLAM* reaction with OLAC followed by ¹H NMR. The dashed line indicates the equivalents of OLAC added to the reaction mixture for the CsPbBr₃ nanoplatforms reported by Toso et al. The comparison was effectuated for the curves obtained at (a) 25 °C, (b) 50 °C, (c) 75 °C and (d) 90 °C. The trend registered from these graphs is to increase the gap between OLAM and OLAM* protonation enhanced the temperature. Therefore, it is not possible to directly deduce the protonation degree only from the comparison at 25 °C, but a temperature studio is required to have an insight on the real protonated amine which participate to the nanocrystal formation.

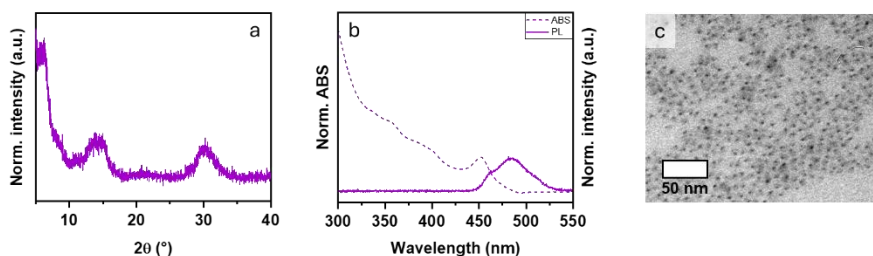
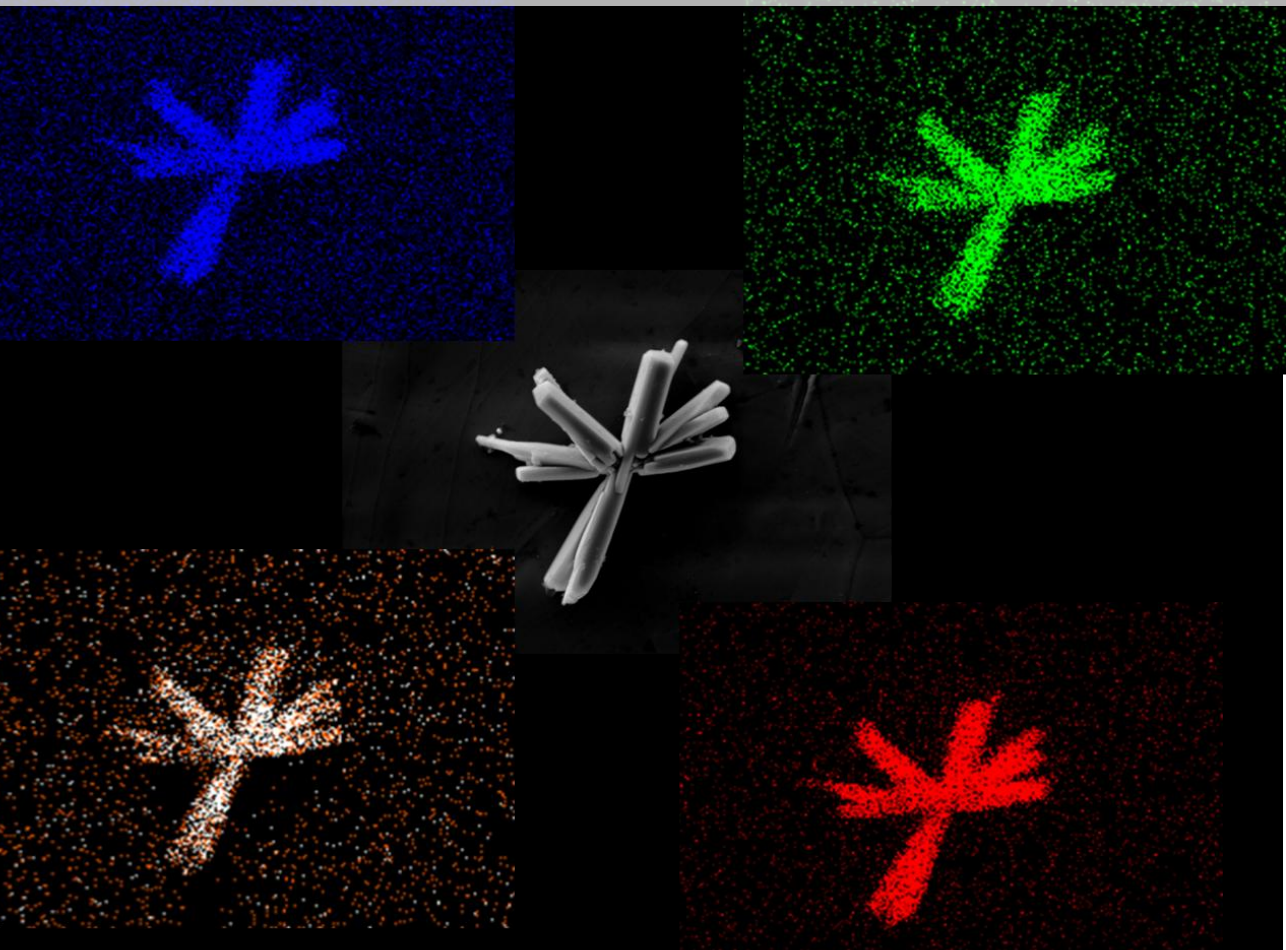


Figure A 8.9 (a) XRD pattern, (b) ABS (dashed line), PL (solid line, λ_{exc} : 365 nm) and (c) low-resolution TEM image of nanocubes synthesized with OLAM* using the procedure reported in Chapter V for the synthesis of the nanoplatforms. In this case the only variation respect the nanoplatforms synthesized as reference was on the amine employed. This experiment confirms the different behaviour of the (S,Z)-nonadec-10-en-2-amine than OLAM.

Chapter IX

Synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$
microcrystals through hot
injection method



Chapter IX: Synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$ microcrystals through hot injection method[†]

Abstract: Mixed-metal chalcogenides have recently gained attention as promising semiconductors for optoelectronic applications due to their tunable bandgaps, abundance of constituent elements, good stability, and absence of heavy metals. Nevertheless, the synthesis of quaternary chalcogenides remains challenging because of their intricate phase behaviour and the thermodynamic tendency to form competing binary and ternary products, which often hinder the formation of the desired quaternary phase. This chapter reports the colloidal synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$ via dual hot-injection protocol. This method allowed the preparation of the desired material as pure, crystalline, and uniformly dispersed microcrystals. The optical bandgap of 1.74 eV is suitable for photovoltaic and photodetection applications. Furthermore, the influence of reaction parameters on the morphology and, finally, the formation mechanism of $\text{Sn}_2\text{SbS}_2\text{I}_3$ were investigated. The work reported in this Chapter was done in the laboratory of the Bernal Institute, University of Limerick, Limerick, Ireland under the supervision of Prof. Shalini Singh.

9.1 Introduction on $\text{Sn}_2\text{SbS}_2\text{I}_3$ material

As reported in Chapter I, LHPs are dual-natured materials, as they exhibit extremely valuable optoelectronic properties while also facing issues related to structural instability and the presence of lead.^{1–8} Despite these challenges, LHPs offer advantages in a broad range of applications,^{4,6,9–13} particularly in solar energy harvesting.^{4,6,14} In 2009, Miyasaka et al. reported the first solar cell based on an LHP material, namely MAPbI_3 , achieving a power conversion efficiency (PCE) of 3.9%.¹⁵ Since then, advancements in this technology have led to efficiencies exceeding 26.7% for devices employing LHPs and up to 34.6% for triple-junction perovskite–perovskite–silicon devices.^{16–18} However, the huge problems derived from the stability and the presence of lead make the search for new materials with similar optoelectronic properties increasingly urgent and important for developing safer and more sustainable alternatives.

Among the studied materials, $\text{Sn}_2\text{SbS}_2\text{I}_3$ has emerged as particularly promising.^{19,20} Recently, Nie et al. demonstrated the potential of the mixed-metal chalcogenide $\text{Sn}_2\text{SbS}_2\text{I}_3$ in solar cell applications, achieving a PCE of 4.04%,²¹ a promising result that surpasses the efficiency reported by Miyasaka et al. for the first LHP solar cell device.

