

Controlled transformations of organozinc precursor systems towards semiconductor nanocrystals

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ABSTRACT

Although numerous synthetic strategies for nanomaterials have been developed to meet increasing demand, scalable and environmentally sustainable approaches remain a significant challenge. To date, most conventional liquid-phase synthetic methods for producing high-quality semiconductor nanocrystals typically require elevated temperatures, expensive solvents, multistep purification processes, and sophisticated stabilizing ligands. In contrast, solid-state chemical transformations offer potential advantages by eliminating the need for solvents and additional stabilizing ligands. However, due to the relatively low reactivity and diffusion rates of chemical species in the solid-state, nanocrystal nucleation and growth are substantially limited. To overcome these energy barrier, thermal and/or mechanical treatment are typically required, making these systems energetically less feasible.

This dissertation introduces a novel all-solid-state synthetic approach for semiconductor nanocrystals that operates under ambient conditions without external energy input. This strategy relies on rationally designed organozinc solid-state precursor based on $[(L)ZnR]_n$ -type molecular clusters, incorporating reactive Zn–C and Zn–N bonds confined within a single-crystal lattice prone to water-mediated hydrolysis.

The first part of the thesis describes design and synthesis of a model solid-state precursor of quantum-sized ZnO nanocrystals. As the model system, the tetranuclear ethylzinc benzamide cluster, $[(BA)ZnEt]_4$, was synthesized and isolated as single crystals, providing a well-defined precursor system to investigate solid-state transformations to semiconductor nanocrystals. This predesigned precursor is reactive towards selected atmospheric components and, upon exposure to air, enables efficient growth of nanocrystals within its own crystalline yet dynamic body, which is prone to rearrangements, thereby overcoming the limitation of efficient mass transport in the solid-state.

To explore the transformation processes at the molecular and nanoscale levels, the second part of the thesis employs a wide range of time-resolved in situ and ex situ characterization methods, including absorption, vibrational, and nuclear magnetic spectroscopies, various diffraction methods, microscopy, and thermal analysis. These comprehensive studies unveil the formation of nanocrystals and their ag-

gregation within the crystalline precursor, as well as within emerging amorphous matrix—an aspect that has remained largely unexplored in solid-state chemistry. Notably, the results highlight the critical role of water molecules in initiating the hydrolysis of $[(\text{BA})\text{ZnEt}]_4$ clusters and the formation of intermediate zinc oxo/hydroxo species alongside the amorphous matrix, which facilitates efficient mass transport and enabling efficient crystal growth in a solid-state environment.

The third and fourth part of the thesis demonstrate the versatility of the presented system. The volatile under vacuum organic matrix based on hydrolysed BA-H ligands, is effectively removed through vacuum-triggered sublimation without using solvents, high temperatures, or complicated surface area activation procedures, yielding a nanocrystalline mesoporous scaffold of semiconductor building blocks. Furthermore, the presented solid-state $[(\text{BA})\text{ZnEt}]_4$ precursor system was successfully extended to other hydrolytic agents. Specifically, hydrogen sulfide was employed as an alternative hydrolytic agent, leading to the successful formation of ZnS nanocrystals, thus confirming the greater scope of the presented system.

The fifth part of the thesis describes complementary studies on water- and water/dioxygen-mediated transformations of the $[(\text{BA})\text{ZnEt}]_4$ precursor in solution, using in situ ^1H NMR spectroscopy. These studies provide not only valuable insights into the reactivity of the model precursor in solution but also highlight significant differences between the processes occurring in the solid-state and those in solution. These results reveal that the reaction pathways in solution depend on the oxygen source used—either a mixture of dioxygen and water (from air) or water alone—whereas in the solid-state, the process is highly selective towards water.

In summary, this dissertation contributes to the development of innovative materials synthesis, addressing the ongoing challenge of developing sustainable synthetic strategies. It presents a simple, cost-effective, and energy-efficient method for producing high-quality semiconductor nanocrystals. Notably, the reported system not only demonstrates, for the first time, the formation of nanocrystals under ambient conditions without the need for external stimuli, but also provides comprehensive molecular-level insights into complex solid-state transformation mechanisms through a range of time-resolved in situ techniques.

STRESZCZENIE

Chociaż opracowano liczne strategie syntezy nanomateriałów w celu zaspokojenia rosnącego zapotrzebowania, wciąż poważnym wyzwaniem pozostają metody proste do skalowania i przyjazne środowisku. Do tej pory większość konwencjonalnych metod syntezy w fazie ciekłej, stosowanych do otrzymywania wysokiej jakości półprzewodnikowych nanokryształów, zazwyczaj wymaga podwyższonych temperatur, drogich rozpuszczalników, wieloetapowych procesów oczyszczania oraz zaawansowanych ligandów stabilizujących. Natomiast chemiczne transformacje prekursorów materiałów funkcjonalnych w ciele stałym oferują potencjalne zalety, eliminując konieczność stosowania rozpuszczalników i dodatkowych ligandów. Jednak ze względu na stosunkowo niską reaktywność i powolną dyfuzję reagentów w ciele stałym, zarodkowanie i wzrost nanokryształów są znacząco ograniczone. Aby pokonać te bariery energetyczne, zazwyczaj wymagane są obróbka termiczna i/lub mechaniczna, co czyni takie systemy mniej korzystnymi energetycznie.

W niniejszej rozprawie zaprezentowano nowatorskie podejście do syntezy półprzewodnikowych nanokryształów w ciele stałym, przebiegającej w warunkach otoczenia, bez dostarczenia energii z zewnątrz. Strategia ta opiera się na racjonalnie zaprojektowanym cynkoorganicznym prekursorze w ciele stałym, zbudowanym z klastrów molekularnych typu $[(L)ZnR]_n$, zawierającym reaktywne wiązania Zn–C i Zn–N uwięzione w sieci monokryształu podatnego na hydrolizę inicjowaną przez wodę.

Pierwsza część rozprawy poświęcona jest projektowaniu i syntezie modelowego prekursora nanokryształów ZnO o rozmiarze kwantowym do transformacji w ciele stałym. Jako modelowy układ zsyntetyzowano i wyizolowano w postaci monokryształów tetranuklearny klaster etylocynkowej pochodnej benzamidu, $[(BA)ZnEt]_4$. Stanowi on dobrze zdefiniowany system, umożliwiający badanie przemian w ciele stałym prowadzących do powstania półprzewodnikowych nanokryształów. Prekursor ten wykazuje reaktywność wobec wybranych składników atmosferycznych i po ekspozycji na powietrze umożliwia wydajny wzrost nanokryształów w obrębie własnej struktury krystalicznej, która dzięki dynamicznej naturze ułatwia przegrupowania i pokonuje ograniczenia transportu masy typowe dla ciała stałego.

Druga część pracy koncentruje się na badaniu procesów transformacji na poziomie molekularnym i nanometrycznym z wykorzystaniem szerokiego zestawu metod *in situ* i *ex situ*, obejmujących spektroskopię absorpcyjną, wibracyjną i NMR, różnorodne techniki dyfrakcyjne, mikroskopowe oraz analizy termiczne. Kompleksowe badania pozwoliły uchwycić powstawanie nanokryształów i ich agregację w obrębie krystalicznego prekursora, jak również w powstającej amorficznej matrycy—zagadnień dotychczas w dużej mierze pomijanych w chemii ciała stałego. Wyniki podkreślają kluczową rolę cząsteczek wody w inicjowaniu hydrolizy klastrow $[(BA)ZnEt]_4$ oraz w powstawaniu pośrednich gatunków hydroksy- i okso-cynkowych wraz z amorficzną matrycą, która sprzyja transportowi masy i umożliwia wydajny wzrost kryształów w środowisku ciała stałego.

W trzeciej i czwartej części rozprawy ukazano wszechstronność systemu. Lotną w próżni organiczną matrycę, powstałą na bazie zhydrolizowanych ligandów BA-H, można skutecznie usunąć poprzez sublimację w warunkach próżniowych, bez użycia rozpuszczalników, wysokich temperatur czy skomplikowanych procedur aktywacji powierzchni. Ponadto prekursor $[(BA)ZnEt]_4$ został z powodzeniem zastosowany z innymi czynnikami hydrolitycznymi. Wykorzystanie siarkowodoru jako alternatywnego czynnika doprowadziło do otrzymania nanokryształów ZnS, potwierdzając szerszy zakres możliwości tego systemu.

Piąta część pracy obejmuje badania uzupełniające dotyczące transformacji $[(BA)ZnEt]_4$ w roztworze z udziałem wody oraz wody i tlenu cząsteczkowego. Zastosowanie spektroskopii ^1H NMR *in situ* umożliwiło uchwycenie różnic między procesami zachodzącymi w ciele stałym, a reakcjami w roztworze. Wyniki wskazują, że w roztworze przebieg reakcji zależy od źródła tlenu—mieszaniny tlenu i wody (z powietrza) lub samej wody—natomiast w ciele stałym proces zachodzi selektywnie w obecności wody.

Podsumowując, rozprawa wnosi istotny wkład w rozwój innowacyjnych metod syntezy materiałów, odpowiadając na wyzwania związane z opracowaniem zrównoważonych strategii otrzymywania nanomateriałów. Zaprezentowana metoda jest prosta, ekonomiczna i energooszczędna, a jednocześnie umożliwia otrzymywanie wysokiej jakości półprzewodnikowych nanokryształów. Co szczególnie istotne, opisany system po raz pierwszy dowodzi możliwości syntezy nanokryształów w łagodnych warunkach otoczenia bez konieczności stosowania zewnętrznych bodźców. Ponadto, przedstawiona rozprawa dostarcza szczegółowych informacji na poziomie molekularnym o złożonych mechanizmach transformacji w ciele stałym, uchwycionych dzięki zastosowaniu szerokiego zestawu nowoczesnych technik *in situ*.

DECLARATION OF AUTHORSHIP

I declare that the research included within this thesis was carried out by myself or with support from others included in the acknowledgments.

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Aleksandra Borkenhagen

September 30, 2025

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ACRONYMS

CP MAS Cross-Polarization Magic Angle Spinning

DOSY Diffusion-Ordered NMR Spectroscopy

DR-UV-Vis Diffuse Reflectance Ultraviolet-Visible Spectroscopy

DRIFT Diffuse Reflectance Infrared Fourier-Transform Spectroscopy

Et Ethyl group

FT-IR Fourier-Transform Infrared Spectroscopy

HOPE Hydrolysable Organometallic Precursor

HRTEM High-Resolution Transmission Electron Microscopy

L Ligand

NC Nanocrystal

NMR Nuclear Magnetic Resonance

PL Photoluminescence Spectroscopy

PXRD Powder X-ray Diffraction

QD Quantum Dot

R Alkyl group

RS Raman Spectroscopy

SAXS Small-Angle X-ray Scattering

SC Single-Crystal

TGA Thermogravimetric Analysis

THF Tetrahydrofuran

INTRODUCTION

"But I am not afraid to consider the final question as to whether, ultimately in the great future we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them? What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have, and of different things that we can do."

- *Richard P. Feynman, 1959*

The development of new functional materials with desired properties is an important key for the continuous forward evolution of science and technology. However, the realization of emerging convergence technology requires the capability to observe, understand, control, and even to predict the reactivity of materials at multi-scale levels including nano-, micro-, and macro-length scales. A key element is the rational organization of nanoscale components into high-quality, well-defined architectures. The revolutionary concept of miniaturization that allowed the design and production of useful nanostructures by manipulating individual atoms or by modifying the structure at the molecular level was presented by physicist Richard Feynman. He emphasized the potential benefits of producing materials in the nanometric range. His visionary talk covered a wide range of concepts and promises,

on which we work today in the meanwhile established field of nanoscience. Feynman's ideas may have been ahead of their time but, considering the many applications that are now utilizing nanotechnology, it is plain to see that he was right: There really is "plenty of room at the bottom"[1].

1.1 Nanotechnology and nanoparticles

Nanotechnology unveils a profound and relatively unexplored world invisible to the human eye—a world that operates on a scale billions of times smaller than what we commonly encounter on an everyday basis. Essentially, nanotechnology involves any technology on a nanoscale that has practical applications in the real world. It is the science of manipulating materials at the atomic level, offering precise control over matter at this minuscule dimension. Nanotechnology extensively contributes to almost every field of science, including physics, materials science, chemistry, biology, computer science, and engineering[2–4].

Nanostructured materials are defined as materials with at least one spatial dimension in the size range of approximately 1 and 100 nanometers[5]. However, it is a broad definition that generally describes the concept of nanotechnology. The most relevant definition is that a structure can be considered nanometric when its size is so small that the physicochemical properties are no longer the same compared to their macroscopic counterparts. At length scales down to the nanoscale regime, one can work with new domains and physics that do not apply at any other scale. With shrinking size, the role of the surface increases, eventually becoming dominant. Size scaling causes a drastic increase in the number of surface atoms compared to volume atoms. Consequently, this results in a very large specific surface of nanomaterials, leading to an increased number of unsaturated coordination sites, defects, and stresses of the crystal lattice. The properties of atoms and surface ions within a coordination environment different from that observed in a perfect crystal lattice are also altered, leading to changes in physicochemical properties, i.e., reactivity, optical, electronic, mechanical, and thermal properties, related to

the reduction of the size of objects[6]. When the size of a material is reduced to a scale comparable to the wavelength of electrons (typically in the range of a few nanometers), the quantum confinement effect becomes significant. In bulk materials, electrons can move freely in three dimensions, whereas in nanostructures only in a well-defined direction that has not become quantum limited due to size. The motion of charged particles in low-dimensional structures can be limited in one, two or all three dimensions, corresponding to the characteristics of two-dimensional (2D) nanomaterials such as thin films[7, 8], one-dimensional (1D) nanomaterials like nanowires, nanotubes and nanorods[9] and zero-dimensional (0D) quantum dots[10], respectively. Limiting the motion of the charge carrier in each dimension leads to a complete quantization of the energy of the system. Hence, quantum-confined structures exhibit size-dependent electronic properties, leading to extra degrees of tunability compared with bulk counterparts and additional levers in the design of materials and devices.

The broad deployment of nanotechnology and nanomaterials in modern society is steadily increasing, with their utilization expanding across an increasing array of commercial applications. As research in the field continues to progress, numerous synthesis methods for nanomaterials have been outlined in the literature, yielding novel techniques and refinements to address the demand for innovative solutions. From both a fundamental perspective and for practical applications, the preparation of nanomaterials remains a primary focus for scientists. While many breakthroughs in nanoparticle synthesis mark significant milestones in the history of nanoscience, these strategies often require careful optimization to achieve scalability, cost-effectiveness, and environmental sustainability. Consequently, the primary objective and major challenge at the forefront of (nano)materials synthesis is the development of sustainable synthetic strategies.

1.2 Semiconductor nanocrystals

Advancements in nanoscience have significantly enhanced our understanding of the nanoscopic arrangement of matter, revealing the unique properties that emerge at the nanoscale. A prime example of these emergent properties is quantum-confined semiconductor nanocrystals (NCs), often referred to as quantum dots (QDs)[11]. These materials usually range from 2 to 10 nanometers in diameter, consisting of hundreds to thousands of covalently bonded atoms, and typically have a quasi-spherical shape. Most colloidal quantum dots feature an inorganic core surrounded by an organic ligand shell[12, 13] (*vide infra*), schematically represented in Figure 1.1a. The concept of quantum dots was first theorized by Alexei Ekimov in the early 1980s in glass matrices[14], and later demonstrated by Louis Brus in colloidal solutions[15]. In the 1990s, Moungi Bawendi revolutionized the chemical synthesis of quantum dots, enabling precise control over particle size and producing high-quality crystals[16]. This breakthrough paved the way for the widespread use of QDs in various applications. In October 2023, Ekimov, Brus, and Bawendi were awarded the Nobel Prize in Chemistry for "*the discovery and synthesis of quantum dots*". Today, these nanocrystals are used in numerous applications, ranging from medicine to electronic and optoelectronic devices, due to their superior size-dependent properties resulting from quantum-confined electronic structures[3, 10, 17–19]. The potential for further uses continues to grow, underscoring that we are still only beginning to explore their full capabilities.

1.2.1 Properties and applications of quantum-confined semiconductor nanostructures

In quantum-confined semiconductor nanostructures, electrons exhibit distinctive behavior compared with that in bulk solids. In bulk semiconductors, the large density of covalently and/or ionically bonded atoms creates a high and broad density of conduction and valence band states[20]. The conduction and valence

bands are energetically separated by the band gap, which is independent of the crystal size. However, when the size of the semiconductor material is reduced to a nanoscale range (typically on the order of a few nanometers), the electronic states become discrete due to the quantum confinement effect[15]. The comparison between the energy levels of nanocrystals and bulk semiconductors on the one side and molecular structures on the other side is exemplified by the Figure 1.1b.

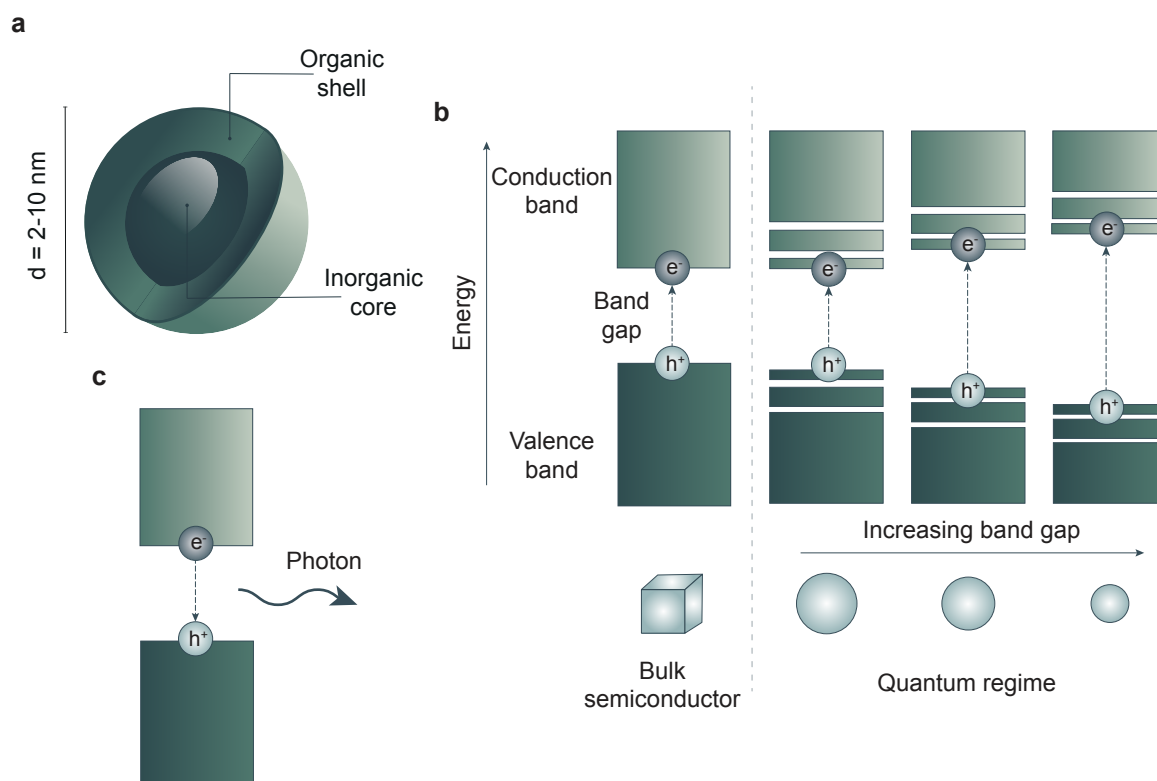


Figure 1.1: Overview of semiconductor nanocrystals. **a**, Schematic representation of semiconductor nanocrystal, consisting of an inorganic core and an outer organic ligand shell. **b**, The quantum confinement effect on the energy levels in semiconductor quantum dots (QDs). The band gap energy increases with decreasing QD size. **c**, Absorption of a photon (the quantized energy of light) causes the electron to transition to a higher energy state, creating a hole in the valence band. A negatively charged electron (e^-) and a positively charged hole (h^+) interact due to Coulombic attraction and an electron-hole pair called an exciton is formed. This state is not permanent, and the excited electron moves to a lower energy state, accompanied by photon emission.

The confinement-induced discrete energy levels have a direct impact on the optical and electronic properties of semiconductor NCs. As shown in Figure 1.1b, the band gap increases and quantized discrete energy levels are formed as the particle size decreases, thus relating the energy gap between the highest occupied and lowest unoccupied states to the NC size. This means that the optical properties, such as

the absorption and emission wavelengths, can be tuned by controlling the size of the nanocrystal (quantum size effect)[21].

Semiconductor NCs feature widely tunable and distinctive optical, electrical, chemical, and physical properties, which make them interesting class of materials for a wide range of potential applications. The bright and size-dependent fluorescence emission of NCs can be applicable in lasers, displays, and light emitting diodes[22–25]. Additionally, their tunable absorption spectrum with high extinction coefficients, which allows for efficient absorption of light across a wide range of wavelengths makes them attractive for ultra-sensitive photodetectors and photovoltaic applications[26]. Semiconductor NCs find significant utility in biomedical research, specifically in labeling, imaging, and sensing applications[27, 28].

1.2.2 Types of semiconductor NCs

Semiconductor NCs can be classified based on their chemical composition or structural and electronic architecture. Compositional classifications typically distinguish three groups: II–VI chalcogenides, III–V chalcogenides, and metal oxides. The most extensively studied are binary II–VI chalcogenides such as cadmium selenide (CdSe), cadmium telluride (CdTe), and lead sulfide (PbS)[3, 29]. Each of these materials has unique properties that makes them well-suited for wide applications. However, they contain toxic metals, possessing significant environmental and health risks. Consequently, there is an urgent need to explore substitute semiconductor NCs with reduced toxicity, aiming to replace the traditional heavy metal-based NCs. For example, III–V semiconductors such as indium phosphide (InP) and indium arsenide (InAs) have appeared as promising alternatives to these heavy-metal-based systems due to their optical properties and lower toxicity. However, the more covalent nature of In-P and In-As bonds, combined with fast and uncontrolled nucleation processes, results in synthetic protocols that are challenging and expensive[30].

To address both the environmental risks arising from heavy-metal-based II–VI NCs and the synthetic complexity of III–V systems, metal oxide NCs have emerged as attractive substitutes. They offer diverse optoelectronic properties, inherent stability, low toxicity, and scalability for large-scale production. Examples include titanium dioxide (TiO_2) for photocatalysis, tin dioxide (SnO_2) for sensing, and iron(III) oxide (Fe_2O_3) for redox and magnetic applications. Within this family, zinc oxide (ZnO) stands out as one of the most promising materials, offering an excellent combination of optical, electronic, and environmental benefits. ZnO is a n-type semiconductor which has been extensively investigated for the past half a century. It is characterized by a broad bandgap of 3.44 eV at low temperatures and 3.37 eV at room temperature[31], and a high exciton binding energy of 60 meV[32] and n-type conductivity[33]. It can exist in three crystal structures: a zinc blende, a rarely observed cubic rock salt, and the most thermodynamically stable at ambient conditions and therefore the most common hexagonal wurtzite structure[34, 35]. The wurtzite structure consists of a hexagonal close-packed array of oxygen anions (O^{2-}), with zinc cations (Zn^{2+}) occupying half of the tetrahedral voids, and each zinc atom surrounded by four oxygen atoms in a tetrahedral arrangement, and vice versa, as shown in Figure 1.2.

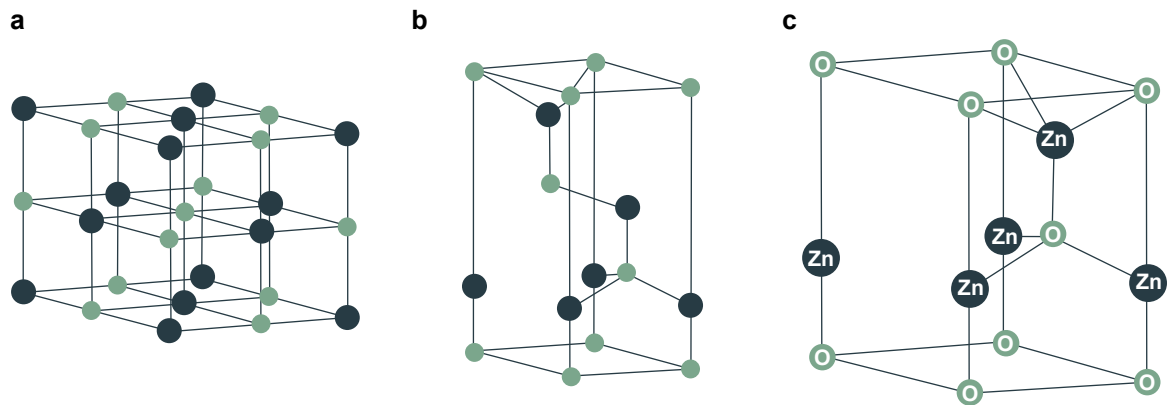


Figure 1.2: Stick and ball representation of ZnO crystal structures. **a**, Cubic rocksalt. **b**, Cubic zinc blende. **c**, Hexagonal wurtzite.

In addition to their compositional diversity, semiconductor NCs can also be engineered in various structural forms that further refine their functionality (Figure 1.3). The simplest architecture is the core-type NC, consisting of a single semiconductor phase that defines the material optical and electronic properties[36]. To

improve photostability and suppress surface-related defects, core-shell structures are commonly employed, where a shell material with a different band alignment is around the core[37, 38]. These can be tailored into Type-I heterostructures, in which both electrons and holes are confined within the core, or Type-II structures, where charge carriers are spatially separated across the core and shell interface, enabling efficient charge separation for applications such as photovoltaics[39]. More complex configurations, such as quasi-Type-II, allow partial carrier localization and offer fine control over recombination dynamics. This architectural versatility, combined with the growing palette of low-toxicity materials, underscores the adaptability of semiconductor NCs for next-generation technologies.

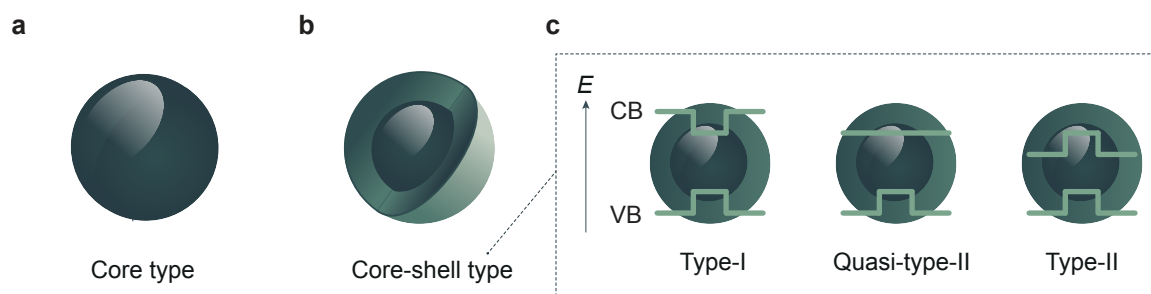


Figure 1.3: Schematic illustration of semiconductor nanocrystal architectures. **a**, Core-type nanocrystal. **b**, Core-shell nanocrystal, and **c**, Type-I, quasi-Type-II, and Type-II band alignment with corresponding carrier localization in core-shell systems.

1.3 Mechanistic insights into nucleation and growth of NCs

Crystallization is one of the most ubiquitous, yet mysterious phenomenon in nature[40, 41]. The mystery lies in how structures with long-range order form from building blocks that only interact with their local neighbors. The process involves complex thermodynamic and kinetic factors which is difficult to detect experimentally. The early stages of crystallization play a critical role in determining the crystal properties. Nucleation controls the location and size of nuclei, whereas growth controls the size, shape, and aggregation of newly formed nanoparticles. Therefore, understanding the crystal nucleation and growth mechanisms in crystallization is an essential step to realize the controllable fabrication of crystalline materials and

consequently their applications[42–44]. This aspect remains an ongoing subject of intensive research, as direct experimental observation of nucleation pathways is inherently challenging. Increasing amounts of evidence show that classical and non-classical mechanisms often coexist and temporally overlap, leading to multi-step nanocrystal formation pathways that complicate precise control of size, shape, and properties[45, 46].

1.3.1 Classical nucleation and growth mechanism

The LaMer's model provides the classical description of the formation mechanism of NCs[46–48]. The model is often used to describe the three stages of a colloidal nanocrystal reaction. Initially, the precursor decomposes or reacts with the initiating agent to form monomers, which act as the building blocks of nanocrystals. Nucleation is triggered once the monomer concentration reaches the critical supersaturation threshold. A growth stage follows this nucleation event and proceeds by the addition of the monomers to the nuclei or by attachment of the nuclei themselves. Organic ligands bind to the surface of nuclei, preventing aggregation and controlling the addition of monomer to the growing nuclei. As growth proceeds, the system reaches equilibrium between monomer in solution and the growing particles. This process is schematically illustrated in Figure 1.4, which outlines the nucleation and growth sequence according to the LaMer model.

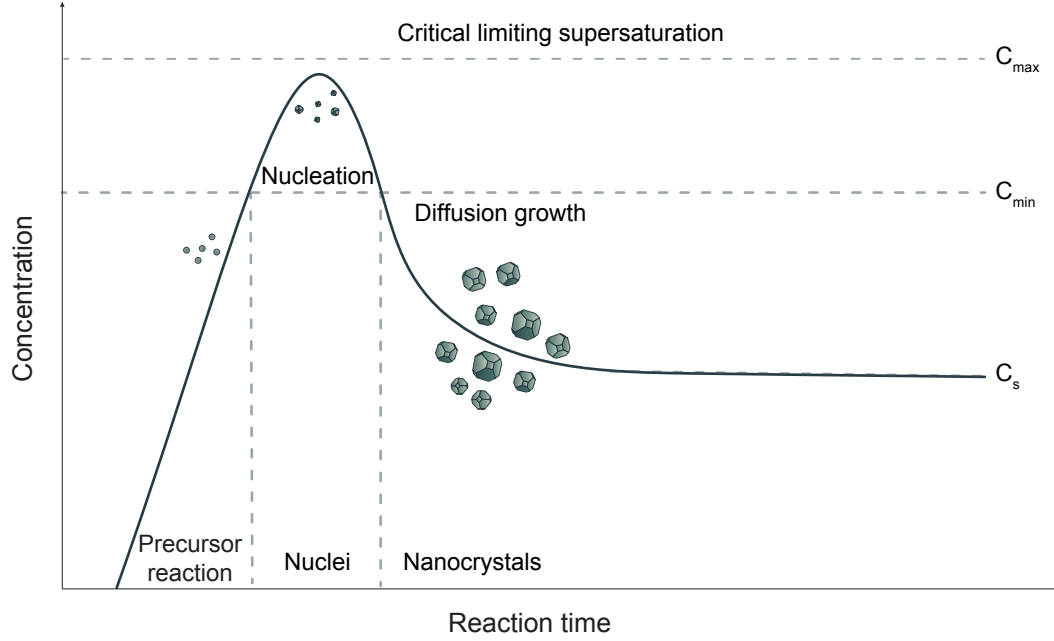


Figure 1.4: Schematic illustration of the nucleation and growth process of NCs in solution-phase in a classical LaMer mechanism. In this model inorganic precursors are initially dissolved in a solvent to form monomers, followed by the generation of nuclei. Subsequent decrease in concentration allows the nuclei to grow into nanocrystals through diffusion-controlled processes.

(i) Classical Nucleation Mechanism

Nucleation is the initial step in the formation of a new thermodynamically favorable phase. In simple words, it is the one-step process, whereby the crystal nuclei are directly generated by spontaneous random aggregation of species (atoms, ions, or molecules) in solution. The classical nucleation theory (CNT) provides a most common theoretical model framework that describes nucleation phenomena in thermodynamic terms[49]. The process of homogeneous nuclei formation can be considered thermodynamically by looking at the total free energy ΔG of a nanoparticle defined as the sum of the surface free energy γ and the bulk free energy ΔG_v . Assuming spherical nuclei with radius r , the change in energy upon nucleation is given by:

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

This thermodynamic relationship is illustrated in Figure 1.5, which shows the balance between surface and bulk free energy contributions to the total free energy of a nucleus (ΔG). The maximum of the curve corresponds to the critical nucleus radius (r_{crit}), below which nuclei are unstable and tend to redissolve, whereas nuclei larger than this threshold can overcome the energy barrier and grow spontaneously.

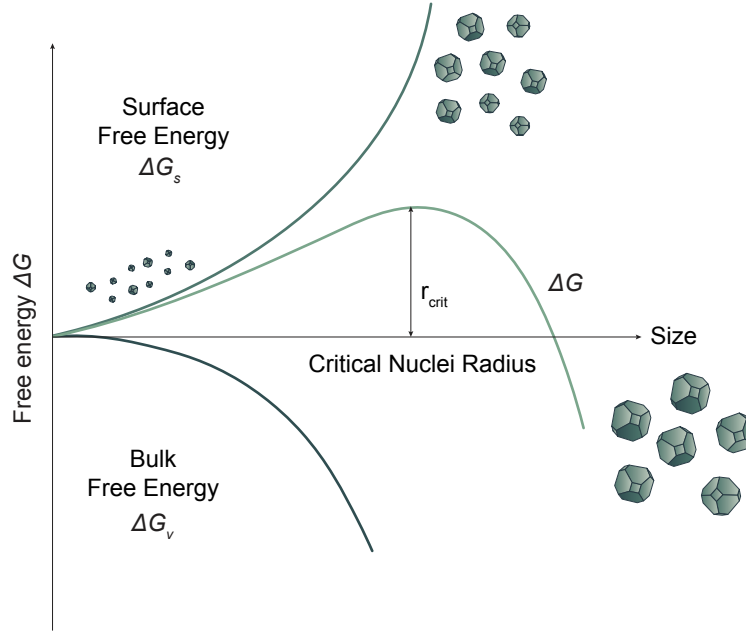


Figure 1.5: Free energy change of nucleation of a spherical particle as a function of particle radius (nucleus size), including volume and surface contributions.

The crystal free energy itself, ΔG_v is dependent upon the temperature T , Boltzmann's constant k_B , the supersaturation of the solution S , and molar volume v of the system. ΔG_v is defined in eq:

$$\Delta G_v = \frac{-k_B T \ln(S)}{v}$$

Thus, when $\frac{dG}{dr} = 0$, the critical nucleus radius r_{crit} can be defined as:

$$r_{crit} = \frac{-2\gamma}{\Delta G_v} = \frac{-2\gamma v}{k_B T \ln S}$$

The critical nucleus radius (r_{crit}) and nucleation energy barrier are the key characteristics for the classical nucleation. The nucleation usually occurs in the metastable state, when the size exceeds a critical value to form a stable nucleus with larger sizes. The critical particle radius r_{crit} corresponds to the minimum size of a stable nucleus in the system. Only the nuclei with $r \geq r_{crit}$ can spontaneously grow into larger particles, whereas if the size of the nucleus is smaller than the critical size ($r < r_{crit}$), the formed nucleus is unstable and can be redissolved in the solution, largely due to their high surface free energy. In the growth stage further size increase takes place from the remaining monomer reservoir.

Significant progress in understanding crystal nucleation has shown that the classical nucleation pathway is not the only route. Classical nucleation theory (CNT) is constrained by simplifying assumptions, and in recent decades, numerous non-classical theories have been proposed that describe multistep nucleation mechanisms[46, 50].

(ii) Classical Growth Mechanism

Once the nuclei are formed, they start to grow by attracting more atoms or molecules from the surrounding solution. This causes the nanocrystals to increase in size without undergoing significant structural changes in the bulk or at the surface. According to the classical growth model, the growth of a NC consists of two processes, i.e., “diffusion-controlled growth” and “reaction-controlled growth”[51, 52]. In the first process, growth of NC nuclei is limited by the rate of diffusion of monomers transported from the solution to the surface of the nuclei (diffusion limited). In the second process, growth of NC nuclei is limited by the rate of reaction of the monomers on the nuclei surface where they are incorporated into the crystal lattice (reaction limited). Based on the Fick’s first law[53] the crystal growth rate (dr/dt) of NCs can be estimated by the increase in particle’s size with time.

If diffusion is the rate limiting process the expression for the radial growth rate is:

$$\frac{dr}{dt} = DV_m \left(\frac{1}{r} + \frac{1}{\delta} \right) (S_b - S_r)$$

where D is the diffusion coefficient; V_m the molar volume of the solid; r the particle radius; δ the thickness of the diffusion layer; S_b the bulk concentration of monomers; S_r the solubility of the particle as a function of its radius r.

And for a rate limiting first order surface reaction the radial growth rate is:

$$\frac{dr}{dt} = kV_m(S_b - S_r)$$

where k is the reaction rate constant.

In the case of “reaction-controlled growth”, the particle growth is mainly controlled by the surface reaction of monomers. The growth rate of NCs is determined by the relative rate of nucleation and the growth rate of monomers on particle surfaces. These two expressions are limiting cases of the same general expression where either $Dk \gg r$ or vice versa. As the nanocrystals continue to grow, they gradually take on their final shape and crystal structure. The growth can be controlled to produce nanocrystals with specific sizes, shapes, and properties, which are essential for tailoring them to various applications in materials science, electronics, medicine, and other fields.

1.3.2 Kinetics and mechanisms of nanocrystal growth

Understanding growth kinetics is essential for controlling particle size, shape, and monodispersity. Progress in this field has long been constrained by the limitations of available analytical tools. Recently, modern in situ characterization techniques have enabled direct evaluation of NC growth processes[50]. Both spectroscopy-

and microscopy-based approaches allow real-time monitoring of nanocrystal formation, providing insights into size evolution, compositional changes, crystallographic development, and morphological transformations.

Growth of nanocrystals proceeds through distinct mechanisms that determine particle size distribution, morphology, and crystallographic order. Among the most common models for nanocrystal growth in colloidal systems are: (i) Ostwald Ripening (OR), considered a classical coarsening mechanism, and (ii) Oriented Attachment (OA), representing a nonclassical growth pathway. These processes play key roles in the structural evolution of nanoparticles as they aggregate and reorganize (Figure 1.6).

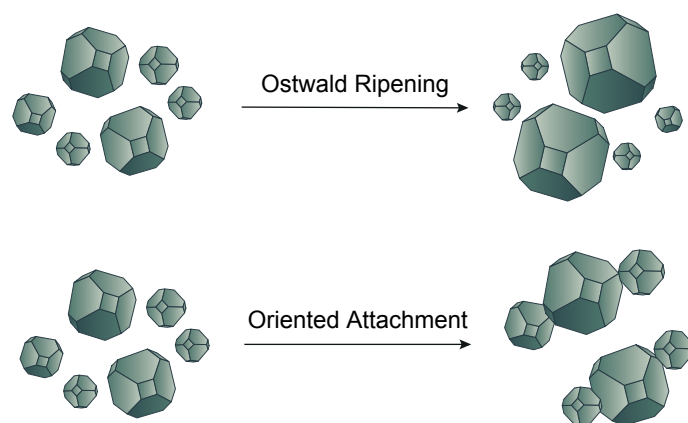


Figure 1.6: Schematic representation of nanocrystalline growth kinetics based on Ostwald ripening model and Oriented attachment model.

(i) Ostwald Ripening (OR)

The most popular mechanism employed to explain the growth kinetics of nanocrystals is the diffusion-limited Ostwald ripening (OR) process following the Lifshitz–Slyozov–Wagner (LSW) theory[54, 55]. In contrast to the simple amplification process in the classical growth model, Ostwald ripening mechanism describes the growth process of larger nanoparticles at the expense of smaller particles in solution. The surface atoms from smaller particles undergo dissolution processes more likely in comparison to surface atoms of bigger particles. This is on account of higher surface energy of smaller particles resulting in their higher instability. Atoms released from smaller particles are further incorporated into larger parti-

cles facilitating their further growth. Ostwald ripening occurs in the later growth stages, particularly in colloidal systems, when stabilizing agents or surfactants are present to prevent aggregation.

(ii) Oriented-Attachment (OA)

This process involves the spontaneous self-organization of adjacent nanocrystals, resulting in the formation of larger crystals with well-defined crystallographic orientations[42, 56–59]. This process occurs when nanoparticles collide and attach to each other in a way that preserves the lattice alignment. Oriented-Attachment (OA) has been observed in various nanocrystal systems, and it is particularly important in the growth of anisotropic nanomaterials, such as nanowires, nanorods, and nanosheets. It is different from conventional coagulation or OR because it leads to the development of high-quality single crystals rather than random aggregation.

The growth of inorganic nanoparticles is generally related to either OR or OA. While both mechanisms are well-recognized, there is limited research that explores their interplay. Notably, these two mechanisms can occur in successive stages or overlapping regimes, depending on the specific conditions of the system[46]. Huang et.al. studied the hydrothermal coarsening of ZnS nanocrystals in the presence of mercaptoethanol, finding that the kinetics corresponded to two distinct, consecutive growth regimes[56]. Thus, in the first step, the coarsening is controlled by OA and the growth curve can be fit by an OA kinetic equation. The second step of crystal growth was fit using an equation based on that for Ostwald ripening[60].

1.4 Synthesis of nanostructured materials

High-quality nanocrystalline materials with controlled size, shape, and surface structure are of fundamental importance because of their unique properties and vast array of promising applications. The NCs must be crystalline, monodisperse in size and shape, and well-passivated to ensure well-defined electronic states free of surface defects. Therefore, to obtain high-quality NCs with controllable physical

or chemical properties, great efforts have been devoted to developing reliable and reproducible synthetic approaches. Generally, depending on the state of the reaction medium, chemical synthetic routes can be generally classified as: (i) the vapor-phase approach, (ii) liquid-phase approach, and (iii) solid-phase approach.

1.4.1 Vapor-phase synthetic approach

The vapor-phase approaches, such as chemical vapor deposition (CVD), involve the reaction of gas-phase precursors to form solid nanomaterials on a substrate. Vapor-phase synthesis of nanomaterials offers numerous advantages, including high purity, high-throughput continuous operation, flexibility in producing a wide range of materials and scalability, which have made it a dominant approach for the commercial synthesis in micro- and nanofabrication technologies[61–63]. However, these methods may require high temperatures and vacuum conditions, specialized equipment and offer relatively limited control over the size and shape of the nanomaterials, especially for more complex nanostructures. Moreover, differences in crystal structure between the substrate and the nanomaterial can lead to lattice mismatches, resulting in structural defects, strain, or poor adhesion at the interface. Scaling up vapor-phase synthesis to produce nanomaterials in large quantities can be complex and costly. In addition to conventional CVD, more advanced techniques such as atomic layer deposition (ALD) and molecular beam epitaxy (MBE) are widely used to achieve precise control over film thickness, composition, and crystallinity at the atomic scale. While vapor-phase methods are crucial for thin films and epitaxial nanostructures, this work emphasizes nanoscale materials synthesized through liquid- and solid-state strategies.

1.4.2 Liquid-phase synthetic approach

Liquid-phase synthesis is the most widely used approach for nanomaterial preparation, in which a solvent facilitates mass transport to promotes chemical reactions

within the reaction medium. Although the use of a liquid medium limits the range of applicable temperature, pressure, and reagent concentration, these constraints are balanced by the broad chemical flexibility offered in the selection of precursors and solvents. A wide range of molecular precursors, such as inorganic salts, organometallic compounds, metal–organic complexes, and so-called single-source precursors, can be used in liquid-phase synthesis. The reaction environment can be further tailored by selecting either polar or non-polar solvents, depending on the solubility and reactivity of the precursors. This flexibility enables precise control over reaction conditions, allowing for the synthesis of high-quality NCs with well-defined size, shape, and crystallinity. Liquid-phase methods include both homogeneous (solution-phase) reactions—such as the hot injection technique—and heterogeneous systems, including precipitation, emulsions, colloidal dispersions, and sol–gel matrices. As a result, liquid-phase synthesis has become one of the leading approaches in nanoparticle research and industrial applications.

(i) Chemical precipitation method

Among the earliest reported synthetic routes for semiconductor nanocrystallites was the chemical precipitation method, in which nanoparticles form through the controlled precipitation of dissolved metal and chalcogenide precursors in a polar solvent. This strategy was first demonstrated by Brus in the early 1980s, where size-dependent optical absorption of CdS nanocrystals was observed following their formation in aqueous solution from Cd^{2+} and S^{2-} precursors[15]. In the following years, this method was applied to various material systems, including CdS, ZnS, and PbS, and became a central focus of early colloidal nanocrystal studies[64–66]. This method typically involves nucleation and growth from supersaturated solutions under ambient or mildly elevated temperatures, without the need for high-boiling coordinating solvents or complex precursor systems. While this approach is simple, cost-effective, and applicable to a wide range of materials, it often results in nanocrystals with broad size distribution and limited control over crystallinity and shape, as the mild reaction conditions lead to slow and often uncontrolled kinetics of nucleation and growth[67]. As a result, nanocrystals obtained via precipitation often exhibit significant polydispersity and poor reproducibility. Despite

these limitations, chemical precipitation remains a key foundational method and played a pioneering role in shaping early development of liquid-phase nanocrystal synthetic strategies.

(ii) Hot-injection method

To overcome these limitations of the precipitation method, Bawendi and colleagues developed the hot-injection method in 1993, which significantly improved control over the size, shape, and crystallinity of semiconductor NCs[16]. In this approach, a highly reactive metal precursor, often an organometallic compound (i.e., dimethylcadmium ($\text{Cd}(\text{CH}_3)_2$)), is combined with a chalcogen precursor of S^{2-} , Se^{2-} , or Te^{2-} ions, typically generated by dissolving elemental chalcogens in a coordinating ligand such as trioctylphosphine (TOP) to form reactive species like TOP-E, where E is S^{2-} , Se^{2-} , or Te^{2-} . This precursor solution (maintained at room temperature) is then rapidly injected into a hot coordinating solvent, typically trioctylphosphine oxide (TOPO), preheated typically in the range of 200–350 °C (Figure 1.8). The high temperature of the reaction medium triggers the decomposition of precursors and a burst of nucleation followed by controlled growth, resulting in nearly monodisperse CdE (E = S, Se, Te) NCs with high crystallinity and narrow size distributions.

Long-chain ligands such as alkylphosphines and alkylphosphine oxides (e.g., TOP and TOPO), long-chain amines (e.g., oleylamine), and carboxylic acids (e.g., oleic acid) not serve as solvents and precursor stabilizers during synthesis, but also passivate the NC surface, controlling their growth and preventing aggregation[68]. Incorporation of such ligands has become standard in colloidal NC synthesis, influencing surface chemistry and stability. However, native ligand shells rarely suit all applications. Pioneering studies by Alivisatos and co-workers demonstrated that ligand exchange and post-synthetic surface modification can be used to precisely engineer the optical, electronic, and chemical properties of nanocrystals, enabling their integration into platforms ranging from biological imaging to photovoltaics and catalysis[13]. Talapin and colleagues later extended these studies to improve charge transport in electronic and optoelectronic devices[17].

The hot-injection method represented a breakthrough in the synthesis of high-quality NCs across diverse material systems, paving the way for large-scale applications of quantum dots in both research and industry. However, despite its advantages, the hot injection method presents technical challenges, as it requires precise temperature control and a deep understanding of reaction kinetics. Additionally, it is more energy-consuming compared to some other synthesis methods, which may limit its efficiency for large-scale industrial production. The method has been particularly effective for II–VI and IV–VI chalcogenide NCs, such as CdS, CdSe, CdTe, PbS, and PbSe, where predominantly ionic or highly polar covalent metal–chalcogen bonds and high precursor reactivity enable fast, well-defined nucleation events and kinetically controlled growth. In contrast, more covalent systems such as ZnO and InP possess higher activation barriers to bond formation, requiring rationally designed precursors to trigger controlled nucleation. Their slower and often overlapping nucleation–growth kinetics limit precise size control, requiring reaction designs that balance precursor reactivity with ligand-mediated surface stabilization. Over the past two decades, advances in precursor chemistry, ligand engineering, and reaction design have enabled more covalent systems to be synthesized with control comparable to ionic systems, thereby broadening the accessible library of high-quality NCs. As such, although it remains a powerful tool for producing high-quality nanomaterials, its limitations, particularly regarding material compatibility, energy consumption, and scalability, must be carefully considered when selecting a synthesis method for industrial applications.

(iii) Sol-gel method

For metal oxide nanocrystals, however, different synthetic strategies are required than those typically applied to chalcogenide systems. Among these, the sol-gel method has emerged as widely used and a versatile chemical route for oxides such as titanium dioxide (TiO₂), zinc oxide (ZnO), and silicon dioxide (SiO₂)[69–71]. This process is distinct from precipitation and hot injection techniques and involves the hydrolysis and polycondensation of precursors, typically inorganic metal salts, to yield a sol, which subsequently transitions into a gel and undergoes further processing to produce nanomaterials[71]. A representative exam-

ple is the sol-gel synthesis of ZnO nanostructures pioneered by Spanhel and co-workers[72]. In this approach, a zinc salt (most commonly zinc acetate dihydrate, $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ or zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is dissolved in an alcohol (ethanol or isopropanol) and gently pre-heated ($<100^\circ\text{C}$) until a transparent sol is formed. Subsequent addition of an alkali hydroxide, typically LiOH, KOH or NaOH, triggers hydrolysis and rapid nucleation, leading to colloidal ZnO NCs ($<10\text{ nm}$). In a general reaction protocol, an ethanolic solution of MOH (where $\text{M} = \text{Li}^+, \text{Na}^+, \text{or } \text{K}^+$) is added to an ethanolic solution of zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) at low temperature ($\approx 0^\circ\text{C}$). The overall reaction for the formation of ZnO nanocrystals can be written as:

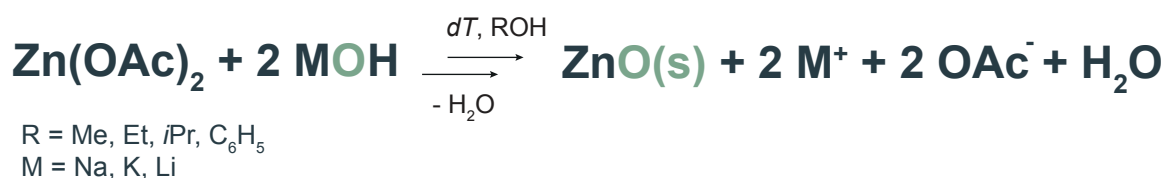


Figure 1.7: Schematic illustration of the sol-gel synthesis of ZnO NCs utilizing zinc acetate as precursor alkali hydroxides.

Spanhel and co-workers proposed that ZnO nanocrystals form through the intermediate assembly of well-defined zinc-oxo-acetate clusters[73]. The most extensively characterized are the tetrahedral $\text{Zn}_4\text{O}(\text{OAc})_6$ unit and its higher homologue $\text{Zn}_{10}\text{O}_4(\text{OAc})_{12}$, which are stabilized in anhydrous alcoholic media. In the presence of alcohols, these species evolve into mixed alkoxy-acetate complexes, $(\text{EtOZnOAc})_n$, which promote one-dimensional growth of NCs. However, the same precursor system under basic conditions in the presence of water leads to the lamellar hydroxyacetate $\text{Zn}_5(\text{OH})_8(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ complexes. Such clusters are considered primary building blocks, whose controlled aggregation and condensation ultimately yield crystalline ZnO nanocrystals. The kinetics of ZnO nanocrystal growth can be tuned by adjusting reaction parameters such as temperature, reaction time, hydroxide concentration, and solvent. Additional control is provided using additional capping agents, which further modulate growth dynamics and surface stabilization. These factors govern nucleation rates and determine the size

and morphology[74–76], optical[77], and catalytic[78] properties of the resulting ZnO nanostructures.

While the sol–gel approach offers several advantages, including synthetic simplicity, versatility, and cost efficiency, it also exhibits some significant drawbacks[79, 80]. The reproducibility of this method is difficult to control, as the formation of quantum-sized ZnO NCs is kinetically controlled. As a result, both the uniformity of particle morphology and the nanocrystal–ligand interface composition, including the density and homogeneity of ligand shells, are often compromised[81]. Moreover, the highly defected and corrugated surface structures obtained in this route can lead to unstable nanocrystal–ligand interfaces[82](*vide infra*; Figure 1.22), with improved stability reported only after extended post-synthetic aging[83]. Advanced ^7Li NMR studies by Lewiński and co-workers further revealed that in sol–gel derived ZnO nanocrystals, Li^+ ions from LiOH become randomly incorporated into the core, subsurface, and surface regions, resulting in interfacial “swelling” and uncontrollable doping[84] (Figure 1.8).

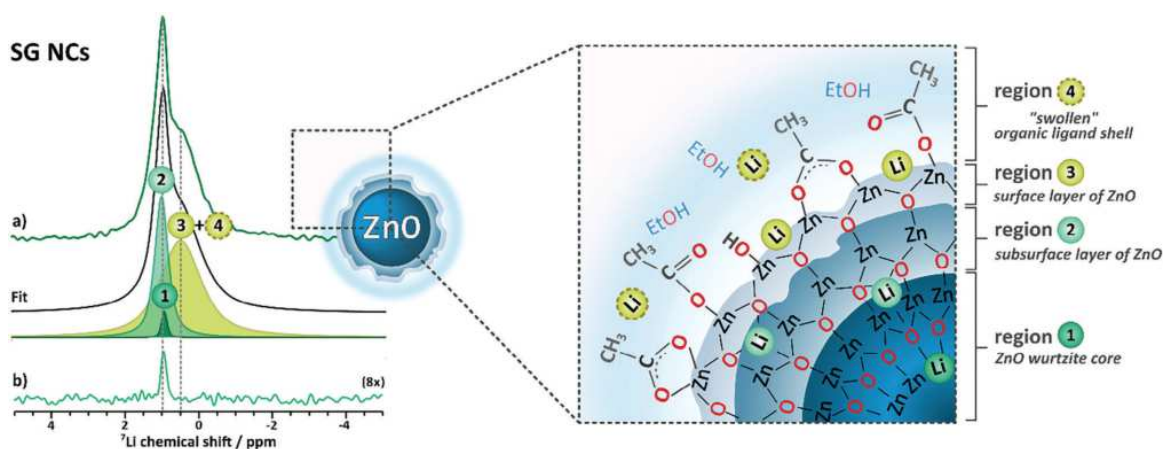


Figure 1.8: ^7Li MAS NMR spectra of sol-gel derived ZnO nanocrystals. **a**, With associated peak deconvolutions (black line represents the sum of the contributions) and **b**, Corresponding ^7Li bulk-filtered MAS NMR spectra. Reproduced from ref.[84] with permission from Wiley-VCH.

(iv) Organometallic method

Taken together, these findings clearly demonstrate the inherent limitations of the sol–gel approach, particularly when high-purity and structurally uniform ZnO nanocrystals are required. Therefore, alternative synthetic strategies have

been explored to overcome these challenges. In this context, the development of organometallic precursors of metal oxides has opened new possibilities for preparation of nanocrystalline materials under mild and controllable conditions. The use of highly reactive organometallic precursors facilitates the synthesis in mild conditions, leading to the well-controlled nanocrystalline products. Organometallic compounds possess lower potential energy barriers for reactions, compared to traditional inorganic precursors, enabling them to react readily under milder conditions (Figure 1.9; see also Chapter 1.5.2). This lower barrier facilitates controlled nucleation and growth processes, allowing for precise control over the size, shape, composition, and organization of the resulting nanocrystals. Additionally, the organic ligands present in the organometallic precursors can influence the reaction kinetics and surface chemistry, further aiding in achieving the desired level of control and uniformity in the nanocrystal synthesis[13].

The formation of NCs can be controlled by regulating type of organometallic precursor and its stoichiometry, temperature, and reaction time. This fine-tuned control is of paramount importance in achieving the desired properties and functionalities essential for advancements in nanomaterials across diverse domains. However, wet-organometallic synthesis of metal oxides often requires air- and moisture-sensitive handling, which requires the use of inert atmospheres and specialized equipment, potentially increasing complexity and cost for both laboratory and industrial implementation (*vide infra*). The organometallic approaches for zinc oxide nanocrystals, which is the focus of this thesis are described in detail in Chapter 1.5.

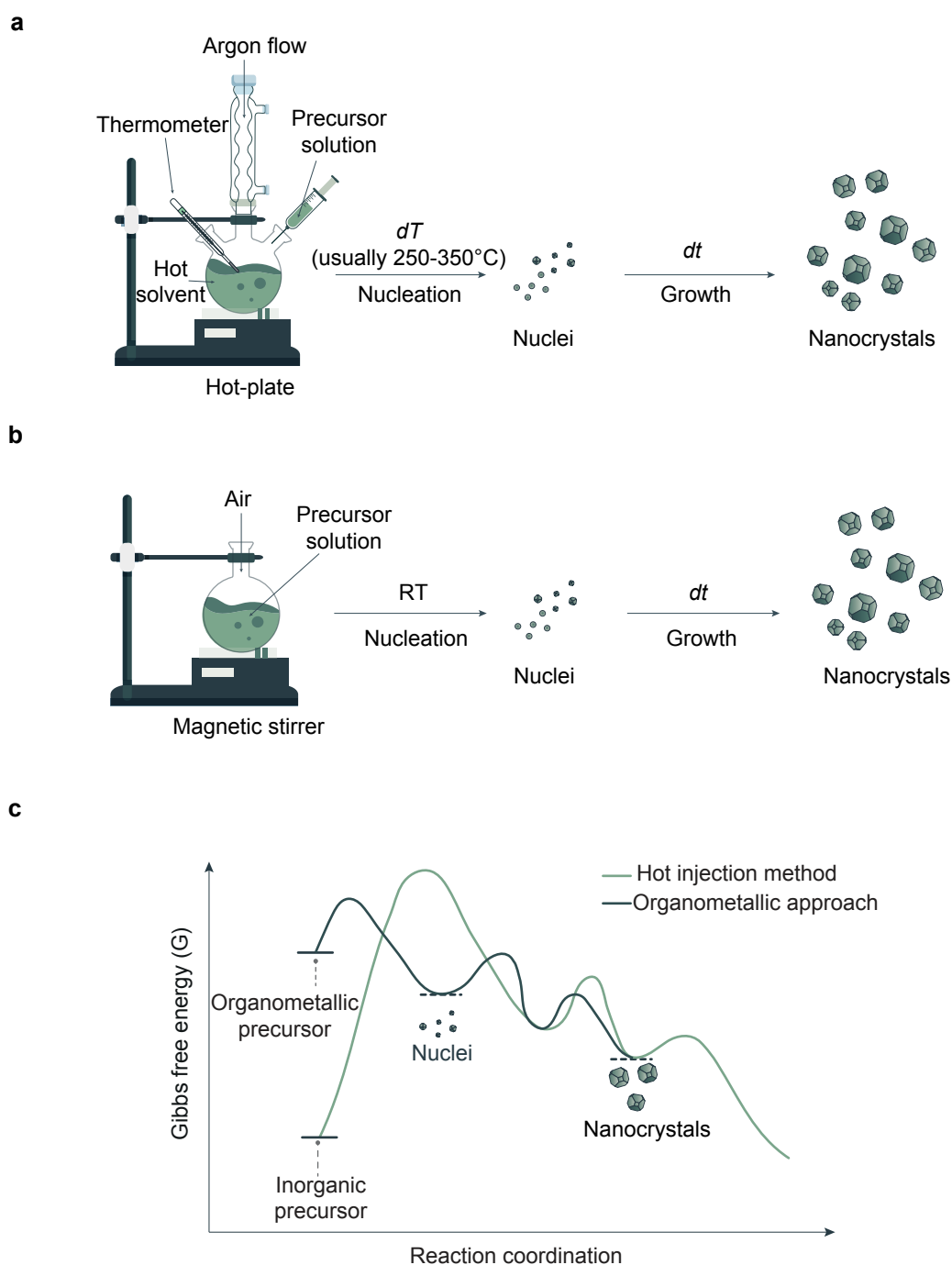


Figure 1.9: The schematic representation of: **a**, Hot-injection method. **b**, Organometallic and inorganic route to synthesis of semiconductor NCs. **c**, Energy landscapes of NCs synthesis.

Beyond these widely adopted routes, additional liquid-phase techniques have also been reported in the literature, including hydrothermal and solvothermal synthesis, microwave-assisted methods, and microemulsion-based strategies. These approaches have demonstrated effectiveness in selected applications, particularly for

metal oxide and hybrid nanomaterials. However, due to their limited applicability to colloidal semiconductor nanocrystals and the need for specialized equipment, they are not discussed in detail in this chapter.

1.4.3 Solid-state synthetic approach

Solid-state transformations are fundamental processes in materials science, playing a pivotal role in many applications. These transformations offer potential attractiveness in the synthesis of NCs as they can avoid the use of solvents and additional stabilizing ligands[85–87]. Unlike well-established solution-based methods, solid-state reactions, which had been at the forefront of traditional inorganic materials chemistry, are quite rarely utilized in the realm of NCs. This occurs because the reactivity of chemical species, as well as NC nucleation and growth, are significantly restricted in the solid-state due to relatively low mass transport in crowded templating environments[88–90]. Consequently, the application of heat[91, 92] and mechanical treatment[93, 94] provides the necessary energy to overcome the activation energy of diffusion, aiding in the mixing of solid reactants. Despite the great progress in synthetic procedures for preparing NCs, there remain significant drawbacks in the reported methods. One of the major challenges is the need for techniques that offer reproducibility, rapidity, scalability to gram quantities, and cost-effectiveness. The high-temperature solid-state reactions can lead to the incorporation of impurities from the reaction vessel or precursors, affecting the purity and quality of the resulting nanomaterials. Solid-phase reactions may have slower reaction kinetics compared to some other methods, leading to longer synthesis times, and potentially affecting production rates. Therefore, understanding and controlling the thermodynamics and kinetics of such transformations are crucial for their practical applications.

1.4.3.1 Fundamentals of solid-state reactivity

Solid state transformations refer to chemical reactions confined within solid materials, where both reactants and products maintain a solid state throughout the process. These reactions typically involve the rearrangement of atoms within the solid lattice structure, resulting in the formation of new compounds or phases[95, 96].

These processes are predominantly governed by diffusion-controlled mechanism, where the reaction rate depends on the diffusion rates of atoms or molecules through the solid matrix[97, 98]. It involves the movement of atoms or ions within the crystalline lattice, allowing for the redistribution of chemical species. The kinetics and mechanisms of solid-state reactions are markedly influenced by the closely packed environment within the crystal lattice (Figure 1.10). This limited mobility of ions and atoms in solids results in slower diffusion rates compared to compared to solution- and gas-phase reactions[88, 99] and contributes to typically long (days) reaction times. Consequently, initiating solid-state reactions between one or more inert solid reactants usually require significant energy input to achieve sufficient interatomic or ionic diffusion to get past energy barriers for product formation[100, 101]. Temperature is one of the most critical factors influencing solid-state transformations. Higher temperatures generally lead to increased diffusion rates, enabling atoms or ions to move more freely within the nanocrystal lattice[100]. This increase in mobility within the nanocrystal lattice at elevated temperatures accelerates the kinetics of transformations (Figure 1.10).

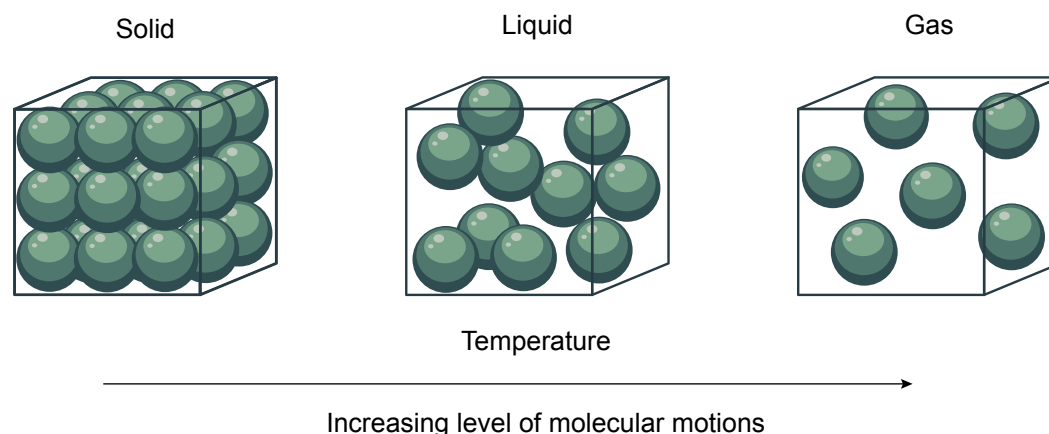


Figure 1.10: Schematic representation of types of matter. Diffusion is faster in liquids than in solids because of the differences in their molecular properties. This distinction in diffusion behavior between solid-state and solution environments underlies their disparate reaction kinetics, with solid-state reactions typically exhibiting slower rates due to the constraints of the crowded lattice. the more rapid diffusion observed in liquids, where reactants can move more freely, facilitated by solvation with solvent molecules.

1.4.3.2 Pathways for solid-state synthesis

Significant progress has been made in achieving a theoretical understanding of solution-state reactions, where solvents facilitate atomic or molecular mixing. In these systems, kinetic and thermodynamic parameters are well-defined, allowing for the development of highly predictive theoretical models. In contrast, solid-state reactions involve numerous chemical species reacting together, making the synthesis of new materials through nucleation and crystal growth largely dependent on the dynamics of bulk, surface, and interface thermodynamics, as well as on transport processes during solid-state diffusion and interfacial phase mixing[102, 103]. The complex interplay between thermodynamics and kinetics makes solid-state synthesis prone to the unpredictable and undesirable formation of impurity phases[104]. To facilitate chemical reactions in the solid-state different accelerating agents can be utilised, i.e., (i) temperature treatment, (ii) mechanical force, or (iii) accelerated ageing (Figure 1.11).

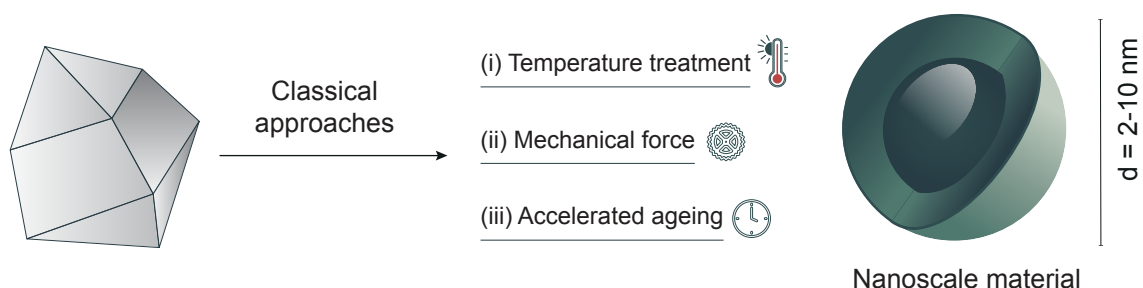


Figure 1.11: Schematic representation of classical solid-state synthesis pathways towards nanoscale materials.

(i) Temperature treatment

In traditional solid-state synthesis, solid compounds are mixed and heated at high temperatures for extended durations to promote atomic diffusion, typically leading to the formation of the most thermodynamically stable product[105, 106]. Numerous inorganic materials are synthesized through the high-temperature solid-state reaction of mixed reagent powders, including metal oxides, intermetallics, and ceramics[96]. Depending on the precursors, the reaction temperature can range from several hundred to over 1000 °C; for many inorganic oxides and ceramics, reaction conditions of 800–1200 °C are common, while some systems require even higher temperatures exceeding 1500 °C. In contrast, reactions involving organic precursors are typically limited to temperatures below 400 °C, since higher values cause decomposition of the organic species. Despite seeming straightforward, the results of solid-state synthesis can often be unpredictable[107, 108]. In situ characterization[109] and ab initio computations[110–112] have significantly advanced our understanding of materials synthesis and are pivotal in enhancing predictive capabilities for synthesizing inorganic solids, particularly regarding their thermodynamic stability[113]. However, even when materials are theoretically stable, their actual synthesis can be complicated by the formation of inert byproducts. These byproducts compete with the desired target material, often resulting in a reduced yield[89, 114]. Metastable materials are typically prepared using low-temperature synthesis routes, where kinetic control can be used to avoid the formation of equilibrium phases[106], though recent work has shown

that metastable phases can also appear as intermediates during high temperature experiments[104, 109, 115]. To optimize the purity of a desired product, whether it be stable or only metastable, requires careful selection of precursors and reaction conditions. Examples for ZnO are discussed in detail in Chapter 1.6.1.

(ii) Mechanical force

The emergence of mechanochemistry has extremely broadened the opportunities of solid-state reactions, yet effectively controlling the formation of nano/microstructures. ‘Mechanochemistry’ refers to reactions, normally of solids, induced by the input of mechanical energy, such as grinding, milling or other types of mechanical action. Mechanical energy is used to break bonds and initiate chemical transformations in solid materials. It is becoming more intensely studied partly because it can promote reactions between solids quickly and quantitatively, with either no added solvent or only nominal amounts[87, 116–118].

Dating back to 1820, the first documented solvent-free mechanochemical reaction was conducted by Faraday, who reduced AgCl to Ag using Zn, Cu, Sn, or Fe through grinding in a pestle and mortar[119]. Despite its ancient origins, mechanochemical methods remained underexplored by chemists for much of the 20th century[96]. However, in contemporary times, mechanochemistry has gained recognition as a highly effective approach within Green Chemistry, emphasizing its environmental benefits and sustainability. Recently, mechanochemistry is undergoing an exciting period of rediscovery, fueled by advancements in synthetic techniques and the advent of tools for real-time mechanistic studies[120–122]. This revival is strongly motivated by the core principles of green chemistry, which prioritize synthetic procedures that are cleaner and more energy- and materials-efficient than existing, solvent-based ones. Modern mechanochemistry is rapidly expanding into almost every area of chemistry and materials science. Initially focused on the synthesis of inorganic materials and mechanical alloying[123–126]—its scope has significantly broadened. Only recently has it been validated as a versatile method to conduct organic[127–129], inorganic[124], and organometallic[130] transformations leading to diverse high-value materials, including pharmaceuticals[131], nanoparticles[132], hybrid[133] and microporous materials[134–138]. Fur-

thermore, mechanochemical routes offer a versatile platform for catalysis[139–143]. Schematic representations of the three main modes of mechanical activation of chemical reactions are presented in Figure 1.12.

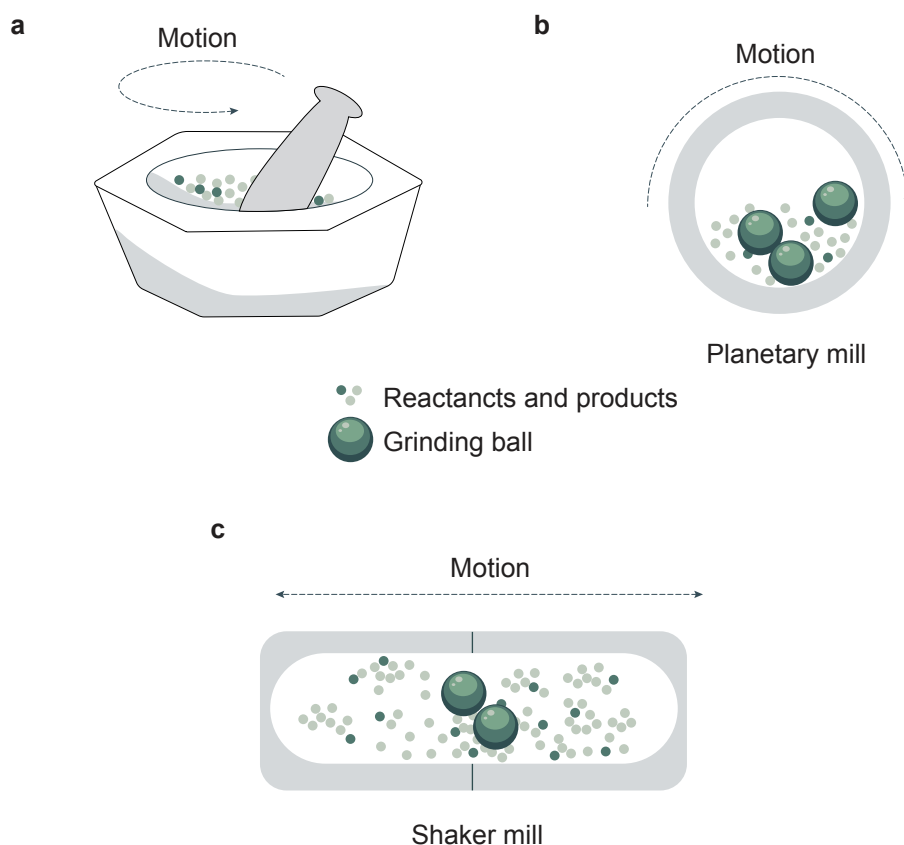


Figure 1.12: Schematic representations of the three main modes of mechanical activation of chemical reactions. **a**, Grinding with mortar and pestle. **b**, Planetary ball milling. **c**, High-speed vibration milling in a mixer mill.

However, despite its rapid growth and promising applications, mechanochemistry faces challenges. Scaling up from lab to industrial levels is difficult due to the specific conditions required. Controlling reaction parameters like temperature and pressure can lead to issues with reproducibility, and mechanical equipment wear can introduce contaminants. Additionally, the underlying mechanisms of many reactions are not fully understood, complicating optimization. While environmentally beneficial, mechanical processing may still involve significant energy consumption, particularly on larger scales.

(iii) Accelerated aging

Accelerated aging reactivity involves diffusion-controlled reactions between initially solid reactants that are accelerated or directed by mild or transient changes in their environment. Inspired by natural processes such as biomineralization and mineral weathering[144–146], these methods rely on prolonged exposure to humidity, vapors, mild catalysts, or simple molecules to trigger and accelerate chemical solid-state transformations[147]. In nature, nanomaterials form primarily through chemical weathering processes involving water, dioxygen, and carbon dioxide as the main factors in the disintegration of rocks and minerals[148–150]. Although the timescale of these chemical processes is impractical from a laboratory perspective, they provide an important hint for designing artificial NC precursor systems, specifically their reactivity towards hydrolytic and/or oxidative species[2].

The guiding principles behind accelerated aging reactions focus on achieving a reaction design that is inherently simple, low-cost, and safe, qualities that enhance scalability and improve the efficiency of material and energy consumption. These reactions typically unfold over hours or days, distinguishing them from the faster solvent-free mechanochemistry or thermochemistry processes, which usually span minutes to hours. However, accelerated aging reactions are significantly quicker than other diffusion-based processes like geological weathering, which can extend over days, years, or even centuries. This positions accelerated aging at a unique crossroads between solution-based chemistry, geochemistry, and various types of solvent-free reactivity, offering a unique opportunity to integrate the strengths of these diverse methodologies. This approach significantly reduces the use of hazardous solvents and energy, aiming for complete consumption of reagents, minimal waste, and the elimination of chemical-intensive purification processes.

In the context of laboratory synthesis, several examples of accelerated aging reactions were reported in the literature. For instance, in 2012 Cliffe et al., investigated how accelerated aging can be applied to the synthesis of zeolitic imidazolate frameworks (ZIFs), exploring the reactivity between zinc oxide and differently substituted imidazoles under mild, solvent-free conditions[151]. Inspired by nat-

ural mineral weathering, they demonstrated that simple and inexpensive precursors such as ZnO and imidazoles (specifically imidazole (Him), 2-methylimidazole (HMeim), 2-ethylimidazole (HEtim), and benzimidazole (HBim)) can be converted into crystalline ZIFs when exposed to catalytic amounts of ammonium salts in a humid atmosphere at moderate temperatures (up to 45 °C). The crystalline products obtained were determined by the ligand, catalyst, and reaction parameters (aging time, temperature, vapor solvent, and humidity). However, such process led only to the formation of non-porous ZIFs.

In the following work published in 2013, Mottillo et al., demonstrated that porous ZIF-8 could be synthesized through accelerated aging by replacing simple ammonium salts as protic catalysts with more complex organoammonium salts, whose larger molecular structure enabled stabilization of the open framework. The same approach was readily applicable to the synthesis of the cobalt(II) analogue, ZIF-67 (Figure 1.13)[144].

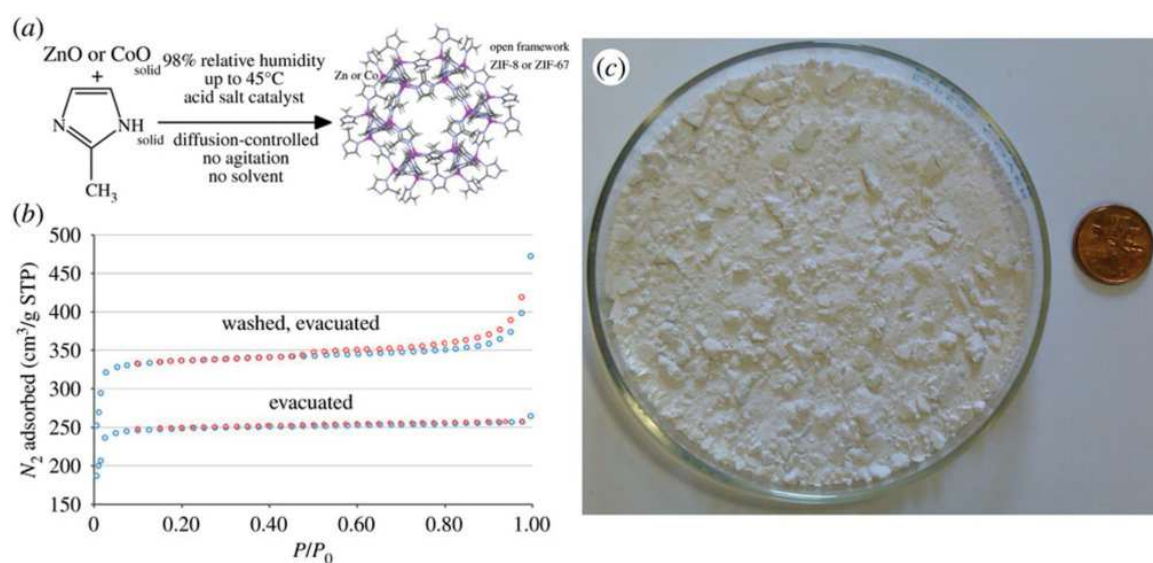


Figure 1.13: Synthesis of zeolitic imidazolate frameworks by geomimetic accelerated ageing. **a**, Schematic of the synthesis of selected zinc- and cobalt(II)-based MOFs. **b**, Nitrogen sorption isotherms for ZIF-8 framework samples obtained by accelerated ageing. **c**, A 5 g sample of ZIF-8 obtained by accelerated ageing. Reproduced from ref.[144] with permission from The Royal Society of Chemistry.

In a related study, Qi and colleagues described the synthesis of metal oxalate coordination polymers by aging mixtures of oxalic acid and metal oxide species at 98% relative humidity[152]. In addition, Užarević and colleagues expanded on this

procedure by using accelerated aging techniques to prepare UiO-66 type MOFs, a zirconium-based material that exhibits a high degree of porosity and catalytic activity[137].

Beyond MOFs, the feasibility of mild solid-state reactivity has also been demonstrated in other systems. For example, Budny-Godlewski and Lewiński showed solvent-free radical transformations involving solid homoleptic organozinc compounds and an intentionally added free stable nitroxyl radical. Such studies represent a significant advance in molecular solid-state chemistry and highlight the potential of radical slow-chemistry reactions[153].

Although accelerated aging has been widely applied to the synthesis of MOFs and other coordination frameworks, analogous strategies for semiconductor NCs under similarly mild thermal and mechanical conditions remain essentially unexplored. In MOFs, metal–ligand bonds typically range from 50–150 kJ/mol, strong enough to stabilize an extended framework yet sufficiently labile to undergo dynamic exchange under relatively mild conditions. This reversibility allows the network to reorganize and anneal itself into the most stable topology even at room temperature. In contrast, semiconductor NCs are stabilized by much stronger ionic–covalent bonds (e.g., Zn–S $\approx$ 285 kJ/mol, Cd–Se $\approx$ 210 kJ/mol), 2–5 times stronger than coordination bonds, and therefore cannot dynamically reorganize without significant external energy input. This raises the question of whether solid-state pathways to semiconductor NCs could be realized under mild conditions, i.e., room temperature. Potentially, these limitations could be addressed by employing suitable molecular precursors that trigger chemical transformations within the reaction system, thereby enabling efficient mass transport in the solid state. In the case of semiconductor metal chalcogenides and oxides, such precursors may be based on coordination complexes, which—similarly to MOF-type materials—feature relatively labile metal–ligand bonds and can undergo transformations that release inorganic components as building blocks for inorganic nanoparticles.

1.5 Wet-organometallic approach for the synthesis of colloidal semiconductor ZnO NCs

This dissertation develops a novel synthesis route for ZnO, one of the most promising semiconductor materials. Therefore, the following section focuses on synthetic strategies specifically developed for ZnO nanocrystals. To date, the synthesis of nanostructures has predominantly employed traditional inorganic precursors such as metal salts or oxides[154, 155]. These methods often necessitate harsh conditions and offer limited control over size, morphology, and composition, leading to inconsistent results and hindered scalability. The use of reactive organometallic precursors facilitates the synthesis in mild conditions, leading to the well-controlled nanocrystalline products[156, 157]. Organometallic compounds possess lower potential energy barriers for reactions, enabling them to react readily under milder conditions compared to traditional inorganic precursors. This lower barrier facilitates controlled nucleation and growth processes, allowing for precise control over the size, shape, composition, and organization of the resulting nanocrystals. Additionally, the organic ligands present in the organometallic precursors can influence the reaction kinetics and surface chemistry, further aiding in achieving the desired level of control and uniformity in the nanocrystal synthesis. The formation of NCs can be controlled by regulating type of organometallic precursor and its stoichiometry, temperature, and reaction time. This fine-tuned control is of paramount importance in achieving the desired properties and functionalities essential for advancements in nanomaterials across diverse domains. A wide range of semiconductor nanomaterials and their synthesis precursors are described in the scientific literature.

1.5.1 Reactivity of R_2Zn organometallic compounds with H_2O

A highly effective approach to synthesizing ZnO nanostructures involves the reaction of organometallic compounds of the type R_2Zn or $RZn(L)$ with H_2O . Particu-

larly, direct reactions between organozinc compounds and H_2O are considered as one of the most efficient methods leading to ZnO. In such processes, an organozinc compound acts as the precursor for the Zn center, while water serves as the oxygen source. These reactions can also lead to well defined molecular zinc hydroxide and oxo species which can be regarded as intermediates on the path to ZnO NCs.

Diorganozinc compounds (R_2Zn) were among the earliest organometallic compounds to be synthesized. In 1852, Edward Frankland prepared diethylzinc (Et_2Zn), the first known organozinc compound, by heating ethyl iodide with metallic zinc[158]. In a typical R_2Zn species, the Zn atom is bonded to two organic groups, (denoted as R), through zinc-carbon (Zn-C) covalent bonds.

Due to the polarized nature of the Zn-C bond, organozinc compounds are highly reactive towards both water and dioxygen, facilitating its relatively low stability[159]. Therefore, when exposed to air, this volatile, colorless liquid inflames spontaneously. Consequently, the preparation and handling of these types of compounds necessitate caution under dry, moisture-free conditions, often within an inert gas atmosphere like nitrogen or argon, to prevent rapid degradation of the compound. Specialized equipment such as Schlenk lines or gloveboxes are employed to maintain an anhydrous environment. The high reactivity of Zn-C bonds towards acidic protons makes the stabilization of organozinc hydroxides a challenging task[160, 161]. Furthermore, the interaction of organozinc compounds with water has remained an area little explored so far. Nevertheless, the significant reactivity of organozinc compounds can be advantageous when the source and stoichiometry of water are strictly controlled, and the reaction conditions (e.g., temperature) are carefully considered[162].

The reactivity of homoleptic R_2Zn compounds towards H_2O has been of interest to researchers for decades. Spectroscopic studies performed by Herold and co-workers in 1963 revealed that direct hydrolysis of Et_2Zn produces ethylzinc hydroxide [EtZnOH] species, that are relatively unstable at temperatures above -60°C and undergo a gradual decomposition (on the order of minutes) into oxozinc clusters via the subsequent evolution of ethane[163]. In 1984 Kuran et al., applied a cryoscopic method to determine the molecular weight in the $\text{Et}_2\text{Zn}/\text{H}_2\text{O}$ reac-

tion system within 1,4-dioxane[164]. This study unveiled that hydrolysis of Et_2Zn initially results in an equilibrium mixture containing dimeric $[\text{EtZnOH}]_2$ and tetrameric $[\text{EtZnOH}]_4$ ethyl(hydroxo)zinc species (Figure 1.14). These systems are unstable and decompose at room temperature with the release of ethane and subsequent gradual aggregation to ethyl(oxo)(hydroxo)zinc compounds $\text{EtZn}(\text{OZn})_3\text{OH}$. Nevertheless, the low stability of low-alkylzinc hydroxides precluded both their isolation and structural characterization and the mechanism and intermediates implicated in the hydrolysis of R_2Zn remained elusive.

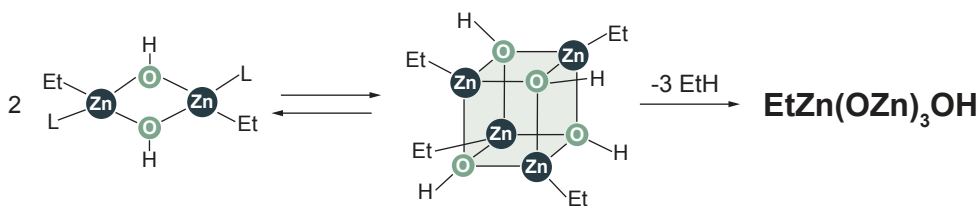


Figure 1.14: Proposed equilibrium between dimeric and tetrameric ethylzinc hydroxide species $[\text{EtZnOH}]$ and their decomposition with subsequent elimination of ethane. The hydrolysis of R_2Zn , containing low-alkyl substituents bonded to the metal centre, leads to an intractable mixture of ethylzinc hydroxides that decompose slowly to ethylzinc (oxo)hydroxide aggregates with concomitant evolution of ethane.

Although examples of structurally characterized organozinc hydroxide complexes are rare, Lewiński and co-workers reported the first reaction system leading to well-defined, stable representative of $[\text{RZnOH}]_n$ -type compounds via direct hydrolysis of homoleptic R_2Zn . Introducing bulky alkyl groups, such as tert-butyl, partially suppresses this uncontrolled reactivity by reducing the accessibility of the zinc center. The equimolar reaction of $t\text{Bu}_2\text{Zn}$ with H_2O led to formation of a novel hexameric tert-butylzinc hydroxide $[(t\text{BuZnOH})_6]$, successfully isolated as crystals[91]. The complex has a characteristic drum-like structure with a core of the Zn_6O_6 formula, which consists of two six-membered and six four-membered Zn–O rings ($[\text{Zn}_3\text{O}_3]$ and $[\text{Zn}_2\text{O}_2]$, respectively). Each hydroxyl group is associated with three zinc centers (see Figure 1.15) The unique intrinsic reactivity of RZnOH -type compounds makes them promising pre-designed single-source precursor (SSP) of ZnO nanostructures, as they can be transformed via simple alkane elimination. For example, the hexameric tert-butylzinc hydroxide cluster reported by Lewiński et al., decomposes to ZnO at approximately 120°C (*vide infra*; Chapter 1.6.1).

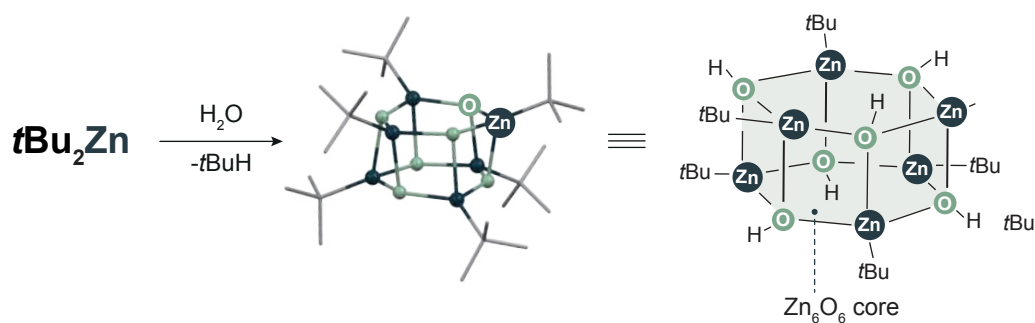


Figure 1.15: Schematic representation of the synthesis of hexameric zinc hydroxide – $[(t\text{BuZnOH})_6]$.

It is noteworthy that, aside from the above-described system, no other stoichiometrically controlled hydrolysis of R_2Zn compounds has resulted in stable, well-characterized alkylzinc hydroxide clusters.

1.5.2 Controlled hydrolysis of R_2Zn -type organometallic precursors to ZnO NCs

The pioneering use of R_2Zn -type compound as a ZnO precursor was demonstrated by Carnes and Klabunde. The reported method involves the transformation of Et_2Zn into an alkoxide prior to hydrolysis[165]. This resulted in the formation of ZnO nanoparticles in powder form, characterized by a crystallite diameter in the 3–10 nm size range. The resulting ZnO particles could further aggregate together to form spherical particles that have a large surface area and enhanced reactivity.

Chaudret and co-workers have extensively explored the hydrolysis of various organozinc precursors to form ZnO nanoparticles. Initially, the authors showed that thermal decomposition of the organometallic precursor—dicyclohexylzinc $[\text{Zn}-(\text{c-C}_6\text{H}_{11})_2]$ in wet solutions leads to the formation of monodisperse spherical Zn nanoparticles of 6 nm mean diameter[166]. Further analysis indicated that the resultant Zn nanoparticles were covered with a thin layer of hexagonal ZnO of wurtzite type. The presence of traces of water in the initial solutions were assumed to be a source of oxygen centers for the formation of ZnO at zinc particle interfaces. Full oxidation of the particles at 600°C led to ZnO particles of similar

size and geometry. These observations align with the results for the anhydrous $\text{Et}_2\text{Zn}/\text{O}_2$ system, which required relatively high temperatures (around 200 °C) to the formation of the NCs[167].

In subsequent studies, it was observed that most organometallic complexes are sensitive to air and undergo exothermic decomposition when exposed to it. The direct exposure at room temperature of the organometallic precursor $[\text{Zn}(\text{c-C}_6\text{H}_{11})_2]$ solution to open air in the absence of ligands leads to agglomerated nanoparticles of ZnO with a zincite structure that display no defined size or shape. However, introduction of long-chain aliphatic ligands [e.g., dodecylamine (DDA), hexadecylamine (HDA), or octylamine (OA)] into the reaction system as supporting stabilizing agent allow to control crystallization of emerging nanostructures and lead to formation of well-defined nano-objects, i.e., spherical, disk or rod-shaped ZnO NCs, the size and shape of which depend upon the reaction conditions[168, 169].

Only recently, Lewiński and co-workers described a one-step organometallic procedure in which commercially available Et_2Zn undergoes controlled transformation in neat dimethyl sulfoxide (DMSO) upon exposure to atmospheric air, where H_2O and O_2 act simultaneously as oxygen sources (Figure 1.16), and DMSO serves both as a solvent and a low-molecular-weight L-type surface protector[170]. In this approach, direct injection of Et_2Zn into neat DMSO under ambient air rapidly produced a turbid mixture that, within two days, evolved from a colorless solution through a white gel-like intermediate into a stable colloidal suspension. Simple syringe filtration afforded a clear nanocolloid of ZnO QDs, whereas centrifugation and subsequent anti-solvent precipitation followed by vacuum drying yielded an air-stable white powder. HRTEM and PXRD analyses confirmed nearly spherical ZnO QDs with a wurtzite structure and an average crystallite size of approximately 4.5 nm. The isolated QDs can be easily re-dispersed in DMSO to form a stable colloidal solution. These colloidal DMSO-capped ZnO QDs were successfully employed for the fabrication of thin films composed of organic ligand-free ZnO QDs, serving as efficient electron transport layers (ETLs) in perovskite solar cells (PSCs)[171]. Further studies have extended the one-pot organometallic strat-

egy toward the use of a series of sulfoxides (e.g., dimethyl, diethyl, and diphenyl sulfoxide), enabling controlled passivation of ZnO QDs while maintaining low surface grafting densities and tunable particle sizes[172].