$\text{Sn}_2\text{SbS}_2\text{I}_3$ can crystallize in *two polymorphs*, namely Cmcm (orthorhombic) and $\text{Cmc}2_1$ (monoclinic), each exhibiting unique structural properties. In the Cmcm structure, $(\text{Sn}_2\text{S}_2\text{I}_2)_n$ forms chains along the *a*-axis, which are tight interconnected by Sb and I. The final structure growth on the *ab*-plane, thereby resulting in the final stoichiometry composition. Conversely, in the $\text{Cmc}2_1$ polymorph, the environmental coordination sphere

[†]**Based on:** *Controlled Colloidal Synthesis of Anisotropic Mixed-Metal Chalcogenides: Insights into Morphology and Phase Evolution*. D. Pratolongo, A. Bora, S. Sen, N.N. Patil, S. Alberti, M. Palabathuni, F. Locardi and S. Singh. *Nanoscale* (2025), 17, 27225–27232

of Sb and Sn differ significantly from those in the Cmcm structure, which lead to the formation of $(\text{Sn}_2\text{SbS}_2\text{I}_3)_n$ chains aligned along the a-axis.^{19,22–25}

DFT calculation predicts a band gap of 1.80 eV for the Cmcm structure.²³ The *direct band gap* characteristic of this material is notable, as it contrasts with the typical indirect band gap observed in many chalcogenide compounds, particularly those that do not feature a mixed-metal composition.²² The presence of a direct band gap in $\text{Sn}_2\text{SbS}_2\text{I}_3$ is indicative of its potential for optoelectronic applications, as direct band gap materials are generally more efficient for light absorption and emission processes.^{26–30}

Although the recent interest on $\text{Sn}_2\text{SbS}_2\text{I}_3$ stoichiometry, the first synthesis was reported by Oliver-Fourcade et al. in 1980.²⁴ In 1990, Starosta et al. extended the studies on $\text{Sn}_2\text{SbS}_2\text{I}_3$.³¹ The same synthetic method, a direct solid-state reaction, was employed to obtain the final material. In recent years, several alternative synthetic strategies were employed to synthesize $\text{Sn}_2\text{SbS}_2\text{I}_3$. Nie et al. employed spin-coating technique to prepare thin films. A solution of SbCl_3 , thiourea and SnI_2 dissolved in DMF was spin-coated at 200 °C, followed by an annealing at 300 °C.²¹ Nicolson et al. synthesized the $\text{Sn}_2\text{SbS}_2\text{I}_3$ single crystal by chemical vapor transport.²³ Roth et al. applied a liquid-phase synthesis approach using the heat-up method to obtain micrometric $\text{Sn}_2\text{SbS}_2\text{I}_3$.³²

In this Chapter, the synthesis and characterization of $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods by hot-injection method are reported. The final product was obtained as a pure phase. Elemental analysis revealed slight variations in the stoichiometry of the material, both in the bulk and at the surface, which can influence the measured bandgap, causing small deviations from the theoretical value. Analysis of the organic fraction indicated that the surface is predominantly capped by amine ligands. Furthermore, the role of the hot-injection parameters on the final microcrystal morphology was investigated in detail. Finally, the formation mechanism of $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods was studied by monitoring the morphological and phase evolution over the course of the reaction.

9.2 Synthesis and characterization

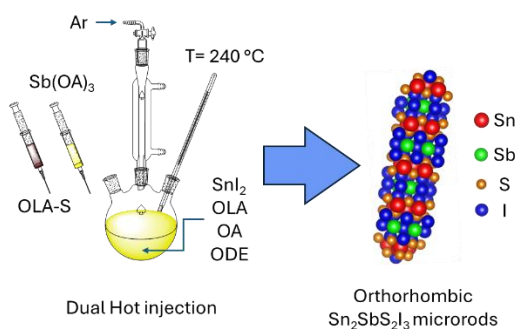


Figure 9.1 Illustration of a dual Hot injection procedure to obtain $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods.

$\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods were prepared via a hot-injection method. Solutions of antimony(III) oleate ($\text{Sb}(\text{OLAC})_3$) and oleylamine sulphur (OLAM-S) were injected at 240 °C into a reaction mixture containing SnI_2 , oleylamine (OLAM) and oleic acid (OLAC) as ligands, with 1-octadecene (ODE) serving as the solvent (see Experimental section for

details). The synthesis employs a sequential injection strategy, with Sb(OLAC)_3 added first, followed by OLAM-S after 5 s (Figure 9.1), to prevent premature redox reactions between the antimony and sulfur precursors and Sn^{2+} ions. This controlled injection order is essential to preserve the correct oxidation states and achieve a phase-pure product.

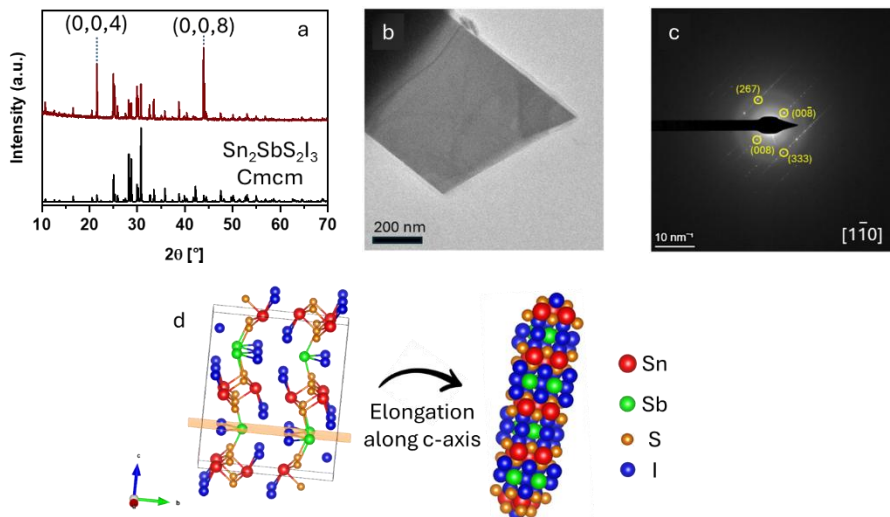


Figure 9.2 (a) X-ray diffraction (XRD) pattern of the as-synthesized $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods (bordeaux line) compared with $\text{Sn}_2\text{SbS}_2\text{I}_3$ Cmcmm reference (ICSD number 23344). (b) High-resolution TEM images and (c) corresponding Selected area electron diffraction (SAED) pattern. (d) Illustration of (002) crystallographic plane (orange plane) of $\text{Sn}_2\text{SbS}_2\text{I}_3$ Cmcmm unit cell (ICSD number 23344). The elongation through c-axis lead to the microrod formation. Indeed, the crystallographic analyses indicate a higher intensity of the peaks related to (002) family.

The as-synthesised $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods were analysed by XRD (Figure 9.2a). The diffraction pattern of the synthesized material shows the characteristic peaks of the Cmcmm orthorhombic phase (ICSD number 23344). Differences in peak intensities compared to the reference can be attributed to a preferred orientation of the microrods on the sample holder. Experimentally, the two most intense reference peaks at 28.2° and 30.8° , corresponding to the (130) and (114) reflections, are significantly diminished in the measured sample. In contrast, reflections with a strong c-axis component, such as those at 21.6° and 44.0° (assigned to the (004) and (008) planes, respectively), show pronounced intensity enhancement. Peaks at 10.7° and 32.6° , indexed as (002) and (006), exhibit milder increases. The (004) plane contains Sb and I atoms, which link the $\text{Sn}_2\text{S}_2\text{I}_2$ chains.¹⁹ These observations suggest *preferential particle growth* along planes perpendicular to the c-axis, consistent with the formation of anisotropic structures (Figure 9.2d). Selected area electron diffraction (SAED) along the $[1\bar{1}0]$ axis (Figure 9.2c) further confirm the rod elongation through (004) plane, since displays (008) reflections along with higher-order planes.

No XRD peaks corresponding to impurities, such as secondary binary or ternary phases (Sb_2S_3 , SbSI , Sn_2SI_2 , Sn_4SI_6 , SnS , SnI_2 etc.), were detected (Figure A9.1).

Additionally, the absence of peaks associated with the monoclinic $\text{Cmc}2_1$ phase of $\text{Sn}_2\text{SbS}_2\text{I}_3$ confirms the phase and compositional purity of the synthesized microrods.

Table 9.1 Elemental distribution calculated by SEM-EDX.

Element	Weight (%)	Atomic (%)
S	9.70	29.24
Sn	27.57	22.44
Sb	17.09	13.56
I	45.64	34.76
Total		100

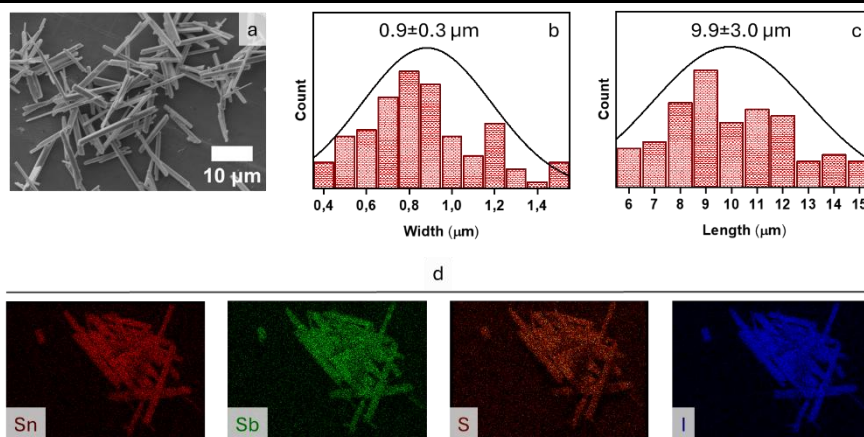


Figure 9.3 (a) SEM imaging of the as-synthesized $\text{Sn}_2\text{SbS}_2\text{I}_3$ reveal its rod-shape. (b) Width and (c) length average of the microrods. (d) Elementary mapping given by SEM-EDX analysis. Sn (red), Sb (green), S (orange) and I (blue) were analyzed.