Figure 1.16: Schematic representation of the one-pot-one-step organometallic synthesis of DMSO-QDs.

Strikingly, extended studies by Lewiński and co-workers on the reactivity of R_2Zn -type compounds toward dioxygen have revealed that zinc alkyls react spontaneously with O_2 . According to the proposed mechanism, in the first stage of the reaction of molecular oxygen with alkyl zinc groups, alkyl peroxide systems ZnOOR are obtained, which are formed by inserting an O_2 molecule into the Zn-C bond[173–176]. The ZnOOR groups, formed through the reaction of molecular oxygen with alkylzinc compounds, are susceptible to subsequent transformations. One such transformation involves the homolytic decomposition of usually unstable in room temperature zinc alkyl peroxide moieties. The homolysis and the O-O bond cleavage gives rise to the formation of $\text{ZnO}\bullet$ and alkoxy radicals $\bullet\text{OR}$ radicals, which in turn are the source of oxyl radicals alongside hydroxide and alkoxy species (Figure 1.17). These oxygenation reactions have been commonly considered as difficult to control on the account of their radical character. For this reason, the nanoparticle product obtained through this method contains not only zinc oxide and the ligand from the precursor but also by-products resulting from peroxide decomposition, such as alcohols and products of oxo radical transformations (Figure 1.17).

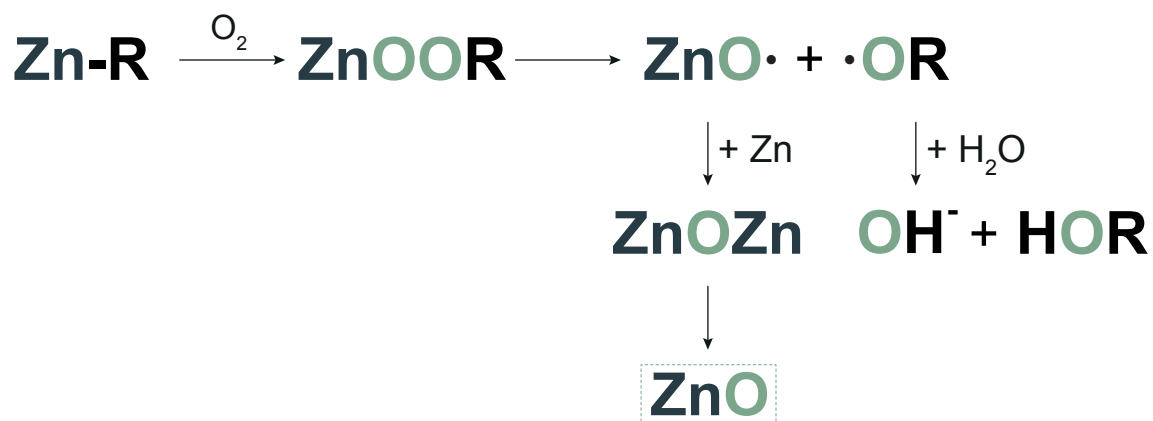


Figure 1.17: Proposed pathway of homolytic decomposition of the O-O bond cleavage.

Consequently, efforts were made to utilize only H₂O as the hydrolytic agent and the solely source of oxygen, aiming to minimize the presence of oxidation products in systems based on [RZn(X)]. Cieřlak et al. introduced an innovative one-pot two-step organometallic synthetic strategy leading to highly luminescent water-soluble ZnO NCs with the well-defined interface[177, 178]. In the first step, Et₂Zn is subjected to controlled hydrolysis to produce pristine luminescent ZnO NCs stabilized by initial ligands (i.e., Zn-Et, Zn-OH species, solvent molecules). The as-prepared NCs are applied as nanocrystalline nuclei to prepare water-soluble ZnO NCs by the subsequent modification of their surface with a supporting pro-ligand, oligo(ethylene glycol) derivative (2,5,8,11-tetraoxatetradecan-14-oic acid; OEG-COOH), bearing a carboxylate anchoring group through controlled interfacial ligand exchange (Figure 1.18).

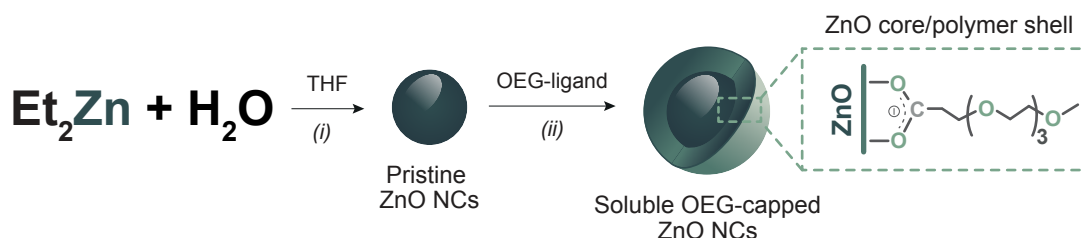


Figure 1.18: Schematic representation of the developed two-step organometallic synthetic strategy leading to highly luminescent water-soluble ZnO NC. The first step involved controlled hydrolysis to produce pristine luminescent ZnO NCs stabilized by initial ligands. In the second step, the as-prepared NCs are further subject to NCs functionalization.

Such well-defined OEG-capped ZnO nanocrystals are highly stable and readily soluble in aqueous media. Furthermore, an appropriate modification of the NCs' inorganic core-organic interface extended the electrons lifetime in the conduction band up to seconds[177]. Notably, the inorganic core- organic ligand interface possesses vacant-spots enabling further sensitization with dye and/or addition of a catalyst[179].

1.5.3 Reactivity of heteroleptic $RZn(L)$ - type alkylzinc complexes incorporating organic ligands with H_2O

While the hydrolysis of homoleptic dialkylzinc compounds typically proceeds through uncontrolled pathways and leads to unstable mixtures of transient hydroxide intermediates, the incorporation of an anionic donor ligand (L) in monoalkylzinc species of the general formula $RZn(L)$ results in a different reactivity toward H_2O [162]. In such heteroleptic systems, the reduced electron density at the Zn center and the stabilization provided by the auxiliary ligand result in enhanced control over the hydrolysis pathway. During the hydrolysis of alkyl zinc complexes the transformation typically begins with the protonation of the alkyl group by a hydrogen atom sourced from the H_2O molecule. This process results in the cleavage of Zn-C bond and evolution of an alkane molecule alongside formation of a hydroxozinc moiety $(Zn-OH)(L)$ or $[Zn(OH)(L)]_n$. Subsequent transformations of this hydroxozinc entity contribute to the eventual formation of oxozinc products. Unlike the hydrolysis of R_2Zn , which often requires cryogenic conditions to prevent rapid decomposition, the hydrolysis of $RZn(L)$ complexes can be conducted under milder conditions. These systems provide valuable mechanistic insight into the hydrolytic transformation of organozinc species and offer a more rational and tunable platform for the design of pre-organized molecular precursors to ZnO nanomaterials in solution.

Among structurally characterized molecular oxozinc clusters, the most representative group consists of species with the general stoichiometry $[Zn_4(\mu_4-O)L_6]$,

where L represents anionic stabilizing ligands. These complexes feature a tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ core, with six ligands coordinated in an octahedral arrangement. Within this family, oxozinc clusters stabilized by organic carboxylate ligands have been particularly intensely investigated. Lewiński et al., introduced an alternative, atom-efficient, and mild synthetic strategy leading to well-defined oxozinc carboxylate complexes, specifically $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CR})_6]$ -type clusters, derived from well-defined alkylzinc precursors[180]. This method involves commercially available Et_2Zn , a carboxylic acid, and H_2O (Figure 1.19).

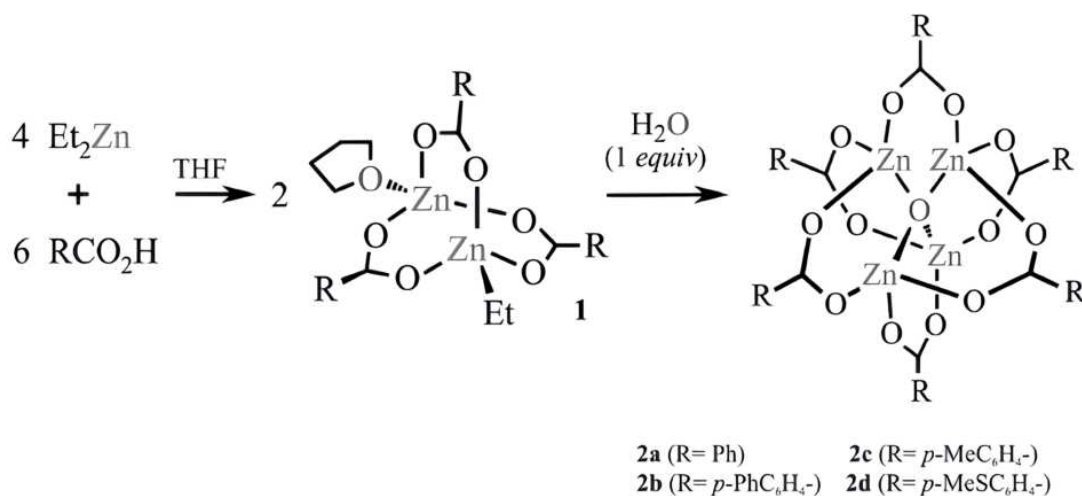


Figure 1.19: Organometallic route for the synthesis of oxozinc complexes $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CR})_6]$. Reproduced from ref. [180] with permission from American Chemical Society.

The relatively high stability and symmetry of carboxylate complexes of the $[\text{Zn}_4(\mu_4\text{-O})\text{L}_6]$ type have contributed to the great popularity of these type of systems as building units of i.e., porous coordination polymers[136]. A variety of structurally analogous oxozinc clusters supported by different organic ligands, such as carbamates[181], amides[136, 182], formamidinate[183], and phosphonates[184], ligands have also been reported. Furthermore, in the equimolar reaction involving oxozinc carboxylate clusters, specifically $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CPh})_6]$, and water, colorless crystals of a cluster with the formula $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})(\text{THF})]_2(\text{THF})$ were isolated from the post-reaction mixture[185] (Figure 1.20). The authors demonstrated that the basic prototypical Zn_4O core can coordinate H_2O or other donor molecules with changing coordination

geometry around zinc centers but preserving the oxozinc core essentially unchanged. These insights reveal oxozinc molecular complexes as excellent model systems to probe reactivity of oxozinc species serving as nodes in metal organic frameworks or as model building blocks of ZnO NCs.

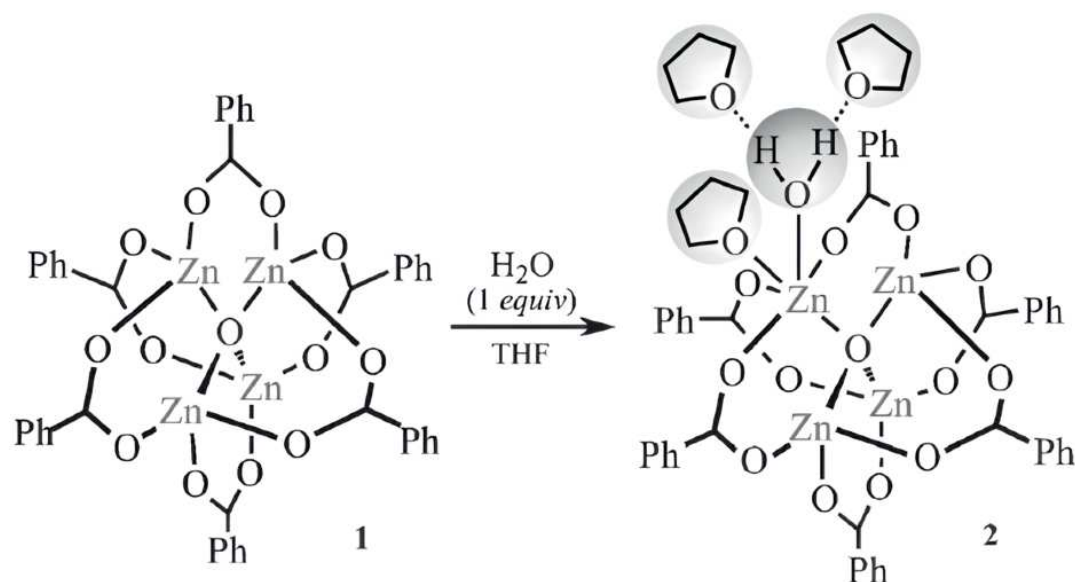


Figure 1.20: Schematic representation of equimolar reaction involving oxozinc carboxylate clusters, specifically $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CPh})_6]$, and water, and the molecular structure of $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})(\text{THF})_2](\text{THF})$. Reproduced from ref. [185] with permission from The Royal Society of Chemistry.

An analogous oxozinc cluster with the $[\text{Zn}_4(\mu_4\text{-O})\text{L}_6]$ stoichiometry was synthesized using benzamide as the supporting ligand in place of carboxylic acid[136]. This zinc-oxo cluster featuring benzamidate ligands with significantly higher basicity paved the way for the development of a new mechanochemical bottom-up approach to ligand-coated ZnO NCs where water plays the role as hydrolytic agent[94] (see Chapter 1.6.2).

In addition to well-defined oxozinc clusters, there are also reports of complexes obtained unexpectedly as by-products of hydrolytic reactions. For example, in the reaction system involving $t\text{Bu}_2\text{Zn}$ and a commercial grade 8-hydroxyquinoline (q-H), the authors observed the formation of a mixture of the expected tert-butylzinc complex stabilized by the quinolate ligand, $[t\text{BuZn}(\text{q})]_3$, and surprisingly an organozinc oxo cluster, $[(t\text{Bu})_3\text{Zn}_5(\mu_4\text{-O})(\text{q})_5]$ [186]. Another example comes from Mitzel

and co-workers, who observed the formation of mixed hydroxyl–hydrazide aggregates $[(\text{MeZn})_4(\text{NHNMe}_2)_3(\mu_3\text{-OH})]$ and $[(\text{EtZn})_4(\text{NHNMe}_2)_3(\mu_3\text{-OH})]$ in moderate yields during one-pot reactions of Me_2Zn or Et_2Zn with 1,1-dimethylhydrazine and H_2O . Both structures contain $\text{Zn}_4\text{N}_3\text{O}$ cages with μ_3 -hydroxide ligands, representing rare examples of alkylzinc hydroxide species stabilized by hydrazide ligands[187].

There is a lack of systematic studies on the alcoholysis reactions of heteroleptic RZn(L) complexes with water (H_2O) and alcohols (ROH). The complexity of these processes is exemplified by a rare report showing that, instead of proceeding through classical alcoholysis, RZn(N,O) -type complexes undergo controlled oxygenation to give zinc alkoxides with unusual structural motifs, such as trimeric and heterocubane aggregates, inaccessible via the conventional pathway[188].

In conclusion, the hydrolysis of alkylzinc compounds of the type RZn(L) leads to products containing oxygen-centered species, such as oxo- or hydroxyl groups, which can be regarded as intermediates in the synthesis pathway towards ZnO NCs [189, 190]. These ligand-supported species serve not only as models for the hydrolytic transformation of organozinc compounds, but also as pre-organized molecular precursors for the synthesis of zinc oxide materials under mild conditions. The following chapter will explore how such RZn(L) -type precursors can be employed in the rational design of ZnO nanostructures via controlled hydrolysis.

1.5.4 Controlled hydrolysis of RZn(L) -type organometallic precursors to ZnO NCs

As discussed in the preceding section, the incorporation of an auxiliary ligand (L) in monoalkylzinc complexes RZn(L) is essential for controlling the hydrolytic reactivity of organozinc species. In the presence of water, these complexes form well-defined hydroxo- and oxo-zinc intermediates that can act as molecular precursors to ZnO NCs . Therefore, precise control over the formation and stability

of hydroxo- and oxo-zinc species through ligand selection is critical for directing ZnO nucleation and growth, positioning $RZn(L)$ complexes as efficient molecular precursors for colloidal ZnO NCs.

Following these findings, the transformation of organozinc precursors under ambient conditions offers a versatile synthetic route to ZnO NCs. This organometallic approach utilizes the high reactivity of Zn–C bonds toward water and/or oxygen, enabling mild processing in aprotic solvents, without the need for elevated temperatures or strongly oxidizing agents. The formation of NCs may be controlled kinetically by changing parameters of the system (i.e., type of organometallic precursor, ligands or surfactants, solvent etc.), ultimately tuning particle size, shape, crystallinity, and surface chemistry.

An innovative advancement in the controlled decomposition of organometallic precursor has become the focus of extensive research by Lewinski and co-workers. Authors presented an one-pot self-supporting organometallic (OSSOM) procedure to produce high-quality quantum-sized ZnO NCs with an organic shell composed of surface-anchored X-type ligands, i.e., carboxylates[191–193], aminoalkoxides[194], phosphates[82], phosphinates[195] and benzamidinates[190]. The OSSOM approach uses controlled transformations of an organozinc $[EtZn(X)]$ -type precursor by exposure to open air (where H_2O and O_2 act simultaneously as a source of oxygen) at room temperature (Figure 1.21).

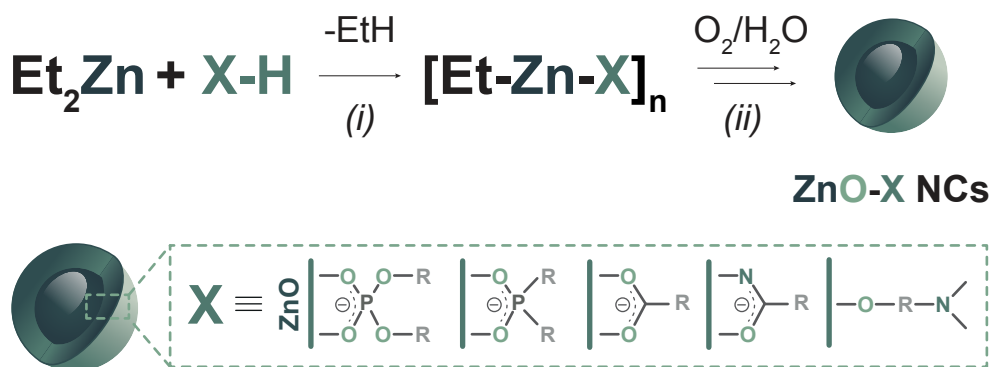


Figure 1.21: Schematic representation of one-pot self-supporting organometallic (OSSOM) procedure. The first step involved the synthesis of an appropriate $[\text{EtZn(X)}]$ -type precursor in an equimolar reaction between commercially available Et_2Zn and the corresponding X-type pro-ligand in THF. In the second step, a THF solution of the respective $[\text{EtZn(X)}]_n$ organometallic precursor is exposed to air to initiate transformations leading to ligand-coated ZnO NCs.

In these precursors, the Zn–R moiety is reactive toward oxygen and water (as oxygen sources), whereas the X-type ligand remains coordinated to Zn and, after transformation, becomes irreversibly anchored on the NC surface. This results in a robust organic shell that preserves the physicochemical properties of the NCs during post-synthetic modifications and further applications[193, 196], in contrast to the dynamic surface chemistry typical of sol–gel-derived ZnO NCs[82], as schematically respresented in Figure 1.22. Consequently, the OSSOM method provides a versatile, safe, and reproducible route to stable ZnO NCs with tailored surface functionality.

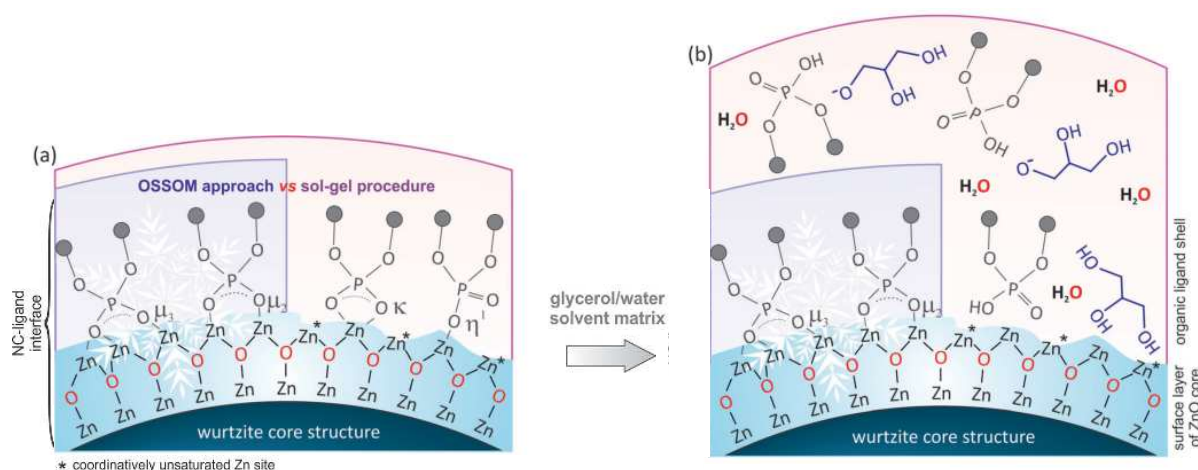


Figure 1.22: Organic ligand shell of organometallic and sol-gel NCs. **a**, Before and **b**, After wetting and aging with a glycerol-based matrix. Reproduced from ref.[82] with permission from Wiley-VCH.

Overall, while solution-phase organometallic approaches have enabled the synthesis of ZnO NCs with precise control over size, shape, and surface chemistry, their broader application is constrained by the need for solvents, multi-step purification to remove unbound ligands, and limited scalability. In this context, solid-state strategies emerge as an attractive alternative, offering solvent-free processing, simplified purification procedures, and inherent scalability. These advantages position solid-state methods as a promising direction for the efficient and sustainable production of high-quality ZnO NCs.

Recently, this methodology was further extended to enable the preparation of colloidal ZnO nanoplatelets (ZnO NPLs) with atomically precise thickness and facet-specific bimodal organic ligand binding, controlled by the amount of water introduced during the hydrolysis of benzamidine-stabilized alkylzinc precursors[190] (Figure 1.23). In this system, the benzamidine ligand plays a crucial role in nucleation and anisotropic growth by coordinating both polar and nonpolar ZnO facets, acting either as an X-type or an L-type donor ligand.



Figure 1.23: Schematic representation of one-pot self-supporting organometallic (OSSOM) procedure for the preparation of ZnO NPLs.

1.6 Solid-state synthesis of ZnO NCs from organometallic precursors

The solid-state synthesis of ZnO from organometallic precursors provides a versatile and efficient approach for producing high-quality ZnO nanomaterials. These precursors offer advantages over traditional precursors, such as inherent molecular preorganization, which ensures precise control and facilitates the formation of high-purity ZnO NCs. By simplifying synthesis pathways and enabling energy-efficient processes, organometallic precursors stand out as a superior choice. Controlled thermal decomposition (usually in the range 250–300 °C) and mechanochemical transformation further enhance the versatility of this method, making it highly effective for fabricating ZnO NCs with desired properties.

1.6.1 Thermal decomposition of Single-Source Precursors towards ZnO NCs

Traditional organometallic methods for synthesizing ZnO nanostructures typically involve the controlled hydrolysis or oxidation of an organozinc precursor, requiring separate sources of zinc and oxygen atoms. Alternatively, the single-source precursors (SSP) strategy employs well-defined precursors consisting of molecular building blocks that contain zinc and oxygen ions in the correct ratio, allowing for straightforward conversion into the desired material, which simplifies the synthesis process.

(i) Alkylzinc alkoxides [RZnOR']

Amongst the various precursors investigated, alkylzinc alkoxides [RZnOR'] with heterocubane structure (where $R' = \text{Me, Et, Bu, } i\text{Pr, } t\text{Bu}$) have received a vast amount of attention as precursors of ZnO nanostructures. Their [Zn₄O₄] heterocubane core has been regarded as a 'preorganized ZnO'. These [RZnOR']₄ compounds can be obtained by a reaction of alkylzinc compounds with corresponding alcohols[197]. Readily accessible alkylzinc alkoxides have long been utilized as SSPs for ZnO-based nanomaterials. These alkoxide precursors yield ZnO either in the solid-state through controlled thermolysis[198–202] under diverse atmospheric conditions, or in solution by reaction with water[203–207] (Figure 1.24). While the resultant ZnO materials have attracted significant interest due to their potential applications in catalysis, the multi-step pathways involved in their decomposition of these precursors to ZnO have remained largely underexplored for a long time.

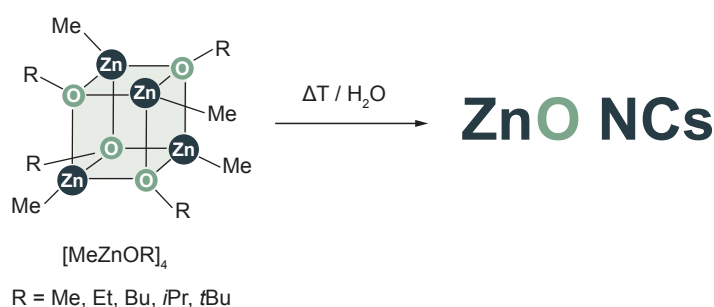


Figure 1.24: Schematic representation of the synthesis of nanometric ZnO using [RZnOR']₄-type precursors.

For example, the temperature treatment (over 250 °C) of the crystalline samples of [MeZnOiPr]₄ and [MeZnOtBu]₄ with various heating rates led to aggregates of nanoparticulate ZnO with a high density of oxygen vacancies[200]. Corresponding catalytic investigations demonstrated that oxygen vacancies in the ZnO lattice are very likely to represent the active sites in the hydrogenative conversion of CO to methanol.

Although extended efforts have been made to understand decomposition pathways, the decomposition mechanism of alkylzinc alkoxides [RZnOR'] has only

been partially understood until recently. A mechanism of gas-phase transformations was proposed in which β -hydrogen atom abstraction from the alkoxide by a zinc center forms a zinc hydride (Zn–H), as the initial step in the decomposition of heterocubane alkylzinc alkoxides[198, 208, 209] (Figure 1.25, path 1). Similar mechanism was also proposed for the solid state thermal decomposition of zinc, magnesium and aluminium alkoxides[210].

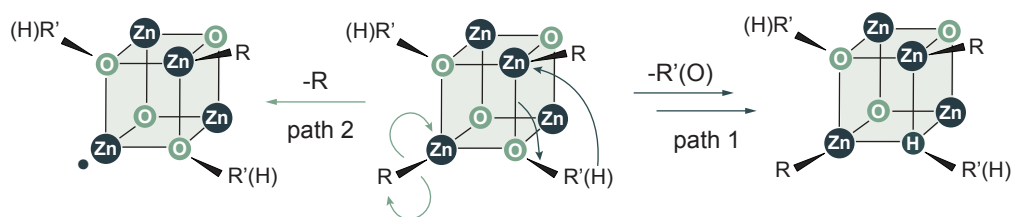


Figure 1.25: Proposed first steps in thermal decomposition of alkylzinc alkoxides to ZnO NCs: β -hydrogen atom abstraction from an alkoxide group (gas-phase, path 1) and homolytic cleavage of a R-Zn bond (solid-state, path 2). Reproduced from ref.[211] with permission from The Royal Society of Chemistry.

However, recent studies, employing a combination of in situ spectroscopic measurements and theoretical simulations, have uncovered a previously unconsidered pathway for the thermal decomposition mechanism of a model pre-organized alkylzinc alkoxide precursor, specifically $[t\text{BuZn}(\mu_3\text{-OtBu})_4]$ [211]. Lewiński and co-workers demonstrated that the structural evolution of the precursor begins with homolytic cleavage of the R-Zn bond, affording a transient radical species of the type $[\bullet\text{Zn}(\mu_3\text{-OR})][\text{RZn}(\mu_3\text{-OR})_3]$ (Figure 1.25, path 2 and 1.26). These intermediates exhibit gapless electronic states, which promote electron delocalization and facilitate radical transformations. Subsequent dimerization, followed by homolytic cleavage of the newly formed Zn-Zn bonds and the concomitant release of alkyl groups, ultimately leads to the formation of $(\text{ZnO})_n$ aggregates. In the final step, these aggregates reorganize into the thermodynamically stable wurtzite ZnO phase. The identification of such gapless-state intermediates not only clarifies the radical cascade preceding ZnO nucleation but may also be relevant to the origin of defect states, such as the singly charged oxygen vacancy (Vo^+), in ZnO nanocrystals.

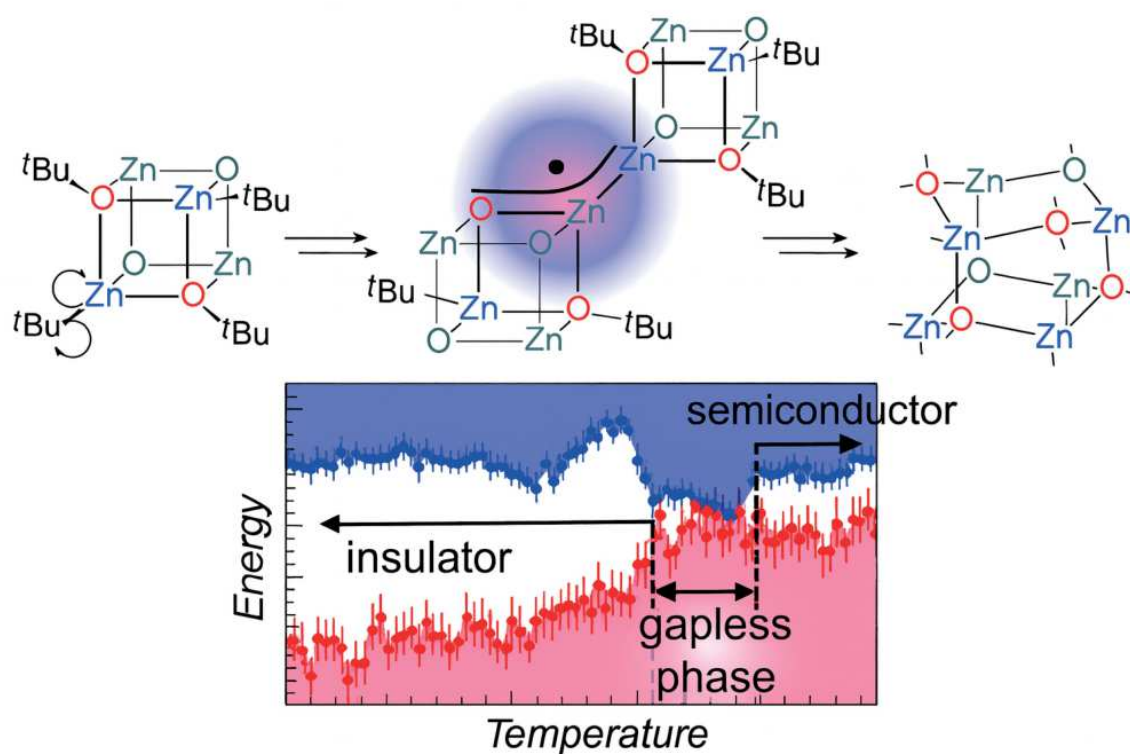


Figure 1.26: Schematic representation of the thermal decomposition pathway of $[t\text{BuZn}(\mu_3\text{-OtBu})]_4$. The process is initiated by homolytic R–Zn bond cleavage, giving rise to transient radical zinc oxo-alkoxide clusters. These intermediates, characterized by gapless electronic states, undergo dimerization followed by Zn–Zn bond cleavage and alkyl release, ultimately forming $(\text{ZnO})_n$ aggregates. The corresponding electronic structure evolution, illustrated in the lower panel, shows the transition from an insulating precursor through a gapless phase to the semiconducting ZnO state. Reproduced from ref.[211] with permission from The Royal Society of Chemistry.

These findings provide valuable insights into the thermal decomposition pathways of alkylzinc alkoxides, a critical step toward harnessing these precursors for the controlled synthesis of ZnO-based nanomaterials. However, both described pathways (path 1 and path 2, proceeding through zinc hydride or radical intermediates) usually yield nonstoichiometric, defect-rich ZnO with excess of Zn or O centres, often containing carbon residues. This highlights the importance of developing new solid-state precursor systems for ZnO in which the transformation proceeds without the need of thermal treatment as described later in this Thesis.

(ii) Alkylzinc hydroxides $[\text{RZnOH}]_n$

The isolation of an unprecedented alkylzinc hydroxide, $[t\text{BuZnOH}]_6$, with a drum-like hexameric structure marks a significant breakthrough. This compound serves

as an excellent example of a predesigned SSP that decomposes smoothly in one step at only 120 °C, yielding wurtzite ZnO NCs with an average size of 5 nm and no carbon impurities[91]. The low decomposition temperature of $[t\text{BuZnOH}]_6$ can be attributed to the presence of Zn-OH groups, which hydrolyze proton-reactive Zn-C bonds, leading to the evolution of an alkane. The drum-like structure of $[t\text{BuZnOH}]_6$ partially resembles a basic unit in wurtzite-type ZnO, suggesting that the breaking of three Zn=O bonds in the zinc hydroxide cluster forms a flexible quasi-molecule. This intermediate can easily stabilize into a ZnO sub-nanocluster (Figure 1.27). Further studies confirmed crucial role of Zn-OH species in the design of organozinc precursors of ZnO nanoparticles (*vide infra*).

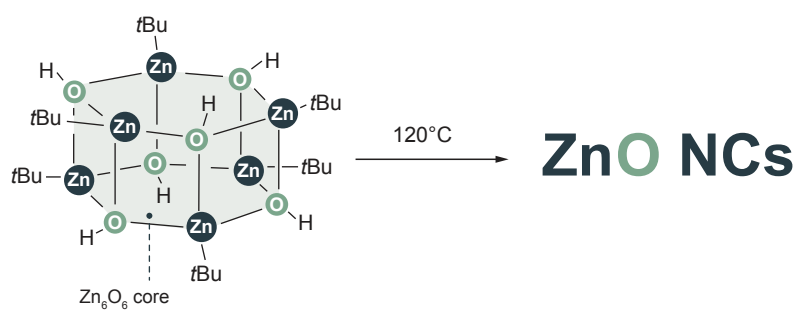


Figure 1.27: Thermal decomposition of predesigned alkylzinc hydroxide SSP towards ZnO NCs.

(iii) Mixed heterocubane alkyl(alkoxy)zincs

An intriguing hybrid of the previously described systems involves the mixing of alkylzinc alkoxides with alkylhydroxyzinc alkoxides. These mixed heterocubane alkyl(alkoxy)zincs were synthesized through a direct reaction between well-defined $[(t\text{BuZnOH})_6]$ (Figure 1.28a) and the $[t\text{BuZn}(\text{OtBu})_4]$ (Figure 1.28b) heterocubane in various molar ratios, leading to the isolation of new mixed cubane aggregates as crystalline solids in a high yield: $[(t\text{Bu})_4\text{Zn}_4(\mu_3\text{-OtBu})_3(\mu_3\text{-OH})]$, $[(t\text{Bu})_4\text{Zn}_4(\mu_3\text{-OtBu})_2(\mu_3\text{-OH})_2]$, $[(t\text{Bu})_4\text{Zn}_4(\mu_3\text{-OtBu})(\mu_3\text{-OH})_3]$ (Figure 1.28c). This reaction results in the formation of a new family of tert-butyl(tert-butoxy)zinc hydroxides, $[(t\text{Bu})_4\text{Zn}_4(\mu_3\text{-OtBu})_x(\mu_3\text{-OH})_{4-x}]$; ($x = 1\text{--}3$), which serve as model single-source precursors for ZnO NCs[92].

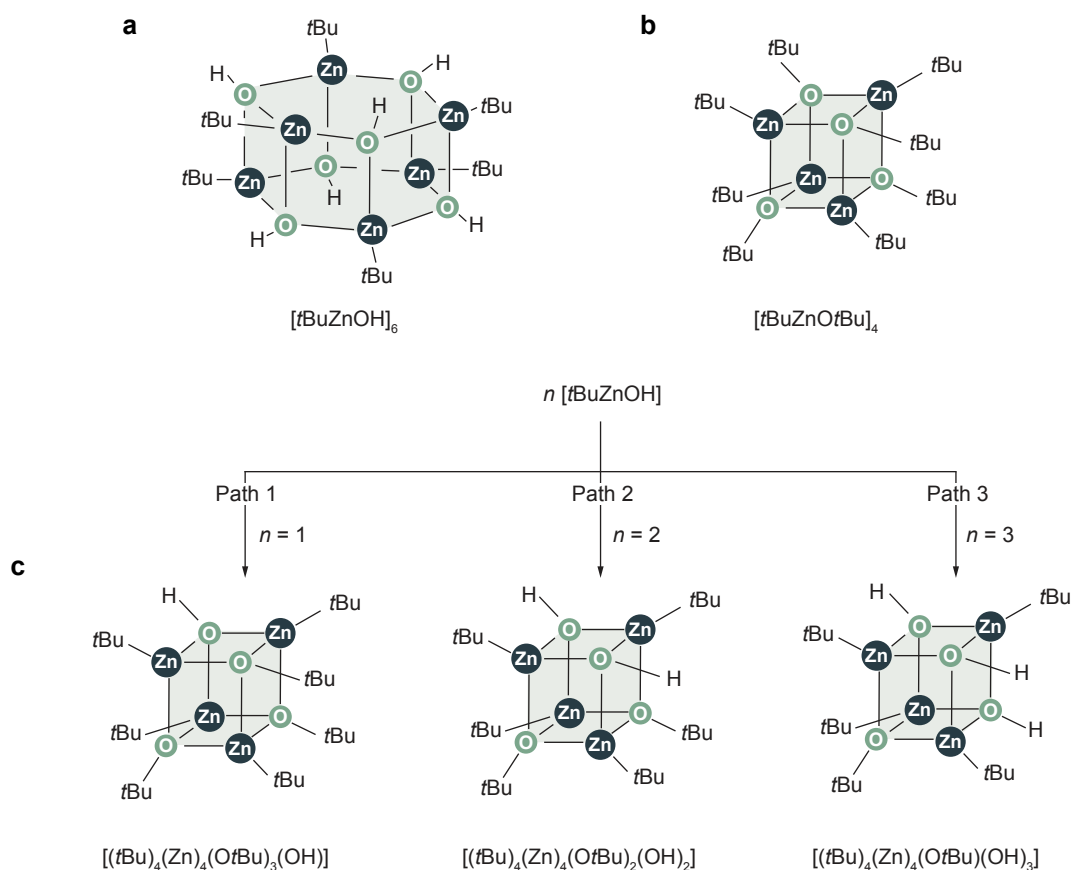


Figure 1.28: Molecular structures of the: **a**, Model alkylzinc alkoxide precursor. **b**, Model alkylhydroxyzinc alkoxide precursor. **c**, Mixed cubane alkyl(alkoxy)zinc hydroxides containing different amounts of alkoxy to hydroxy ligands.

The successful synthesis of the first series of well-defined mixed cubane alkyl(alkoxy)zinc hydroxides, enabled the investigation of the effect of hydroxy species in alkylzinc precursors on their thermolysis behavior toward ZnO nanostructures. The investigations revealed that the decomposition temperature of mixed alkyl(alkoxy)zinc hydroxides decreases in conjunction with an increasing amount of hydroxyl groups in their molecular structure (Figure 1.29). Moreover, while $[(\text{tBuZnOH})_6]$ decomposes in a simple single-step manner, the thermal decomposition of mixed alkyl(alkoxy)zinc hydroxides displayed a more complicated pattern. Therefore, the Zn-OH groups appear to be a desirable structural feature for designing SSPs that act as a source of protons required to initiate the decomposition process and decrease the decomposition temperature of crystalline precursors.

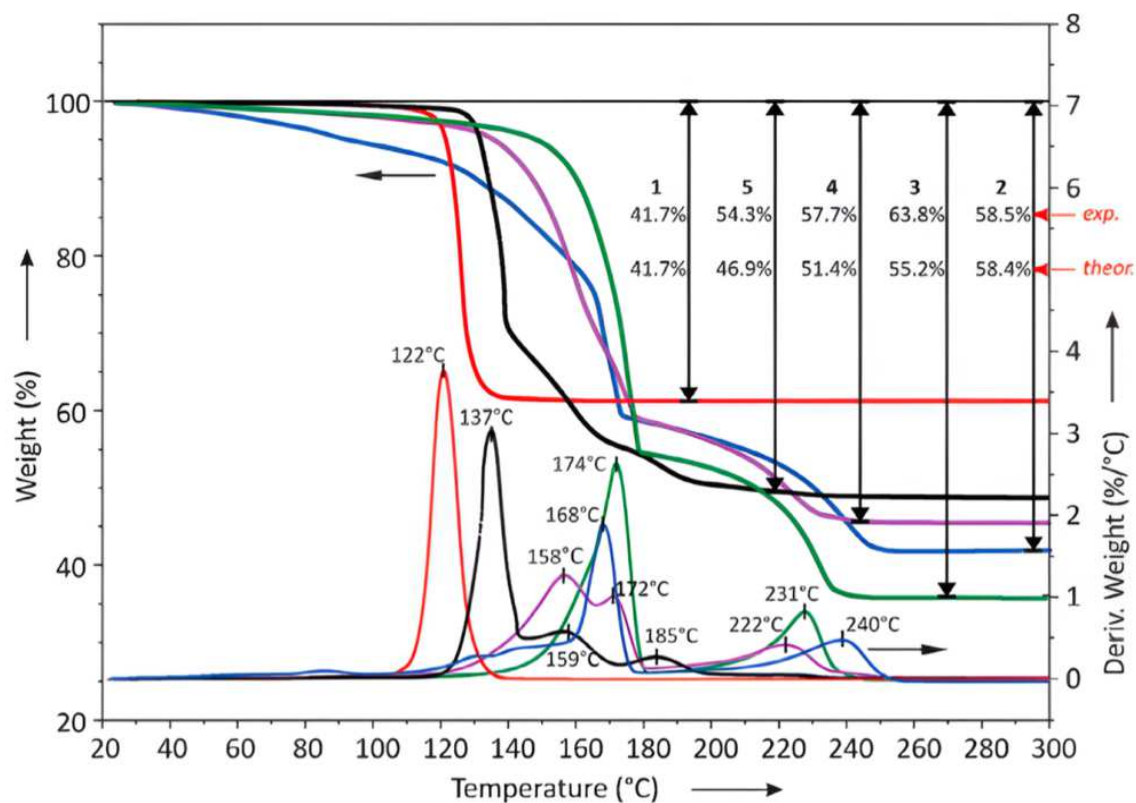


Figure 1.29: Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) traces showing the decomposition of mixed cubane alkyl(alkoxy)zinc hydroxides in an inert (Ar) atmosphere. Reproduced from ref.[92] with permission from Wiley-VCH.

1.6.2 Mechanochemical transformation of a predesigned organozinc precursors towards ZnO NCs

The first successful example of obtaining semiconductor nanostructures through mechanochemical strategy using molecular precursors involved the previously mentioned hexameric zinc hydroxide $[t\text{BuZn}(\mu\text{-OH})]_6$ complex. It was assumed that the presence of 'pre-organized ZnO' groups in the form of the Zn_6O_6 core and hydroxyl groups as a source of protons in the structure would enable mechanochemical transformation into ZnO NCs. Grinding of predesigned alkylzinc hydroxide complex for 20 min at room temperature led to straightforward transformation to wurtzite ZnO NCs with a mean diameter of approximately 3.5 nm (Figure 1.30)[212]. The resulting white powder emitted yellow luminescence under UV lamp.

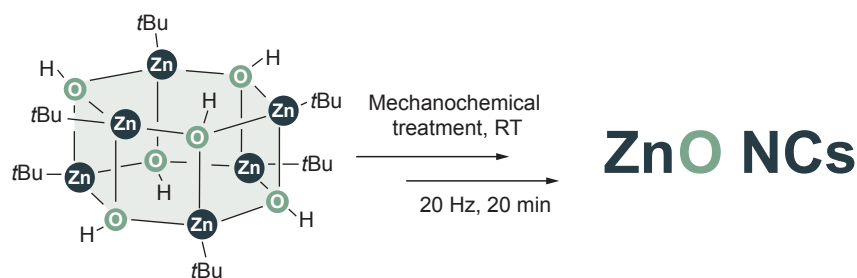


Figure 1.30: Schematic representation of mechanochemical transformation of $[t\text{BuZn}(\mu\text{-OH})]_6$ towards ZnO NCs.

Mechanochemical synthesis was applied to a rapid mild-conditions transformation of a predesigned molecular oxo-zinc precursor to ligand-coated ZnO NCs[93]. In this process, the oxo-zinc benzamidate complex, $[\text{Zn}_4(\mu_4\text{-O})(\text{NHOCPh})_6]$, was milled for about 15 min in the presence of water (Figure 1.31). The resulting pristine ZnO NCs were coated by organic ligand, which enabled further post-synthetic modification by mechanochemical capping with β -cyclodextrin, thereby enhancing their dispersion stability in both aqueous and organic environments.