The SEM image in Figure 9.3a shows that the synthesized $\text{Sn}_2\text{SbS}_2\text{I}_3$ exhibits a clear rod-like morphology. The microrods display an average length of $9.9 \pm 3.0 \mu\text{m}$ and a width of $0.9 \pm 0.3 \mu\text{m}$ (Figure 9.3b and c). SEM-EDX mapping confirms a homogeneous distribution of all the elements along the rods (Table 9.1 and Figure 9.3d). The atomic ratios derived from EDX correspond to an overall composition of $\text{Sn}_{1.65}\text{SbS}_{2.16}\text{I}_{2.56}$, indicating a slight enrichment in Sb and S compared to the nominal stoichiometry.

X-ray photoelectron spectroscopy (XPS) was carried out to further examine the elemental composition, chemical environment, and oxidation states present in the synthesized microrods (Figure 9.4). Surface analysis yields a composition of $\text{Sn}_{1.56}\text{SbS}_{1.78}\text{I}_{2.24}$, indicating that the rod surfaces are even more enriched in Sb than the bulk, while the sulfur content is comparatively lower at the surface.

In the high-resolution Sb 3d spectrum (Figure 9.4a), peaks at 540 eV and 541.5 eV proper of Sb (V) are observed, corresponding to the spin-orbit doublet levels Sb 3d_{5/2} and Sb 3d_{3/2}, respectively, with an energy separation of 1.5 eV. The Sn 3d region (Figure 9.4b) shows the characteristic spin-orbit doublet Sn 3d_{5/2} and Sn 3d_{3/2}, placed at 487.5 eV and 496.0 eV, respectively, separated by roughly 8.5 eV. Deconvolution confirms a single component for each peak. The energy separation between the two peaks, together with

the deconvolution analysis and the asymmetric peak shape, confirms the presence of Sn(II) and the absence of other oxidized species, since Sn(IV) typically exhibits a symmetric peak at an energy very close to that of Sn(II).³² The S 2p spectrum (Figure 9.4c) displays a peak at 163.2 eV, arising from the typical S 2p doublet, with the 2p_{3/2} and 2p_{1/2} components at 163.1 eV and 165.4 eV and separated by 2.3 eV, consistent with S²⁻. Finally, the I 3d region (Figure 9.4d) features a clear doublet corresponding to I 3d_{5/2} and I 3d_{3/2} spin-orbit split levels at 620.1 eV and 631.4 eV, respectively, with an 11.3 eV separation, characteristic of I⁻. The lack of additional signals associated with oxidation, binary/ternary oxide phases, or other side products in the high-resolution XPS spectra underscores the effectiveness of the dual-injection synthesis strategy developed here for producing phase-pure metal chalcogenides.

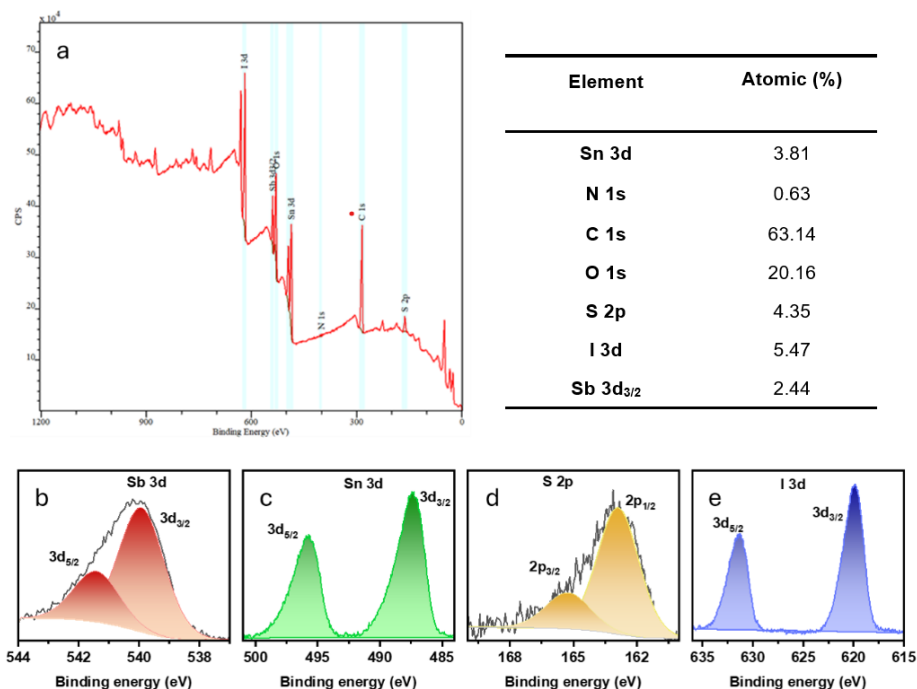


Figure 9.4 (a) X-ray photoelectron spectroscopy (XPS) analysis of the as-synthesized microrods with the atomic percentage calculated from the peak integration which reveal a elemental ratio between Sn:Sb:S:I of 1.56:1:1.78:2.24. High-resolution XPS spectra of (a) Sb 3d, (b) Sn 3d, (c) S 2p, and (d) I 3d.

The reflectance spectrum of the Sn₂SbS₂I₃ microrods (Figure 9.5a) shows a marked decrease in reflectance between 600–800 nm, corresponding to the onset of the valence-to-conduction band transition. No additional spectral features appear, supporting the phase purity of the material. The Tauc plot in Figure 9.5b, obtained by applying the Kubelka–Munk transformation to the reflectance data and assuming a direct allowed transition, indicates an optical band gap of 1.74 eV. This value aligns well with the 1.80 eV band gap predicted for orthorhombic Cmcm Sn₂SbS₂I₃.²³

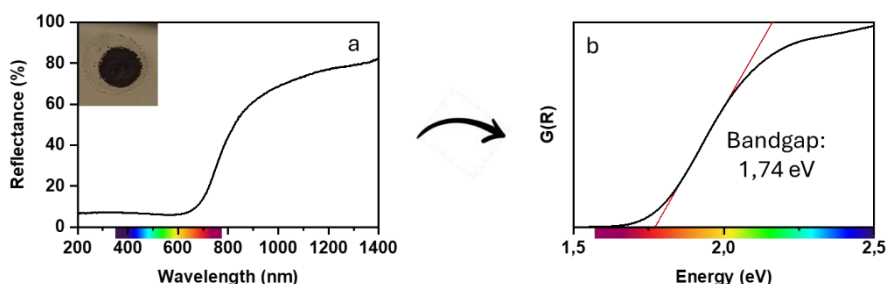


Figure 9.5 (a) Reflectance spectrum of the $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods. The inset shows a photograph of the dried product deposited on a zero-background silica wafer. (b) Tauc plot obtained from the reflectance data after applying the Kubelka–Munk transformation ($y = G(R) = (F(R) \cdot hv)^2$ with $F(R) = (1 - (\text{reflectance}/100))^2 / (2 \cdot (\text{reflectance}/100))$ and $x = hv = 1240/\text{Wavelength}$). The optical band gap, determined by extrapolating the linear region of the plot to $y = 0$ (red line), is 1.74 eV.

The small deviation between experimental and calculated band gaps may arise from several factors. Although the microrods are far larger than the quantum confinement regime, their anisotropic shape could still affect the electronic structure. A similar morphological influence was shown by Tsai et al. for TiO_2 nanorods, where reflectance characteristics varied with nanorod length and differed from bulk TiO_2 , despite the quantum confinement regime were not achieved.³³ In addition, Nicolson et al. reported that static cation disorder, which develops when these materials are synthesized above 127 °C, results in a reduced band gap.²³

Moreover, SEM-EDX and XPS analyses reveal that both surface and bulk compositions deviate slightly from the ideal $\text{Sn}_2\text{SbS}_2\text{I}_3$ stoichiometry. According to the density of states (DOS) analysis by Kavanagh et al., the conduction band minimum primarily arises from interactions between Sb p and I p orbitals, while the valence band maximum is dominated by antibonding interactions among the Sn $5s^2$ lone pair and S^{2-}/I^- p states.^{19,22,23} Since all these ions contribute to the frontier bands, variations in their relative abundances can shift the corresponding energy levels and modify the band gap. Taken together, we attribute the observed band gap difference to a combination of morphology-dependent electronic effects and thermally induced cation disorder.

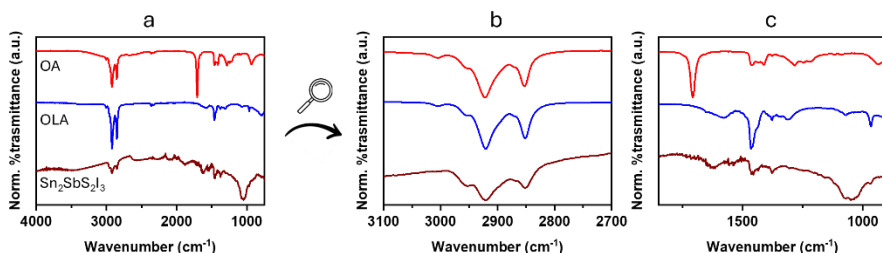


Figure 9.6 (a) Fourier Transform Infrared (FTIR) spectroscopy analysis of as-synthesized $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods. Expansion in range (b) 3100 – 2700 cm^{-1} and (c) 1850 – 900 cm^{-1} to evidence the C-H stretching (first range) and the N-H bending (second range). The peak of C=O result not visible, indicating a low amount of the acid ligand on the microrod surface.

FTIR spectrum of as-synthesised $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods (Figure 9.6), recorded in the 500–4000 cm^{-1} range, was used to examine the organic species present on their surface. The peaks at 2955, 2920, 2850 cm^{-1} correspond to sp^3 C–H stretching vibration, while the band at 1450 cm^{-1} derived from the sp^3 C–H bending of the ligands carbon chain. The little peak at ~ 3000 cm^{-1} derived from the sp^2 C–H stretching displayed in the FTIR spectra of the ligands result not visible probably for the relative low amount of ligand on the microcrystal surface. Further insights into the bound ligands come from the 1700–1300 cm^{-1} region. A feature at 1630 cm^{-1} is assigned to the asymmetric bending of N–H groups, indicating the presence of amine functionalities. Importantly, the absence of a peak near 1700 cm^{-1} , typically associated with the C=O stretching of oleic acid, suggests that this ligand is either present at very low levels or largely absent at the microrod surface. Lastly, the broad signal around 1040 cm^{-1} , located within the fingerprint region, is too broad to differentiate between OLAM and OLAC.

9.3 Influence of the synthetic parameter on the microcrystals

Table 9.2 The table reports reaction performed for studying of the H_{inj} parameters influence on the final $\text{Sn}_2\text{SbS}_2\text{I}_3$ microcrystal. The table reported the length and the width of the microrods obtained varying the reaction parameters, whereas the pure product has been obtained. Entry 0 corresponds to the standard synthesis conditions described in the Experimental section, and the associated width and length values are reported accordingly.

Entry	OLAC (mL)	OLAM (mL)	ODE (mL)	Inj. T (°C)	Annealing T (°C)	XRD analysis	SEM images and analysis	Width (μm)	Length (μm)
0	1.5	0.5	5	240	240	Figure 9.2a	Figure 9.2a	0.9 ± 0.3	9.9 ± 3.0
1	1.5	1	5	240	240	Figure 9.7	Figure A9.2a	-	-
2	3	0.5	5	240	240	Figure 9.7	Figure A9.2b, c, d	1.1 ± 0.6	12.6 ± 4.2
3	0.5	0.5	5	240	240	Figure 9.7	Figure A9.2e, f, g	1.2 ± 0.5	19.7 ± 7.8
4	1.5	0.5	15	240	240	Figure 9.7	Figure A9.2h, i, j	0.8 ± 0.3	10.9 ± 3.5
5	1.5	0.5	5	150	240	Figure 9.7	Figure A9.2k, m, n	0.9 ± 0.4	4.8 ± 1.7

Control experiments in which key parameters were systematically varied were carried out to understand how different reaction conditions influence one another during synthesis and to identify possible correlations between them. The reactions were carried out as detailed in the Experimental section, varying the amounts of OLAC, OLAM, and ODE, as

well as the injection and annealing temperatures, according to the conditions listed in this table. The quantities of the reagents and the annealing time were kept constant throughout all experiments. Each sample was examined by XRD (Figure 9.7) to verify the crystalline phase, and by SEM to assess the morphology and determine the size distribution (Figure A9.2). A summary of the tested parameter variations is provided in Table 9.2. Surprisingly, changes in ligand concentrations (OLAM and OLAC), injection temperature or dilution of the reaction mixture all consistently led to the formation of $\text{Sn}_2\text{SbS}_2\text{I}_3$, as displayed to the XRD patterns reported in Figure 9.7. Among them, only the sample synthesized with a double amount of OLAM led to an incomplete transformation of Sb_2S_3 into the desired phase.

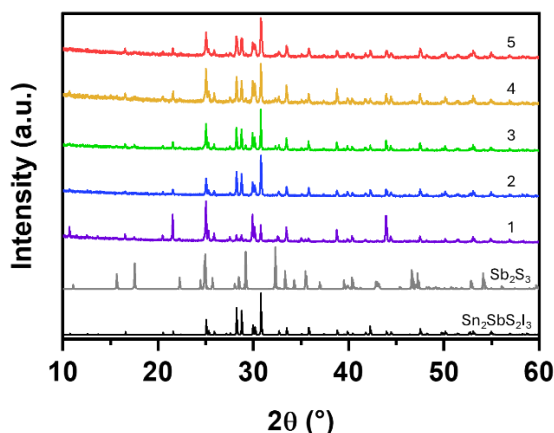


Figure 9.7 Comparison between $\text{Sn}_2\text{SbS}_2\text{I}_3$ orthorhombic Cmc $\bar{m}$ phase (ICSD number 23344) and Sb_2S_3 orthorhombic Pn $\bar{m}$ a phase (ICSD number 22176) with the product obtained from reactions 1, 2, 3, 4, 5 (reaction parameters reported in Table 9.2). Only 1 showed a pattern derived from an overlapping of the two reported phases, while the others present a pure $\text{Sn}_2\text{SbS}_2\text{I}_3$ phase.

The only noticeable influence of these variations was observed on the *morphology* of the anisotropic crystals (Table 9.2 and Figure A9.2). For example, reducing the OLAC concentration by half resulted in longer microrods, whereas doubling the OLAC concentration led to a broader length distribution. *Acid–base interactions* play a key role in defining crystal morphology, particularly at the nanoscale, because they generate oleate anions and oleylammonium (OLAM-H) cations.³⁴ FTIR analysis indicates a stronger presence of amine species relative to acid-derived ones on the microrod surface, suggesting that OLAM and OLAM-H dominate the surface coverage and thus control the final morphology and size distribution.

As reported in XPS analysis (Figure 9.4), microcrystal surface presents an elemental distribution which slightly differ from the nominal $\text{Sn}_2\text{SbS}_2\text{I}_3$ by an increasing of Sn^{3+} and, above all, a decreasing of S^{2-} . Therefore, approximately 39% of the surface is composed of elements that preferentially act as *Lewis acids*, such as Sn^{2+} and Sb^{3+} . In contrast, S^{2-} behaves as a Brønsted acid and would therefore be expected to interact more strongly with ammonium species, while I^- shows no particular affinity toward either amine or ammonium groups. Moreover, the acidity of S^{2-} is further reduced due to its coordination

within the crystal lattice. On the other hand, Sn^{2+} and Sb^{3+} readily form coordination complexes with electron-pair-donating amine ligands,^{35–39} which bind to the microrod surface as L-type ligands.⁴⁰ The abundance of amine species is consistent with more effective passivation and stabilization along a growing rod, enabling the formation of longer microrods. However, when the amine concentration exceeds the optimal range for chalcogenide synthesis, incomplete conversion of Sb_2S_3 into $\text{Sn}_2\text{SbS}_2\text{I}_3$ (Table 9.2, entry 1, Figure 9.7 and A9.2a). Under these conditions, Sn^{2+} and the Sb_2S_3 particles become *excessively stabilized* by the amine-rich environment, thereby hindering the progression and completion of the reaction.

9.4 Insight into formation mechanism

To monitor the reaction progress and to investigate the kinetic factors governing the formation pathway of $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods, aliquots at different times were collected and analyzed. Each aliquot was purified as described in the Experimental section and subsequently analysed by XRD and SEM (Figure 9.8), enabling the simultaneous assessment of crystal phase evolution and morphological development throughout the reaction.

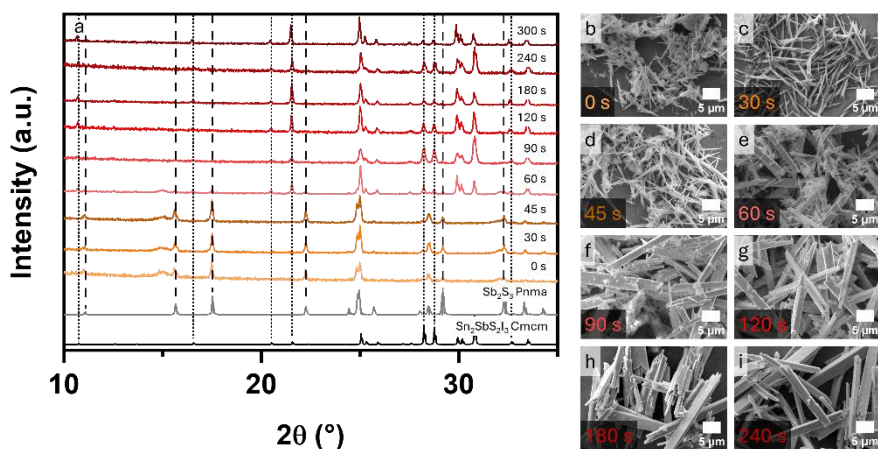


Figure 9.8 (a) XRD patterns of aliquots collected at various stages of the reaction, shown together with reference diffractograms for $\text{Sn}_2\text{SbS}_2\text{I}_3$ orthorhombic Cmc21 phase (ICSD number 23344) and Sb_2S_3 orthorhombic Pnma phase (ICSD number 22176). The reflections associated with $\text{Sn}_2\text{SbS}_2\text{I}_3$ and Sb_2S_3 are marked by dotted black and dashed black lines, respectively, aiding the assignment of peaks in the aliquot patterns. SEM images of aliquots withdrawn at (b) 0 s, (c) 30 s, (d) 45 s, (e) 60 s, (f) 90 s, (g) 120 s, (h) 180 s, and (i) 240 s.