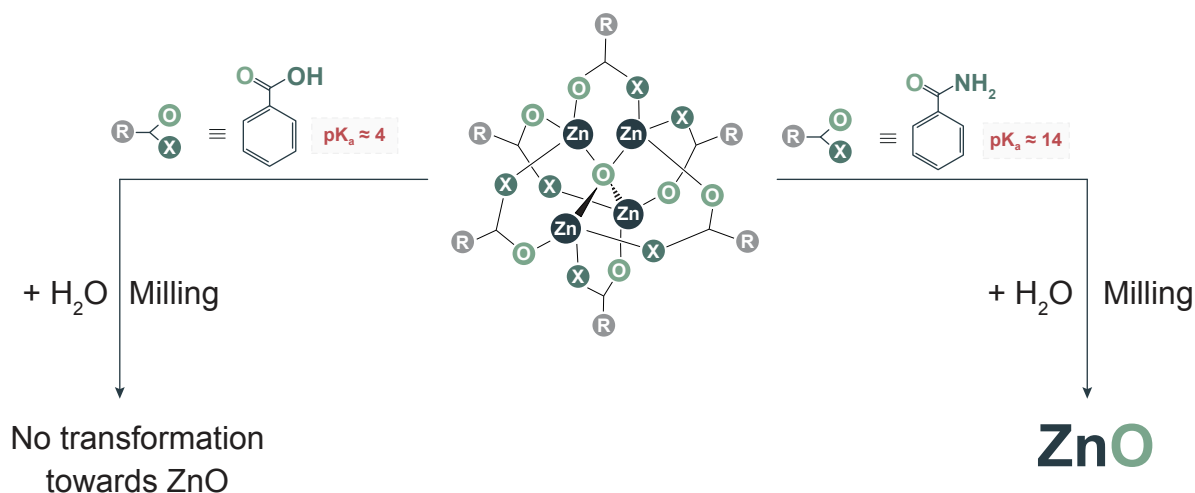


Figure 1.31: Mechanochemical bottom-up approach for the synthesis and modification of ZnO NCs using a predesigned zinc-oxo cluster.

The further advancement of the previously described mechanochemical strategy led to the development of novel organozinc ureate complexes incorporat-

ing N-phenylureate or N,N-dicyclohexylureate ligands[94]. These alkylzinc ureate compounds proved to be effective self-supporting precursors in the mechanochemical synthesis of ureate ligand-coated ZnO NCs. The resulting ZnO-urea NCs differ significantly from previously reported amide-coated ZnO NCs in terms of both core size and the nature of the organic–inorganic interface. These preliminary studies suggest that size-controlled mechanochemical synthesis of ZnO NCs is feasible.

Despite extensive research on the development of solid-state precursors, no system has yet been identified that decomposes into ZnO without the application of thermal or mechanical energy. This represents a critical limitation in existing approaches and emphasizes the need for innovative solutions to achieve energy-independent decomposition processes for ZnO synthesis. Such advancements could open new pathways for more sustainable and efficient production methods, with broad implications for nanomaterial fabrication and industrial applications.

OBJECTIVE AND OUTLINE OF THE THESIS

The introduction section (Chapter 1) of this dissertation presents recent progress in the synthetic strategies of semiconductor nanocrystals, with a particular focus on molecular organozinc precursors and their solid-state transformations to nanocrystalline ZnO. Although heat and mechanical treatment have been successfully applied to transform solid-state precursors into various nanoscale materials, the mild and stimulus-free formation of semiconductor nanocrystals, such as quantum dots, remains largely unexplored. These limitations are primarily due to the intrinsic restriction of mass transport in the solid-state, a fundamental barrier that has so far not been overcome through rational precursor design. This raises the important question of whether it is possible to rationally design solid-state molecular precursors that can overcome the limitations of mass transport, a concept distinct from currently known nanoparticle precursor systems. Inspiration can be drawn from nature, where nanoscale materials form under moderate temperatures through chemical weathering driven by water, oxygen, and carbon dioxide, the key factors in the breakdown of rocks and minerals[148–150]. Although the timescale of these chemical processes is impractical from a laboratory perspective, they provide an important hint for designing artificial NC precursor systems, specifically their reactivity towards hydrolytic and/or oxidative species[2]. Such approach could pave the way for solvent-free, room-temperature synthesis of semiconductors, while potentially also revealing new intriguing growth and self-organization pathways of NCs in the solid state.

The main aim of this dissertation is to design and develop new organozinc precursors of ZnO NCs, including a well-defined solid-state system for the synthesis of ZnO nanostructures under ambient conditions, i.e., without the input of energy through thermal treatment or mechanical forces. An integral part of this objective is the comprehensive investigation of the solid-state transformation processes using single crystals of a selected model organozinc precursor, as well as the nucleation, growth, and self-organization of NCs. Detailed studies of the reactivity of model organozinc systems in solution are essential to reveal the fundamental differences between solid-state and solution-phase transformations. These complementary studies will aim to identify reaction intermediates and provide molecular-level insights into ZnO formation in the system where the precursor molecules are well solvated, thereby enhancing the understanding gained from solid-state investigations and offering a more complete mechanistic picture. Understanding the reactivity of organozinc precursors in the solid-state may potentially enable their application in the synthesis of semiconductor materials beyond zinc oxide, i.e., other zinc chalcogenides. This work, therefore, bridges the gap between molecular precursor design and solid-state chemistry, demonstrating how rationally engineered organozinc systems can unlock new pathways for the controlled, mild, and sustainable synthesis of ZnO NCs.

The following chapters present the proof of concept and original results and discussion, covering the design and synthesis of the model precursor and its solid-state transformations to ZnO nanocrystals (Chapter 3), mechanistic investigations at the molecular and nanoscale level (Chapter 4), further developments toward semiconductor mesoporous systems (Chapter 5) and other semiconductor nanomaterials (Chapter 6), as well as complementary studies of the reactivity of the model precursor in solution (Chapter 7). The results and discussion section is followed by the general conclusions and perspectives (Chapter 8), while the final chapter (Chapter 9) contains the detailed experimental procedures together with supplementary data.

SOLID-STATE ORGANOMETALLIC MOLECULAR SYSTEM FOR THE SYNTHESIS OF SEMICONDUCTOR NANOCRYSTALS

Designing and conducting solid-state reactions under mild conditions is both a major challenge at the forefront of (nano)materials synthesis and a key objective in the development of sustainable strategies. Solid-state chemistry, despite numerous advances in preparation of coordination complexes and nanocrystals through thermal treatment or mechanical force, is still often described as a “black box”[103], typically explored through systematic and extensive empirical iteration, requiring substantial experimental expertise[111]. To date, well-defined systems capable of transforming crystalline precursors into inorganic NCs under ambient conditions are still lacking. Inspiration can be drawn from nature, where nanoscale materials form under moderate temperatures through chemical weathering driven by water, oxygen, and carbon dioxide, the key factors in the breakdown of rocks and minerals[148–150]. Although natural timescales are impractically long for laboratory synthesis, they highlight the potential of hydrolytic and oxidative processes to drive solid-state transformations in a solvent-free manner[2].

This important gap motivates the present work, which aims to demonstrate how predesigned crystalline organozinc precursors can be transformed into quantum-sized semiconductor NCs under ambient conditions, thereby establishing a new pathway in solid-state nanochemistry.

3.1 Design, synthesis, and characterization of a molecular precursor for solid-state nanocrystal formation

The rational choice of molecular precursors is a major consideration in the solid-state synthesis of NCs. However, the development of such precursors that can undergo transformations under mild conditions (i.e., room temperature) is hampered by a limited insight into general principles allowing their rational design through selection of suitable structures and functionalities. As the formation of a new nanocrystalline solid phase occurs through nucleation and growth processes, that are driven by a complex interplay of bulk, surface, and interface thermodynamics, a subtle balance between structure and reactivity of a predesigned NC precursor needs to be considered[107].

In particular, an optimal solid-state precursor for NCs, which is susceptible to water-mediated hydrolysis processes, should possess specific characteristics. First, it is expected to exhibit good thermal stability to endure the synthesis conditions. This stability would prevent premature decomposition or unwanted reactions during the transformation process. Additionally, the precursor needs to display moderate reactivity towards components present in the surrounding air to prevent side reactions or contamination. Furthermore, the synthetic environment in which the transformation occurs plays a critical role in the successful formation of NCs. This environment should facilitate efficient mass transport to enable the precursor's transformation and the subsequent nucleation and growth of emerging NCs.

3.1.1 Design principles of an organozinc molecular precursor

In the parent group, research has long focused on the controlled transformation of alkylzinc derivatives into quantum-sized ZnO NCs in solution through exposure to air. A broad library of organic ligands has been successfully employed, including carboxylates[191–193], aminoalkoxides[194], phosphates[82], phosphinates[195], and benzamidinates[190]. These findings suggested that amidate-type

ligands could play a crucial role in directing precursor reactivity; however, the chemistry of amides in this context remains insufficiently explored. Building on these insights, [(amidate)ZnR]_n-type molecular clusters were selected as representative precursors for solid-state transformations. The synthetic approach presented in this dissertation relies on organometallic [(X)ZnR]_n-type molecular clusters (where X = monoanionic organic ligand), featuring reactive Zn-C and Zn-N bonds prone to water-mediated hydrolytic processes.

Benzamide (BA-H) was chosen as the model ligand because it combines relatively high basicity with a rigid and planar aromatic structure that promotes ordered crystal packing, and favorable intermolecular interactions such as hydrogen bonding and π - π stacking. These features may provide a defined environment that enables the growth of well-ordered single crystals, in contrast to aliphatic amides, typically do not crystallize, yielding only powders or disordered solids. Therefore, a well-defined single-crystal system incorporating the tetranuclear ethylzinc benzamide cluster, [(BA)ZnEt]₄, was selected as a model precursor to investigate in detail the solid-state transformation towards semiconductor nanocrystals. This cluster “encodes” functional features in its molecular structure, that is (i) reactive Zn-carbon bonds and (ii) readily hydrolysable Zn-coordinated ligand (here deprotonated benzamide - BA, pK_a = 14) both exhibiting relatively weak acidity and acting as a Brønsted bases[213–215] as shown in Figure 3.1. The incorporation of these functionalities is critical as such organometallic precursor can undergo efficient transformations in the contact with water traces, i.e., moisture from air, acting as an acid and facilitating hydrolysis of both Zn-C and Zn-BA bonds. In such a system, the hydrolysable BA ligand may act as a source of supramolecular organic matrix in the form of hydrolyzed protonated BA-H. In combination with H₂O molecules, this matrix can potentially (i) support the mass-transport of reactants and (ii) kinetically control the nucleation and growth of the NCs formed during the described processes. The proof of concept is shown in Figure 3.1.

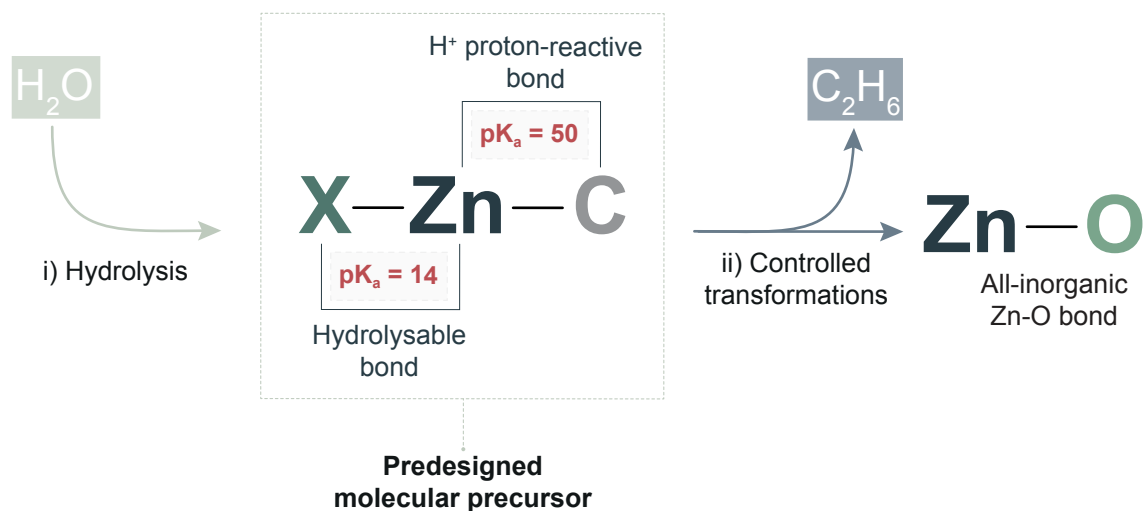


Figure 3.1: Design principles of the molecular single-crystal precursor for solid-state transformation towards semiconductor NCs. The use of these functionalities with high pK_a values is critical as such precursor should undergo i) hydrolysis in the contact with water traces, such as moisture from the air, following by ii) water-mediate hydrolysis processes effectively leading to ZnO NCs.

3.1.2 Synthesis and characterization of the molecular single-crystal precursor, $[(\text{BA})\text{ZnEt}]_4$

Single crystals of an ethylzinc amide derivative were prepared as a model system for investigating solid-state transformations towards ZnO NCs. The precursor was by an equimolar reaction between diethyl zinc (Et_2Zn) and BA-H, as illustrated below in Figure 3.2. The solution of BA-H in dichloromethane (DCM) was cooled to -78°C and Et_2Zn was added dropwise. The mixture was allowed to warm up spontaneously to room temperature and stirred for an additional 24 hours. The reaction product was then isolated quantitatively from the post-reaction mixture at -24°C on the gram scale as colorless single crystals (Figure 3.3).

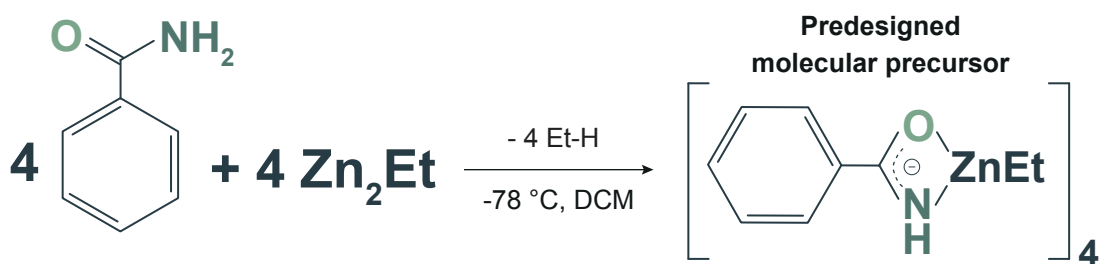


Figure 3.2: Schematic representation of an organometallic procedure for the preparation of a model molecular single-crystal precursor—[(BA)ZnEt]₄.

3.1.2.1 Optical microscopy studies of the [(BA)ZnEt]₄ precursor

Optical microscopy was employed to capture images of the resultant precursor single-crystals stored within an inert atmosphere (Figure 3.3). These images reveal that the crystals are transparent, exhibit a rectangular shape and sizes in a range of 0.3 and 0.6 mm.

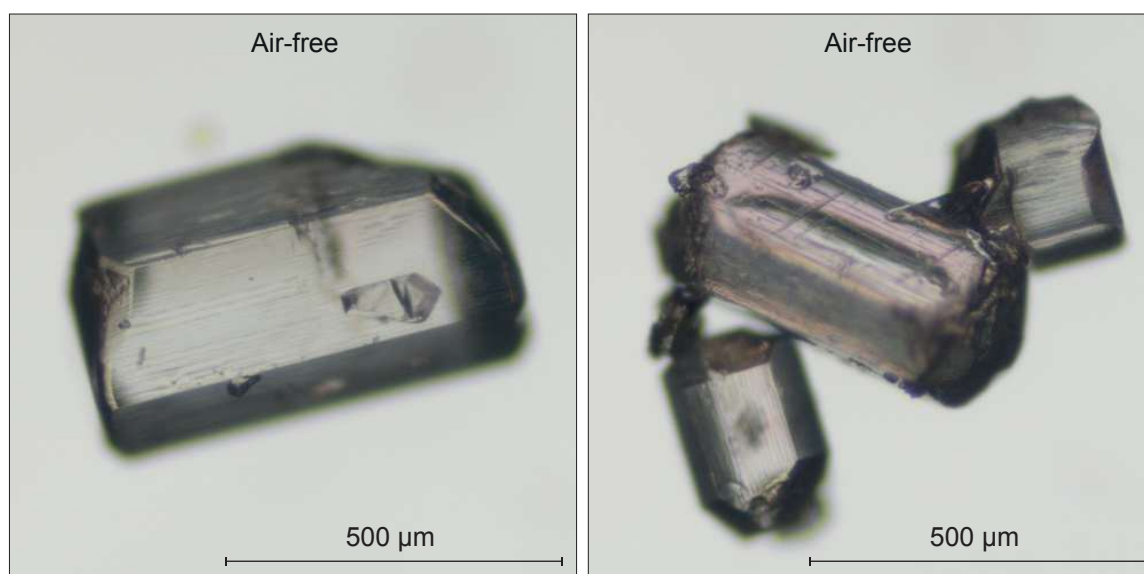


Figure 3.3: Representative optical microscopy images of the SC precursor stored under an inert atmosphere.

3.1.2.2 Molecular and crystal structure characterization of the [(BA)ZnEt]₄ precursor

The molecular and crystal structure of the model single-crystal precursor was confirmed by single-crystal and powder X-ray diffraction (SC-XRD and PXRD,

respectively). Ethylzinc derivatives of BA-H, [(BA)ZnEt] crystalize in the space group P-1 as tetrameric complexes, [(BA)ZnEt]₄, consisting of four Zn-Et moieties which are arranged in a quasi-tetrahedral geometry with a slightly distorted Zn₄O₄ heterocubane structure (Figure 3.4). The Zn centers occupy the four corners of a distorted tetrahedron, connected by four deprotonated amide ligands in such a way that the amide oxygen center bridges-up two different Zn atoms, while the amide nitrogen atom is coordinated to a third Zn center (for selected geometrical parameters, see Table 9.4 in the Experimental Section).

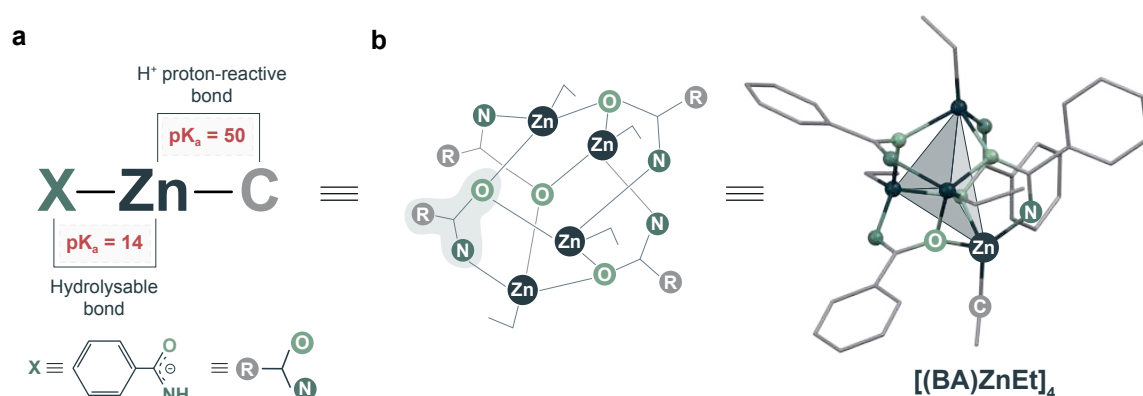


Figure 3.4: Molecular structure of the predesigned solid-state single-crystal precursor. **a**, Design principles of the solid-state precursors for weathering and schematic representation of amidate ligands used in the presented studies. **b**, Molecular structure of the [(BA)ZnEt]₄ precursor.

Non-specific noncovalent interactions-driven self-assembly of the tetranuclear clusters leads to a close packed non-porous crystal lattice with no solvent molecules entrapped (Figure 3.5a). Importantly, the Zn-C and Zn-N bonds are positioned at the periphery of the central cluster (tetrahedron corners) located within a nest-like discrete microcavities surrounded by phenyl groups from the BA ligands, being exposed to reagents, i.e., small molecule hydrolytic agents that potentially can initiate hydrolysis (Figure 3.5b). The spatial arrangement of the [(BA)ZnEt]₄ clusters in the crystal lattice ensures uniform exposure of these reactive N-Zn-C sites across all three crystal facets, suggesting isotropic reactivity in the solid state. Hirshfeld surface analysis of the crystal structure reveals the distribution and nature of intermolecular interactions[216, 217], highlighting the crucial role of noncovalent forces in stabilizing the self-assembly of the [(BA)ZnEt]₄ clusters. This analysis emphasizes

the arrangement of reactive chemical sites within discrete microcavities, which are key to understanding the $[(BA)ZnEt]_4$ cluster solid-state reactivity. The mapping of the Hirshfeld surface provides detailed insights into various interactions, including hydrogen bonding, van der Waals forces, and π - π stacking, while also pinpointing regions of high electron density that may serve as hotspots for chemical reactivity. The visualization in Figure 3.5b further supports this, showing how the electron-dense micropockets indicate potential sites for hydrolytic reactions. The exposure of these reactive regions across the crystal lattice offers valuable insight into the clusters' solid-state behavior and highlights how the spatial arrangement of these chemical entities facilitates efficient hydrolysis.

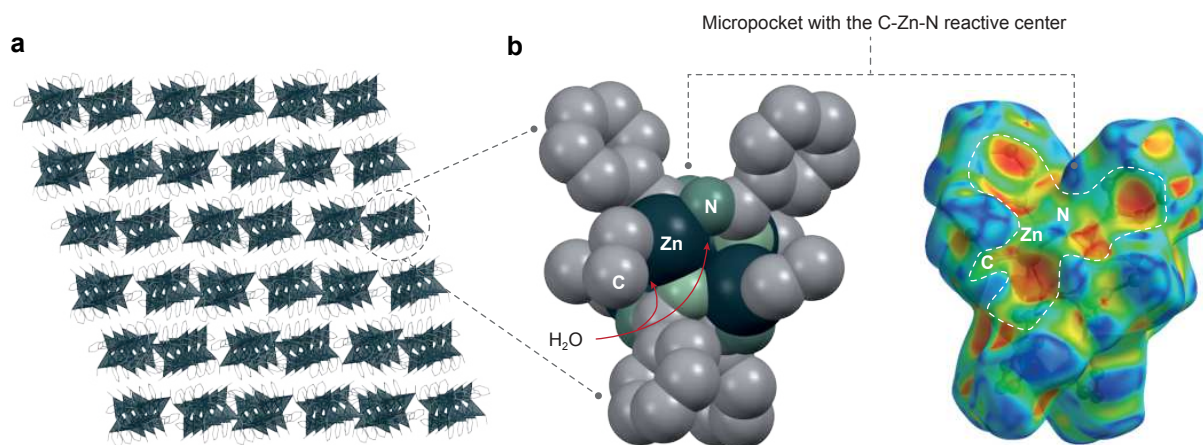


Figure 3.5: Crystal structure of the predesigned solid-state single-crystal precursor. **a**, Crystal structure of the $[(BA)ZnEt]_4$ precursor. **b**, Microcavities incorporating reactive N-Zn-C chemical entities; (left) space filling mode, (right) calculated Hirshfeld surface mapped with shape index. Red color indicates concave regions and blue color indicates convex regions. Hydrogen atoms are omitted for clarity.

The PXRD experiment confirms that the model precursor sample has a crystalline structure that is in good agreement with the simulated pattern (Figure 3.6). The matching of peak positions and the absence of additional peaks in the experimental diffractogram indicate that the material is homogeneous and free from contamination.

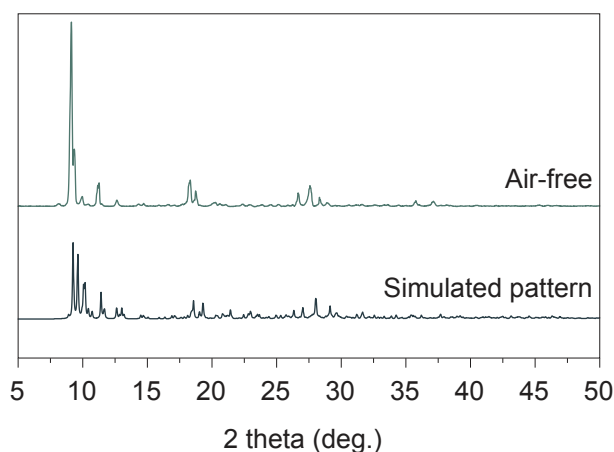


Figure 3.6: PXRD patterns for the $[(BA)ZnEt]_4$ single-crystals under air-free atmosphere and a simulated pattern based on SC-XRD measurements. The close match between the two patterns confirms the initial crystalline structure of the precursor material.

3.1.2.3 Spectroscopic characterization of the $[(BA)ZnEt]_4$ precursor

The $[(BA)ZnEt]_4$ precursor was further comprehensively analyzed using a combination of ^{13}C and ^{15}N cross-polarization magic angle spinning (CP MAS) NMR, and Fourier transform infrared (FTIR) spectroscopy techniques. These complementary solid-state methods provide detailed insights into the bonding interactions between the BA ligand and the Zn centers within the $[(BA)ZnEt]_4$ complex.

The CP MAS ^{13}C NMR spectrum of the $[(BA)ZnEt]_4$ is presented in Figure 3.7. Signals observed at 175 ppm correspond to the carbonyl carbon of the deprotonated BA ligand while signals at 129 ppm are characteristic of aromatic BA groups. Signals at 13.4 ppm and -0.82 ppm are assigned to the ethyl group coordinated to Zn centers within the complex. The CP MAS ^{15}N NMR spectrum (Figure 3.7) displays a sharp signal at approximately -225 ppm, indicative of the nitrogen atom of the deprotonated BA amide group coordinated to zinc center. The presence of sharp peaks in both solid-state spectra is characteristic for highly crystalline samples with well-ordered crystal structure.

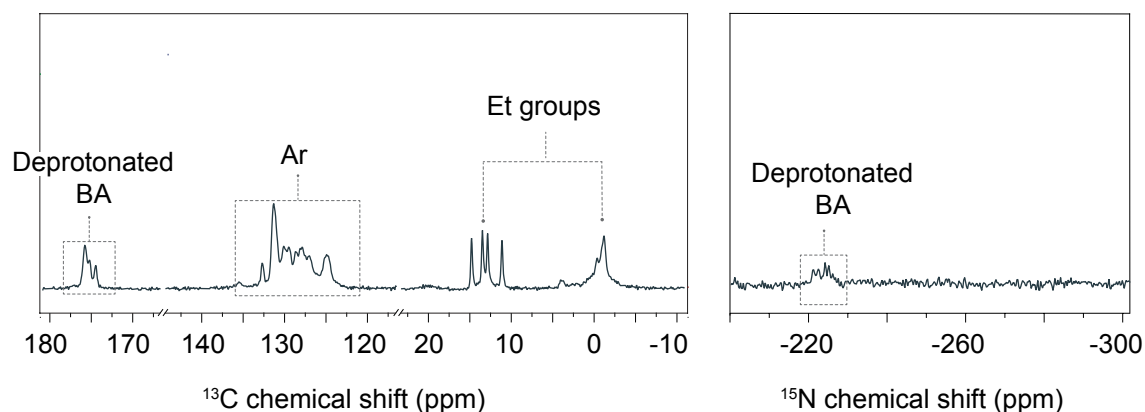


Figure 3.7: Solid state CP MAS ^{13}C and ^{15}N NMR spectra of $[(\text{BA})\text{ZnEt}]_4$ complex at room temperature.

To gain further insights into the nature of the chemical bond between the deprotonated BA ligands and Zn centers, FTIR spectra of the protonated BA-H ligand and the $[(\text{BA})\text{ZnEt}]_4$ precursor were compared and presented in (Figure 3.8). The spectrum of benzamide reveals several key absorption bands characteristic of its molecular structure. The broad absorption between $3200\text{--}3400\text{ cm}^{-1}$ corresponds to the N-H stretching vibration of the amide group ($\text{C}(\text{O})\text{--NH}_2$), while the strong band near 1650 cm^{-1} is indicative of the carbonyl ($\text{C}=\text{O}$) stretch, a signature feature of the amide functional group. The band around $1550\text{--}1600\text{ cm}^{-1}$, corresponding to N-H bending coupled with C-N stretching $1400\text{--}1450\text{ cm}^{-1}$.

Significant shifts in the $\text{C}=\text{O}$ stretch and N-H stretching bands of the BA-H ligand are observed in $[(\text{BA})\text{ZnEt}]_4$ complex. Specifically, the shift of the $\text{C}=\text{O}$ stretching frequency (1650 cm^{-1}) to lower wavenumbers (1590 cm^{-1}) implies interaction between the carbonyl oxygen and the zinc center. Additionally, changes in the N-H stretching region ($3200\text{--}3400\text{ cm}^{-1}$) and its shift to $3260\text{--}3280\text{ cm}^{-1}$ as well as presence of a band assigned to the asymmetric Zn-O vibrations at 488 cm^{-1} indicating that the benzamide ligand is coordinated to the metal center as corroborated by crystallographic analysis. Moreover, the presence of an N-H in-plane bending frequency at 1562 cm^{-1} , alongside the absence of the NH_2 scissoring band typical of free benzamide (1622 cm^{-1}), confirm that there are no uncoordinated benzamide ligands or impurities in the sample.

The strong bands observed at 1677 cm^{-1} and 1454 cm^{-1} are attributed to C=O and C-N stretching vibrations, respectively, and provide further support for the coordination of benzamide.

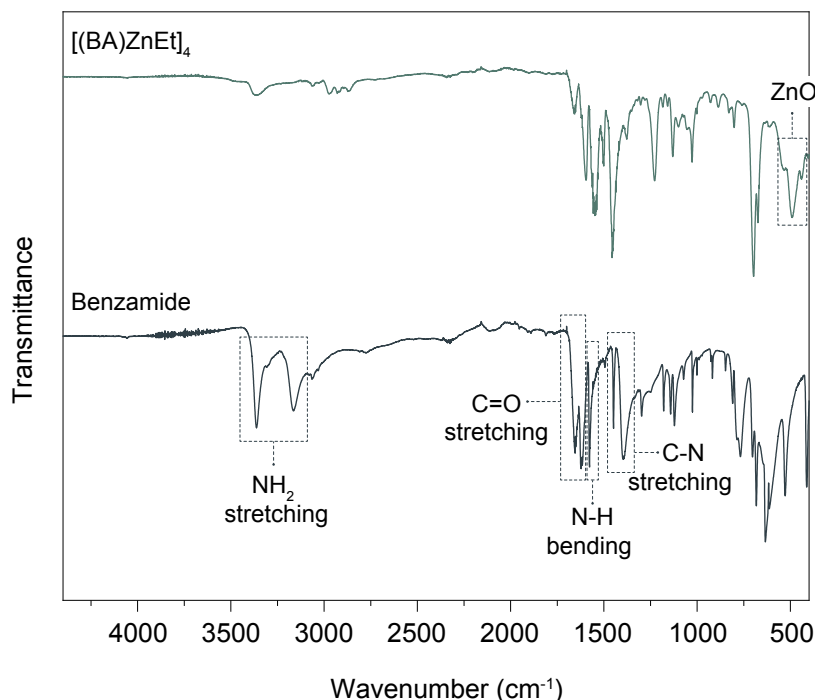


Figure 3.8: FTIR-ATR spectra of the $[(BA)ZnEt]_4$ precursor and free BA-H ligand.

These observations indicate a bidentate coordination mode, where both the carbonyl oxygen and the nitrogen of the deprotonated benzamide ligand are coordinating to the zinc center, reflected in the distinctive shifts and new bands in the FTIR spectrum of the $[(BA)ZnEt]_4$ precursor. In a typical bidentate coordination mode, the ligand uses two different atoms (in this case, the oxygen and nitrogen) to bind to the metal center. Bidentate coordination is common for amides, particularly when deprotonation occurs, as the lone pairs on both the oxygen and nitrogen can be used for bonding with the metal[218].

3.1.2.4 Thermogravimetric analysis of the $[(BA)ZnEt]_4$ precursor

To demonstrate the thermal stability of the $[(BA)ZnEt]_4$ precursor, the thermogravimetric analysis (TGA) was conducted under an argon atmosphere. The sample was heated from $20\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ at a constant rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. As shown in

Figure 3.9, the TGA profile reveals two main decomposition steps with a maximum decomposition rate at approximately 150 °C and 235 °C. The decomposition step at approximately 150 °C corresponds to the release of ethane driven by decomposition of Et-Zn units (weight losses of 14.9%). The decomposition step at approximately 235 °C corresponds to sublimation and/or decomposition of benzamide (weight losses of 55.8%).

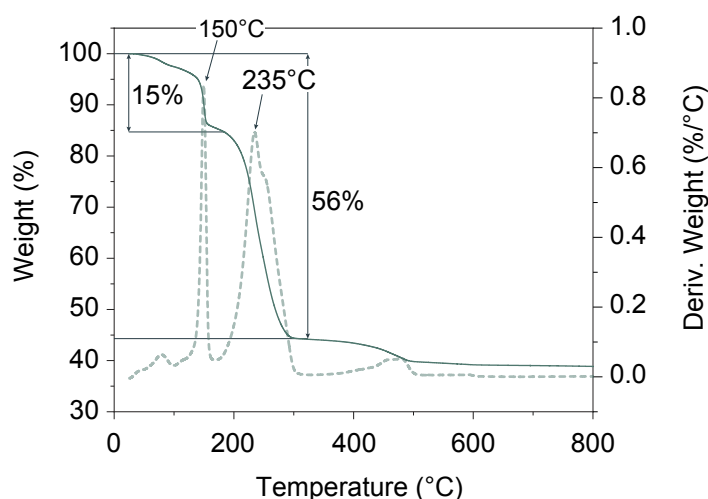


Figure 3.9: Thermogravimetric analysis (TGA and DTG) of the $[(BA)ZnEt]_4$ precursor in an inert (Ar) atmosphere.

The good thermal stability of the $[(BA)ZnEt]_4$ precursor, combined with the presence of R-Zn and Zn-X units that are susceptible to water-mediated hydrolytic processes, makes it a promising candidate for further studies on solid-state transformation processes.

3.2 Solid-state transformations of the organozinc precursor to ZnO NCs with preserving the crystal shape integrity

Solid-state precursor transformation into the solid-state final product offers a route to avoid the use of solvents and costly purification methods, and to have, in general, more efficient material production. However, solid-state chemical reactions are usually impeded by relatively low diffusion rate at low temperatures[88, 90, 99]. The introduction of a single-crystal host matrix prone to water-mediated hydrolytic

process in contact with air components could possibly overcome this limitation, allowing efficient transformations in ambient temperatures.

To test the hypothesis—that the crystalline network, consisting of both reactive zinc-carbon (Zn-C) and zinc-nitrogen (Zn-N) bonds, confined within a single-crystal (SC) lattice prone to water-mediated hydrolytic processes, can undergo efficient transformations to nanocrystalline oxides in mild conditions—single crystals of the $[(BA)ZnEt]_4$ were exposed to humid air at room temperature. On account of these highlighted chemical properties, the $[(BA)ZnEt]_4$ complex was named Hydrolysable Organozinc PrEcursor (HOPE). An overview of single-crystal to nanocrystals transformations is shown in Figure 3.10.

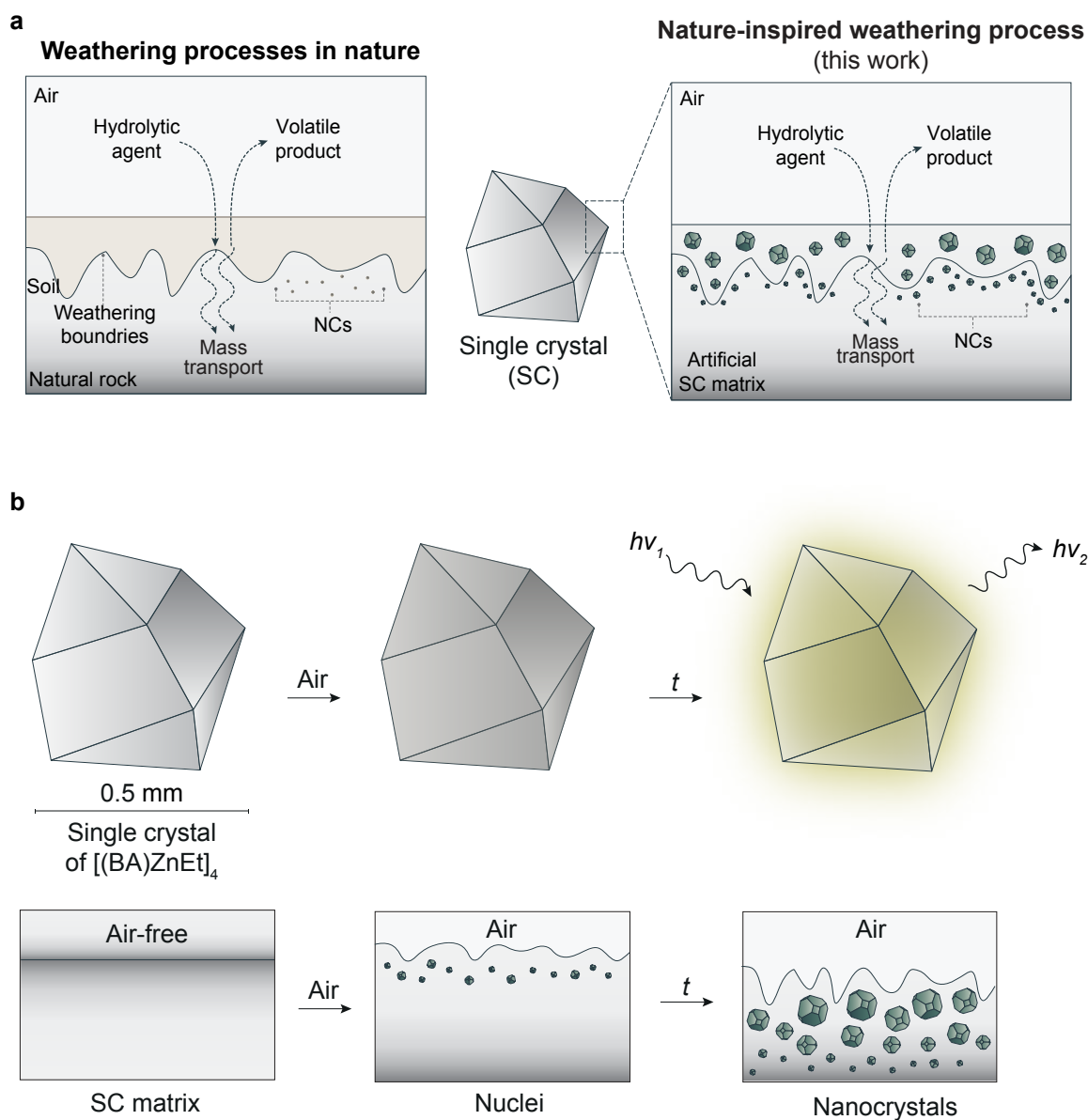


Figure 3.10: Schematic representation of: **a**, Weathering processes in nature (left) and nature-inspired weathering processes of molecular single-crystals described in this work (right). **b**, Nature-inspired weathering processes in the single-crystal HOPE system ($[(BA)ZnEt]_4$) leading to the formation of ZnO NCs.

3.2.1 Characterization of the resultant nanocrystalline material upon air exposure

Upon exposure to air at room temperature, HOPE single-crystals undergo gradual transformations over a period of 96 hours, ultimately forming ZnO NCs while preserving the integrity of the crystal shape. The PXRD patterns of the gently grinded

material obtained after 96 hours of air exposure, revealed broad reflections within the 2θ range of 32° - 38° , which can be indexed to the (100), (002), and (101) planes of the hexagonal wurtzite ZnO structure (Figure 3.11). Sharp peaks observed at lower values of 2θ (5° - 30°) are consistent with the crystalline phase of benzamide (BA-H). The complete disappearance of the distinct diffraction peaks characteristic of the pristine HOPE SCs confirmed efficient transformation of the starting material into ZnO NCs and BA-H.

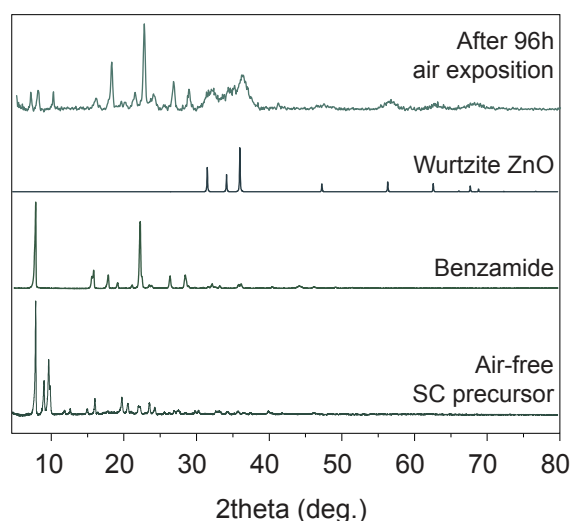


Figure 3.11: The PXRD pattern of the HOPE precursor and resultant material based on ZnO NCs.

The average size of the ZnO crystalline domains was estimated using the Scherrer equation, applied to the full width at half maximum (FWHM) of the (101) reflection of wurtzite ZnO (see Experimental section for more details). This analysis yielded an average crystalline domain size of approximately 4.65 nm. High-resolution transmission electron microscopy (HRTEM) micrographs (Figure 3.12) revealed a network of interconnected, nearly spherical NCs with an average diameter of 4.6 ± 0.6 nm; consistent with the PXRD analysis. The measured interplanar distances (d -values) of $2.47 \text{ \AA}$ were consistent with the (101) planes of wurtzite ZnO, further confirming the crystalline nature of the nanostructures.

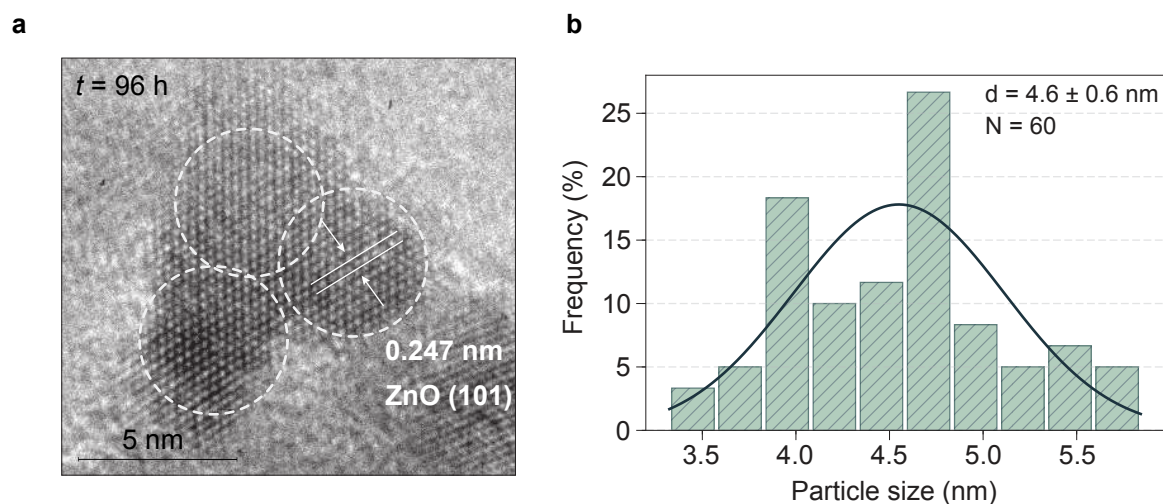


Figure 3.12: Characterization of the resultant ZnO NCs. **a**, The representative HRTEM image of the final ZnO NCs with average size of 4.6 ± 0.6 nm. **b**, Particle size distribution histogram.

Optical characterization of the resultant material under UV irradiation ($\lambda = 365$ nm) revealed a strong yellow luminescence centered at 530 nm (Figure 3.13). Such emission is characteristic of ZnO NC surface defect states, typically associated with surface structural vacancies[72, 219, 220] and are strongly related to the synthesis method, structural defects and surface chemistry.

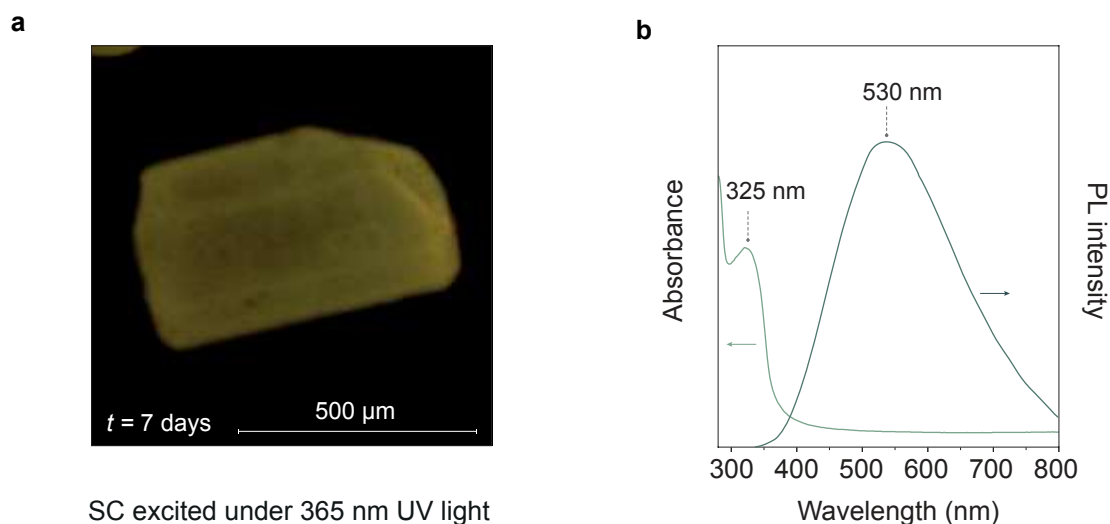


Figure 3.13: Characterization of the resultant ZnO NCs. **a**, Optical microscope image of SC after transformation, photoexcited with 365 nm wavelength. **b**, UV-Vis and PL spectra of ZnO NCs obtained by air exposure of HOPE single crystals for 96h.

In summary, the characterization of the material obtained via air exposure reveals a successful transformation of the HOPE precursor into ZnO nanocrystals. In sharp contrast to other solid-state systems, the HOPE system does not involve any temperature or mechanochemical treatment and the transformation occurs at room temperature through simple exposure to air. This is unlike previously reported systems, which required high-temperature treatments of predesigned molecular precursors. For instance, $[t\text{BuZnOH}]_6$ decomposed at 120 °C, while crystalline samples of $[\text{MeZnOiPr}]_4$ and $[\text{MeZnOtBu}]_4$ required temperatures above 250 °C to decompose. These differences underscore the unique, low-temperature nature of the HOPE system.