Immediately after the simultaneous injection of $\text{Sb}(\text{OLAC})_3$ and OLAM-S into the reaction flask containing SnI_2 , OLAM, and OLAC at 240 °C, *rapid formation of Sb_2S_3* is observed. XRD patterns confirm the presence of orthorhombic Sb_2S_3 (Pnma) for up to 45 s after injection. The corresponding SEM images (Figure 9.8b, c and Figure A9.3) show the formation of microrods with a narrow size distribution. No incorporation of Sn into Sb_2S_3 , nor formation of any tin sulphide phase, is detected within the first 45 s. However,

Sb_2S_3 crystals are short-lived: between 45 and 90 s, XRD patterns reveal the *coexistence of Sb_2S_3 and the final quaternary chalcocalide* ($\text{Sn}_2\text{SbS}_2\text{I}_3$). Consistently, the microrod size distribution (Figure 9.8d, e) broadens during this interval, reflecting the mixed-phase composition of these aliquots. After 90 s, the XRD patterns show a gradual disappearance of Sb_2S_3 reflections and the emergence of distinct peaks exclusively corresponding to $\text{Sn}_2\text{SbS}_2\text{I}_3$. The SEM images of the aliquots (Figure 9.8f–i) show an enlargement in rod dimensions (length and width) and a progressive narrowing of the size distribution.

These observations support a *formation mechanism* initiated by the dissociation of SnI_2 in the reaction flask. Given its bond dissociation energy (200–250 kJ/mol),³² SnI_2 is expected to partially dissociate at 240 °C before the injection of the Sb and S precursors, generating Sn^{2+} and I^- species that become stabilized by OLAC and OLAM. Upon injection, OLAM reduces $\text{Sb}(\text{OA})_3$, forming a transient metal–amido complex that is rapidly sulfurized by the OLAM–S precursor, yielding anisotropic Sb_2S_3 crystals instantly. In the presence of reactive Sn and halide species, as well as OLAM, these Sb_2S_3 crystals likely undergo partial dissolution followed by reprecipitation into the final mixed-metal chalcocalide $\text{Sn}_2\text{SbS}_2\text{I}_3$. With extended reaction time, a ripening process takes place, leading to further growth and a progressive narrowing of the microrod size distribution.

9.5 Conclusion

In summary, this Chapter illustrates a robust colloidal synthesis strategy for producing phase-pure $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods via a dual hot-injection approach. By precisely controlling the injection parameters and precursor chemistry, we achieved uniform anisotropic structures with reproducible morphological features. Systematic aliquot studies enabled us to track the evolution of the reaction intermediates and to elucidate the formation pathway of this complex chalcocalide. The synthesis initiates with the rapid nucleation of needle-like Sb_2S_3 seeds immediately after the introduction of the antimony and sulfur precursors. These transient seeds undergo partial dissolution, triggering a reassembly process in which Sn^{2+} and I^- species from the reaction mixture drive the conversion of the binary Sb_2S_3 phase into the final quaternary $\text{Sn}_2\text{SbS}_2\text{I}_3$ compound. This transformation ultimately yields phase-pure crystalline microrods. Overall, this work not only provides mechanistic insight into the synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$ but also highlights the dual hot-injection strategy as a versatile and accessible route for controlling stoichiometry in the synthesis of other quaternary chalcocalides.

9.6 Experimental Section

Materials. Antimony(III) acetate ($\text{Sb}(\text{OAc})_3$, Sigma-Aldrich, 99.99%), hexane (Hex, Honeywell, $\geq 97.0\%$), isopropanol (iPrOH, Honeywell, $\geq 99.9\%$), 1-octadecene (ODE, Sigma-Aldrich, for synthesis), oleic acid (OLAC, Sigma-Aldrich, 90% technical grade), oleylamine (OLAM, Sigma-Aldrich, 70%), sulphur powder (S powder, TCI, $>99.0\%$), tin(II) iodine (SnI_2 , Sigma-Aldrich, 99.99%).

Preparation of sulphur precursor (OLAM-S). The stock solution of the sulfur precursor was prepared by combining 160.1 mg (4.99 mmol) of sulfur powder with 5 mL of OLAM in a 10 mL vial. The mixture was stirred at room temperature inside an Ar-filled glove box. Over the course of 2 hours, the initially turbid yellow solution gradually turned into a clear dark red solution. The resulting transparent dark red solution (1 M) was stored in the glove box and used as the stock solution for the synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$.

Preparation of antimony oleate ($\text{Sb}(\text{OLAC})_3$). The stock solution of $\text{Sb}(\text{OLAC})_3$ was prepared by combining 434.5 mg (1.45 mmol) of $\text{Sb}(\text{OAc})_3$ with 5 mL of OLAC in a 25 mL three-neck flask connected to a Schlenk line. The mixture was heated to 100°C under vacuum with continuous stirring and maintained under these conditions for 1 hour. The resulting transparent pale-yellow solution (0.3 M) was then transferred into the glove box and used as a stock solution for the synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$.

Synthesis of $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods. A 25 mL three-neck flask connected to a Schlenk line was loaded with 75.5 mg (0.20 mmol) of SnI_2 , 1.5 mL of OLAC, 0.5 mL of OLAM, and 5 mL of ODE. The mixture was stirred under vacuum at 120°C for 30 min. The temperature was then raised to 240°C under an Ar atmosphere, during which the solution changed from yellow to orange. At this temperature, 0.35 mL of $\text{Sb}(\text{OLAC})_3$ (0.3 M) was rapidly injected, followed 5 s later by 0.2 mL of OLAM-S (1 M). After 5 min, the reaction was quenched using an ice bath. The resulting black mixture was centrifuged at 5000 rpm for 3 min, and the precipitate was washed three times with a Hex:iPrOH (1:2) solution. The final black solid was dried and stored under ambient conditions for further characterization.

X-ray diffraction (XRD) analysis. XRD measurements were performed using an Empyrean X-ray diffractometer. Samples were prepared by drop-casting the final product, dispersed in hexane, onto a zero-background boron-doped P-type silica wafer. Diffractograms were collected using a 1.8 kW Cu ceramic X-ray tube (Cu K α radiation) operating at 45 kV and 40 mA, with a PIXcel3D 2×2 area detector. Data were recorded over a 2θ range of 5° – 80° , with a step size of 0.013° and a scan speed of $0.094^\circ \text{ s}^{-1}$.

Scanning electron microscopy (SEM) and scanning electron. SEM images and elemental analysis via energy-dispersive X-ray spectroscopy (SEM-EDX) were acquired using a Hitachi SU-70 microscope operating at 5–20 kV. Samples were prepared by drop-casting the final product, dispersed in hexane, onto a stainless-steel substrate fixed to the sample holder with carbon tape. Image analysis and processing were performed using ImageJ software.⁴¹

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out on a Kratos AXIS ULTRA spectrometer equipped with a monochromatic Al K α X-ray source (1486.58 eV). The C 1s peak at 284.8 eV was used for calibration. Spectra construction and peak fitting were performed using CasaXPS software.⁴² Samples were prepared by drop-casting a dispersion of microrods in toluene onto p-type boron-doped silicon substrates.

Reflectance measurements. The reflectance spectrum was recorded using a Shimadzu UV–2600i spectrophotometer equipped with an integrating sphere coated with BaSO_4 . Measurements were taken over the 200–1400 nm range with a step size of 1.0 nm and a scan time of 6 min per spectrum (scan speed 0.0028 nm s^{-1}). The reflectance data were converted using the Kubelka–Munk function, and a Tauc plot was constructed to determine the optical band gap.

Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were collected using a Nicolet iS20 spectrometer (Thermo Fisher Scientific) in attenuated total reflectance (ATR) mode. For each sample, 32 scans were acquired over a collection time of 95.44 s, with a resolution of 4000 cm^{-1} and 12,415 scan points, covering the $500 - 4000 \text{ cm}^{-1}$ range. Data are reported as % transmittance. Both powder and liquid samples were deposited directly onto the diamond crystal prior to measurement. Spectral processing was performed using OMNIC™ Series Software.⁴³

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Appendices

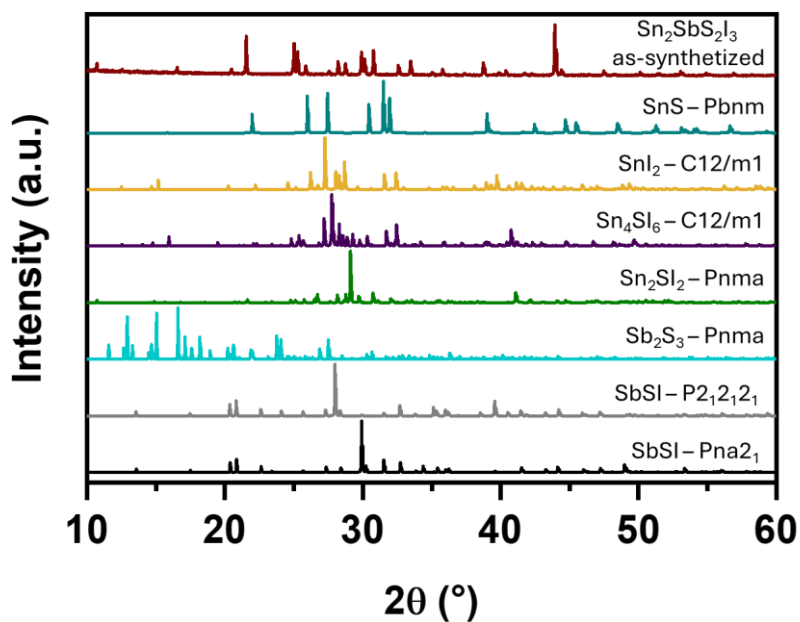


Figure A 9.1 XRD pattern of as-synthesised $\text{Sn}_2\text{SbS}_2\text{I}_3$ microrods (bordeaux), in comparison with the reference patterns of potential by-products: SbSI (Pna2₁, ICSD 26924), SbSI (P2₁2₁2₁, ICSD 85298), Sb₂S₃ (Pnma, ICSD 22176), Sn₂SI₂ (Pnma, ICSD 50), Sn₄SI₆ (C12/m1, ICSD 12165), SnI₂ (C12/m1, ICSD 2831), and SnS (Pbnm, ICSD 41739).

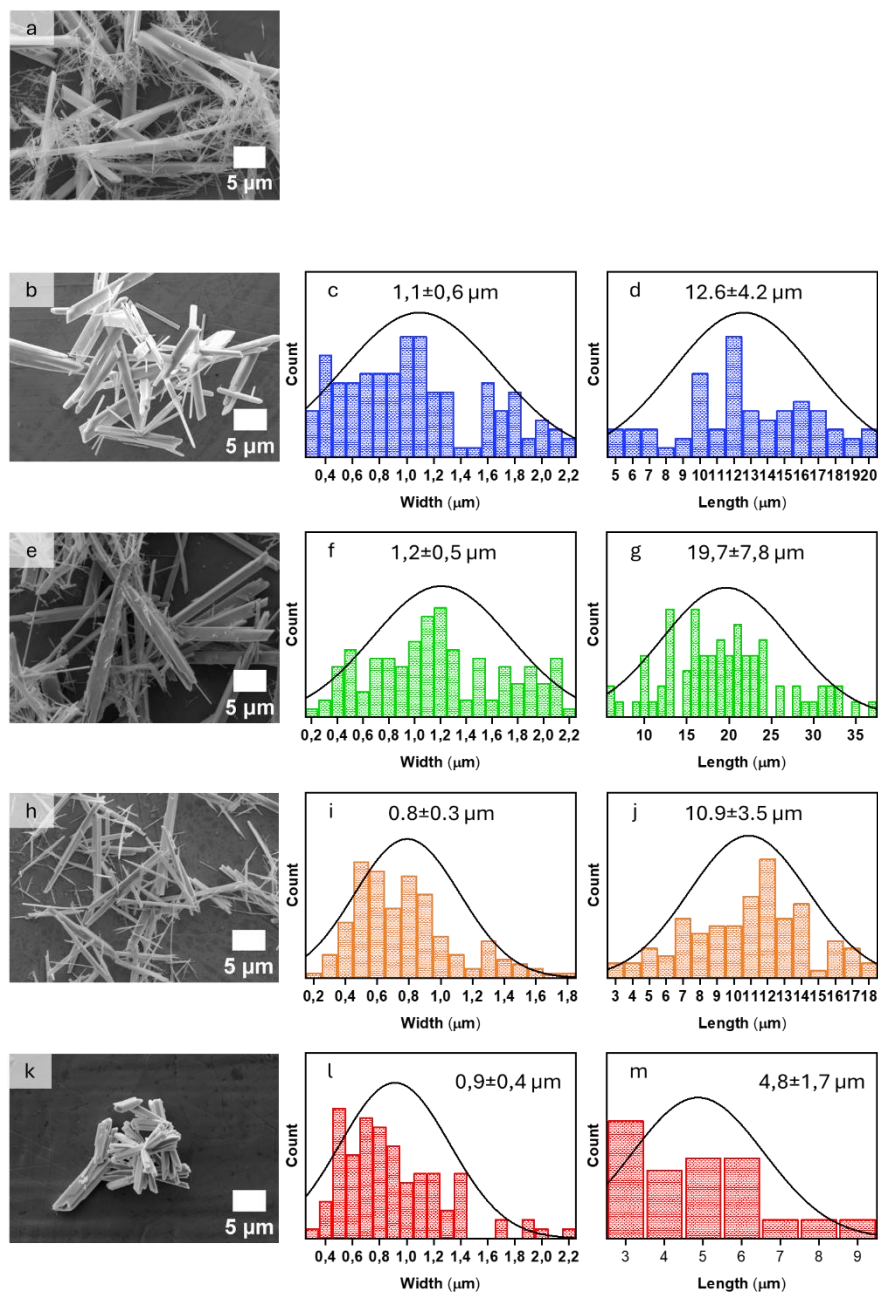


Figure A 9.2 SEM images, along with width and length distributions, of $\text{Sn}_2\text{SbS}_2\text{I}_3$ synthesized under the conditions reported in Table 9.2 are shown. The samples correspond to the following synthesis entries: (a) 1, (b–d) 2, (e–g) 3, (h–j) 4, and (k–n) 5. 1 exhibits two distinct phases, visible in the SEM image as thick rods and thin needle-like rods; due to this heterogeneity, no size distribution was calculated. Variations in reaction parameters notably influence the final rod morphology, particularly the size distribution. Increasing the OA amount (2) primarily affects the width distribution (54%), whereas reducing the OA content (3) impacts both the length ($19.7 \mu\text{m}$) and the size distribution

(42%). Diluting the reagent and ligand concentrations by increasing the ODE volume (4) produces only minor changes, with rods showing a width of 0.8 μm and a length of 10.9 μm . For sample 5, where the injection temperature (150 $^\circ\text{C}$, held for 3 min) was separated from the annealing temperature (240 $^\circ\text{C}$, held for 5 min), SEM imaging reveals rod-like particles, contrasting with the spherical morphology of Sb_2S_3 formed under similar conditions (Figure A9.4). This indicates that the final $\text{Sn}_2\text{SbS}_2\text{I}_3$ morphology is not determined by the initial Sb_2S_3 structure. The rods in 5 measure 0.9 μm in width and 4.8 μm in length, approximately half the length of rods produced under standard synthesis conditions. For comparison, microrods synthesized following the standard procedure (Table 9.2, entry 0 and Experimental Section) exhibit a width of 0.9 μm and a length of 9.9 μm , with size distribution percentages of 33% and 30%, respectively.

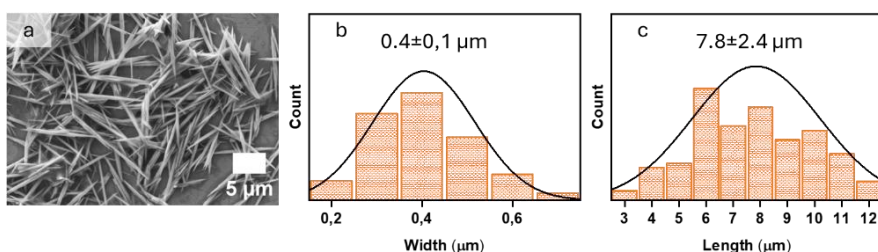


Figure A 9.3 (a) SEM imaging of the needle-shape Sb_2S_3 giving by the aliquot taken after 30 s from the dual hot injection. (b) Width and (c) length average of the needle-shape particles.

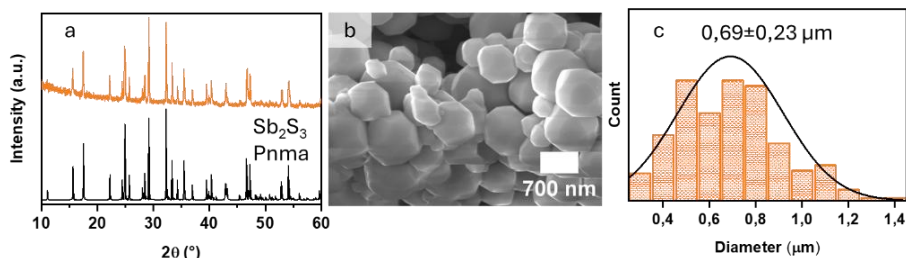


Figure A 9.4 (a) XRD pattern, (b) SEM image, and (c) particle diameter distribution of Sb_2S_3 synthesized via co-injection of $\text{Sb}(\text{OLAC})_3$ and OLAM-S at 150 $^\circ\text{C}$ into a solution containing 1.0 mL OLAC, 0.5 mL OLAM, and 5 mL ODE, followed by annealing at 240 $^\circ\text{C}$ for 5 min. The reaction was quenched by rapid cooling in an ice bath. The resulting product corresponds to the orthorhombic Sb_2S_3 Cmcm phase (ICSD 22176) and consists of spherical particles with an average diameter of 0.69 μm . This contrasts with the spiky, rod-shaped Sb_2S_3 particles obtained when the precursors are injected directly at 240 $^\circ\text{C}$ (Figure A9.3).