3.2.2 Monitoring of air-triggered transformations of the HOPE single crystal using optical microscopy

To gain macroscopic insights into the transformation process, an optical microscopy experiment was performed on the HOPE single crystal, capturing real-time observations during air exposure (Figure 3.14). A single crystal was placed in an open square glass cuvette and monitored using an optical microscope. Images were recorded at defined intervals: every 5 minutes for the first hour, every hour from 1 to 12 hours, every 2 hours between 12 and 24 hours, every 6 hours from 24 to 48 hours, and finally every 24 hours for the remainder of the experiment. The experiment lasted 7 days, during which no visible changes in the crystal structure were observed.

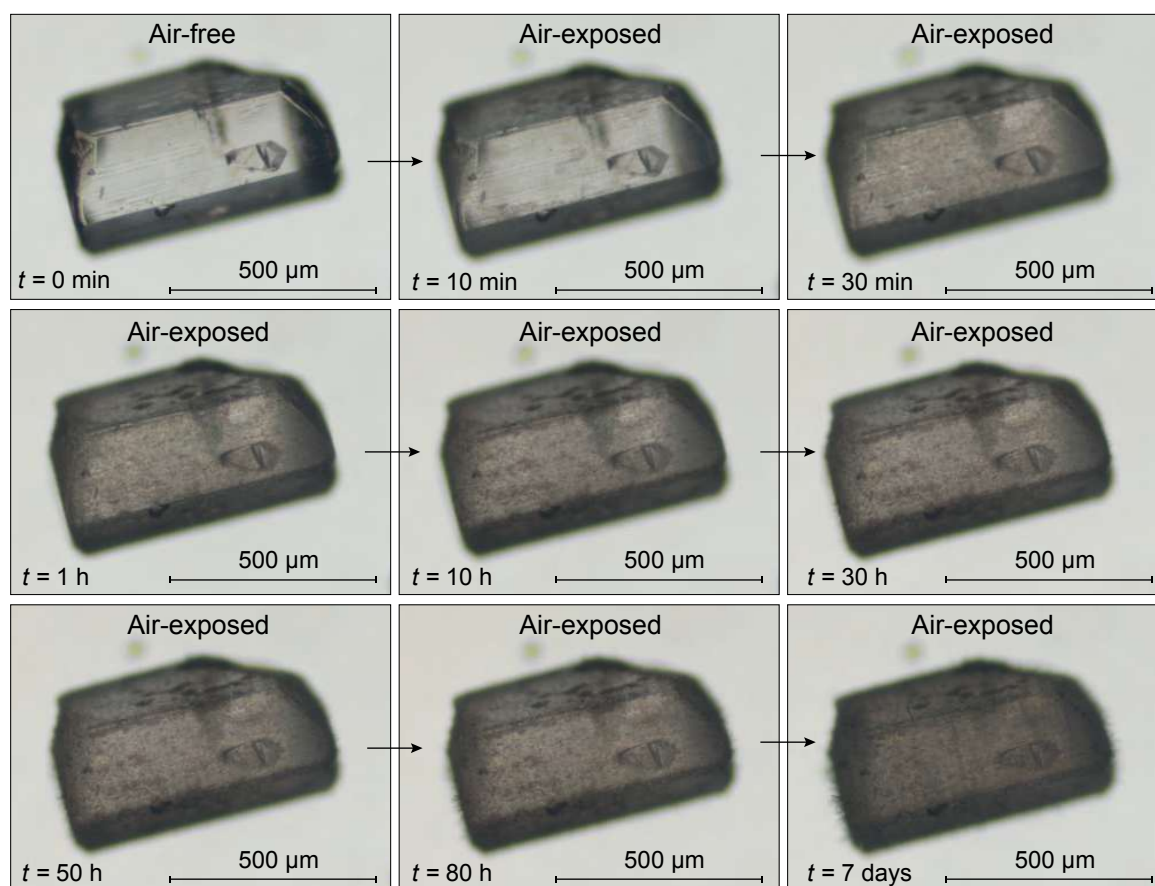


Figure 3.14: Insights into sequential transformation of the HOPE single crystal upon exposure to air using optical microscope imaging.

An overview of the observed processes is described below and presented in Figure 3.16. During air exposure, water molecules initially adhere to the single crystal interfaces, initiating hydrolysis processes. These processes lead to evolution of ethane (EtH) and the formation of free hydrolyzed amorphous BA-H ligands, and zinc hydroxide/oxide species. This is followed by observed crystallization of the hydrolyzed BA-H ligands forming needle-like crystals at the HOPE surfaces (Figure 3.15 and 3.16), which is consistent with PXRD studies.

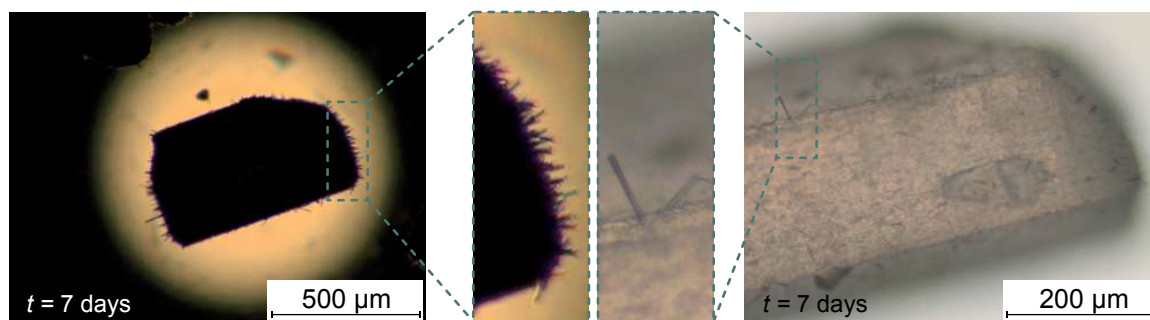


Figure 3.15: Optical microscopy images of the HOPE single crystal after weathering processes. The collected images revealed crystallization of the hydrolyzed BA-H ligands forming needle-like crystals at the HOPE surfaces.

Both the evolution of gaseous EtH and the BA-H crystallization can be regarded as thermodynamic driving forces, ultimately providing a disorder into the precursor crystal lattice, allowing efficient mass transport of both water molecules and emerging zinc hydroxide/oxide species towards inner parts of the precursor. The hydrolyzed Zn centers, acting as a carrier of hydroxide species, undergo further condensation to yield ZnO NCs (*vide infra*). The emerging amorphous BA-H matrix observed during the transformation can be regarded as an intermediate “solvent” existing in the nucleation processes of other solid–solid transitions reported recently[221]. Notably, during this transformation, the HOPE SC maintain its initial shape and volume (less than 1% of their original size) throughout the entire process, implying that the amorphous BA-H matrix likely plays a critical role as dynamic metastable matrix for ZnO NCs’ nucleation and growth[222].

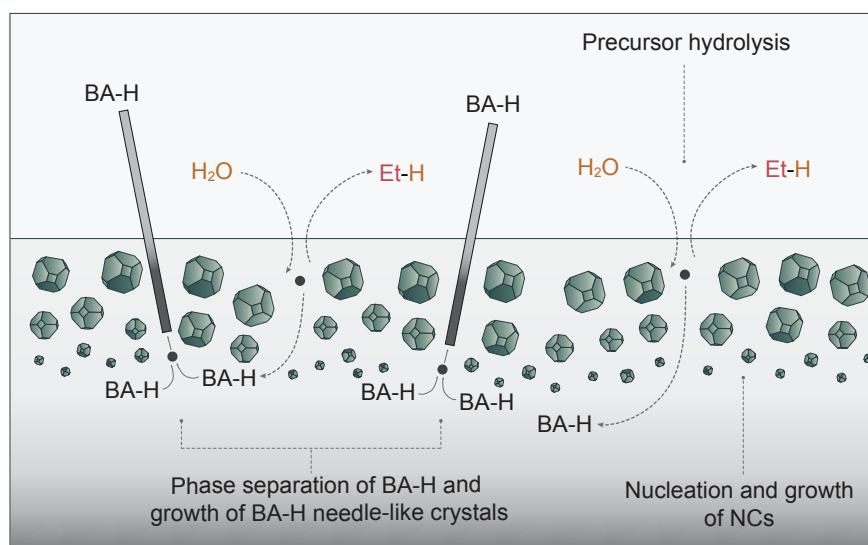


Figure 3.16: Schematic representation of BA-H needle-like crystal growth and nanocrystal formation during precursor hydrolysis.

3.3 Conclusions

Overall, the experiments described in this chapter demonstrate that simple air exposure of the predesigned $[(\text{BA})\text{ZnEt}]_4$ organometallic precursor leads to the formation of the high-quality semiconductor NCs on a multigram scale under ambient conditions, without the use of solvents—reminiscent of natural chemical weathering. This single-crystal system relies on a $[(\text{X})\text{ZnR}]_n$ -type Hydrolysable Organozinc PrEcursor (HOPE), in which reactive zinc–carbon (Zn–C) and zinc–nitrogen (Zn–N) bonds are confined within a crystal lattice prone to water-mediated hydrolytic processes. The system interacts effectively with selected air components, allowing for the efficient growth of NCs within its crystalline yet dynamic body prone to rearrangements, overcoming the limitation of efficient mass transport in the solid-state while preserving the integrity of the crystal shape. Moreover, the progressing hydrolytic transformations generate a new chemical environment providing efficient mass transport within the emerging host matrix alongside highly controlled conditions for the NCs’ nucleation and growth. The following chapter explores the mechanism behind this transformation, utilizing a range of in situ spectroscopic and diffraction techniques.

INSIGHTS INTO NANOCRYSTALS FORMATION UPON CHEMICAL WEATHERING OF THE SINGLE-CRYSTAL PRECURSOR

This chapter explores the processes governing the formation of ZnO NCs during solid-state transformations. By utilizing advanced in situ techniques, previously unknown pathways in the nucleation, growth, and self-assembly of ZnO NCs are uncovered. The study highlights the critical role of hydrolytic processes in overcoming the inherent limitations of low diffusion rates at low temperatures in solid-state reactions. It demonstrates how these hydrolytic reactions unlock efficient mass transport within the system, facilitating chemical transformations that drive nanocrystal growth. This challenges conventional understanding of nanocrystal formation, revealing dynamic solid matrices as active environments for nanosynthesis. The insights gained from this work offer new avenues for the design of molecular precursors and their controlled transformations towards functional nanomaterials.

4.1 Molecular-level insights into transformation of the solid-state precursor towards ZnO NCs

4.1.1 Elucidating air components active in the solid-state transformations of the [(BA)ZnEt]₄ precursor

Water molecules are essential for the activation HOPE single-crystals via hydrolysis of both Zn-N and Zn-C bonds (*vide infra*), starting the reaction chain and initiating complex transformations towards ZnO NCs. In a control experiment (Figure 4.1), the exposure of HOPE crystals to H₂O vapors under N₂ atmosphere (no molecular oxygen involved) at room temperature led to efficient formation of ZnO NCs within 12 hours as indicated by PXRD (Figure 4.2).

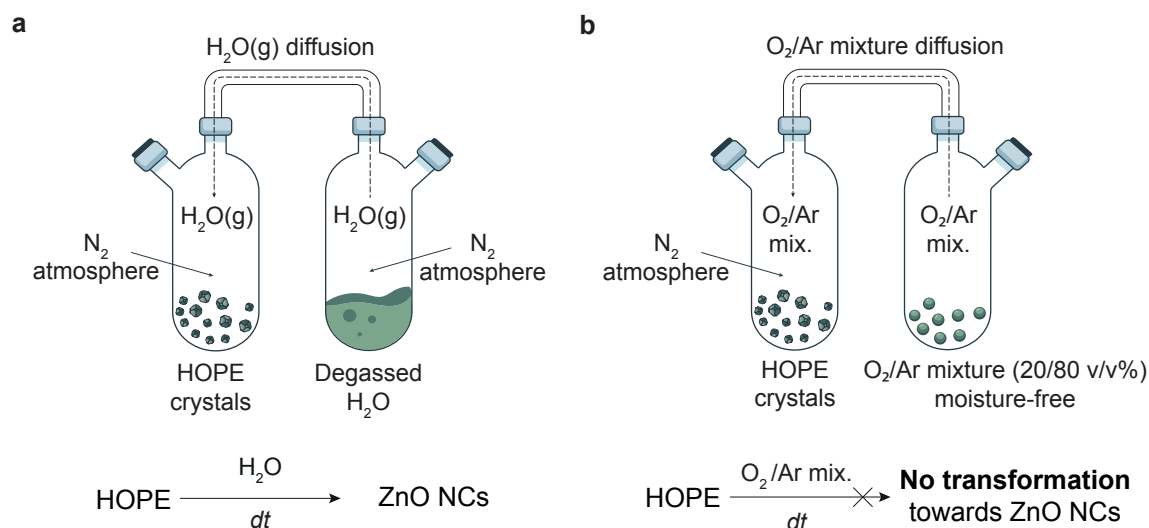


Figure 4.1: The experimental setup for precursor reaction with vapors (H₂O) or dry synthetic air (20/80 v/v% mixture of O₂ in Ar) in a closed system.

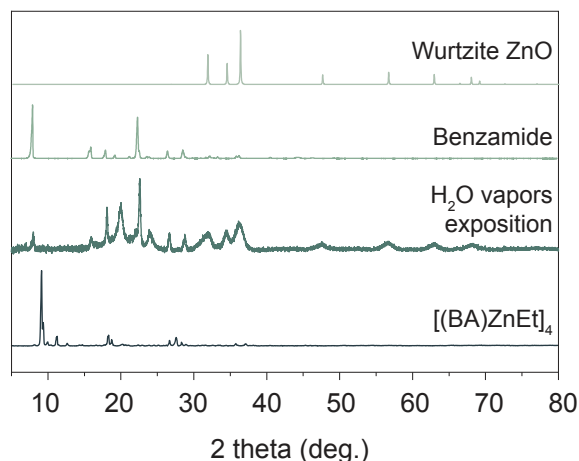


Figure 4.2: PXRD patterns of the HOPE single crystals after exposure to a water vapors.

However, when the HOPE SCs were exposed to a dry synthetic air (20/80 v/v% mixture of O₂ in Ar) no transformation to ZnO NCs occurred (Figure 4.3). This set of experiments confirms that water molecules are an indispensable component of air responsible for efficient conversion of HOPE to the nanoparticulate semiconductor material. This observation is in line with the mechanism of activation of molecular O₂ on Zn-C bond proposed previously by Lewiński and co-workers, where dioxygen can be activated only on coordinatively unsaturated, i.e., three-coordination Zn centres[223]. In the solid state, the [(BA)ZnEt]₄ precursor consists of four four-coordinate (saturated) Zn centers which renders it unreactive towards O₂.

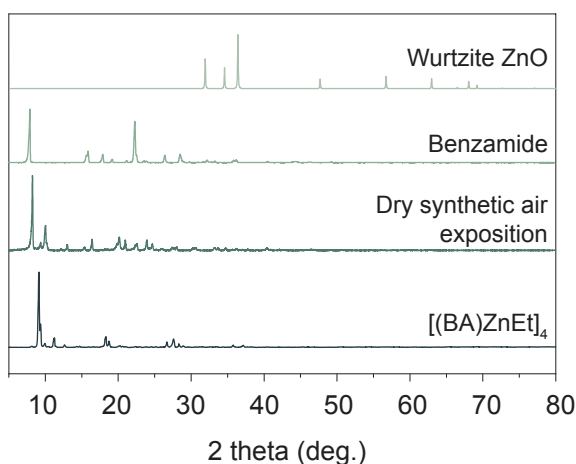


Figure 4.3: PXRD patterns of the HOPE single crystals after exposure to a dry synthetic air (20/80 v/v% mixture of O₂ in Ar).

4.1.2 The impact of ligand acidity on the transformations of organozinc precursors in the solid-state

The impact of ligand acidity on the transformation of alkylzinc complexes was examined. It was found that the alkylzinc amidate complex, $[(BA)ZnEt]_4$, with monodeprotonated benzamide (BA, $pK_a = 14$) as the Zn-coordinated ligand, effectively interacts with certain air components and undergoes complex hydrolytic processes, leading to successful NC formation (Figure 4.4a). In contrast, the alkylzinc carboxylate analogue $[PhCO_2ZnEt]_6$, where $PhCO_2H$ (benzoic acid, $pK_a = 4$) serves as the ligand^[176], showed no such reactivity. Exposure of its microcrystalline solid to air produced an intractable mixture of products, with PXRD confirming the absence of ZnO NC formation (Figure 4.4b).

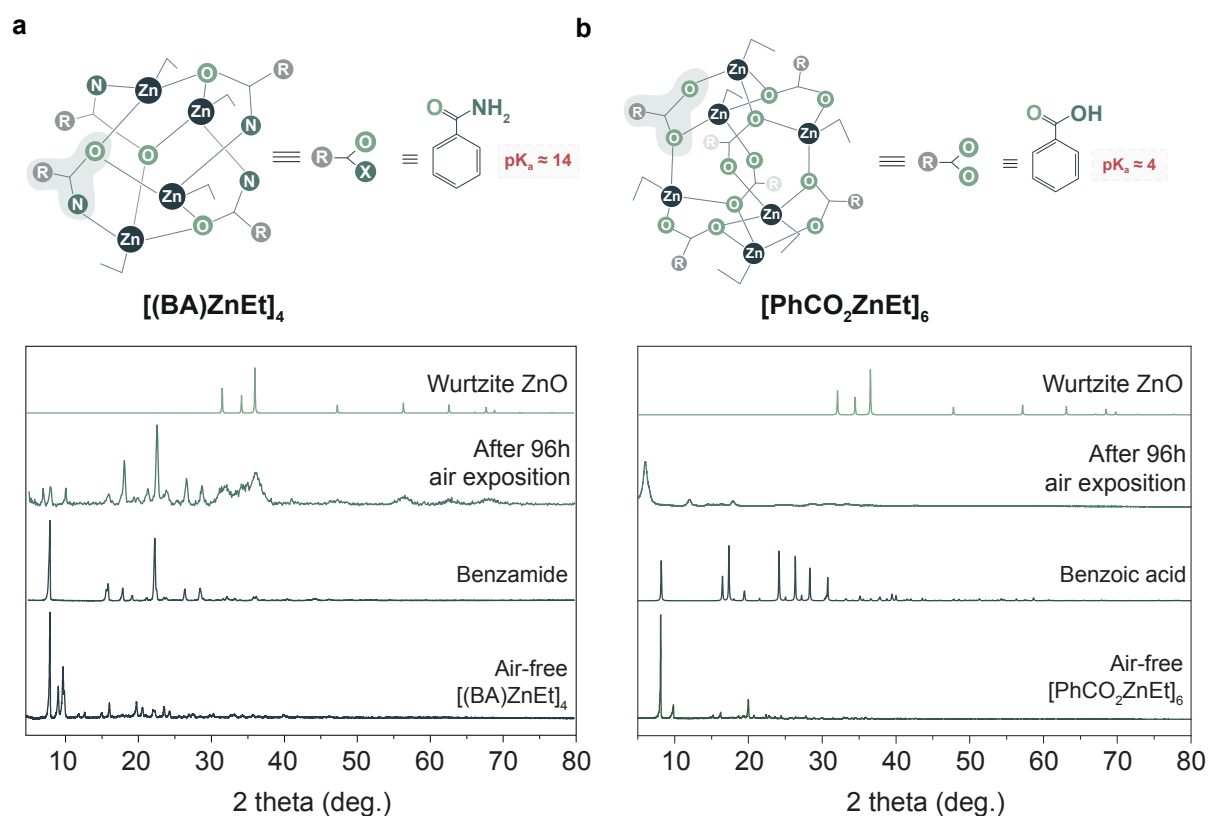


Figure 4.4: Comparison of the influence of ligand pK_a on the reactivity of zinc complexes towards ZnO nanocrystal formation, with PXRD patterns of **a**, The alkylzinc amidate complex $[(BA)ZnEt]_4$ and **b**, The alkylzinc carboxylate complex $[PhCO_2ZnEt]_6$ before and after air exposure.

Remarkably, previously Lewiński and co-workers reported distinct reactivity of oxo-zinc complexes based on benzamide and benzoic acid ligands[136]. In their work, researchers developed a mechanochemical strategy achieving the first successful mechanosynthesis of IRMOFs using an oxo-centered secondary building unit (SBU). In the described strategy, ligand exchange between oxo-zinc complexes (i.e., $[\text{Zn}_4(\mu_4\text{-O})(\text{L})_6]$) and an organic linker (carboxylic acid) was driven by hydrolysis processes, mediated by proton transfer from the organic linker to the more basic ligand L. Initially, the researchers tested a model oxo-zinc benzoate cluster $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CPh})_6]$ as a mechanochemical precursor to IRMOFs. However, they discovered that efficient mechanochemical reactivity required switching to its amidate analogue $[\text{Zn}_4(\mu_4\text{-O})(\text{HNOCPh})_6]$ based on more basic benzamide ligand which readily undergoes hydrolysis in the presence of acidic protons. This study demonstrated that controlling the acid–base relationship between reagents is crucial for the successful mechanochemical synthesis of IRMOF structures.

In summary, the studies presented in this chapter reveal that ligand acidity plays a crucial role in NC formation during alkylzinc complex transformations. High pKa ligands (basic) facilitate effective interactions of $[(\text{BA})\text{ZnEt}]_4$ complexes with water driving hydrolytic processes and leading to successful NC formation, whereas a low pKa ligand (acidic) impedes these reactions and prevents NC formation. This emphasizes the importance of acid-base equilibria and the basic nature of high pKa ligands in promoting interactions with water and hydrolytic processes.

4.1.3 Spectroscopic investigations of elementary reaction pathways from the organozinc precursor towards ZnO NCs and BA-H based organic matrix

To provide further insights into the molecular-level formation of ZnO NCs, an array of spectroscopic techniques, i.e., CP MAS ^{13}C and ^{15}N NMR, diffuse reflectance infrared Fourier transform (DRIFT) and Raman (RS) spectroscopy, was employed.

CP MAS ^{13}C and ^{15}N NMR spectroscopies were applied to directly monitor the functional zinc-amide (Zn-BA) and zinc-ethyl (Zn-Et) bonds, as well as emerging hydroxide intermediates (Zn-OH), within the HOPE system upon its exposure to air, and to identify the resultant products. Additionally, the CP MAS NMR spectra shown in Figure 4.5 support the described transformation pathways and provide insight into changes in sample crystallinity during the hydrolysis process.

The CP-MAS ^{13}C NMR data indicate that both the BA ligands (signals at 175 ppm for the carbonyl group and complex signals at 130 ppm for the phenyl group) and the alkyl groups (signals at 13 ppm and -2 ppm) are protonated over time. Within the first 24 hours, a progressive broadening and chemical shift of the resonances corresponding to Zn-bound BA ligands is observed. After 24 hours, broad resonances centered at ≈ 172 ppm and ≈ 125 ppm become clearly visible in the spectrum and are assigned to a mixture consisting of chemical species incorporating both deprotonated and protonated benzamide ligands. This broadening of the signals is likely due to the emerging inhomogeneity of the chemical environment and appearance of local amorphization domains within the sample.

A small fraction of crystalline BA-H matrix (sharp resonance at 172 ppm) is observed after 5 hours of the weathering process, with its signal intensity increasing over time. Upon extended exposure, the crystalline BA-H matrix becomes the dominant fraction after ca. 96 hours, which is attributed to the evolution of ethane as collaborated by DRIFT and RS as well as TGA (*vide infra*). Notably, new signals characteristic for zinc peroxides or ethanol as products of reactions with molecular oxygen are not visible in the spectra indicating that the transformations of the HOPE precursor in the solid-state are predominantly driven by hydrolytic processes (please compare with Chapter 7 describing reactions in solutions).

The initial amorphization and subsequent crystallization of BA-H fraction are further observed in the CP-MAS ^{15}N NMR experiment, where the signal of deprotonated BA at -222 ppm shifts to a broad resonance around -250 ppm (amorphous phase), which subsequently transforms into a well-shaped peak at -273 ppm, characteristic of crystalline BA-H.

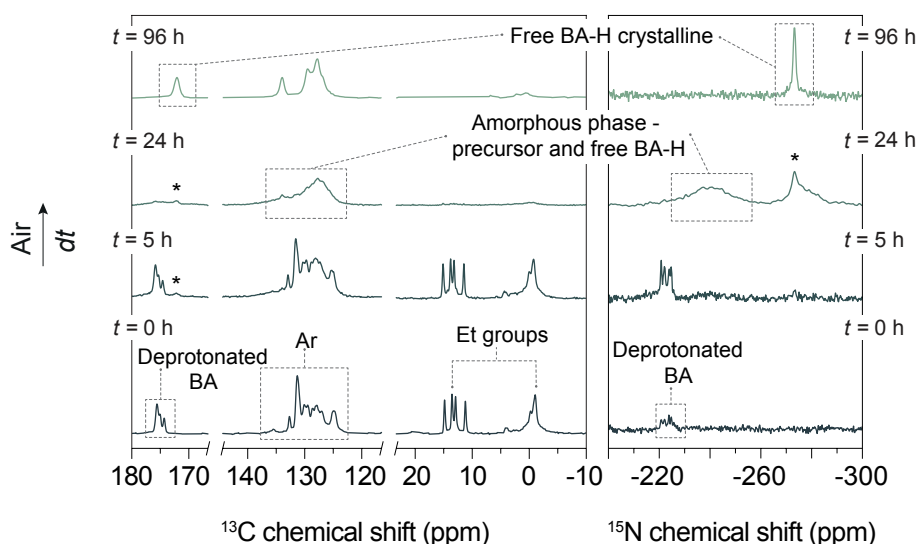


Figure 4.5: Ex situ ^{13}C CP MAS and ^{15}N CP MAS NMR studies on transformation of HOPE towards ZnO NCs.

Time-resolved DRIFT and Raman spectroscopies were further applied to provide insights into the initial steps of the HOPE precursor transformations. DRIFTS is a surface related technique providing useful information about chemical composition and processes at material interfaces. Time-resolved DRIFTS experiments on a HOPE micronized sample exposed to air reveal that the successive hydrolysis steps start from relatively rapid protonolysis of BA ligands of the pristine $[(\text{BA})\text{ZnEt}]_4$ clusters (Figure 4.6). The bands at 3370 cm^{-1} and 3185 cm^{-1} , corresponding to the asymmetric and symmetric stretches of the NH_2 group in the released BA-H molecules, appear within the first seconds of air exposure (Figure 4.6). The rapid development of these bands, along with broad bands in the $3000\text{--}3400\text{ cm}^{-1}$ range, indicates the progressing hydrolysis mediated by penetrating water molecules and concurrent formation of intermediate zinc hydroxide- and oxide species. After the first 30 minutes, the process slows down, however the subsequent hydrolysis of the Zn-C bonds becomes evident (as seen in the decrease of C-H stretching bands of the Zn-Et units at 2850 cm^{-1} ; also observed in the Raman spectrum at 2880 cm^{-1}).

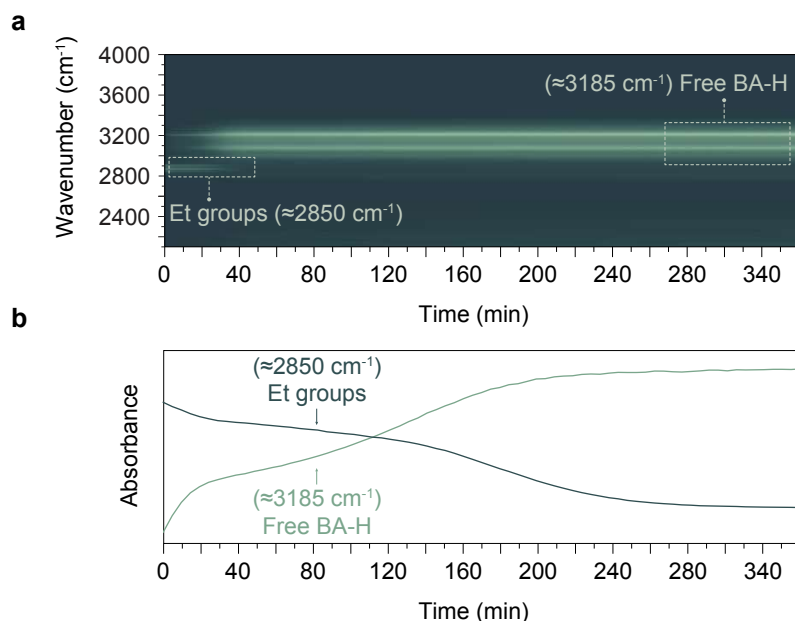


Figure 4.6: In situ DRIFT studies on transformation of HOPE towards ZnO NCs upon exposure to humid air. **a**, 2D contour map. **b**, Evolution of selected signals over time.

The gathered DRIFT data were further corroborated by the Raman spectrum, showing the emergence of a band at 3630 cm^{-1} (Figure 4.7) characteristic for the O-H stretching modes and indicating zinc hydroxide intermediates in the reaction medium[224]. After approx. 4 hours two new bands are observed at 583 cm^{-1} and 1156 cm^{-1} , assigned to the ZnO-stretching vibrations, indicative for the formation of NCs. Notably, both the DRIFT and Raman spectra indicate that the hydrolysis of Zn-Et groups, leading to the release of volatile ethane, lags behind the BA ligands protonolysis.

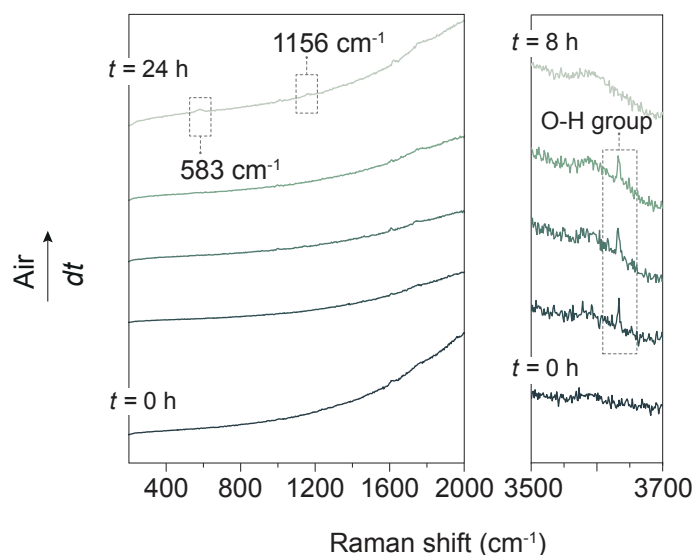


Figure 4.7: In situ Raman studies on transformation of HOPE towards ZnO NCs upon exposure to humid air.

Altogether, the described spectroscopic data provide comprehensive insights into the initial steps of hydrolytic processes within the HOPE system, where the hydrolysis of Zn-N and Zn-C bonds is critical. These hydrolysis processes progressively introduce disorder throughout the HOPE crystal structure, which together with release of ethane molecules create a water-permeable dynamic matrix essential for efficient mass transport of both water molecules and emerging zinc hydroxide- and oxide intermediates. Subsequently, these intermediates act as secondary precursors for nucleation and growth of ZnO NCs. The revealed acid–base relationship between the Zn-BA and Zn-Et units is likely a key to the successive formations of zinc hydroxide- and oxide- species followed by nucleation and growth of NCs within an emerging hydrogen-bonded host organic matrix composed from the hydrolysable amidate ligands. The described transformation processes involve following steps: (i) initial hydrolysis of $[(BA)ZnEt]_4$ cluster, (ii), formation of zinc hydroxide- and oxide intermediates, (iii), nucleation and growth (Figure 4.8).

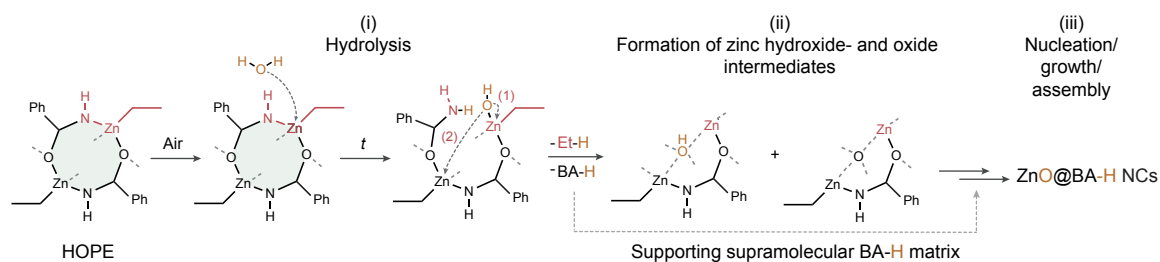


Figure 4.8: Proposed mechanism of HOPE system transformation to ZnO NCs involving: (i) initial hydrolysis of [(BA)ZnEt]₄ cluster, (ii), formation of zinc hydroxide- and oxide intermediates, (iii), nucleation and growth.

4.1.4 In situ isothermal thermogravimetric analysis

In situ isothermal thermogravimetric analysis (TGA) was employed to monitor mass changes of the HOPE sample under ambient conditions during the weathering process, providing time-resolved insights into the release or uptake of volatile species. This technique could offer complementary information to the spectroscopic analyses (Figure 4.9), enabling direct correlation between mass variations and underlying chemical transformations, and identifying which functional groups leave the system.

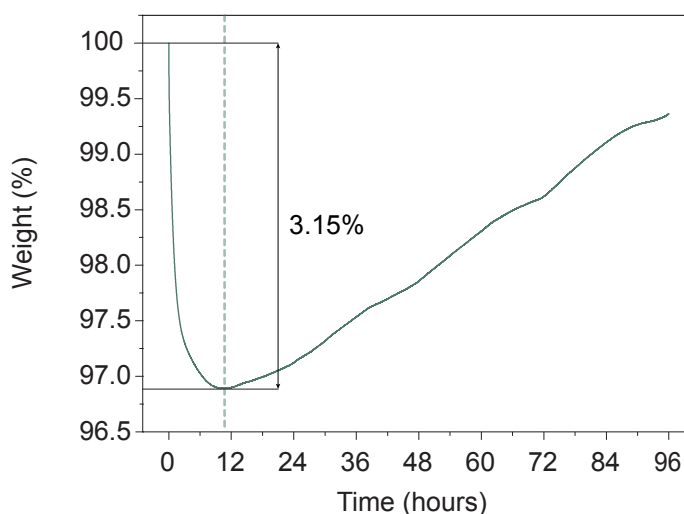


Figure 4.9: Isothermal TGA measurement of changes in the mass of the sample as a function of time at room temperature.

The isothermally registered weight change for the HOPE sample as a function of time exhibits an asymmetric parabolic character (Figure 4.9). The weight loss is observed primarily within the initial 10 hours of the weathering process, consistent with the evolution of gaseous ethane (Et-H) resulting from the hydrolysis of Zn-Et units. The recorded weight loss of 3.15% is lower than the calculated mass drop of 5.57% estimated for the total hydrolysis of Zn-C bonds, accompanied by the formation of ZnO/ZnOH sequestered units supported by BA ligands (*vide supra*); note that the hydrolyzed BA-H molecules do not leave the system but form the host organic matrix. This discrepancy suggests that, parallel to the hydrolytic processes, moisture permeation occurs, and additional water molecules (formally ca. 1.3 H₂O molecules per one Zn center) are absorbed by the sample at this stage. In the subsequent period from 10 to 96 hours, the combination of water adsorption, progressing hydrolytic reactions, and NC nucleation and growth processes, is evidenced by the observed slightly non-monotonic weight gain of the sample.

4.2 Studies on nucleation, growth, and self-assembly of the ZnO NCs in single-crystal matrix

In the literature, in situ experimental techniques have been widely utilized to elucidate the mechanisms underlying crystal nucleation and growth during crystallization[50]. These in situ methods are particularly effective in monitoring the nucleation and growth of NCs in real-time, precisely under the conditions in which these processes occur. Such approaches offer invaluable insights into the kinetics, mechanisms, and properties of the resulting nanocrystals, enhancing the understanding of these complex phenomena.

In the current investigation, to gain deeper insights into the solid-state reaction pathways and the nucleation and growth of ZnO NCs, a series of time-resolved in situ experiments were conducted employing PXRD, UV-Vis spectroscopy, and small-angle X-ray scattering (SAXS). The [(BA)ZnEt]₄ precursor crystals were exposed to air, and data were meticulously collected at regular intervals over a 96-

hour period. The results of these in situ experiments are presented in the following discussion, providing a comprehensive analysis of the crystallization process of ZnO NCs.

4.2.1 Monitoring of structural changes and phase transformations using in situ PXRD

In situ PXRD is a powerful technique that allows for real-time monitoring of structural changes and phase transformations, particularly during processes such as the nucleation and growth of nanocrystals[225]. By collecting diffraction patterns directly under reaction conditions, it is possible to track the formation and evolution of crystalline phases, determine crystallite size changes from peak broadening, and follow lattice parameter variations that reflect compositional changes or strain. This information provides valuable insights into growth kinetics, coarsening mechanisms, and reaction pathways.

Figure 4.10 presents the in situ PXRD patterns of the HOPE single-crystals exposed to air, with diffractograms collected every 30 minutes over a 96-hour period. Analysis of the diffraction patterns reveals a complex solid-state transformation starting from the initial crystalline precursor via amorphous intermediate phase and ultimately forming crystalline final product. The reflections characteristic of the $[(\text{BA})\text{ZnEt}]_4$ precursor (inset, Figure 4.10) decreases relatively fast in intensity, vanishing quantitatively within the first 30 min. This loss of precursor crystallinity is likely associated with the consecutive adsorption of water vapor and the relatively rapid hydrolysis of the parent $[(\text{BA})\text{ZnEt}]_4$ clusters. This process leads to the formation of various zinc-oxo molecular clusters, followed by a series of complex hydrolysis reactions. These initial stages result in an amorphous phase, likely composed of loosely packed zinc hydroxo/oxo intermediate species[162, 176, 180, 185], along with a mobile phase based on BA-H molecules. Subsequently, the released BA-H molecules contribute to the formation of a new crystalline phase, identified as the classical polymorph of benzamide[226] (indicative peaks at 5° - 30° , inset Fig-

ure 4.10), and a hydrogen-bonded host supramolecular network based on BA-H with entrapped water molecules. This mobile phase maintains the crystal shape integrity while facilitates efficient mass transport of the reactants, which is essential for the nucleation and growth of ZnO NCs capped by BA ligands. Following these initial steps, after approximately 3 hours, new diffraction peaks corresponding to the emerging wurtzite-type ZnO NCs become apparent. By the 72-hour mark, distinct peaks indicative of the benzamide phase are visible, alongside increasingly sharp and defined NC reflections. Ultimately, after 96 hours, the final size of the inorganic core of NCs was determined to be 4.4 nm, consistent with the HRTEM data.

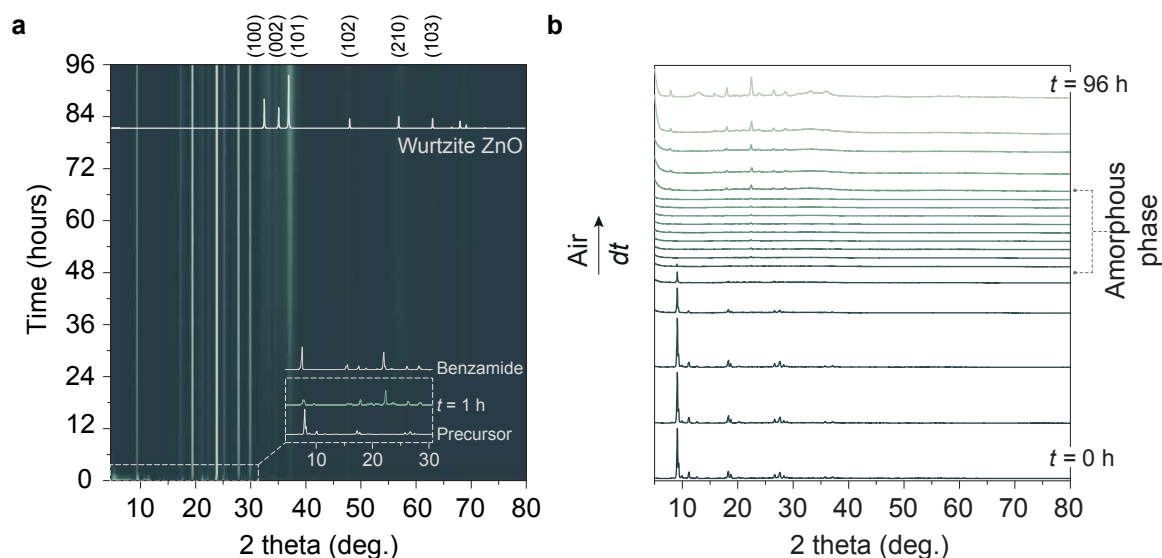


Figure 4.10: The evolution of the PXRD pattern during the HOPE system transformation to ZnO NCs upon exposure to humid air. **a**, 2D contour map of in situ PXRD patterns. **b**, Corresponding in situ PXRD patterns showing the formation of an amorphous phase.

4.2.2 Monitoring of NCs' growth using in situ UV-Vis

The ZnO NCs growth was investigated using in situ UV-Vis spectroscopy, allowing real-time monitoring of changes in absorption peaks, thereby offering essential insights into nanocrystal size evolution and growth kinetics throughout the nucleation and growth stages[72]. While PXRD was initially employed to monitor the growth process, significant broadening of the diffraction peaks in the early stages

hindered accurate determination of crystal size. Consequently, in situ UV-Vis spectroscopy was employed to (i) track the growth kinetics and (ii) monitor the growth both within the first 24 hours and following this initial period.

The evolution of calculated NC diameter (see Experimental section for detailed NC size calculation) versus reaction time is shown in Figure 4.11. The data reveal two distinct quantum-sized crystal growth stages: a rapid initial growth of NCs during the first 24 hours, followed by a slower growth in the later stages. The initial stage exhibits an exponential growth profile, saturating after approximately 24 hours, that corresponds to NCs reaching a diameter of around 4 nm. Following this, the growth rate decreases by a factor of 10, transitioning into a quasi-linear process. Over the course of the chemical weathering process, the NCs reach a diameter of 4.40 nm after 96 hours. The significant lack of further crystallite growth indicates the key presence of organic ligands and high stability of the system over time[227].

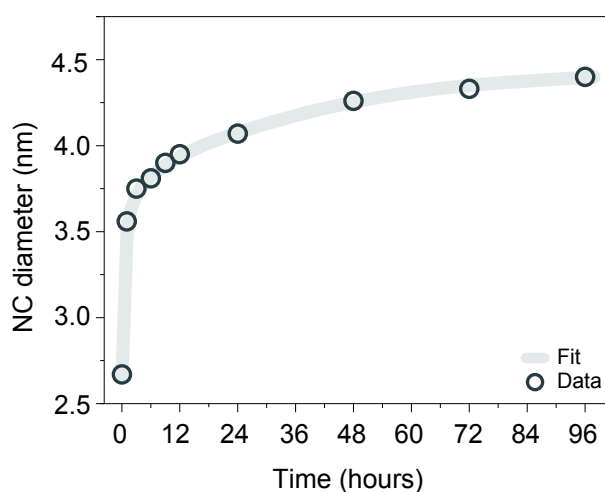


Figure 4.11: Experimental data and kinetic fitting of ZnO NC growth from UV-Vis analysis.

To gain deeper insight into these growth dynamics, the experimental data were subsequently modeled and fit to kinetic equations representative of the underlying processes. As outlined in the literature review, nanocrystal growth is frequently interpreted in terms of either oriented attachment (OA) or Ostwald ripening (OR) mechanisms. In the present study, however, the observed kinetic behavior could not be adequately described by either model separately. To accurately capture the observed NC growth kinetics, a combined growth model that integrates both

the-non-classical OA and the classical Ostwald ripening OR mechanisms was employed. This model reflects a sequential process: an initial rapid growth phase governed predominantly by OA, followed by a slower, diffusion-controlled OR phase[56, 59]. The model is expressed as:

$$D = \frac{D_0 (\sqrt[3]{2k_1t + 1})}{(k_1t + 1)} + k_2^{(1/n)}$$

where D is the particle diameter at any time, D_0 is the initial particle diameter, k_1 and k_2 are the rate constants, and t is time.

This combined model provides an excellent fit to the experimental data, capturing the complete trajectory of nanocrystal growth across both regimes. The early-stage growth ($t < 12$ h) is well described by the OA model[42, 56, 57]. In the studied system, this process likely involves anisotropic interactions that assemble NCs into chain-like quasi-fractal structures[42] (see also Chapter 4.2.3). However, while the data support an OA-based pathway, other mechanisms may also contribute to the crystal growth at this stage, such as growth of primary NCs at the expense of these molecular Zn-oxo and Zn-hydroxo clusters, which are present in high concentrations during the early stages. The subsequent NC growth stage (after 24 hours), characterized by a distinct and much slower NC growth rate, can be described by the classical OR process. In this regime, the less stable, smaller crystalline domains, together with residual hydroxy- and oxo-clusters that likely exhibit higher mobility in the organic matrix, decay in favor of larger and more stable ZnO nanocrystalline phases[60]. As the emerging organozinc precursor-derived NCs are inherently coated with organic ligands[82] and embedded in the organic matrix, once their growth is completed, the neighboring NCs do not coalesce preserving their size and shape[227].

4.2.3 Monitoring of NCs' aggregation mechanism using in situ SAXS

Small-angle X-ray scattering (SAXS) is a powerful technique for structural characterization of nanoparticles in their native environment[228–230]. To investigate the aggregation behavior of emerging NCs during the HOPE single-crystal transformation, time-resolved in situ SAXS measurements were performed. These experiments provide detailed insights into the NC formation and aggregation. Figure 4.12a presents the evolution of SAXS profiles throughout the initial stage of transformation ($t < 2$ h). The observed increase in scattering intensity in the small- q region ($q < 0.05 \text{ \AA}^{-1}$) is characteristic of transformations on the molecular level, and the NC nucleation and growth. Although the collected data did not allow for accurate particle-size determination, likely due to the surface-driven nature of these processes and the random orientation of NCs (*vide infra*), it still provided valuable insights into how the NCs aggregate and the overall structure of their aggregates.