Chapter IX

Summary and outlook



Chapter X: Summary and outlook

Abstract: Since 1993, the hot-injection method has become a cornerstone of colloidal synthesis due to its ability to synthesize high-quality, monodisperse nanocrystals. The precise control over the reaction parameters enables the synthesis of nanocrystals with different stoichiometries as well as a wide range of morphologies. This level of control has facilitated a deeper investigation of size-dependent properties and quantum confinement effects, as well as the integration of these materials into functional devices. For these reasons, the hot-injection method has emerged as one of the most prominent synthetic strategies in the field of nanotechnology. The hot-injection method represents the backbone of this thesis, as all the studies conducted herein are based on, or rely upon, this powerful synthetic approach. Chapter X summarizes the results reported along this thesis, giving an outlook about the possible implementation of materials, ligands and methodology in the future research.

10.1 Green solvent in hot injection method

Nowadays, there is increasing concern about environmental issues across the entire field of chemistry, from production and use to the end-of-life disposal of products. In the field of nanocrystals, significant efforts have been devoted to developing materials with enhanced performance while using safer and earth-abundant starting elements that are incorporated into the final structure, such as studies focused on replacing lead in lead halide perovskites with less toxic alternatives. Nevertheless, relatively few studies have addressed the *sustainability of the synthetic process* itself. In particular, colloidal synthesis methods typically produce a large amount of waste compared to the mass of the final product, with the reaction solvent that forms the majority of this waste. Therefore, the use of *environmentally friendly solvents* represents an important strategy to improve the sustainability of these reactions.

Chapters IV and V have addressed the synthesis of colloidal nanoparticles using *limonene* and *pinene* as alternative solvents to the conventional 1-octadecene.

Chapter IV focused on the synthesis of CsPbX_3 ($X = \text{Cl, Br, I}$) nanocubes through (*R*)- and (*S*)-limonene as *green* solvent. Although lead halide perovskites possess environmental concerns primarily due to the presence of lead in their crystal structure, this stoichiometry was selected as a reference system because of the extensive literature available. The nanocubes synthesized using both limonene enantiomers exhibited properties comparable to those obtained in the conventional solvent. Furthermore, the physicochemical properties of limonene, especially its relatively low boiling point, enable easy removal under vacuum from the final product, as well as efficient solvent recovery from the reaction waste via simple distillation. The overall process was evaluated through life cycle assessment, revealing trends that depend on the specific stoichiometry. Specifically, the environmental impact of CsPbCl_3 NCs production was higher when limonene was used instead of ODE. In contrast, CsPbI_3 NCs showed comparable impacts, while in CsPbBr_3 NCs production using limonene proved environmentally favourable. Overall, this study demonstrated that limonene is a valid alternative to conventional solvents in the hot-injection method.

The results of this work were published in the paper: *Lead Halide Perovskites Nanocrystals Synthesized in a Green, Reusable Solvent*. (*Small* 2500535 (2025)).

Chapter V build upon the results obtained from the limonene-based study. Accordingly, (1*R*)- α -pinene, (1*S*)- α -pinene and (1*S*)- β -pinene were employed as alternative solvents in the hot-injection method. The use of these solvents enabled syntheses that extended beyond the synthesis of CsPbX₃ (X = Br, I) nanocubes. Indeed, pinenes proved to be particularly promising solvents for the synthesis of nanocrystals with different morphologies (nanoplatelets) and compositions (Cs₂NaInCl₆). In particular, it was observed that β -pinene behaves more similarly to the solvents typically used in nanoparticle synthesis, whereas α -pinene lead to different results, suggesting the possibility of tuning the properties, and especially the morphology, using this family of solvents. Therefore, this work proved that even these *green* solvents result suitable for the hot injection method.

10.2 Chiral ligand for colloidal nanoparticles

Chapter VI and VII related to the employment of a *new chiral ligand* for the LHP nanocrystals synthesis.

Chapter VI described the *synthetic route* developed to obtain (S,Z)-nonadec-10-en-2-amine. This molecule was selected because of its *similarity in carbon-chain* length to the commonly used oleylamine in colloidal nanocrystal synthesis. The synthetic strategy proved to be effective for producing this new compound starting from a readily available precursor, namely oleyl alcohol. Although this approach was applied specifically to the synthesis of (S,Z)-nonadec-10-en-2-amine, the methodology could be extended to the preparation of “chiral oleylamine” analogues bearing different substituents at the α -carbon, through the straightforward use of Grignard reagents with different substituents than the methyl group. Finally, a preliminary study on the large-scale production of (S,Z)-nonadec-10-en-2-amine was carried out. In order to reduce reaction time and, in particular, solvent consumption, the purification steps typically performed after to the oxidation and the imine formation were omitted. Consequently, the crude imine was directly employed in the subsequent nucleophilic addition of the Grignard reagent. The ¹H NMR analysis of the reaction crude indicated that the impurities present did not significantly affect the outcome of the reaction. Apart from the signals attributable to iodobenzene, subproduct derived from the first oxidation step, the spectrum mainly showed the proton signals corresponding to the desired product, together with a minor signal attributable to the secondary stereoisomer. The effectiveness of this simplified protocol is further supported by the similar d.r. value obtained under these conditions. Although the synthetic sequence was not completed within the timeframe of this study, and therefore the final yield and enantiomeric excess of the target product are not yet available, these results highlight the potential of this strategy for simplifying the synthetic procedure and reducing solvent consumption in the context of larger-scale production.

Chapter VII naturally followed Chapter VI, as it focuses on the *effective use* of (S,Z)-nonadec-10-en-2-amine as ligand in LHPs nanocrystals synthesis. In particular, CsPbBr₃ nanocubes and nanoplatelets were successfully synthesized and characterized. The increased steric bulk of this ligand compared to oleylamine required slight modifications to the synthetic protocol and influenced the properties of the resulting nanocrystals, particularly their morphology. Specifically, the nanocubes exhibited a slightly larger size,

while the nanoplatelets crystallized in four monolayers, compared to the two-monolayer thickness typically achieved using oleylamine. Furthermore, the interplay between the chiral amine and chiral solvent was investigated by synthesizing CsPbBr₃ nanoplatelets into (R)/(S)-limonene, highlighted the different interaction of (S,Z)-nonadec-10-en-2-amine with the two enantiomers used as solvent. Finally, the chiroptical properties were evaluated, revealing that only the layered structures exhibited a promising chiroptical activity.

10.3 Sn₂SbS₂I₃ microcrystals synthesized through hot injection method

Chapter IX explored the synthesis of mixed-metal chalcogenide materials via the hot-injection method. In particular, Sn₂SbS₂I₃ crystals were obtained with a microrod morphology. The product was extensively characterized, revealing high crystallinity of the microrods and a stoichiometry slightly deviating from the ideal composition, which likely accounts for the small shift in the measured bandgap (1.74 eV) compared to the theoretical value (1.80 eV). Furthermore, the influence of reaction conditions on the final material was systematically investigated, demonstrating that the amine ligand plays a crucial role in the synthesis. Finally, the study of the formation mechanism revealed the immediate formation of Sb₂S₃ needle-shaped particles, which partially dissolve and subsequently re-precipitate as Sn₂SbS₂I₃ microrods.

The results of this work were published in the paper: *Controlled Colloidal Synthesis of Anisotropic Mixed-Metal Chalcogenides: Insights into Morphology and Phase Evolution*. (*Nanoscale* (2025), 17, 27225-27232).

10.4 Outlook

The results of this thesis further highlight the hot-injection method as a *powerful strategy* for the synthesis of high-quality nanoparticles.

The introduction of natural apolar solvents as reaction media may inspire the nanomaterials research community to further explore the sustainability of the synthetic methodologies, extending the use of green solvents beyond lead halide and double perovskites. Further studies aimed at optimizing solvent recovery processes, particularly for the pinene family, are certainly warranted. Beyond the *green* aspects, the inherent enantiomeric nature of these solvents may provide a chiral reaction environment that can be exploited for the synthesis of a wide range of chiral nanoparticles.

In this context, the straightforward synthetic route developed for the preparation of chiral oleylamine analogues offers new opportunities to investigate chiroptical properties beyond those accessible with conventional chiral amines. Indeed, the simplicity of the synthetic approach described in this thesis allows systematic evaluation of the effects of different substituents. In particular, it would be interesting to investigate bulkier substituents than the methyl group, such as isopropyl groups, or substituents with electronic effects, such as phenyl groups. These new ligands could induce different surface distortions in nanocrystals compared to (S,Z)-nonadec-10-en-2-amine, thereby influencing the resulting chiroptical properties. Finally, the synthetic route for the production of the new chiral ligands could be further improved to enable large-scale synthesis, particularly from an environmental perspective. The reported procedure involves several steps, each followed by purification by chromatography. During this work,

it was shown that only two of the synthetic steps actually require purification, whereas the crude products from the other steps can be directly used in the subsequent reactions. Unfortunately, due to time constraints, this aspect could not be investigated in depth. Nevertheless, the preliminary results are promising, suggesting that it may be possible to reduce the number of purification steps and consequently decrease the amount of organic solvents used.