The SAXS patterns were fitted using a simplified sphere-approximation model that captures sample polydispersity, as well as the type and geometry of the emerging assemblies[231] (see Experimental section for details). Polydispersity was analysed to track particle size distribution and its evolution during the reaction, with higher values indicating a broader range of sizes and lower values reflecting more uniform nanocrystal dimensions[232]. An initial rise in polydispersity ($t < 12$ h) followed by its subsequent decrease, indicates a complex interplay between aggregation and growth of NCs (Figure 4.12b). This increase in polydispersity is typical of the nucleation phase, where particles form and grow at different rates, leading to a broad size distribution. As the reaction progresses, polydispersity decreases, suggesting that the nanocrystals become more uniform in size as the system stabilizes, likely due to the onset of slower, more controlled aggregation mechanisms, i.e., reaction-limited aggregation (*vide infra*). This transition from a broad distribution of particle sizes to more uniform NCs is an essential indicator of the stabilization of the nanocrystal assemblies.

The intensity of scattering data may follow a power-law behavior ($I \sim q^n$) at intermediate q values, which can offer insights into the shape of the particles or the presence of fractal structures. The exponents of the power law in the Porod regime (high- q range ($q > 0.05 \text{ \AA}^{-1}$)) were determined by fitting the scattering profiles in $0.05\text{--}0.2 \text{ \AA}^{-1}$ regime to the SAXS profiles, revealing variation in the power law value over time and establishing a clear threshold at the 12 hour-time point (Figure 4.12c). In the literature, it is well established that from the slope of the scattering curve, one can deduce the mechanism of aggregation, such as reaction-limited or diffusion-limited growth[233–236]. At the early stage ($t < 12 \text{ h}$), a rapid growth of the exponent p for the Porod law is observed from 2.4 to 3.4 within the first 12 h, then the growth rate decelerates continually, being effectively arrested with a value of 3.6 until the end of the process. The linear growth rate of the fractal dimension exponent indicates diffusion-limited aggregation (DLA) processes (within the first 12 hours), in line with the concurrent increase in polydispersity[237]. In contrast, the stable value of the exponent after the 12-hour mark suggests that reaction-limited aggregation (RLA) is in place, which results in progressively decreasing polydispersity (Figure 4.12c).

In DLA, particles move randomly through the surrounding medium, and growth occurs when a diffusing particle collides with an aggregate or cluster. Due to the lack of strict preferences for size or orientation in these collisions, this process promotes a broad distribution of aggregate sizes, leading to increased polydispersity. In RLA, particles also approach clusters within the medium, but their movement and subsequent attachment are slower, as the aggregation is limited by the rate of chemical or surface reactions rather than by diffusion. Unlike in DLA, particles in RLA must overcome an energy barrier or react chemically to bind a cluster, introducing selectivity in the attachment process. This selective attachment results in more compact and ordered structures, which limits the variability in aggregate sizes and leads to a decrease in polydispersity over time. As a result, the growth and assembly of NCs progress from the formation of primary ZnO NCs, followed by their rapid assembly to form quasi-fractal, open structures with higher polydispersity of the aggregates structures. After this initial phase, the

processes slow down, allowing the formation of closed-packed, more ordered NC aggregates in the final material (lower polydispersity of the aggregated structures; Figure 4.12c and 4.12d).

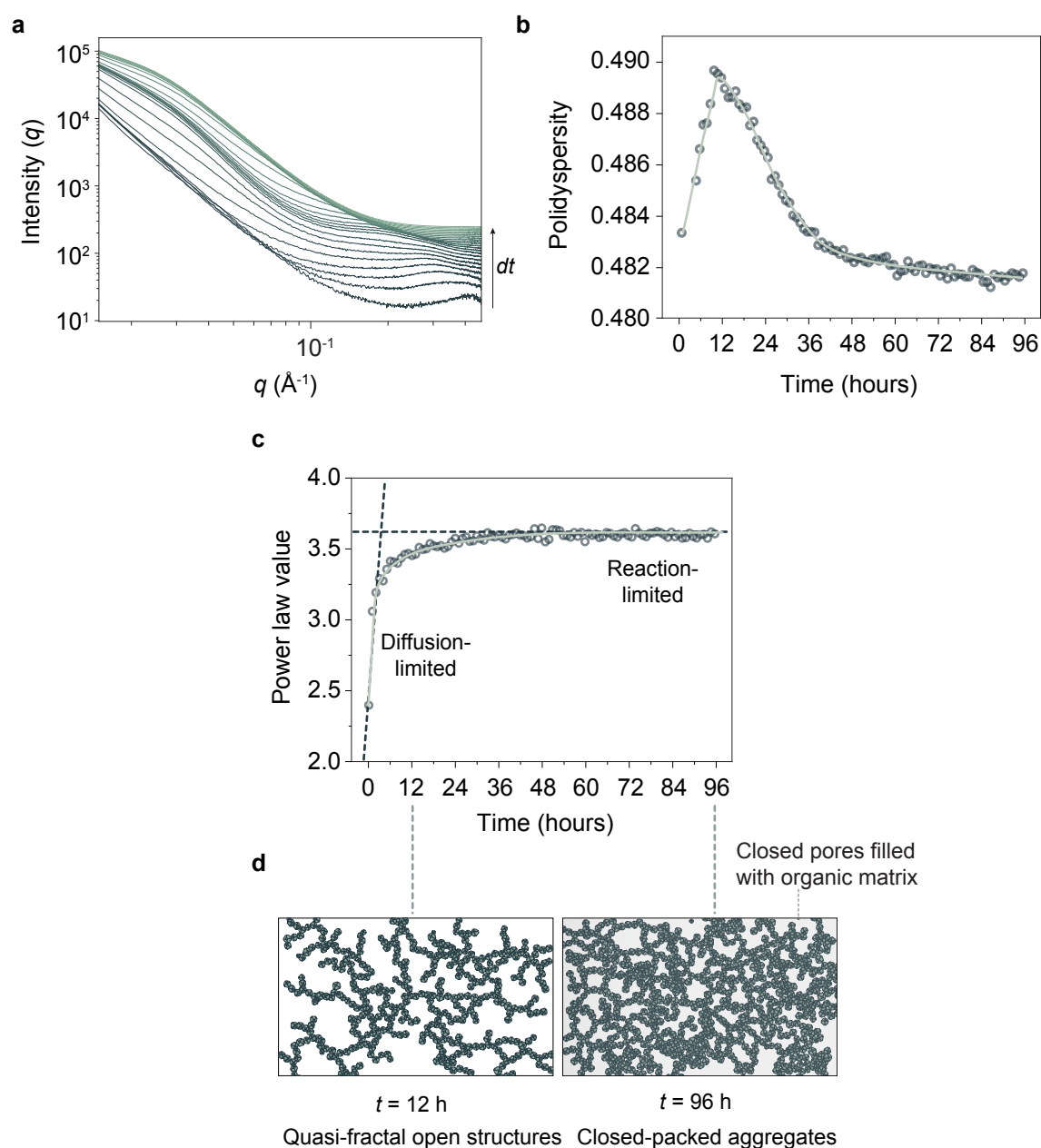


Figure 4.12: Insight into the aggregation processes during HOPE SC transformation. **a**, The evolution of the in situ SAXS pattern during the HOPE SC transformation. **b**, Polydispersity parameter determined by the fit of the SAXS patterns. **c**, Power law value determined by the fit of the SAXS patterns. **d**, Schematic representation of quasi-fractal open structures and closed-packed aggregates.

Notably, the clear threshold within the first 24 hours was also observed in in situ UV-Vis experiments, suggesting two distinct kinetic processes: (i) one associated

with the OA-type mechanisms, accompanied by the complex growth of primary NCs through the absorption of molecular zinc hydroxide- and oxide clusters, followed by (ii) the classical OR crystal growth (*vide supra*). These two stages of NC growth correspond to the DLA and RLA processes, respectively, as observed in the SAXS experiments. Similarly to DLA, the initial OA processes can lead to increased polydispersity due to the fusion of primary particles or clusters with variable sizes and orientations[238]. The resultant broad size distribution later narrows as particles coalesce into more stable configurations. RLA processes, typically characterized by decreased polydispersity of the resulting aggregates, occur in the system together with OR processes also yielding lower polydispersity. Collectively, the SAXS and UV-Vis data suggest that the initial phase of the HOPE transformation, with relatively high freedom for the diffusion of intermediate zinc hydroxide/oxide nanoclusters alongside primary ZnO NCs, allows for rapid and more random NC growth and aggregation. In contrast, the later stages are dominated by processes that yield higher monodispersity of the final material, both at the level of individual NCs and NC aggregates.

4.3 Conclusions

The findings presented in this chapter reveal that the transformation from the model precursor to the final NCs proceeds through several complex developmental stages and the assembly of their arrays within a crystalline network. This demonstrates that dynamic solid matrices can serve as effective environments for nanosynthesis. This breakthrough not only challenges traditional liquid-phase synthesis methods but also highlights the critical role of hydrolytic reactions in enabling efficient mass transport and facilitating crystal growth in a solid-state environment. The ability to control nucleation and growth processes in these constrained environments opens up new possibilities for fine-tuning nanomaterial properties. Collectively, these insights provide a new perspective on the potential of solid-state transformations in the synthesis of functional nanomaterials.

VACUUM-ASSISTED FORMATION OF SEMICONDUCTOR AEROGELS

The chemical synthesis of nanomaterials has been essential for the progress of nanotechnology. In just a few decades, thousands of different methods have been reported for the preparation of a wide variety of nanoscale materials, typically in the form of colloidal dispersions. However, the majority of applications for colloidal nanocrystals necessitate further purification or surface modification process following nanocrystal growth.

Purification is essential for separating the nanocrystals from reaction by-products, ligands, and unreacted precursors[13, 239]. Typically, this is achieved by adding a polar solvent such as ethanol, methanol, or acetone to the reaction mixture[240]. The change in solvent polarity induces flocculation, causing the nanocrystals to precipitate out, while excess ligands and residual precursors remain dissolved in the solvent. The nanocrystals are then separated via centrifugation, followed by redispersion in non-polar solvents such as hexane, toluene, or chloroform.

While this conventional purification method is widely used, there is an ongoing need for simpler, more efficient techniques. In this chapter, a novel approach to purifying nanomaterials through sublimation under reduced pressure is described, to the best of my knowledge, for the first time. This method offers a straightforward, effective alternative to traditional purification techniques, providing new opportunities for optimizing nanomaterial processing.

5.1 Vacuum-assisted activation of ZnO@BA NCs embedded within BA-H organic matrix

In the preceding discussion (Chapter 3 and Chapter 4), the role of the emerging organic matrix within the HOPE system was explored, revealing its auxiliary function in mass transport, which facilitates the formation of NCs. The presence of free BA-H ligands within the ZnO@BA material, embedded within BA-H organic matrix, raises the question of whether the BA-H-based matrix can be post-synthetically removed to generate porosity in the remaining scaffold based on ZnO@BA core-shell NCs.

The relative mass of the organic matrix and the residual mass of the inorganic ZnO in the material after transformation were estimated from the TGA data to be 60% and 40%, respectively (*vide infra*; Figure 5.5). The commonly observed critical effect of organic molecules on the photophysical properties of NC materials[3], i.e., electrical conductivity, led to attempt to remove the described organic matrix from the system. However, washing or thermal removal of organic surface ligands from the NC systems often generate mid-gap charge carriers, reduces chemical stability, leads to the sintering of inorganic cores, and dramatically reduces surface area of the resultant material. Thus, it was conceptualized that the volatile under vacuum organic matrix based on BA-H could be readily extracted and separated from ZnO NCs through a vacuum-triggered sublimation (Figure 5.1). This would potentially allow to prepare a microporous material based on semiconductor NCs without using any solvents, temperatures necessary to decompose organic molecules (usually $>400\text{ }^{\circ}\text{C}$), or complicated surface area activation procedures[241, 242].

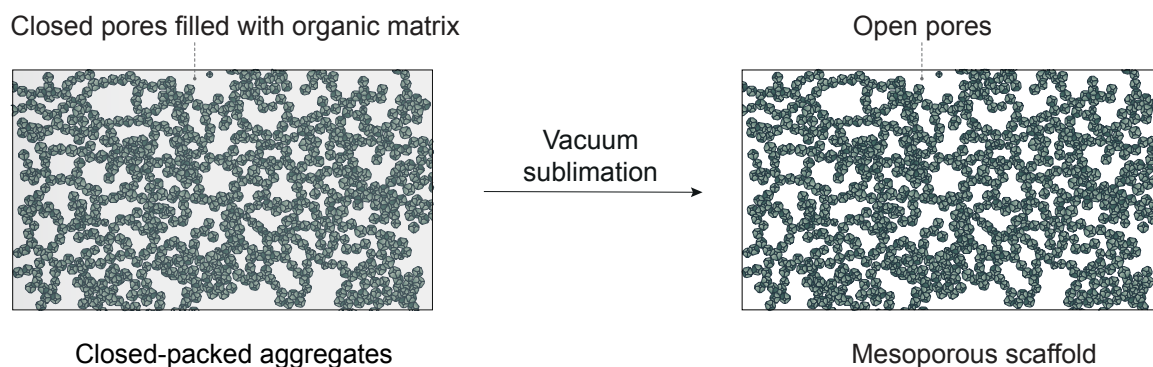


Figure 5.1: Schematic representation of activation of the mesoporous material by vacuum-assisted sublimation of the BA-H organic matrix.

The resultant ZnO NCs embedded within the organic matrix, ZnO@BA/BA-H, were exposed to a reduced pressure of $4 \cdot 10^{-3}$ mbar while the temperature was gradually increased to 120°C over a 2-hour period (as analyzed in the TGA; *vide infra*). Schematic representation of experimental set up of vacuum-assisted sublimation of the BA-H organic matrix is shown on Figure 5.2. This controlled heating and reduced pressure environment facilitated the sublimation of the organic BA-H matrix, effectively removing it from the system without the need for additional solvents or complex chemical procedures. As a result, a white crystalline material was obtained.

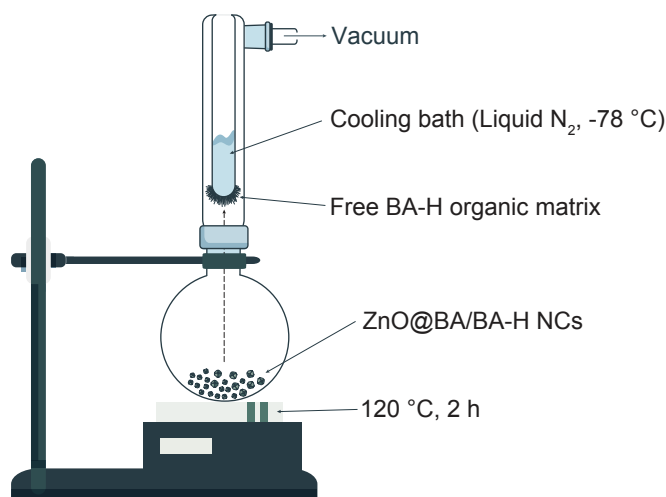


Figure 5.2: Schematic representation of experimental set up of vacuum-assisted sublimation of the BA-H organic matrix.

The nanopowder exhibits a low bulk density of $0.10 \text{ g}\cdot\text{cm}^{-3}$, which corresponds to just 1.4% of the density of a single crystal of ZnO ($5.61 \text{ g}\cdot\text{cm}^{-3}$)[243]. This drastic

reduction in density suggests that the material is highly porous, a characteristic feature of aerogels. Aerogels are known for their low density and high internal surface area, resulting from a network of air-filled pores[244–247]. The significant porosity of the nanopowder, combined with its extremely lightweight nature, allows it to be classified as an aerogel, which retains a solid framework while being composed mostly of air. This porosity is a direct consequence of the sublimation process, which removes the organic matrix without collapsing the nanostructure, preserving the aerogel-like properties.

5.2 Porosity analysis of the ZnO nanocrystalline aerogel

The porosity of the hybrid materials, obtained after vacuum-assisted activation, was confirmed by nitrogen (N_2) adsorption measurements at 77 K (Figure 5.3). The isotherm exhibits a type IV profile, characteristic of mesoporous materials[248, 249]. The material demonstrated a maximum nitrogen uptake of $220 \text{ cm}^3 \cdot \text{g}^{-1}$, revealing its substantial pore volume. The calculated Brunauer–Emmett–Teller (BET) surface area was determined to be $83 \text{ m}^2 \cdot \text{g}^{-1}$ and the average pore diameter is approximately 9.2 nm. To further support the mesoporous nature of the material, a Barrett-Joyner-Halenda (BJH) pore-distribution analysis was performed. The resulting pore volume distribution curve shows a maximum centered around 10 nm within the mesopore size range (2–50 nm). Collectively, these results demonstrate that the surface area of the resultant mesoporous aerogel was successfully activated.

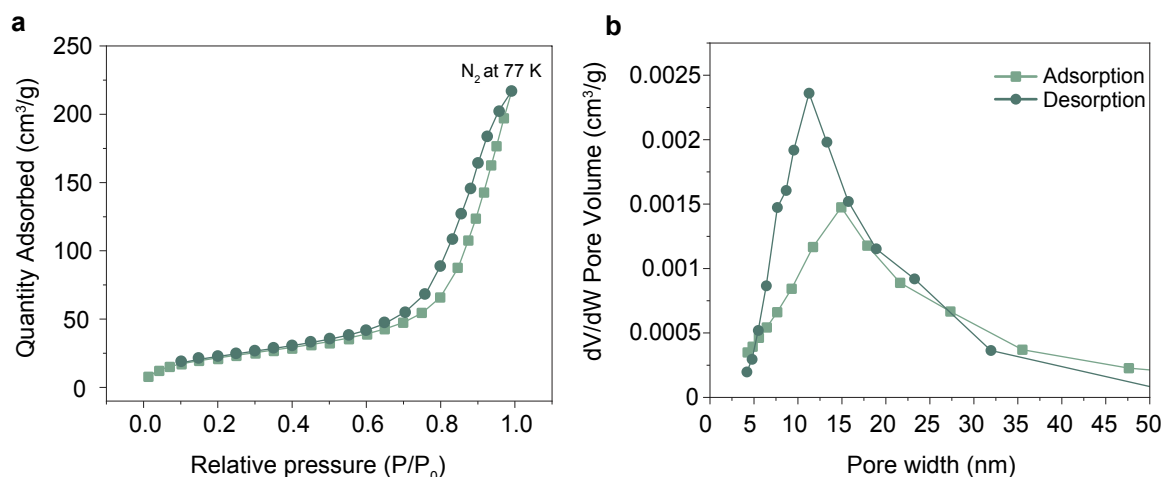


Figure 5.3: Porosity analysis of the ZnO nanocrystalline aerogel. **a**, N₂ gas sorption isotherm for the mesoporous material based on ZnO NCs and **b**, BJH pore-size distribution curves.

5.3 Characterization of the mesoporous network of ZnO NCs

PXRD analysis confirmed the successful activation of the material by demonstrating the removal of free BA-H from the system (Figure 5.4). The diffraction patterns revealed the absence of peaks associated with the organic matrix, indicating its complete sublimation. Additionally, the characteristic peaks corresponding to the crystalline ZnO nanostructure were preserved, confirming that the material's structural integrity was maintained post-activation. This evidence supports the efficient removal of the BA-H molecules without compromising the crystallinity of the ZnO.

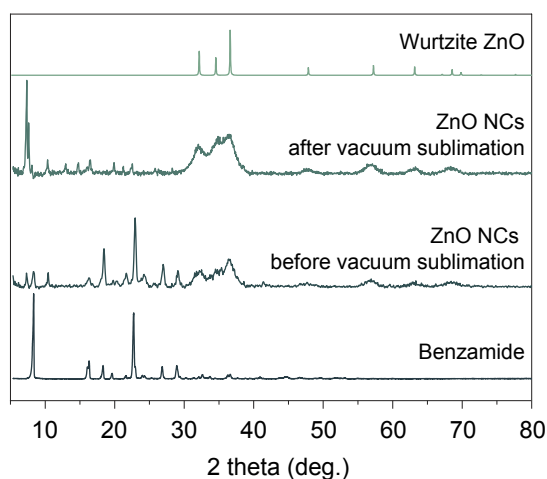


Figure 5.4: PXRD pattern for the mesoporous material based on ZnO NCs.

TGA analysis shown in Figure 5.5 indicates that the organic fraction of the material was reduced from 60% to 30% following the applied sublimation process. Based on this TGA data, the grafting density of BA ligands on the nanocrystal surfaces was estimated to be approximately 8.7 molecules per nm², assuming a spherical shape for the nanocrystals. This ligand density is consistent with previously reported values for ligands on ZnO nanocrystal surfaces[193]. These findings suggest that the resulting mesoporous scaffold consists of ZnO@BA nanocrystals capped with a thin layer of residual organic BA ligands, maintaining the structural integrity of the nanocrystals while achieving porosity.

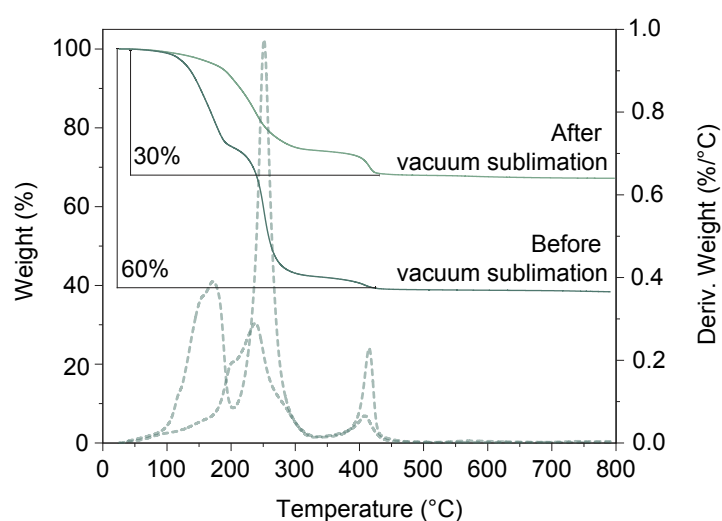


Figure 5.5: TGA for the mesoporous material based on ZnO NCs.

To gain further insights into the nature of the interaction between the BA ligands and surface Zn centers, the FTIR spectra of the free BA-H ligand, the HOPE precursor alongside the ZnO@BA/BA-H material and the ZnO@BA core-shell NCs after sublimation were compared (Figure 5.6). The amide stretching vibrations region of the spectrum of the purified ZnO@BA core-shell NCs is distinct from that of the ZnO@BA/BA-H material. The spectrum of the purified NCs shows a broad band below 600 cm^{-1} that is characteristic of the ZnO core[250]. Moreover, the NH_2 stretching bands at 3370 cm^{-1} and 3185 cm^{-1} characteristics of protonated BA-H are not in the spectrum of ZnO@BA core-shell NCs, conclusively confirming the successful removal of free BA-H molecules from the studied ZnO NC system. The changes in the amide N-H bending vibrations region ($500\text{--}800\text{ cm}^{-1}$) are also observed, suggesting that the BA ligands are anchored to the ZnO surface in the deprotonated form. A more in-depth comparison of the spectrum of purified ZnO NCs with the analogous data for HOPE crystals clearly shows that the BA ligands coordinated to the zinc atoms display the same coordination environment as in the designed precursor. Therefore, BA ligands forming the capping shell of NCs are coordinated to Zn surface sites both through the oxygen and nitrogen centers of the amide group. The presented FTIR data confirms that the resultant porous aerogel is composed of ZnO NCs that are inherently coated with tightly bound BA ligands anchored to the Zn surface sites in deprotonated form.

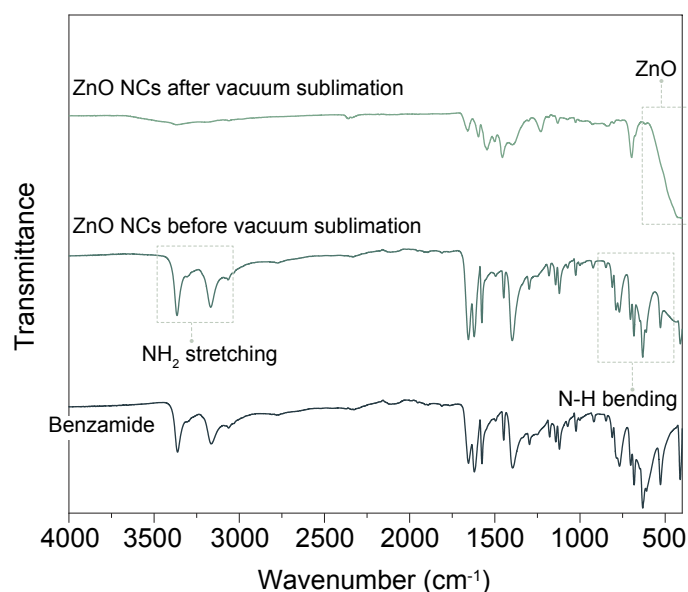


Figure 5.6: FTIR for the mesoporous material based on ZnO NCs.

Elemental analysis (EA) of the materials performed before and after sublimation shows significant changes in the levels of carbon, hydrogen, nitrogen, and oxygen contents, indicating the removal of unbound benzamide ligands from the pristine material (Figure 5.7). Carbon content for the activated ZnO@BA sample dropped by ca. 60% compared to the carbon content in the ZnO@BA/BA-H material before sublimation, suggesting that the applied sublimation procedure effectively removed free organic ligands; corroborated by TGA (Figure 5.5). Similarly, the decrease in hydrogen content (from 3.26% (non-activated) to 1.66% (activated)) and nitrogen content (from 6.43% (non-activated) to 2.98% (activated)) aligns with the removal of unbound BA-H molecules. After sublimation, the residual carbon (15.60%) and nitrogen (2.98%) indicate that some BA ligands remained coordinated to the ZnO surface. These tightly bound ligands are likely deprotonated and coordinated to the Zn atoms, forming a stable capping layer; consistent with FTIR data (Figure 5.6.). The increase in overall oxygen content by 5.48% in the ZnO@BA sample suggests greater mass fraction of ZnO species (ca. 28% more) after sublimation; in good agreement with TGA data (30%). Overall, sublimation removed the loosely attached benzamide molecules, while the tightly bound ones remained on the surface, helping to stabilize the mesoporous network and prevent its collapse upon ligand removal.

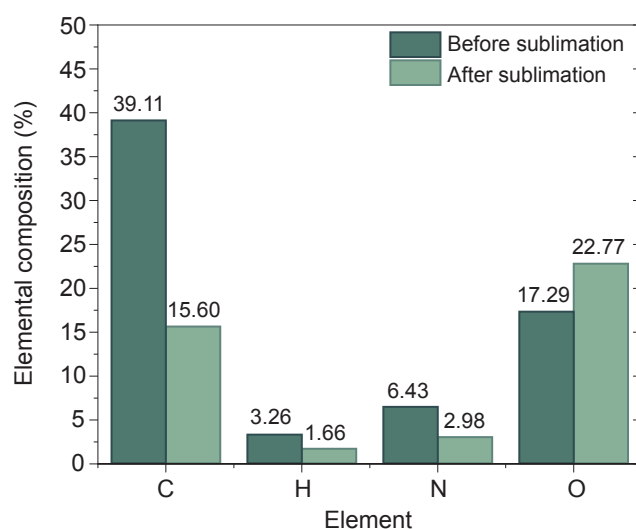


Figure 5.7: Elemental composition analysis of the resultant ZnO NCs before and after sublimation process.

5.4 Conclusions

The majority of known aerogels based on nanoparticulate semiconductor building blocks are synthesized through time-consuming processes, often requiring weeks and involving complex activation procedures such as supercritical CO₂ treatment[251]. In contrast, for the first time, a novel, straightforward sublimation process has been applied to activate solid ZnO nanocrystalline material embedded in an organic matrix. This method, free of solvents and complicated surface area activation procedures, presents an attractive alternative for creating mesoporous materials with highly activated surfaces.

This innovative approach involves the sublimation of the organic matrix via a vacuum-based process, transforming the embedded ZnO nanocrystalline material into a highly porous semiconductor aerogel without the use of solvents or complex chemical treatments. Compared to traditional methods, this sublimation process efficiently purifies the material while maintaining the structural integrity of the ZnO nanocrystals. It effectively removes the free BA-H matrix, leaving behind a stable scaffold of semiconductor building blocks capped with a thin layer of tightly bound ligands.

These results confirm that the sublimation-based activation strategy is a promising, straightforward method for producing mesoporous semiconductor aerogels, offering advantages in terms of synthesis simplicity, material stability, and functional surface. Additionally, the described sublimation process offers a significant reduction in the time and complexity of NC aerogel preparation methods, demonstrating an innovative and cost-effective approach for producing mesoporous materials.

EXPLORING THE VERSATILITY OF THE HOPE SYSTEM

Building upon the foundation established in the preceding chapters, where the concept of a solid-state hydrolysable organozinc precursor was introduced, attention was turned to expanding the scope of the HOPE system to incorporate hydrolytic agents other than water, such as hydrogen sulfide (H_2S), hydrogen selenide (H_2Se) and hydrogen telluride (H_2Te). The observation that simple air exposure can transform a solid-state system into high-quality semiconductor NCs under ambient conditions just by simple air exposure is highly attractive, prompting exploration of new possibilities for translating the HOPE system. In this chapter, the focus will be on further investigating the versatility of the HOPE system by testing various hydrolytic agents (Figure 6.1).

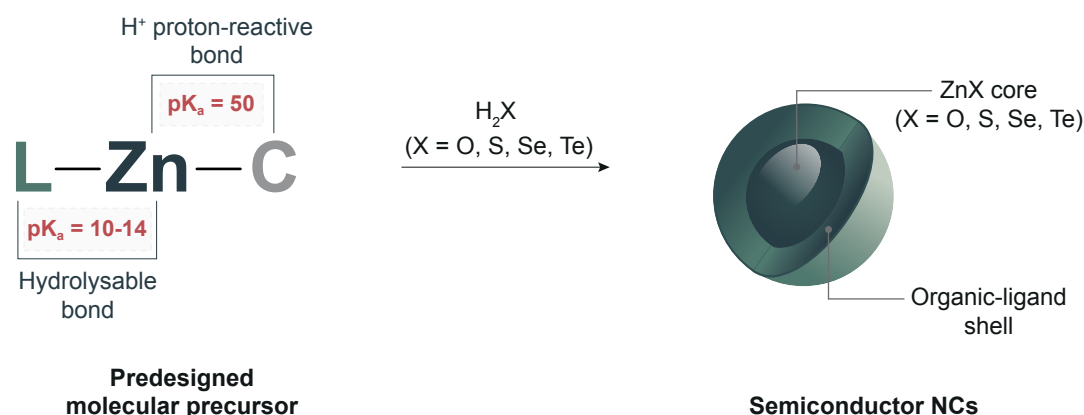


Figure 6.1: Schematic representation of the versatility of the HOPE system in tunable semiconductor NCs synthesis via controlled transformations.

6.1 Exploring HOPE reactivity with H₂S as other hydrolytic agent

6.1.1 Introduction to synthesis of metal sulfide nanocrystals

Increased interest in metal sulfide NCs is largely driven by their unique photo- and electrochemical properties, making them good candidates for applications in photocatalysis, solar energy conversion, and electronic devices. The synthesis of these NCs typically involves a metal source, (i.e., metal salts) and a sulfur sources and involves various chemical synthetic methods, including chemical vapor deposition (CVD), hydrothermal synthesis, sol-gel techniques, and precipitation methods[252]. Commonly used sulfur sources include sodium sulfide, thiourea, thioacetamide, and elemental sulfur, each selected based on the method used. Wet chemical routes typically utilize thiourea and thioacetamide for their simplicity, while elemental sulfur is favored in high-temperature techniques like “hot-injection” synthesis of QDs[253–256] and spray pyrolysis for scalable production[257–259]. However, there are only few examples in the literature where a precursor is exposed to H₂S vapors for the direct synthesis of NCs[260, 261]. This underexplored approach presents an intriguing opportunity for nanocrystal formation.

Based on the analogy to water molecules acting as both a hydrolytic agent and a source of oxygen centers in the synthesis of ZnO NCs via controlled hydrolysis of HOPE crystals, H₂S was selected as the subsequent hydrolytic agent and source of sulfur centers. This potentially introduces a distinct chemical pathway, leading to the formation of zinc sulfide (ZnS) NCs and opening new possibilities in the synthesis of metal sulfides. The choice of H₂S as a hydrolytic agent results in notable differences, particularly in its acidity compared to water. H₂S has a pK_a of around 7.0 at 25 °C[262], making it significantly more acidic than H₂O, which has a pK_a of 14.0 at 25 °C[263]. This stronger acidity is due to the weaker H–S bond compared to the H–O bond, which arises from sulfur’s larger atomic size relative to oxygen. The longer and weaker H–S bond facilitates proton release, increasing acidity. Additionally, sulfur’s larger size stabilizes the HS[−] anion more effectively

than oxygen stabilizes OH^- , enhancing the reactivity of H_2S in hydrolytic reactions involving organometallic precursors.

6.1.2 H_2S -assisted solid-state synthesis of ZnS NCs from the organozinc precursor

In this experiment, the HOPE system was placed in a sealed glass vessel, while a separate vessel contained a 0.8M H_2S solution in tetrahydrofuran (THF). The two vessels were connected in a closed system without air exposure. The reaction was initiated by vapors of H_2S leaving the THF solution and being transported into the vessel containing the crystalline precursor, allowing the H_2S to react with the precursor under controlled conditions. The experimental setup provides an air-free environment, as shown in Figure 6.2. After 4 days of exposure, the material was stored under a nitrogen atmosphere to prevent any reactions with moisture or oxygen. To remove excess ligand, the material was subsequently washed with a small portion of fresh THF and then dried under vacuum.

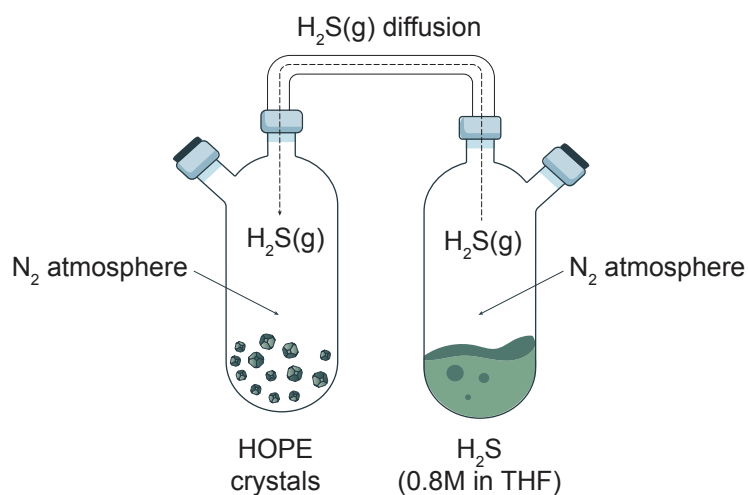


Figure 6.2: The experimental setup for precursor reaction with H_2S in a closed system.

6.1.3 Characterization of ZnS NCs

The structural and optical properties of the synthesized ZnS NCs were systematically investigated using PXRD, HRTEM, as well as UV-Vis, PL, and FTIR spectroscopies. PXRD analysis confirms the crystalline structure of the ZnS NCs, with diffraction peaks consistent with both the wurtzite and zinc blende phases (Figure 6.3). The average crystallite size of about 3.10 nm was estimated according to the line width analysis of the (111) diffraction peak based on the Scherrer formula.

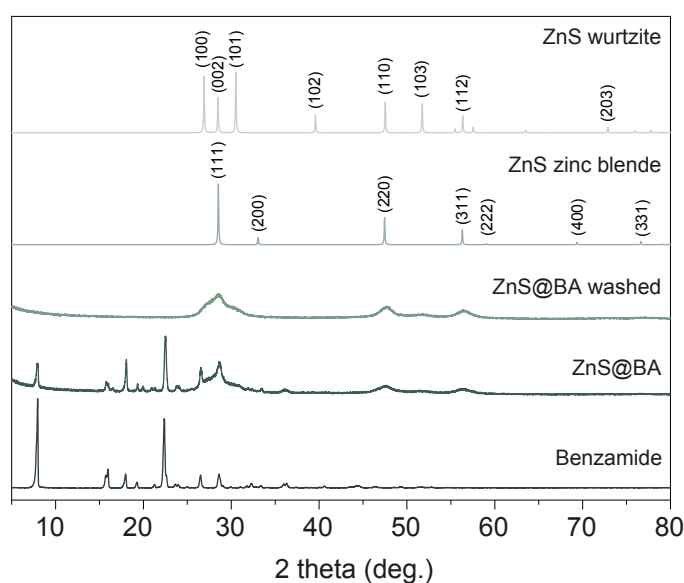


Figure 6.3: PXRD patterns of the resultant ZnS NCs.

HRTEM imaging (Figure 6.4) further corroborates PXRD data, revealing well-defined ZnS nanocrystals with an average size of 3.4 ± 0.4 nm. The nanocrystals exhibit a uniform quasi-spherical morphology with narrow size distribution, as shown in the corresponding particle size histogram. The measured lattice fringes display a d-spacing of 3.10 Å, which can be indexed to the (111) plane of the zinc blende phase of ZnS[264, 265].

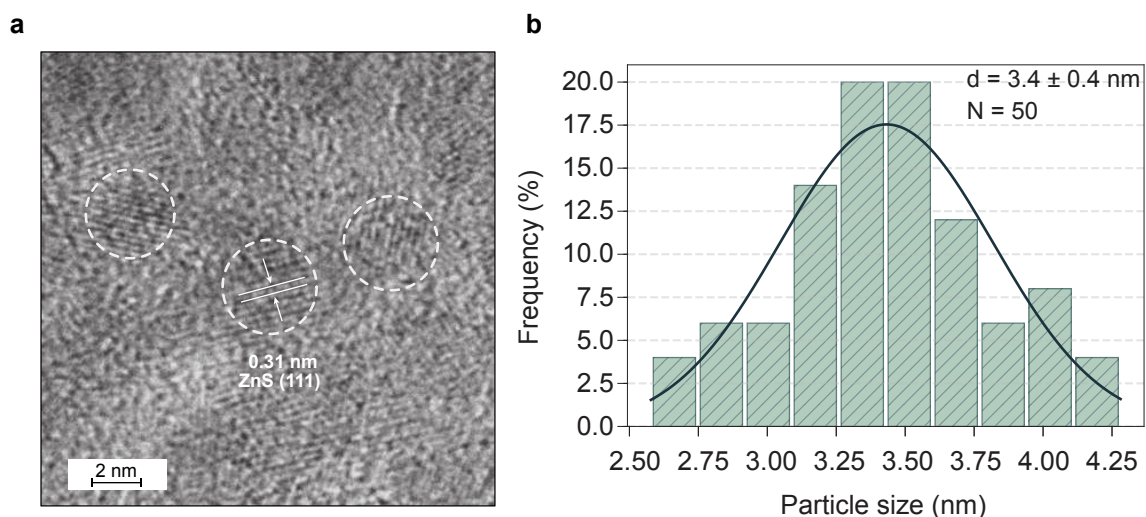


Figure 6.4: Characterization of the resultant ZnS NCs. **a**, Representative HRTEM image; fringes with $d = 0.31$ nm indexed to ZnS (111). **b**, Particle-size histogram ($N = 50$) and Gaussian fit showing an average of 3.4 ± 0.4 nm.

The optical properties were investigated by UV-Vis absorption and PL spectroscopy (Figure 6.5). The UV-Vis absorbance spectrum exhibits a distinct peak at 290 nm. The corresponding optical diameter is 3.80 nm, in good agreement with the HRTEM size distribution and the PXRD crystallite-size estimate. The PL spectrum displays a broad emission peak centered at 550 nm[266]. This intense emission in the visible range is characteristic for doped ZnS NCs and is likely attributed to defect-related emissions, potentially involving sulfur vacancies or surface states[267–269].

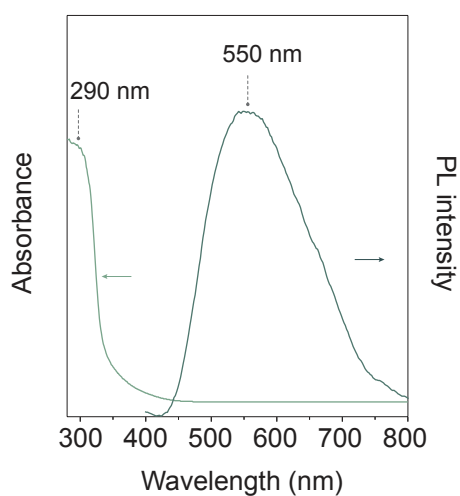


Figure 6.5: UV-Vis absorption and PL spectra of the resultant ZnS NCs.

The FTIR spectra in Figure 6.6 provide additional evidence for the successful formation of ZnS nanocrystals and the presence of organic surface ligands, primarily benzamide. The band at $\approx 620\text{ cm}^{-1}$ is attributed to the Zn–S stretching vibration of ZnS[270]. In addition, the peaks at $1600\text{--}1700\text{ cm}^{-1}$, corresponding to C=O stretching, together with N–H stretching vibrations in the region of $3000\text{--}3500\text{ cm}^{-1}$, confirm that benzamide acts as a capping agent, stabilizing the nanocrystal surface. Moreover, the absorption band in the range of $1200\text{--}1110\text{ cm}^{-1}$ is assigned to C–O stretching vibrations[271], further supporting the presence of benzamide-derived functionalities on the ZnS surface.

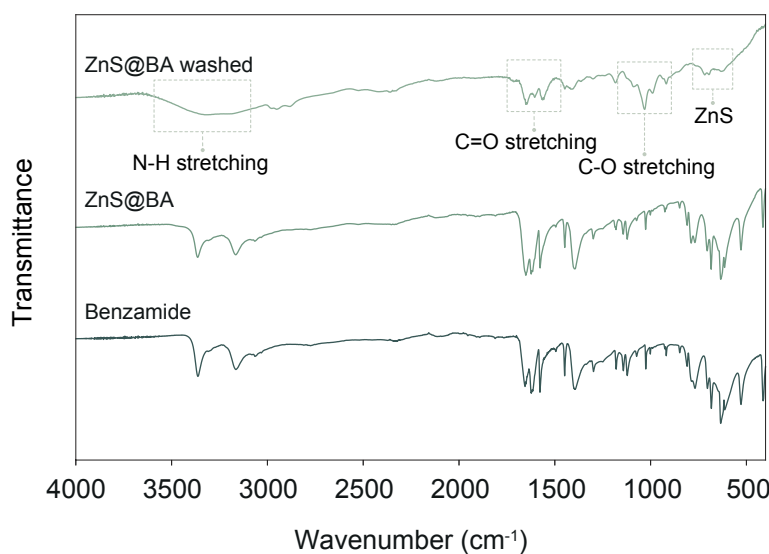


Figure 6.6: FTIR spectra of ZnS NCs.

6.1.4 Conclusions

In summary, the combination of analytical techniques confirmed the successful formation of ZnS NCs. These promising results pave the way for further exploration into the reaction pathway using alternative hydrolytic agents such as H_2Te and H_2Se . However, it is important to note that, regrettably, these particular studies were not conducted within the scope of this dissertation. The decision to omit investigations involving H_2Te and H_2Se was influenced by the associated safety concerns. Both hydrogen telluride and hydrogen selenide are known to be highly toxic

and hazardous substances, necessitating rigorous safety measures and specialized equipment for their handling. Given these challenges and constraints, the focus of this dissertation remained centered on the innovative use of H_2S as an alternative hydrolytic agent, offering new reactivities into field of solid-state organometallic precursor reactions. Exploring the complexities of H_2Te and H_2Se in similar contexts represents a compelling direction for future research and the advancement of scientific knowledge. The unique optical and electronic properties of ZnSe and ZnTe , particularly their effective absorption in the visible range, make them key materials for advancing next-generation optoelectronic devices[272, 273].

REACTIVITY OF THE MODEL ORGANOZINC PRECURSOR IN SOLUTION

Organometallic synthetic approaches, in which a solution of an organozinc precursor is exposed to air, have been extensively employed for the synthesis of colloidal ZnO NCs[191, 193, 194, 274]. However, in situ monitoring of molecular transformations during these processes remains limited. The formation of ZnO nanoparticles in such systems involves a complex sequence of consecutive transformations, each dependant on fundamental molecular-level transformations. Understanding the decomposition pathways of preorganized alkylzinc species into ZnO NCs, including the identification and characterization of key intermediates, is essential for elucidating the mechanistic foundations of these transformations. Such insights are crucial for optimizing synthesis strategies and achieving precise control over NC properties.

Chapters 3 and 4 of this dissertation describe design, synthesis and characterization of the predesigned single-crystal precursor of ZnO NCs and its transformations triggered by air exposure in the solid-state. It is evident that the developed solid-state process not only allows for the synthesis of high-quality NCs under mild conditions, but also, due to the highly controlled reaction environment, the resulting material is free from impurities originating from side reactions with molecular oxygen. For instance, during the precursor transformation, no formation of peroxides or ethyl alcohol was observed, and the process proceeds through a clean

pathway, where water leads to the hydrolysis of both the ethyl group, resulting in the release of ethane, and the amide ligand, along with the formation of crystalline benzamide as a separate phase. As the result, the final material consisted of ZnO NCs stabilized by deprotonated amide ligands.

With these observations in hand, the author of this thesis considered how the new solid-state system compares to classical organometallic reaction systems in solution, which lead to the formation of ZnO NCs upon exposure to air. Of particular interest was how the reactivity toward oxygen and water influences the chemical composition of the final reaction mixtures.

Therefore, in this Chapter, the reactivity of the well-defined $[(BA)ZnEt]_4$ precursor with water and water/oxygen systems in organic solvents (toluene- d_8 and THF- d_8) is examined using in situ ^1H NMR spectroscopy. These studies provide direct insights into the sequential transformations, including the evolution of functional groups and intermediates that drive ZnO NC formation. To complement this studies, diffusion-ordered NMR spectroscopy (DOSY) was employed to determine the aggregation level of $[(BA)ZnEt]_n$ species in solution. Together, these results highlight the critical role of the solvent environment—whether coordinating or non-coordinating—and the reaction pathway, governed either by exposure to air or direct hydrolysis, in modulating reaction kinetics and stabilizing intermediates.

7.1 Structure and degree of aggregation of $[(BA)ZnEt]_n$ species in solution

The structure and aggregation level of the $[(BA)ZnEt]_n$ species were investigated in toluene- d_8 and THF- d_8 as non-donor and donor solvents, respectively. As described in Chapter 3.1.2.2 the ethylzinc derivative of benzamide in the solid-state exist as tetranuclear cluster, $[(BA)ZnEt]_4$. To investigate the reactivity of the precursor in solution it was critical to provide insights into degree of aggregation and whether the solution consist of a mixture of different aggregates.

The well-defined crystalline complex $[(BA)ZnEt]_4$ was dissolved in a selected dry and deoxygenated deuterated solvents (2% w/v) at room temperature in a glove-box and initially kept in a Young Precision NMR tube under nitrogen.

The ^1H NMR spectrum of the $[(BA)ZnEt]_n$ system in toluene- d_8 (Figure 7.1a) shows signals for the aromatic protons of the benzamide ligand in the chemical shift range of 7.0 to 7.8 ppm. The amide protons (-NH) are observed around 6.5 ppm as a singlet. Furthermore, the ^1H NMR spectrum shows the signals of the alkyl group bound to the zinc atom: a characteristic triplet with an NMR shift at 1.8 ppm (CH_3CH_2-Zn) and a quartet with an NMR shift at 0.9 ppm (CH_3CH_2-Zn), with a 3:2 proton signal intensity ratio.

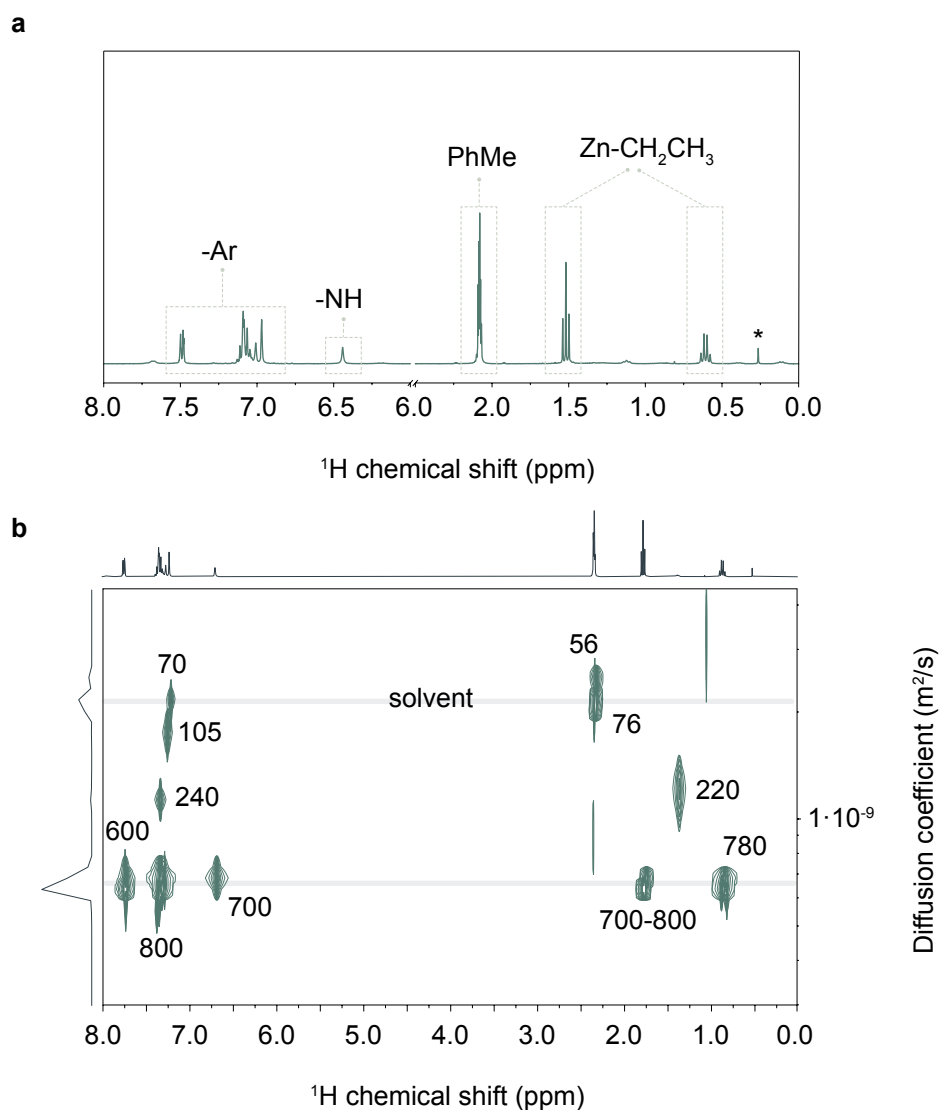


Figure 7.1: ^1H NMR and 2D DOSY spectra of $[(BA)ZnEt]_n$ in toluene- d_8 at room temperature. The peaks marked with asterisk (*) are from grease impurities.

The degree of aggregation of alkylzinc species in solution depends on the coordination environment[275, 276]. Analysis of the DOSY ^1H NMR spectra of the $[(\text{BA})\text{ZnEt}]_n$ in toluene- d_8 (Figure 7.1b) shows that tetrameric moieties ($n = 4$), with the estimated molecular weight (MW) of about $700\text{--}800\text{ g}\cdot\text{mol}^{-1}$, are favored. The presence of species with a MW around $600\text{ g}\cdot\text{mol}^{-1}$ also suggests the coexistence of a trimeric ($n = 3$) alkylzinc species, though tetramers remain predominant under these conditions. This equilibrium between trimeric and tetrameric species is illustrated in Figure 7.2.

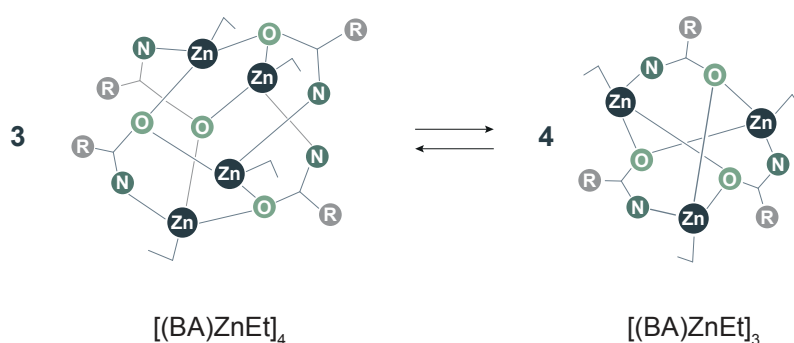


Figure 7.2: Equilibrium between tetrameric $[(\text{BA})\text{ZnEt}]_4$ and trimeric $[(\text{BA})\text{ZnEt}]_3$ clusters in toluene- d_8 at room temperature.

In the ^1H NMR spectrum of the $[(\text{BA})\text{ZnEt}]_n$ species in THF- d_8 (Figure 7.3a), the aromatic protons from the benzamide ligand are observed within the chemical shift range of 7.0 to 8.0 ppm. The methyl group protons from the ethyl group are observed in the range 0.9 - 1.2 ppm ($\text{CH}_3\text{CH}_2\text{-Zn}$), while protons from the methylene group appear in the range of -0.2 to 0.2 ppm ($\text{CH}_3\text{CH}_2\text{-Zn}$). The singlet observed around 0.85 ppm arises from traces of ethane generated by the partial hydrolysis of the ethyl group due to residual water impurities. The sharper ^1H NMR signals in toluene- d_8 and broadened signals in THF- d_8 are primarily due to the differences in solvent coordination and the resulting interactions of the $[(\text{BA})\text{ZnEt}]_n$ aggregates with the solvent molecules. Toluene, as a non-coordinating solvent, interacts weakly with the system, resulting in sharper peaks, whereas THF, as a coordinating solvent, induces stronger yet dynamic complex-solvent interactions (*vide infra*) changing local chemical environment and leading to broader peaks.

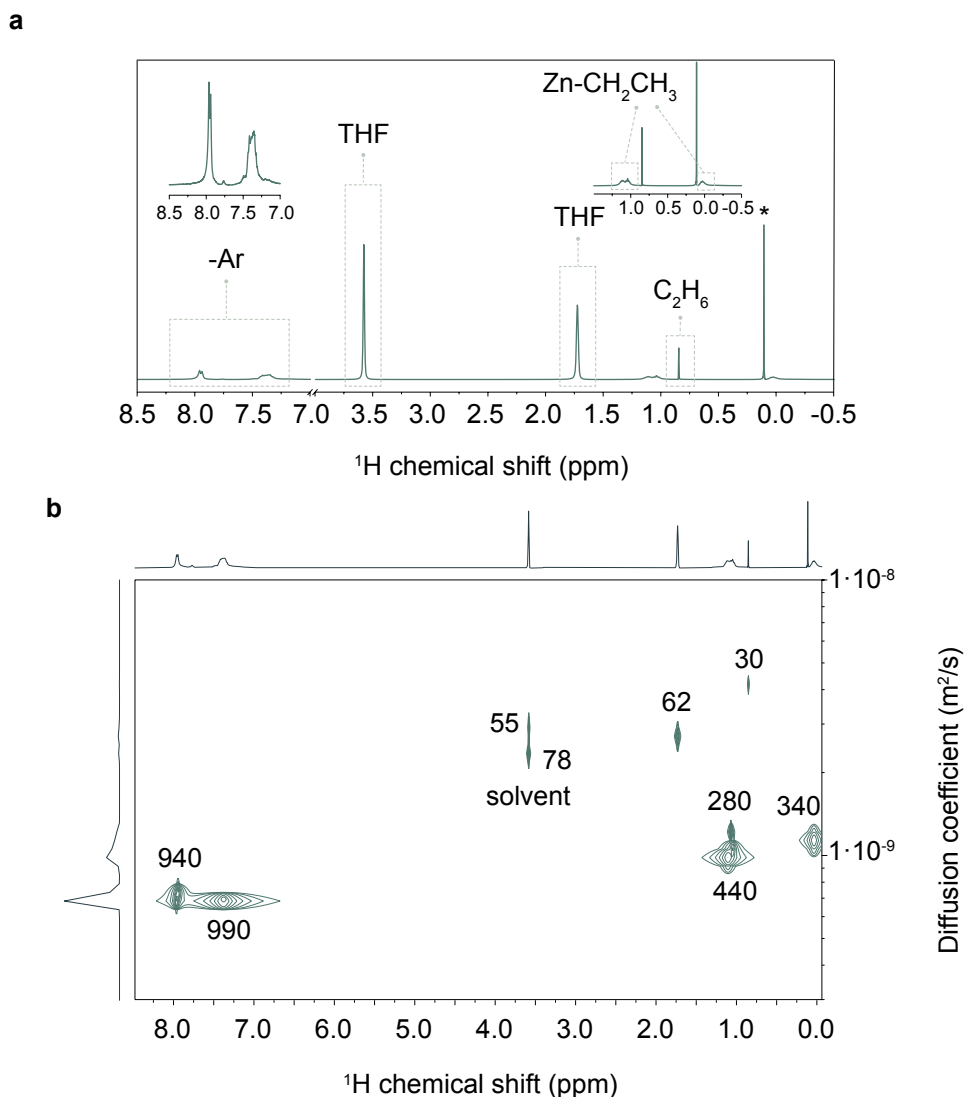


Figure 7.3: ^1H NMR and 2D DOSY spectra of $[(\text{BA})\text{ZnEt}]_n$ in THF-d_8 at room temperature. The peaks marked with * are grease impurities.

The DOSY ^1H NMR spectrum of the $[(\text{BA})\text{ZnEt}]_n$ system in THF-d_8 reveals the presence of multiple aggregate states involved in the Schlenk-type equilibria. The Schlenk equilibrium refers to the dynamic balance between different organozinc species in solution. First described for Grignard reagents nearly a century ago, the Schlenk equilibrium is now recognized as a general phenomenon in heteroleptic organometallic systems. These equilibria often generate to complex mixtures of species with distinct reactivity. Despite extensive studies on the oxygenation of alkylzinc compounds, the role of the Schlenk equilibrium in modulating their reactivity towards O_2 has not been systematically addressed. Characterizing organozinc reactants and intermediates is challenging due to their complex solution behav-

ior, often involving a variety of aggregated forms and non-stoichiometric species resulting from Schlenk equilibria[277, 278]. The analysis of the $[(\text{BA})\text{ZnEt}]_n/\text{THF-d}_8$ system revealed the presence of two main components with the MW of $940 \text{ g}\cdot\text{mol}^{-1}$ and $280 \text{ g}\cdot\text{mol}^{-1}$ in the aromatic and alkyl region respectively, which likely indicates the presence of trimeric bis-chelate complex, $[(\text{BA})_2\text{Zn}]_3$, and ZnEt_2 adduct with THF, $[(\text{THF})_2\text{ZnEt}_2]$. The proposed Schlenk equilibrium shifted towards products almost quantitatively is presented in Figure 7.4.

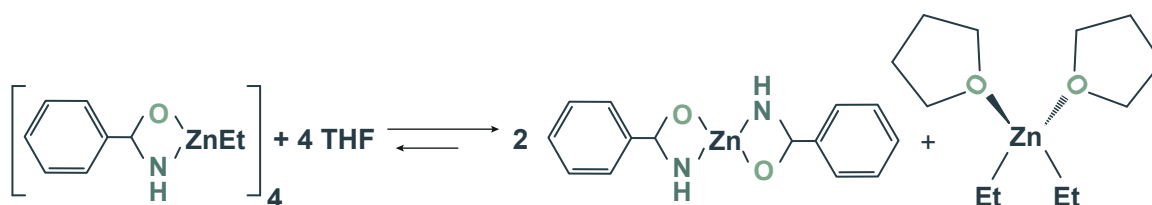


Figure 7.4: Schlenk equilibrium of the $[(\text{BA})\text{ZnEt}]_n$ species upon dissolving in THF-d_8 at room temperature.

In summary, while solid-state studies of the model precursor provide detailed and precise structural information, they may not fully represent the species present in dynamic solution-phase reaction systems, which are critical for a comprehensive understanding of the system reactivity. The DOSY ^1H NMR study revealed that, although the $[(\text{BA})\text{ZnEt}]_n$ system exists as a tetramer in the solid state, multiple aggregate states are observed in solution. The DOSY ^1H NMR spectra clearly illustrate that the $[(\text{BA})\text{ZnEt}]_n$ system forms larger aggregates in toluene- d_8 , a non-coordinating solvent. In contrast, in THF-d_8 , solvent molecules coordinate to Zn centers shifting the Schlenk equilibria towards Zn-ligand bischelate complexes and diethylzinc $[(\text{THF})_2\text{ZnEt}_2]$ moieties. This difference is due to the ability of THF to coordinate to the zinc center, reducing aggregation and increasing the dynamic exchange processes within the solution. Understanding solvent effects remains challenging, particularly when reaction intermediates exhibit differential behavior in distinct solvents[275, 276]. Notably, in the THF based systems the $[(\text{THF})_2\text{ZnEt}_2]$ moieties act most likely as the direct precursor of ZnO NCs through the interactions with dioxygen and/or water from air (Chapter 7.2.1.2).

7.2 In situ ^1H NMR studies on reactivity of the $[(\text{BA})\text{ZnEt}]_n$ system towards water and water/dioxygen in solution

To investigate the sequence of elementary steps of the reaction between $[(\text{BA})\text{ZnEt}]_n$ system and dioxygen and/or water from air, the process was monitored by ^1H NMR spectroscopy. In situ ^1H NMR spectroscopy allows for direct monitoring of the functional groups (that is BA-Zn and Zn-C bonds) within alkylzinc complexes upon its transformation to ZnO NCs, identifying the intermediates and resulting products. For the ^1H NMR experiments, the well-defined model complex of $[(\text{BA})\text{ZnEt}]_4$ was first dissolved in dry and deoxygenated toluene- d_8 or THF- d_8 (2% w/v) at room temperature in a glovebox and then stored in a Young Precision NMR tube under nitrogen. For the controlled exposure experiments, the NMR tube was slightly unsealed to allow gradual contact of the sample with air. In situ ^1H NMR spectra were recorded in 5-minute intervals over the first 12 hours to capture the initial transformation stages and subsequently at 24-hour intervals until transformation completion. The endpoint of the transformation was confirmed by the visible luminescence of the complex under a UV lamp, indicating the formation of ZnO NCs.

7.2.1 In situ ^1H NMR studies of exposure of the $[(\text{BA})\text{ZnEt}]_n$ system to humid air

7.2.1.1 $[(\text{BA})\text{ZnEt}]_n$ in toluene- d_8 solution during air exposure

The in situ ^1H NMR experiments in toluene- d_8 provide insight into the transformation pathway of the $[(\text{BA})\text{ZnEt}]_n$ precursor in toluene- d_8 upon controlled air exposure (Figure 7.5). After the first hour, broad signals appear in the 4.70–4.15 ppm range, attributed to zinc hydroxide groups, Zn-OH (Figure 7.4a). In the presented system, zinc hydroxide species act as intermediates on the way to zinc oxide species and are result of direct hydrolysis of Zn-C bonds by water molecules or

gradual decomposition of zinc peroxide groups. As the reaction progresses, a hydroxide peak at 4.30 ppm increases in intensity over 24 hours, and shifts eventually matching the neighboring peak at 4.45 ppm; both peaks gradually disappear over the following days as broad signals characteristic of free benzamide (6.0–5.0 ppm) emerge. This shift indicates progressing hydrolysis of the amide ligand and release of free benzamide. After 48 hours, a new signal appears at 4.85 ppm, potentially associated with new Zn-OH species, suggesting ongoing reorganization of zinc hydroxide and oxide intermediates. Although this signal cannot be directly assigned to Zn-O-Zn bonds, it may represent zinc hydroxide species in a bridging coordination mode, Zn-O(H)-Zn, or other proton-containing intermediates involved in the reaction. As the Zn-OH groups condensate, likely forming zinc oxo bridges, Zn-O-Zn, further hydrolysis of the amide ligands is facilitated, eventually leading to ZnO nanocrystal formation. Notably, new peaks emerge in the 0.4–0.55 ppm range, indicating the formation of water molecules during the condensation process (Figure 7.5b). These water signals suggest that the condensation of Zn-OH groups to form Zn-O-Zn bridges releases water as a byproduct as represented in Figure 7.5b, further supporting the transformation pathway toward ZnO NCs formation.

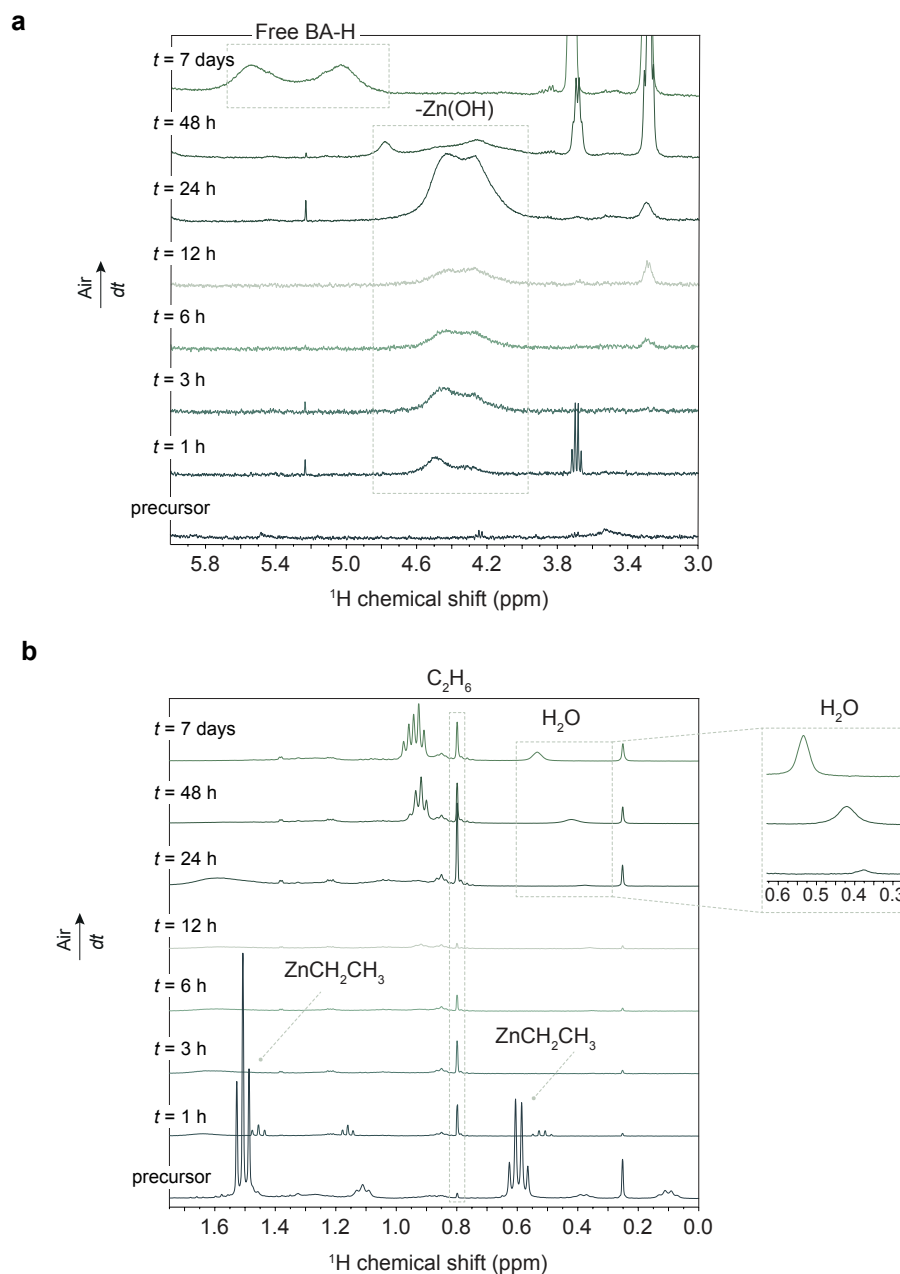


Figure 7.5: In situ ^1H NMR studies of the $[(\text{BA})\text{ZnEt}]_n$ system during air exposure in toluene- d_8 at room temperature. **a**, Release of free benzamide (BA-H) and formation of hydroxyl intermediates. **b**, Release of water molecules during condensation.

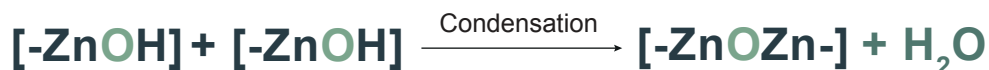


Figure 7.6: Schematic representation of hydrolysis and condensation reactions in the toluene- d_8 /air and THF- d_8 /air systems towards ZnO NCs.

Notably, in the investigated system, well-defined multiplets appear in the 3.75–3.70 ppm region within the first 5 minutes, indicating the formation of oxidation products, specifically zinc peroxo species, $\text{Zn-OOCH}_2\text{CH}_3$, as shown in Figures 7.7a and 7.7b. The intensity of these signals gradually decreases, completely disappearing quantitatively after 2 hours, highlighting the relatively high stability of these peroxides at room temperature in this system. The presence of Zn-OOR species alongside ethylene ($\text{CH}_2=\text{CH}_2$, singlet at 5.25 ppm) indicates a concomitant transformation pathway in which O_2 inserts into the Zn-C bond, forming an Et-O-O-Zn species. This pathway further involves the homolytic cleavage of the O-O bond, yielding an ethyl ($\text{Et-O}\cdot$) and $\cdot\text{O-Zn}$ radical species. The ethyl radical subsequently react with hydrogen species (i.e., protons) present in the reaction system, potentially leading to the formation of ethanol byproducts ($\text{C}_2\text{H}_5\text{OH}$) as indicated by new signals at 3.4 and 1.4 ppm. This mechanism aligns with the previous findings, which describes similar ethylene elimination upon O_2 insertion and subsequent decomposition in an analogues alkylzinc systems supported by benzoic acid[176]. The presence of both free ethanol and ethylene in the NMR spectra thus supports this oxidative pathway, wherein Zn-C bonds undergo transformation upon reaction with O_2 , leading to byproducts like ethanol and ethylene through radical mediated processes.

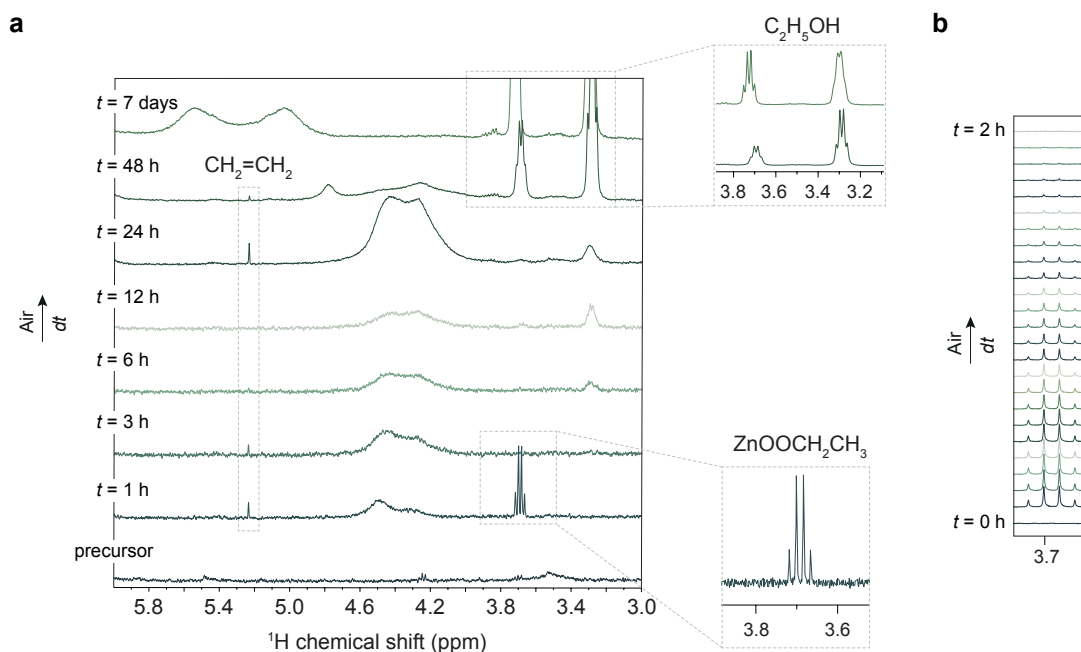


Figure 7.7: In situ ^1H NMR studies of the $[(\text{BA})\text{ZnEt}]_n$ system during air exposure in toluene- d_8 at room temperature. **a**, Spectra showing oxygenated intermediates during precursor decomposition. **b**, Magnified region showing the emergence of intermediates during the first 2h.

7.2.1.2 $[(\text{BA})\text{ZnEt}]_n$ in THF- d_8 solution during air exposure

The transformation pathway of the $[(\text{BA})\text{ZnEt}]_4$ precursor dissolved in THF- d_8 upon air exposure exhibit notable differences compared to the toluene- d_8 system, highlighting the influence of the solvent environment and resultant equilibria on the reaction course (Figure 7.8). As noted above, based on ^1H DOSY experiments for $[(\text{BA})\text{ZnEt}]_4$ in THF- d_8 , the most likely organozinc species reactive in this system are $[(\text{THF})_2\text{ZnEt}_2]$ moieties, which can directly interact with dioxygen and/or water from the air, leading to the formation of ZnO NCs. This sheds new light on the reactivity of alkylzinc precursors in donor solvents[191–193, 195].

Broad signals corresponding to Zn-OH intermediates at the range 4.05 - 4.20 ppm emerge after around 3 hours and remain pronounced/evident for an extended period. These observations indicate that, the THF-system stabilizes the reaction intermediates more effectively (*vide infra*). Notably, the singlet at 2.50 ppm, indicative of water formation from the condensation of Zn-OH groups, emerge much

later—only after 7 days—suggesting that the condensation process (formation of Zn-O-Zn species on the expense of Zn-OH systems with evolution of water molecules) and subsequent formation of ZnO NCs are delayed in THF. At the same time, broad resonances in the 7.25–6.50 ppm region confirm the gradual release of free benzamide during the course of the reaction.

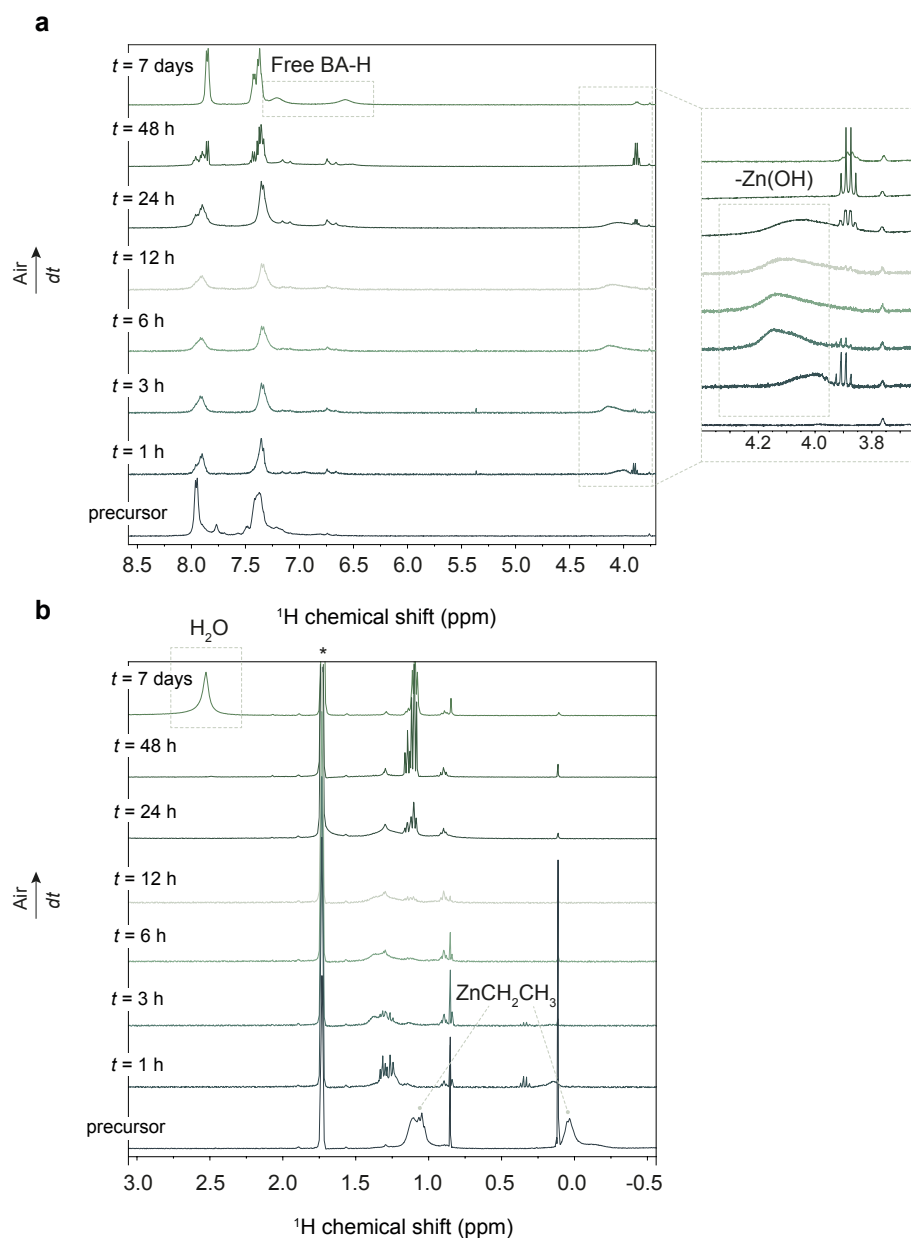


Figure 7.8: In situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_n$ system during air exposure in THF-d_8 at room temperature demonstrating: **a**, Release of free benzamide (BA-H) and formation of hydroxyl intermediates. **b**, Release of water molecules during condensation. The peak marked with * is from THF-d_8 .

The initial formation of $\text{Zn-OOCH}_2\text{CH}_3$ species is observed within the first few hours, with signals appearing in the 3.80–3.95 ppm region. Interestingly, these signals remain longer than in the system based on toluene- d_8 , suggesting a slower progression of the transformations in the THF- d_8 system. Ethylene ($\text{CH}_2=\text{CH}_2$) formation, detected as a singlet at 5.35 ppm, is observed for a shorter time in THF-based system in comparison to toluene- d_8 . The ethanol ($\text{C}_2\text{H}_5\text{OH}$) byproduct signals (3.60 – 3.30 ppm and 1.20 – 1.00 ppm) appear only after 24 hours, indicating prolonged radical-driven decomposition processes of zinc peroxides in THF.

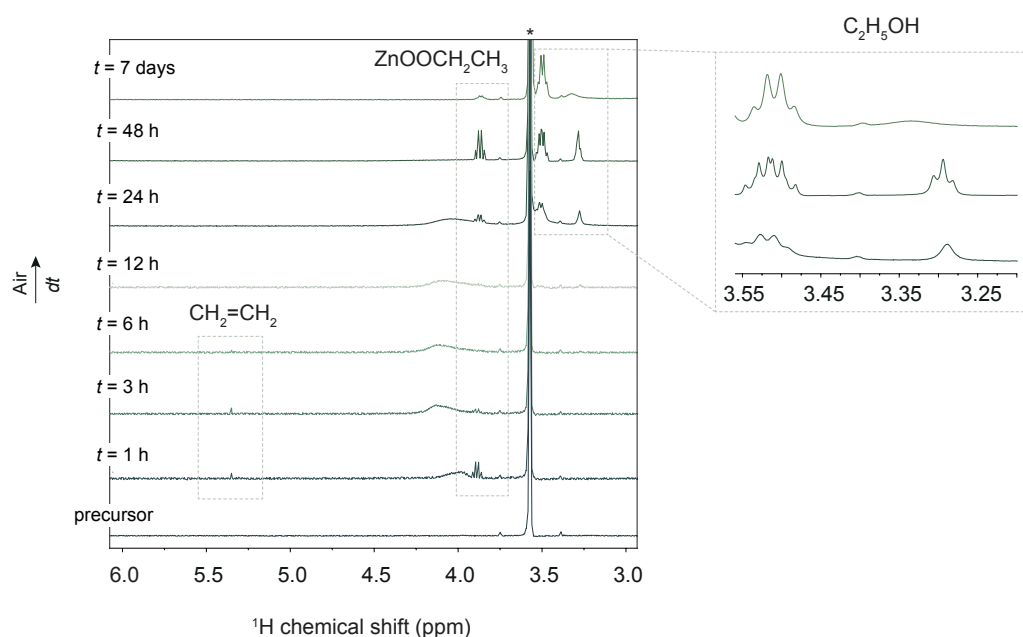


Figure 7.9: In situ ^1H NMR studies of the $[(\text{BA})\text{ZnEt}]_n$ system during air exposure in THF- d_8 at room temperature presenting oxygenated intermediates during precursor decomposition. The peak marked with * is from THF- d_8 .

Overall, these findings underline the slower reaction rate, more efficient stabilization of intermediates, and much delayed formation of nanocrystalline products in THF- d_8 . The kinetics of $[(\text{BA})\text{ZnEt}]_n$ transformation differ significantly between THF- d_8 and toluene- d_8 , primarily due to different coordination strength of the solvents and stabilizing effect of THF. In THF- d_8 , reactions with H_2O and O_2 are slower, with intermediates such as $\text{Zn-OOCH}_2\text{CH}_3$ and Zn-OH persisting for a longer time. In the THF system, formation of water and ZnO NCs through condensation are significantly delayed, with water signals appearing only after 7 days.

In contrast, toluene- d_8 promotes faster oxidative and hydrolysis pathways, with faster hydrolysis, formation of water molecules on an earlier stage (after only 1 day), and faster ZnO NCs formation.

To visualize the described systems on the macroscopic level, additional experiments were carried out in which $[(BA)ZnEt]_4$ precursor was dissolved in both solvents (THF- d_8 and toluene- d_8), placed in vials at room temperature, and monitored during air exposure (Figure 7.10). This experiment revealed distinct differences of the transformations occurring in each environment, further corroborating the data obtained from the in situ NMR studies. In the coordinating solvent system (THF), the formation of a gel-like material was clearly observed, reflecting the stabilization of Zn-OH species, which aggregate over time to form three-dimensional network stabilized by hydrogen-bonding interactions, kinetically hindered from fast nucleation towards crystalline ZnO. Conversely, in the non-coordinating solvent system (toluene), turbidity of the sample developed quickly and precipitation of nanopowders rather than gels was observed. THF, as a donor solvent containing oxygen donor center, propagates hydrogen bonding interactions that significantly influence the reaction dynamics of $[(BA)ZnEt]_n$, distinguishing it from non-donor solvents like toluene. The gelation behavior observed in THF reflects the prolonged existence of intermediates and the kinetic arrest of smaller ZnO structures, such as sub-nanometric oxo- and hydroxozinc clusters, delaying their condensation into larger ZnO nanostructures. In contrast, toluene enables faster transformations, leading to efficient ZnO NC formation, as intermediate stabilization and hydrogen bonding are less pronounced.

In conclusion, the timing of water formation in the investigated systems dictate the course and efficiency of the ZnO nanocrystallization. In THF, condensation of ZnOH species is delayed and, as a consequence, formation of water molecules occurs later. THF stabilizes intermediates, promotes gelation, and hinders nucleation, allowing precise control over ZnO structure. Conversely, in toluene, elimination of water molecules from Zn-OH species at early stages accelerates condensation processes and facilitates efficient ZnO NC formation, making it more suitable for rapid ZnO production in a powder form.

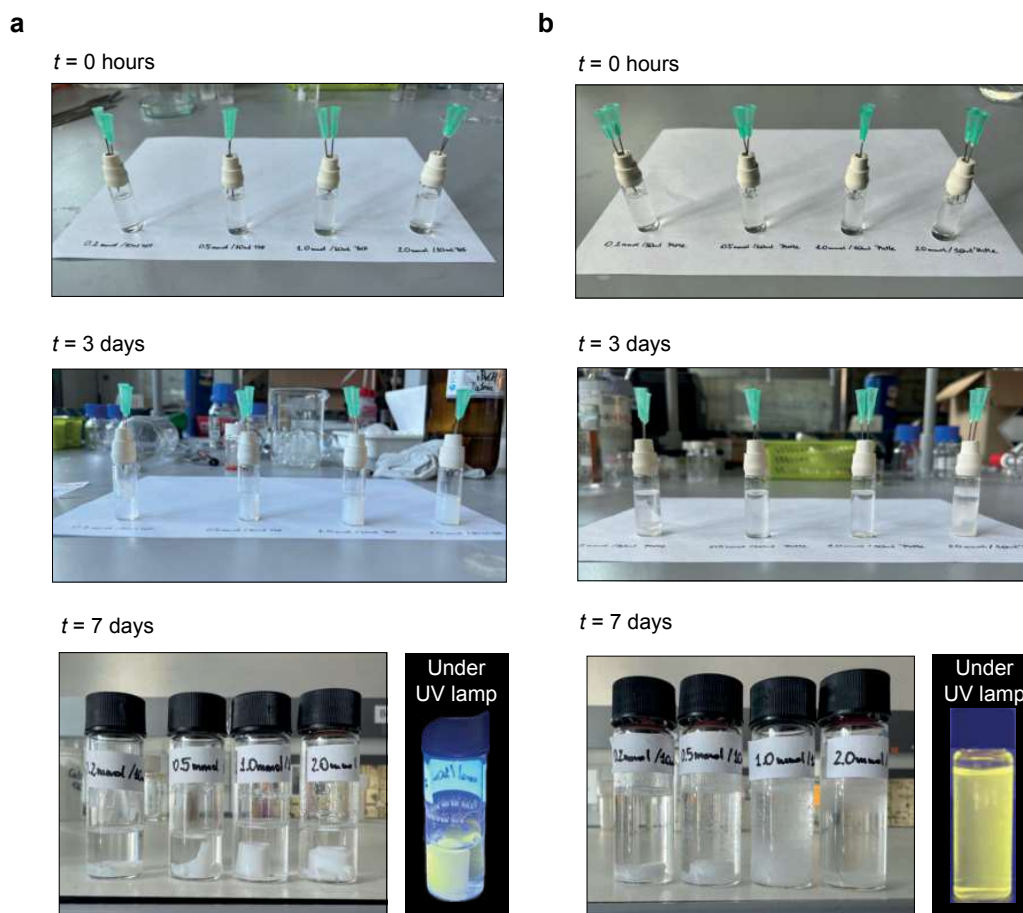


Figure 7.10: Comparative analysis of $[(BA)ZnEt]_n$ transformation over time after air exposure in: **a**, THF- d_8 /air system and **b**, toluene- d_8 /air system.

7.2.2 In situ ^1H NMR studies of the $[(BA)ZnEt]_n$ species hydrolysis

7.2.2.1 Reactivity of $[(BA)ZnEt]_n$ system with H_2O in toluene- d_8

For the experiment on the reactivity of $[(BA)ZnEt]_n$ with H_2O , a 1.7 μl (92 μmol) of water was added to the $[(BA)ZnEt]_4$ precursor (10mg; 46 μmol) dissolved in toluene- d_8 (2:1 molar ratio) and reaction progress was monitored with ^1H NMR spectroscopy. The ^1H NMR spectra reveal a transformation pathway distinct from that observed during air exposure (Figure 7.11). Within the first few minutes, a strong peak at 0.82 ppm is observed, indicating rapid cleavage of Zn–C bonds and the subsequent release of ethane (C_2H_6). After around 12 h, weak broad signals appear in the 5.3–4.8 ppm region, which increase in intensity over the following 24 h. At

longer times these signals evolve into distinct peaks centred at 5.8 and 5.2 ppm, consistent with hydrolysis of the amide ligands and the release of free benzamide.

A singlet at around 0.55 ppm appears after approximately 48 h, corresponding to water molecules released during the condensation step. Notably, signals associated with Zn-OH species are not observed in this system, likely on account of interaction of zinc hydroxide moieties with water molecules and rapid proton exchange, which is fast on the NMR timescale and results in extensive line broadening beyond detection. Strikingly, signals from water molecules are initially not visible in the spectra and only appear after 48 hours, indicative of condensation processes and the elimination of free water molecules. Weak multiplets appear in the 3.9–3.7 ppm region within the first 1–3 h, consistent with Zn-OOCH₂CH₃ species. These signals are most likely assigned to trace peroxide intermediates arising from residual oxygen contamination introduced during water injection through the septum. Importantly, no additional oxidative byproducts such as ethylene or ethanol are detected, confirming that the radical pathways and O₂-insertion processes are not involved in this transformation.

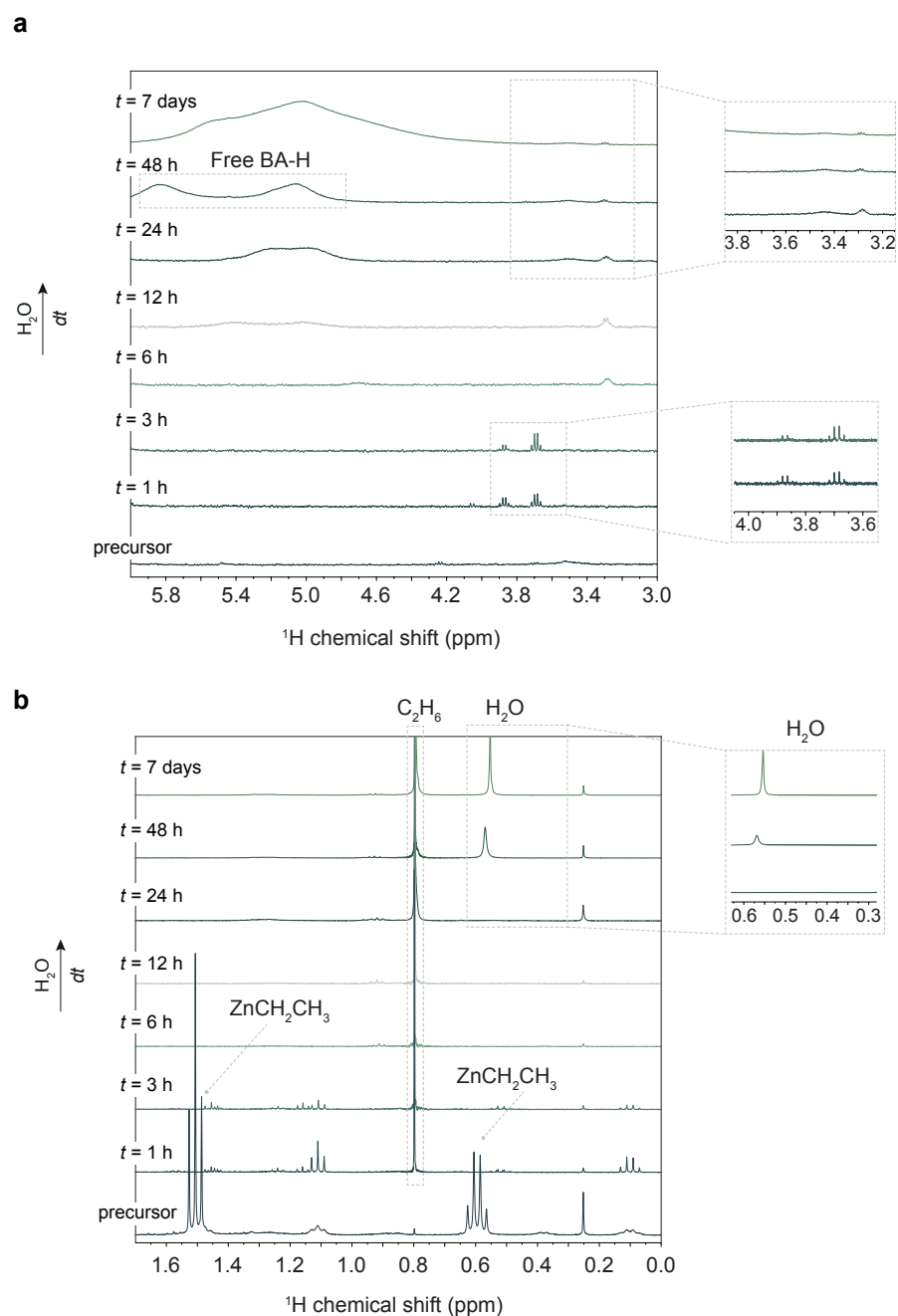


Figure 7.11: In situ ^1H NMR studies of the $[(BA)ZnEt]_n$ system in toluene- d_8 upon addition of water droplet at room temperature. **a**, Release of free benzamide (BA-H) **b**, Release of water molecules during condensation.