Finally, the study on $\text{Sn}_2\text{SbS}_2\text{I}_3$ further confirms the potential of this stoichiometry for solar energy harvesting applications, owing to its suitable bandgap of 1.74 eV. Other mixed-metal chalcogenide compositions, such as $\text{Sn}_2\text{SbSe}_2\text{I}_3$ or $\text{Sn}_2\text{BiS}_2\text{I}_3$, may also be promising in this regard and would be worthwhile to explore via the hot-injection method. Moreover, since the morphologies obtained in this work lie in the micrometre range, quantum confinement effects were not observed. Reducing these materials to the nanocrystal regime could significantly modify the properties of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and related compounds; therefore, a systematic study of these nanostructured systems would be particularly interesting.

List of abbreviations

0/1/2/3D 0/1/2/3 Dimensional	E_l Left-Circularly Polarized
1-DDT 1-dodecanethiol	E_r Right-Circularly Polarized
a₀ Exciton Bohr radius	E_s Resultant Vector
ABS Absorption	FA Formamidinium
AFM Atomic-Force Microscopy	FE-PV Ferroelectric Photovoltaic Effect
ATP Adenosine Triphosphate	f_{i→f} Oscillator Strength
BAIB (Diacetoxyiodo)benzene	FTIR Fourier Transform Infrared Spectroscopy
B_{CPL} CPL Brightness	FWHM Full Width Half Maximum
BzCl Benzoyl Chloride	G Reciprocal Lattice Vector
CB Conduction Band	g_{ABS} Kuhn's Dissymmetry Factor
CD Circular Dichroism	g_{lum} Luminescence Dissymmetry Factor
CL Cathodoluminescence	GPP Geranyl Diphosphate
CNT Classical Nucleation Theory	GWP Global Warming Potential
CoA Coenzyme A	Ĥ Hamiltonian Operator
CPL Circularly Polarized Luminescence	ħ Planck Constant
CsOLAC Caesium Oleate	h⁺ Hole
d.r. Diastereomeric Ratio	HDA Hexadecylamine
DACH 1,2-diaminocyclohexane	Hinj Hot-Injection Method
DC Direct Current	HMG 3-hydroxy-3-methylglutaryl
DDAB Didodecyldimethylammonium Bromide	HOMO Highest Occupied Molecular Orbital
DDAC Didodecyldimethylammonium Chloride	ħν Energy
DESS Deep Eutectic Solvents	ILs Ionic Liquids
DFT Density Functional Theory	ICP-AES Inductive Coupled Plasma
DMAP 4-dimethylaminopyridine	IPP Isopentenyl Diphosphate
DMAPP Dimethylallyl Phosphate	IR Infrared Light
DMSO-d₆ Deuterated Dimethyl Sulfoxide	k Particle Momentum Wavevector
DOE Dioctyl Ether	LARP Ligand-Assisted Re-Precipitation Method
DOS Density Of States	LCA Life Cycle Assessment
DPE Diphenyl Ether	LEDs Light-Emitting Diodes
e⁻ Electron	LHP NCs Lead Halide Perovskite Nanocrystals
E Energy eigenvalue	LHPs Lead Halide Perovskites
e.e. Enantiomeric Excess	LPP Linalyl Diphosphate
EDX Energy Dispersive X-ray Spectroscopy	LSW Lifshitz–Slyozov–Wagner Growth
E_g Bandgap	LUMO Lowest Unoccupied Molecular Orbital
EL Electroluminescence	

$\vec{m}$ Magnetic Dipole Moment	$R_{i \rightarrow f}$ Rotational Strength
MA Methylammonium	RL Radioluminescence
MBA Methyl Benzyl Amine	Sb(OLAC)₃ Antimony(III) Oleate
m_e Electron Mass	SCF Supercritical Fluid
MEP Methylerythritol Phosphate	S_{crit} Critical Saturation Concentration
m_h Hole Mass	SEM Scanning Electron Microscopy
MOs Molecular Orbitals	S_{min} Minimal Saturation Concentration
MVA Mevalonate Acid	S_{sup} Supersaturation Level
NEA 1-(2-naphthyl)ethylamine	t Goldschmidt Tolerance Factor
NMR Nuclear Magnetic Resonance	t-Bu Tert-butyl Group
NPP Neryl Diphosphate	T_c Critical Temperature
NPs Nanoplatelets	T_{deg} Degradation Temperature
ODE Octadecene	TEM Transmission Electron Microscopy
OIHPs Organic–Inorganic Hybrid Lead Halide Perovskites	TEMPO Tetramethylpiperidine 1-oxyl
OLAC Oleic Acid	tol-d₈ Deuterated Toluene
OLAM Oleylamine	TOP Trioctylphosphine
OLAM* (S,Z)-nonadec-10-en-2-amine	TOPO Trioctylphosphine Oxide
OLAM-H Oleylammonium	TPP Thiamine Pyrophosphate
OLAM-I Oleylamine Iodine	UV Ultraviolet Light
OLAM-S Oleylamine Sulphur	VB Valence Band
P_c Critical Pressure	Vis Visible Light
PCE Power Conversion Efficiency	VOCs Volatile Organic Compounds
PL Photoluminescence	XPS X-ray Photoelectron Spectroscopy
PLQY Photoluminescence Quantum Yield	XRD X-ray Diffraction
PQXs Poly(quinoxaline-2,3-diyl)s	δ Chemical Shift
R&D Research and Development	ΔG Gibbs Free Energy
r_c Critical Radius	ϵ Molar Extinction Coefficient
RF Radiofrequency	λ Wavelength
	$\vec{\mu}$ Electric Dipole Moments
	ψ Wavefunction

Publications

D. Pratolongo, M. Campolucci, M. Vocciante, L. Pugliesi, E. Di Giorgio, C. Lambruschini, L. Manna, and F. Locardi. **Lead Halide Perovskites Nanocrystals Synthesized in a Green, Reusable Solvent.** *Small* 2500535 (2025).

D. Pratolongo, A. Bora, S. Sen, N.N. Patil, S. Alberti, M. Palabathuni, F. Locardi and S. Singh. **Controlled Colloidal Synthesis of Anisotropic Mixed-Metal Chalcogenides: Insights into Morphology and Phase Evolution.** *Nanoscale* (2025) 17, 27225-27232.

Contributions to Conferences and PhD school

1. CDCF50, congress of the physical chemistry division 2025 and 5th ECPC, European conference on physical chemistry 2025, June 29th – July 3rd, 2025, Pisa, Italy

- ❖ F. Locardi, **D. Pratolongo**, M. Campolucci, M. Voccianti, E. Di Giorgio, L. Manna, C. Lambruschini, *Green solvents for nanocrystals synthesis: a step toward environmental sustainability* (Oral)

2. MATSUS Spring 2025 Conference, Material for Sustainable Development Conference, March 3rd - 7th, 2025, Seville, Spain

- ❖ **D. Pratolongo**, N. Patil, M. Palabathuni, A. Bora, S. Sen, F. Locardi, S. Singh, *Sn₂SbS₂l₃ rods synthesized by Hot-injection method* (Oral)
- ❖ F. Locardi, **D. Pratolongo**, M. Campolucci, M. Voccianti, E. Di Giorgio, C. Lambruschini, L. Manna, *CsPbX₃ (X = Cl, Br, I) nanocrystals synthesized in green solvent* (Oral)

3. XI Workshop Nazionale – Green chemistry – chimica sostenibile, October 24th - 25th, 2024, Turin, Italy

- ❖ F. Locardi, **D. Pratolongo**, M. Campolucci, M. Voccianti, E. Di Giorgio, L. Manna, C. Lambruschini, *Colloidal nanocrystals synthesis in green solvent* (Oral)

4. XLIX Congress of the Physical Chemistry Division of the Società Chimica Italiana, September 4th - 7th, 2023, Turin, Italy

- ❖ **D. Pratolongo**, L. Pugliesi, S.V. Ochoa Meza, M. Campolucci, C. Lambruschini, B. Benedetti, M. Ferretti, F. Locardi, *Halides perovskites nanocrystals synthesized in green solvents* (Oral)
- ❖ L. Pugliesi, **D. Pratolongo**, M. Campolucci, B. Benedetti, M. Ferretti, F. Locardi, *Optimization of lead halide perovskites nanocubes' in green solvents through experimental design* (Poster)

5. School of Physical Chemistry 2023, June 19th - 23rd, 2023, Verbania, Italy

- ❖ **D. Pratolongo**, L. Pugliesi, M. Campolucci, C. Lambruschini, B. Benedetti, M. Ferretti, F. Locardi, *Lead halides perovskites nanocrystal synthesis in green solvents* (Poster)