In conclusion, the water-induced reaction is characterized by the replacement of ethyl groups with hydroxyl groups and accelerated condensation reactions. Although signals assigned to Zn–OH intermediates are not directly observed, their transient presence is indicated by the subsequent appearance of a singlet at 0.55 ppm, corresponding to water molecules released during condensation. This

progression indicates the stepwise formation of Zn–O–Zn bridges, ultimately leading to ZnO nanocrystals (Figure 7.12). Notably, signals of water molecules are only visible after the condensation processes of zinc hydroxide species are initiated, indicating strong involvement of water molecules present in the system (as the reagent) at earlier stages of the hydrolytic transformations. This pathway highlights the efficiency of water as a hydrolytic agent, driving rapid ligand exchange and condensation reactions without requiring oxidative intermediates, in contrast to the slower, O₂-mediated transformations observed during air exposure.

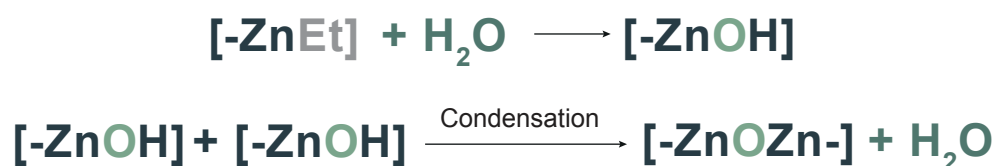


Figure 7.12: Schematic representation of hydrolysis reaction and condensation step in the toluene-d₈/H₂O and THF-d₈/H₂O systems towards ZnO NCs.

7.2.2.2 Reactivity of the [(BA)ZnEt]_n system in THF-d₈ solution with H₂O

For the experiment on the reactivity of [(BA)ZnEt]_n with H₂O, a 1.7 μL (92 μmol) water was added to the [(BA)ZnEt]₄ precursor (10 mg; 46 μmol) dissolved in THF-d₈ (2:1 molar ratio) and reaction progress was monitored with ¹H NMR (Figure 7.13). Within the first hour, a sharp increase in the signal at 0.82 ppm is observed, assigned to the ethane (C₂H₆) release, indicating rapid Zn–C bond cleavage similar to the toluene system. Broad signals at 2.8–2.6 ppm are assigned to water molecules present in hydrogen-bonded clusters, which are observed during the first 12 h. After this time, a sharp singlet at 2.65 ppm appears, corresponding to free water released during Zn–OH condensation, ultimately leading to the formation of ZnO NCs. In parallel, broad multiplets assigned to coordinated benzamide ligands (8.00–7.00 ppm) progressively decrease, while sharper signals characteristic of free benzamide (BA–H) appear, confirming progressive hydrolysis of the amide ligands. Zn–OH species are not directly observed in this system, consistent with rapid proton exchange and their dynamic interactions with water. As in

toluene- d_8 , these processes broaden the Zn–OH signals beyond detection on the NMR timescale.

The dynamics of water release, however, differ between the two solvents. In THF, the higher polarity accelerates proton exchange and leads to the earlier release of water, observed as a distinct, narrow signal. This contrasts with the toluene system, where slower kinetics and weaker hydrogen-bonding interactions result in delayed condensation and a less pronounced water signal. Ultimately, in both solvents the process leads to the formation of ZnO nanocrystals. Importantly, no additional oxidative byproducts are detected in this system, confirming that the radical pathways and O_2 -insertion processes are not involved.

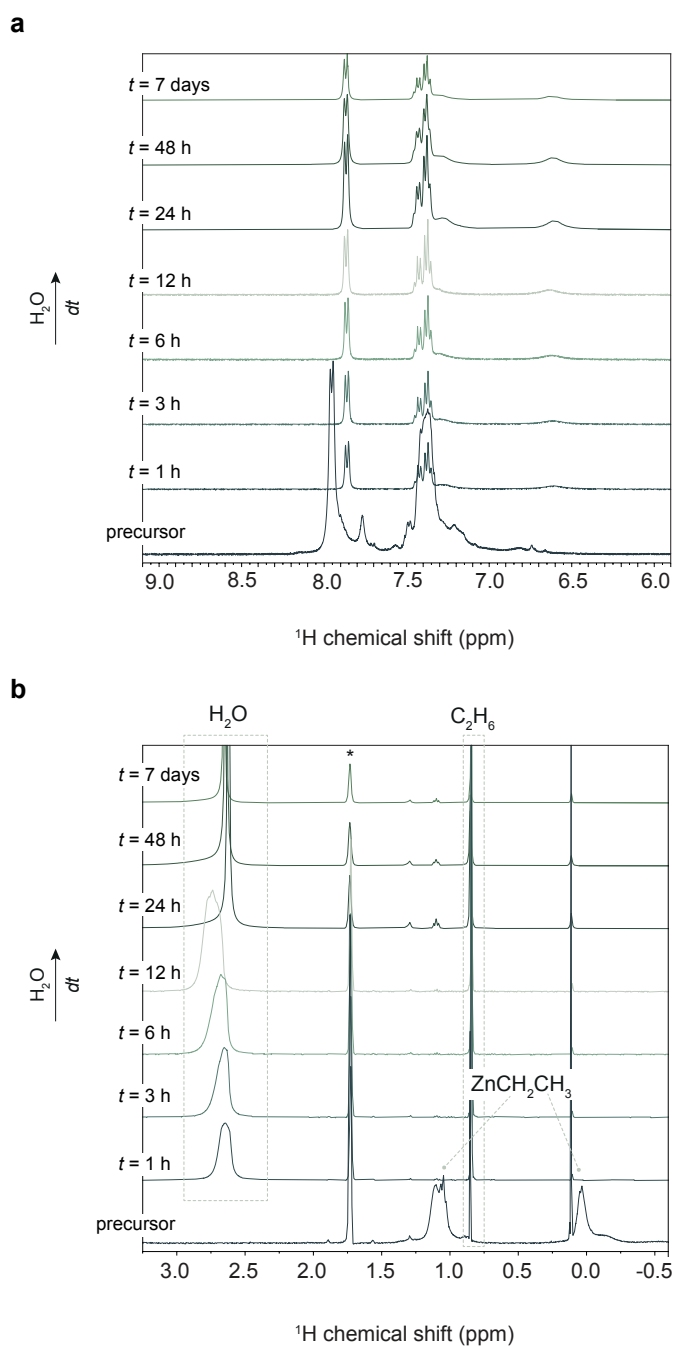


Figure 7.13: In situ ^1H NMR studies of the $[(\text{BA})\text{ZnEt}]_n$ system in THF-d_8 upon addition of water droplet at room temperature. **a**, Release of free benzamide (BA-H) **b**, Release of water molecules during condensation. The peak marked with * is from THF-d_8 .

7.3 Conclusions

The in situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_n$ transformations in toluene- d_8 and THF-d_8 under air exposure and water-mediated hydrolysis reveal distinct mech-

anistic pathways. Both systems ultimately lead to ZnO NC formation, but the reaction rates and intermediates differ substantially, dictated by the solvent environment and the oxygen source (air or water).

Air exposure of the $[(BA)ZnEt]_n$ precursor proceeds through both the hydrolytic and oxidative pathway involving $Zn-OOCH_2CH_3$ peroxides. This mechanism, involving O_2 insertion into $Zn-C$ bonds, produces byproducts such as ethylene ($CH_2=CH_2$) and ethanol (C_2H_5OH). $Zn-OH$ species appear later as intermediates before the condensation step, wherein water molecules are eliminated from zinc hydroxide intermediates, leading to the further formation of ZnO NCs. The overall process is slower due to the sequential nature of radical-mediated oxidative steps and limited by oxygen diffusion from the air to the sample. In contrast, direct hydrolysis with water follows a non-oxidative pathway. The $Zn-C$ bonds cleave almost immediately, releasing ethane (C_2H_6) as the volatile product, while $Zn-OH$ species undergo rapid condensation. This leads to earlier ZnO NC formation compared to air-driven transformation. The transformations of $[(BA)ZnEt]_n$ are highly solvent-dependent, toluene facilitates rapid oxidative and hydrolytic processes, while THF stabilizes intermediates through hydrogen bonding, resulting in slower reaction kinetics and delayed ZnO NC formation. It was noted, that based on ^1H DOSY experiments for the precursor in THF- d_8 , the most likely organozinc species reactive in this system are $[(THF)_2ZnEt_2]$ moieties and not $(L)ZnR$ -type clusters. This sheds new light on the reactivity of alkylzinc precursors in donor solvents and suggests that simple mixtures of Et_2Zn with a selected ligand can be used in synthetic protocols[191–193, 195].

The solution studies also highlight the distinctive advantages of the HOPE solid-state system (see Chapter 3 and Chapter 4). Unlike in solution, millimetre-sized precursor crystals, when exposed to humid air, undergo hydrolytic transformations that ultimately lead to the formation of ZnO NCs without oxidative byproducts (such as ethylene and ethanol).

This highlights the crucial role of the crystalline network, which mediates selective reactivity with components of air and provides a well-defined environment for the efficient nucleation and growth NCs. In solution, oxygen and water diffuse from

the air and react with organozinc species through competing pathways—namely hydrolysis and oxidation—leading to undesired oxidative byproducts. In stark contrast, the $[(\text{BA})\text{ZnEt}]_4$ clusters in the solid-state exhibit high selectivity toward water. The highly hygroscopic nature of $[(\text{BA})\text{ZnEt}]_4$ single crystals promotes efficient interactions between water molecules and their surfaces. These water molecules remain on the crystal surfaces long enough to trigger hydrolytic reactions. Conversely, oxygen molecules are unable to effectively diffuse through the surface layer or the non-porous crystal lattice and therefore do not efficiently react with the organometallic centers, even those that are partially hydrolyzed. Instead, due to their high kinetic energy and low affinity for the crystal surface, oxygen molecules tend to scatter back rather than engage in productive reactions.

It should be noted that the final ZnO nanocrystals obtained in these transformations were not subjected to detailed structural or morphological characterization. These solution-based studies were carried out to support the previously described solid-state investigations. The aim was to analyse the intermediates and provide complementary molecular-level insights into ZnO formation, thereby strengthening the solid-state investigations and offering a more complete mechanistic picture.

CONCLUSIONS

Development of solid-state reactions is a major challenge and one of the key targets for sustainable synthetic strategies. However, to date, only a few artificial solid-state synthetic strategies that lead to predesigned products under ambient conditions, without the addition of external energy, have been described. Moreover, there is a scarcity of examples where molecular precursors, typically reactive in solutions, are employed for the solid-state synthesis of nanocrystalline materials.

The main aim of this dissertation was to design and develop of a well-defined solid-state precursor system for the controlled synthesis of ZnO nanocrystals at ambient temperature without external stimuli, as well as to comprehensively investigate its transformation at the molecular and nanoscale level into quantum-sized nanostructures (i.e., quantum dots). Additionally, this thesis focuses on uncovering the differences between the developed solid-state synthetic approach and classical organometallic processes conducted in solution. This work demonstrates that rationally designed organozinc precursors can overcome the intrinsic barrier of limited mass transport in the solid-state, thereby opening new pathways to the sustainable synthesis of functional materials.

Initially, an organozinc solid-state precursor was designed based on $[(L)ZnR]_n$ -type molecular clusters, incorporating reactive Zn–C and Zn–N bonds confined within a single-crystal lattice prone to water-mediated hydrolysis. Specifically, the ethylzinc benzamide complex $[(BA)ZnEt]$ was synthesized and crystalized as a tetranuclear $[(BA)ZnEt]_4$ cluster, and its single crystals were employed as a well-defined model precursor to investigate solid-state transformations

into semiconductor nanocrystals. These non-porous molecular single-crystals are highly reactive towards water molecules, while preserving the integrity of the crystal shape upon air exposure. Such a predesigned synthetic matrix enables the efficient growth of ZnO NCs within its crystalline yet dynamic body, which is susceptible to rearrangements, thereby overcoming the limitation of efficient mass transport in the solid-state.

Subsequently, the development of a comprehensive in situ methodology employing absorption, vibrational, and nuclear magnetic spectroscopies, diffraction and scattering techniques, microscopy, and thermal analysis was pivotal for investigating complex solid-state transformations pathways at both the molecular and nanoscale levels. Together, these complementary methods unveiled the formation of NCs and their aggregation mechanism within a crystalline matrix—an aspect that has remained largely unexplored in solid-state chemistry. Notably, the studies unveiled the critical role of water molecules in initiating the hydrolysis of $[(\text{BA})\text{ZnEt}]_4$ clusters, leading to the formation of zinc hydroxide/oxide intermediate species and an amorphous matrix from hydrolysed BA-H ligands, thereby facilitating efficient mass transport and enabling efficient crystal growth in a solid-state environment. Furthermore, the predesigned single-crystal precursor is highly selective toward water, enabling the controlled synthesis of ZnO nanocrystals without impurities typically associated with reactions involving molecular oxygen.

The developed solid-state methodology was further extended by employing hydrogen sulfide as an alternative hydrolytic agent, leading to the successful formation of ZnS nanocrystals from the model organozinc precursor. These results confirmed the generality of the solid-state precursor approach and opened the possibility for its extension to other chalcogenides such as ZnSe and ZnTe, which are of great interest for optoelectronic applications. Although these latter systems were not investigated within the scope of this dissertation due to their limited availability and safety constraints, the conceptual framework established here clearly indicates their feasibility.

Complementary studies in solution further enriched the mechanistic understanding of the model organozinc precursor reactivity, thereby strengthening the solid-

state investigations and providing a more complete mechanistic picture. The studies revealed reaction pathways depending on the oxygen source used—either a mixture of dioxygen and water (from air) or water alone. In strong contrast to the solid state, where the precursor reacts selectively with water, solution-phase transformations proceeded simultaneously with oxygen and water when exposed to air, often resulting in undesired side reactions and byproducts. These results underscored the selectivity advantage of the developed solid state system, where the crystalline lattice confines reactivity to a single (hydrolytic) pathway, leading to high-quality nanocrystals.

The main scientific achievements of this dissertation can be summarized as follows:

1. The development of the well-defined solid-state system for the synthesis of ZnO NCs at ambient temperature without the input of external energy.

A well-defined solid-state organozinc system that enables controlled transformations towards quantum-sized NCs under ambient conditions, was developed through rational molecular design of precursors for the first time. The developed system resembles natural weathering processes, where minerals are exposed to atmospheric conditions; it operates without the need for additional external energy input and is highly selective toward water molecules from air, minimizing dioxygen-mediated pathways. This selectivity enables a clean transformation free from impurities and byproducts associated with reactions involving oxygen.

2. The elucidation of the mechanism of nucleation, growth, and aggregation in the solid-state. Within this dissertation, a comprehensive methodology for in situ monitoring of processes in the solid state was developed. This development allowed for a detailed understanding of the nucleation, growth, and aggregation of ZnO nanocrystals in the solid-state environment, uncovering previously unknown pathways in solid-state transformations at both the molecular and nanoscale levels. The findings demonstrate a critical role of hydrolytic processes in overcoming the inherent limitations of low diffusion rates at low temperatures in solid-state reactions, thereby facilitating

efficient mass transport and enabling efficient crystal growth in a solid-state environment. The results also show that the initial stage of the precursor transformation, with relatively high freedom for the diffusion of intermediate zinc hydroxide/oxide nanoclusters alongside primary NCs, allows for rapid and more random NC growth and aggregation. In contrast, the later stages are dominated by processes that yield higher monodispersity of the final material, both at the level of individual NCs and NC aggregates.

3. **The development of an effective vacuum-assisted method for a preparation of semiconductor aerogels.** An innovative activation process of NCs was developed, in which the organic matrix was removed through a vacuum-assisted sublimation step, transforming the embedded ZnO nanocrystalline material into a highly porous semiconductor aerogel without the use of solvents or complex chemical treatments. Compared to traditional methods, the presented sublimation process efficiently purified the nanocrystalline material while preserving the structural integrity of the ZnO NCs.
4. **The translation of hydrolysable synthetic systems to other semiconductor materials, exemplified by the H₂S-assisted solid-state synthesis of ZnS NCs.** It was demonstrated that water, as a component of air, is responsible for the complex hydrolytic processes leading to the formation of oxo- and hydroxo-intermediate products, which in turn enable efficient mass transport and formation of ZnO NCs in the solid-state. Understanding this mechanism allowed to extend the methodology to other hydrolytic agents, such as H₂S, which enabled the preparation of high-quality luminescent ZnS NCs. Potential developments of the presented synthetic methodology include the use of H₂Se and H₂Te; however, these were not investigated here due to their limited availability under laboratory conditions.
5. **The comparison of the reactivity of the model organozinc precursor in the solid-state and in solution.** It was demonstrated that the transformation pathways in the solid-state and in solution differ dramatically: in the solid-state the reaction proceeds selectively with water, without the participation of oxygen, whereas in solution the transformation occurs simultaneously with

both water and oxygen when exposed to air, leading to the formation of undesired byproducts. Therefore, the solid-state system offers dramatically enhanced selectivity, as the crystalline lattice confines reactivity to a single pathway, resulting in high-quality nanocrystals.

In summary, this dissertation advances the understanding of nanosynthesis in the solid-state and its mechanistic foundations. The reported artificial system employs a sub-millimeter-sized molecular single crystal acting as a “chemical reactor” for the synthesis of semiconductor nanocrystals, driven by water-fuelled reaction under ambient conditions and thereby mimicking natural chemical weathering processes. In presented system, the crystal matrix plays a dual role acting both as a precursor of metal centres and as a “solvent”, providing the chemical environment for the reaction to proceed. The reported system unveils the formation of nanocrystals and the assembly of their arrays within a crystalline network, revealing dynamic solid matrices as useful environments for highly controlled nanosynthesis. The presented research also provides insights into selection rules for other classes of high-pK_a ligand systems (e.g., amines or other primary and secondary amides), which, in combination with organozinc species, are likely to perform well as solid-state precursor systems for semiconductor materials.

Finally, the results bridge molecular precursor design with solid-state chemistry and demonstrate that mild, selective, and sustainable strategies can be developed for the synthesis of functional semiconductor nanomaterials. These findings provide not only a conceptual advance, but also a practical methodology for the rational design of next-generation nanostructured materials with potential applications in catalysis, optoelectronics, and energy conversion.

EXPERIMENTAL SECTION

9.1 General remarks

Materials. All chemicals were obtained from commercial vendors i.e., benzamide (Sigma-Aldrich, 99% purity) and diethylzinc (ABCR, 99.9998% Zn purity), and were used as received. Solvents were dried and distilled prior to use with an MBraun SPS solvent purification system. Air-sensitive manipulations were performed under a dry, oxygen-free nitrogen atmosphere by using a glovebox (water and oxygen concentration level below 0.1 ppm) and standard Schlenk techniques.

Synthesis of [(BA)ZnEt]₄. Et₂Zn (10 mmol) was added to a suspension of benzamide (10 mmol) in dichloromethane (DCM) (15 ml) at -78 °C and then the reaction mixture was allowed to warm to 20 °C and stirred for an additional 24 h. Colorless crystals were obtained after crystallization with the addition of hexane at 20 °C; isolated yield ca. 87%.

The general protocol for solid-state transformation of [(BA)ZnEt]₄. An appropriate amount of [(BA)ZnEt]₄ single-crystals were exposed to humid air at room temperature (25 °C) and relative humidity (45-55%). The resultant material was collected after 96 h.

Vacuum-assisted sublimation of NCs. The resulting NCs were carefully transferred to a vacuum chamber maintained at a reduced pressure of $4 \cdot 10^{-3}$ mbar.

Gentle heating was applied, gradually raising the temperature up to 120 °C over a period of 2 hours.

9.2 Characterization techniques

Single crystal X-ray diffraction. The crystal was selected under Paratone-N oil, mounted on the nylon loops, and positioned in the cold stream of nitrogen on the diffractometer. The X-ray data for complex [EtZn(BA)]₄ was collected at (100 ± 2) K on a SuperNova Agilent diffractometer using graphite monochromated CuK α radiation (λ = 1.54184 Å). The data were processed with CrysAlisPro[279]. The structure of [EtZn(BA)]₄ was solved by direct methods using the SHELXT program and was refined by full-matrix least-squares on F² using the program SHELXL[280]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealised coordinates and refined as riding atoms.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). CCDC: **2428973** ([EtZn(BA)]₄).

Powder X-Ray diffraction. Diffractograms were collected on a PANalytical Empyrean diffractometer with Ni-filtered Cu K α radiation (λ = 1.5406 Å), a secondary graphite (002) monochromator, and an RTMS X'Celerator (Panalytical) in an angle range of 2θ = 5 ° to 80 °, by step scanning with a step of 0.02 degree.

Small angle X-Ray scattering. The small angle X-ray diffraction patterns were collected with the Bruker Nanostar system fitted with a CuK α ₁ radiation source (Incoatec); the patterns were registered with an area detector VANTEC 2000. Precursor powder was sealed in a hermetic Kapton cell in a glovebox and transferred to a diffractometer. The sample holder section of the instrument has not been evacuated and one of the vacuum ports was left open to allow the exchange of air with

the ambient air in the laboratory. After the collection of the first scattering pattern ($t = 0$), the Kapton windows were punctured to admit the ambient air (RH = 55%) into the cell. The temperature of the sample was stabilized at 25 ± 0.1 °C throughout the experiment. The signal intensities vs. wavevector q were obtained through the integration of the pattern over the azimuthal angle. The scattering data were analyzed using SASView software[281], assuming a spherical form factor and a lognormal distribution of the particle size.

Solid-state Cross-Polarization Magic Angle Spinning ^1H NMR, ^{13}C NMR Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR, ^{15}N NMR). CP-MAS NMR spectra were recorded on a Bruker Avance II 500 MHz spectrometer. For ^{13}C MAS NMR spectra were measured at a spinning frequency of 8 kHz and for ^{15}N MAS NMR at a spinning frequency of 6 kHz. All CP-MAS NMR spectra were performed at 298K and were referenced to glycine as an external standard.

Raman spectroscopy. RS spectra were measured with a Renishaw inVia spectrometer.

Fourier-transform infrared (FTIR) spectroscopy. FTIR spectra were measured with a Bruker Tensor II spectrometer equipped with an ATR (attenuated total reflection) accessory.

Diffuse reflectance infrared fourier-transform (DRIFT) spectroscopy. DRIFT spectra were measured with a Bruker Tensor II spectrometer equipped with a diffuse reflectance accessory (Pike Technologies).

Ultraviolet and visible light spectroscopy. UV–Vis spectra were acquired on a UV 2600 spectrometer (Shimadzu), and measurements were performed on solid powders located on the BaSO_4 surface in reflectance mode with the integrating sphere as a detector in the range 186–1400 nm by 5 nm wide scanning with a step of 1 nm.

PL spectroscopy. PL emission was measured using Quantaurus τ (Hamamatsu C11367).

Thermogravimetric analysis. TGA was performed using open alumina crucibles (5 mm diameter) on a TA Instruments Q600. Standard characterization of the sample was performed with temperature ramping of $5^{\circ}\cdot\text{min}^{-1}$ in the range between 20 and 800°C under a flow of artificial air. In situ experiment with isothermal TGA (temperature is kept constant and the sample weight is recorded as a function of time) was performed under no flow (for hydrolysis reaction).

Optical microscopy. Optical microscopy images were recorded on an Olympus BX53 microscope in transmission mode. The instrument was equipped with two linear polarizers (Olympus U-POT), which were oriented as indicated, and an Olympus DPT2 camera (Olympus Schweiz AG, Volketswil, Switzerland).

High-resolution transmission electron microscopy. HRTEM images were obtained using a JEM 2100 microscope (JEOL Ltd, Japan) with an operation voltage of 200 kV.

Gas adsorption experiments. Gas sorption studies were undertaken using an ASAP 2020 system, Micromeritics Instrument Corporation (Norcross, Georgia, USA). Approximately 100 mg of HOPE SCs were transferred to a sample tube and evacuated under vacuum at 25°C on the gas adsorption apparatus until the outgassing rate was $<5\ \mu\text{m Hg}$ to give fully desolvated material. All gases used were of 99.999% purity. Helium was used for the free-space determination after sorption analysis. Adsorption isotherms were measured at 77 K using a liquid nitrogen bath.

9.3 Data processing and calculations

9.3.1 Calculation of NCs size using Debye–Scherrer relation

In order to estimate the average crystallite size of the NCs, peak broadening in the powder XRD patterns was analyzed using the Debye–Scherrer relation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

where 0.89 is the Scherrer constant, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum (FWHM) of the primary diffraction peak (in radians), θ represents the Bragg's diffraction angle.

The analysis was performed on the (101) reflection of ZnO, yielding a crystallite size of 4.65 nm.

Table 9.1: Crystallite size of ZnO NCs calculated using the Scherrer.

2θ (°)	Reflection	FWHM (° 2θ)	Crystal size (nm)
35.985	(101)	1.777	4.65

9.3.2 Calculation of NCs size from UV-Vis spectra

UV–Vis diffuse reflectance spectra were acquired using the instrument's software, which provided absorbance as a function of wavelength. For further analysis, spectra corresponding to selected reaction time points were selected and exported.

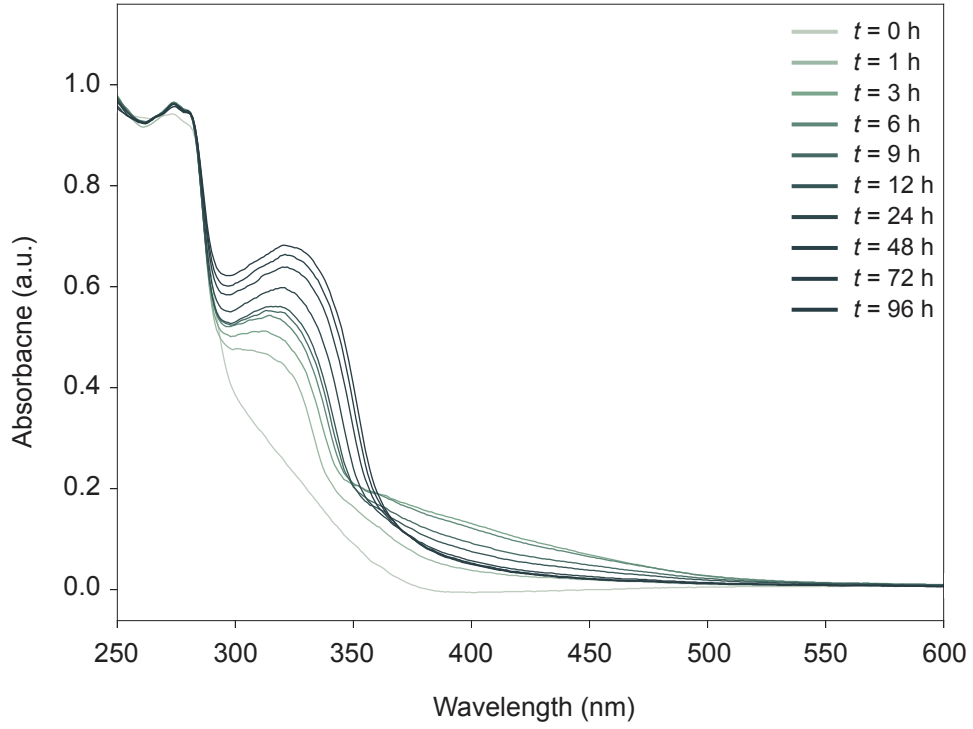


Figure 9.1: Selected UV-Vis experimental data.

The optical band gap (E_g) of ZnO nanocrystals was estimated using the Tauc relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g),$$

where α is the absorption coefficient, $h\nu$ is the photon energy, and A is a proportionality constant.

Tauc plots were obtained by plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$, eV). The band gap value E_g for each sample was determined from the x -intercept of the linear portion of the plot, extrapolated to $(\alpha h\nu)^2 = 0$.

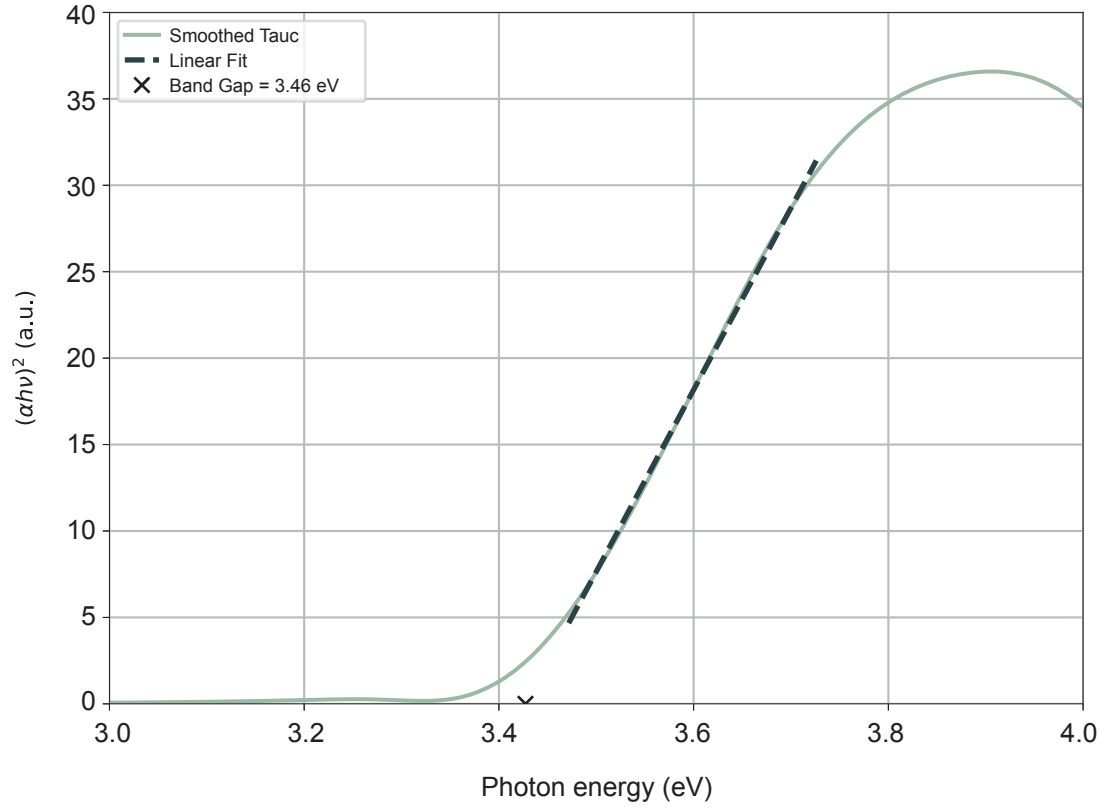


Figure 9.2: Representative Tauc plot.

The nanocrystal radius (r) was subsequently estimated using the Brus equation:

$$E_g(r) = E_{\text{bulk}} + \frac{h^2\pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r},$$

where $E_{\text{bulk}} = 3.37 \text{ eV}$, $m_e^* = 0.24m_0$, $m_h^* = 0.59m_0$, and $\epsilon_r = 8.5$.

By solving this equation for r , the nanocrystal size was obtained. The extracted band gap values and corresponding nanocrystal sizes are summarized in Table below.

Table 9.2: Evolution of E_g and particle size over time (minutes converted to hours).

Time (h)	E_g (eV)	d (nm)
0	4.03	2.67
1	3.63	3.56
3	3.58	3.75
6	3.56	3.81
9	3.54	3.90
12	3.53	3.95
24	3.51	4.07
48	3.48	4.26
72	3.47	4.33
96	3.46	4.40

9.4 Additional data

9.4.1 X-Ray crystallographic data

Table 9.3: Crystal data and structure refinement for [(BA)ZnEt]₄.

Empirical formula	C ₃₆ H ₄₄ N ₄ O ₄ Zn ₄
Formula weight	858.23
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit-cell dimensions	a = 9.9332(3) Å α = 74.349(3)° b = 19.1019(7) Å β = 88.420(3)° c = 19.8507(8) Å γ = 88.828(3)°
Volume	3625.2(2) Å ³
Z	4
Density (calculated)	1.565 Mg·m ⁻³
Absorption coefficient	3.347 mm ⁻¹
F(000)	1744
Theta range for data collection	2.312–66.599°
Index ranges	–11 ≤ h ≤ 10; –22 ≤ k ≤ 22; –23 ≤ l ≤ 23
Reflections collected	19962
Independent reflections	19962 (<i>R</i> _{int} = 0.706)
Completeness to θ = 66.599°	99.7%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	19962 / 0 / 874
Goodness-of-fit on <i>F</i> ²	0.995
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0677, <i>wR</i> 2 = 0.1984
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0882, <i>wR</i> 2 = 0.1953
Largest diff. peak and hole	1.23 / –1.20 e Å ⁻³

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

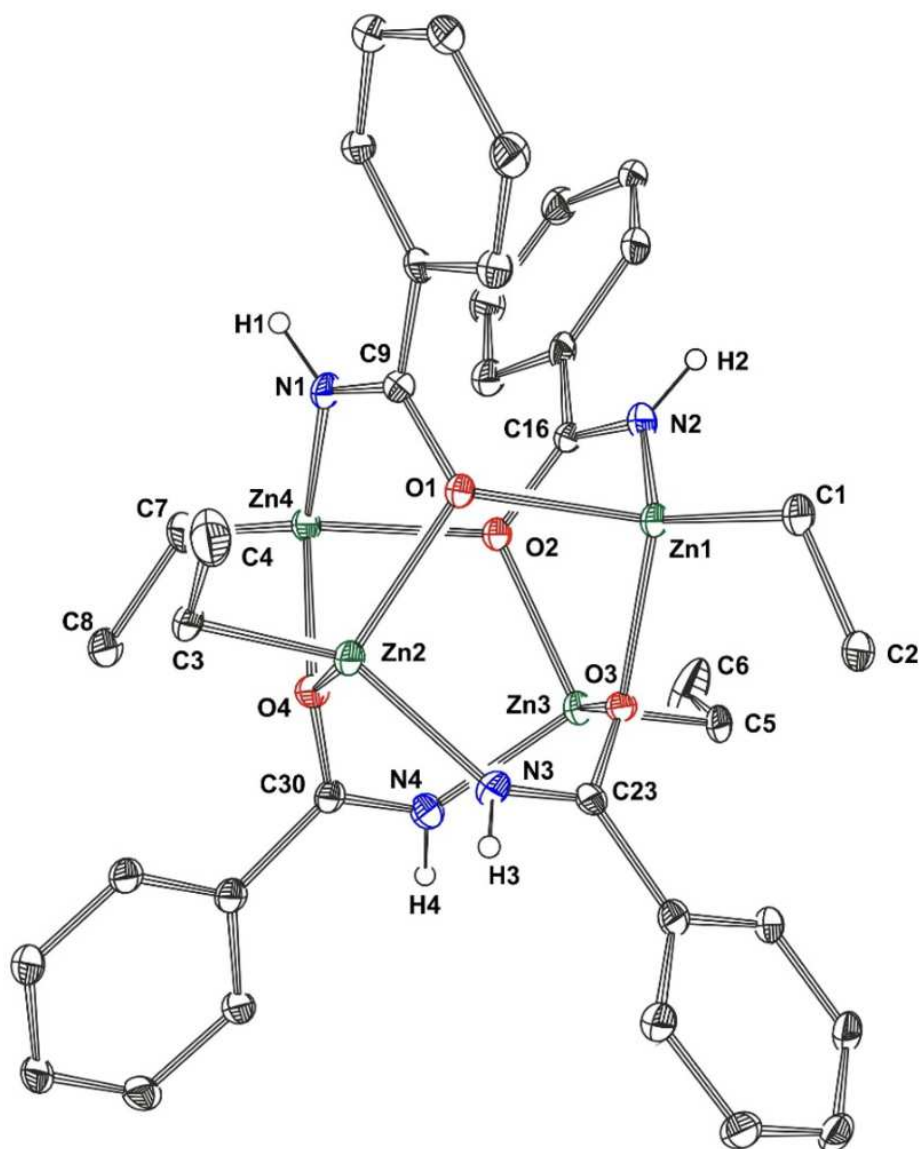


Figure 9.3: The molecular structure of $[(BA)ZnEt]_4$ with thermal ellipsoids set at 30% probability. N-H hydrogen atoms are placed at idealized positions; C-H hydrogen atoms are omitted for clarity.

Table 9.4: Selected intermolecular bond lengths (Å) and angles (°) for [(BA)ZnEt]₄.

Bond Lengths (Å)					
Zn1–O1	2.105(5)	Zn3–O2	2.081(4)	O1–C9	1.303(8)
Zn1–O3	2.086(4)	Zn3–O3	2.123(5)	O2–C16	1.303(8)
Zn1–N2	1.994(6)	Zn3–N4	1.983(6)	O3–C23	1.291(9)
Zn1–C1	1.977(7)	Zn3–C5	2.006(7)	O4–C30	1.296(8)
Zn2–O1	2.083(4)	Zn4–O2	2.128(5)	N1–C9	1.304(9)
Zn2–O4	2.120(5)	Zn4–O4	2.073(4)	N2–C16	1.313(9)
Zn2–N3	1.991(6)	Zn4–N1	2.001(6)	N3–C23	1.300(10)
Zn2–C3	1.981(7)	Zn4–C7	1.982(7)	N4–C30	1.297(10)
Bond Angles (°)					
O1–Zn1–C1	121.0(3)	O4–Zn2–C3	113.9(3)	Zn3–N4–C30	128.7(5)
O1–Zn1–O3	93.34(17)	O4–Zn2–N3	95.1(2)	Zn3–O2–Zn4	115.9(2)
O1–Zn1–N2	95.3(2)	N3–Zn2–C3	133.8(3)	O2–Zn4–C7	119.7(3)
O3–Zn1–N2	102.9(2)	Zn2–O4–C30	125.3(4)	O2–Zn4–O4	92.96(18)
O3–Zn1–C1	110.8(2)	Zn2–O4–Zn4	110.8(2)	O2–Zn4–N1	95.3(2)
N2–Zn1–C1	127.3(3)	O2–Zn3–C5	113.4(2)	O4–Zn4–C7	111.7(2)
Zn1–O1–C9	121.1(4)	O2–Zn3–N4	99.5(2)	N1–Zn4–C7	127.6(3)
Zn1–O1–Zn2	116.3(2)	O3–Zn3–C5	116.2(2)	Zn4–N1–C9	130.0(5)
Zn1–O3–Zn3	111.7(2)	O3–Zn3–N4	95.3(2)	Zn4–O2–C16	121.0(4)
O1–Zn2–C3	111.6(2)	N4–Zn3–C5	130.3(3)	Zn4–O4–C30	120.8(4)
O1–Zn2–O4	96.44(18)	O2–Zn3–O3	95.56(18)		
O1–Zn2–N3	99.1(2)	Zn3–O2–C16	118.5(4)		

9.4.2 Fit of SAXS data

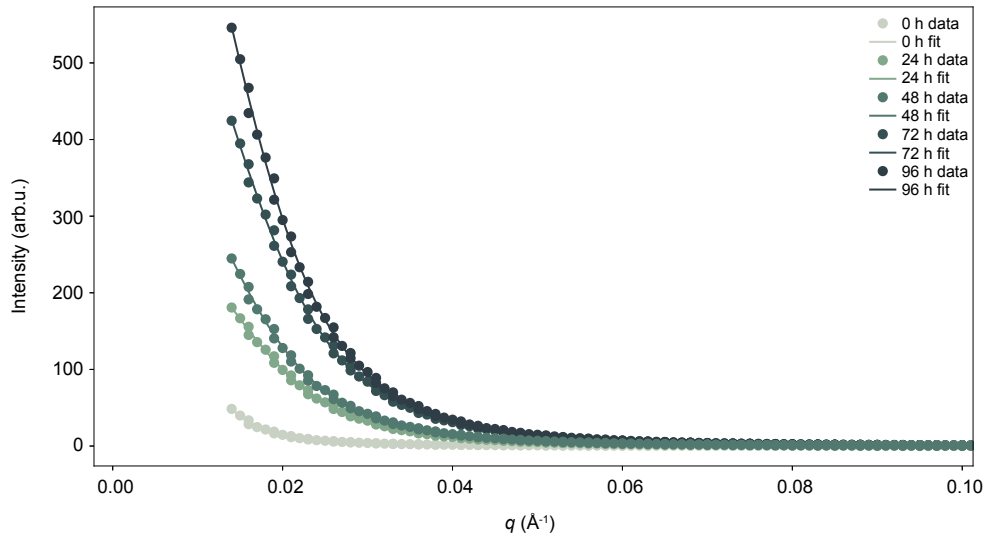


Figure 9.4: Selected SAXS experimental data and corresponding fits shown in a linear scale.

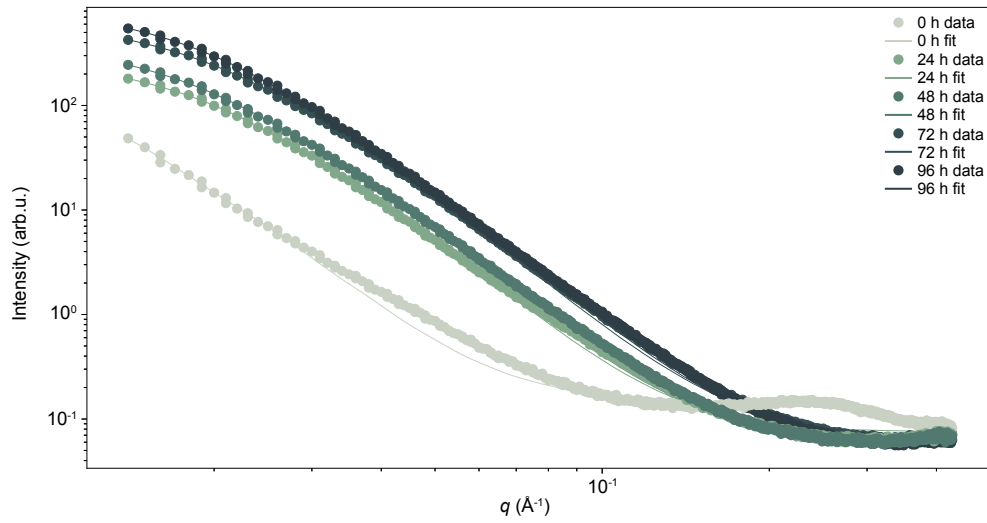


Figure 9.5: Selected SAXS experimental data and corresponding fits in a log-log scale.

9.4.3 In situ ^1H NMR spectra illustrating the reactivity of the model organozinc precursor in solution

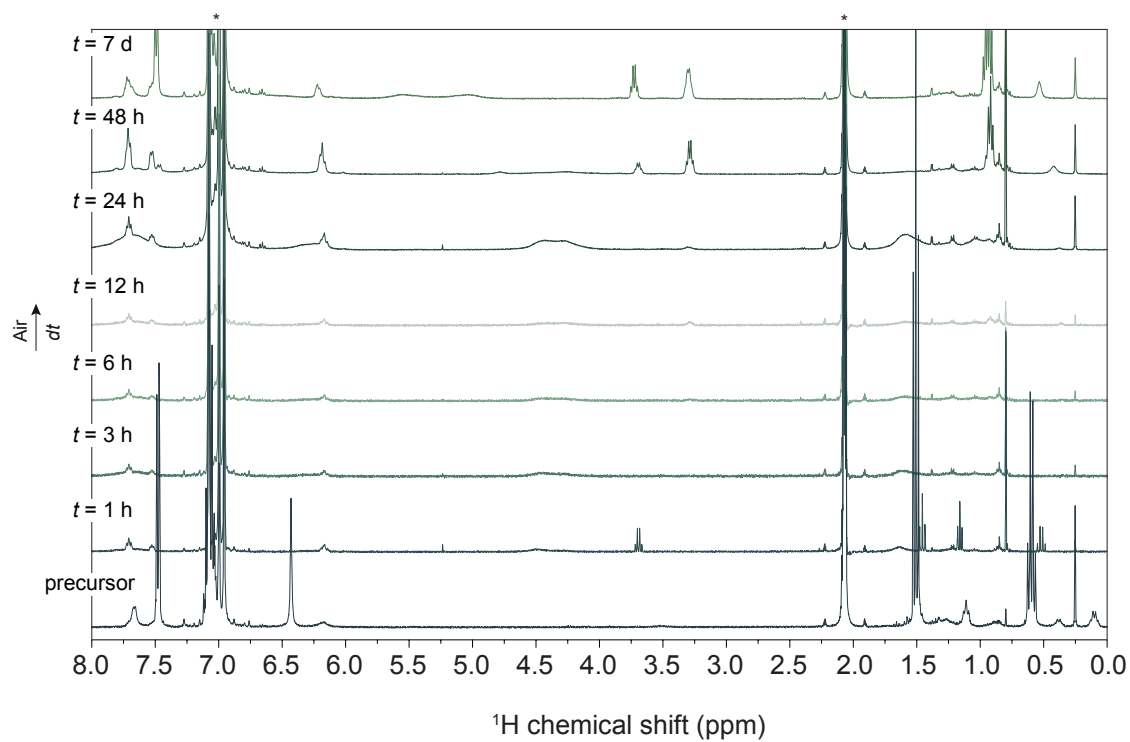


Figure 9.6: In situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_4$ reactivity in toluene- d_8 during air exposure.

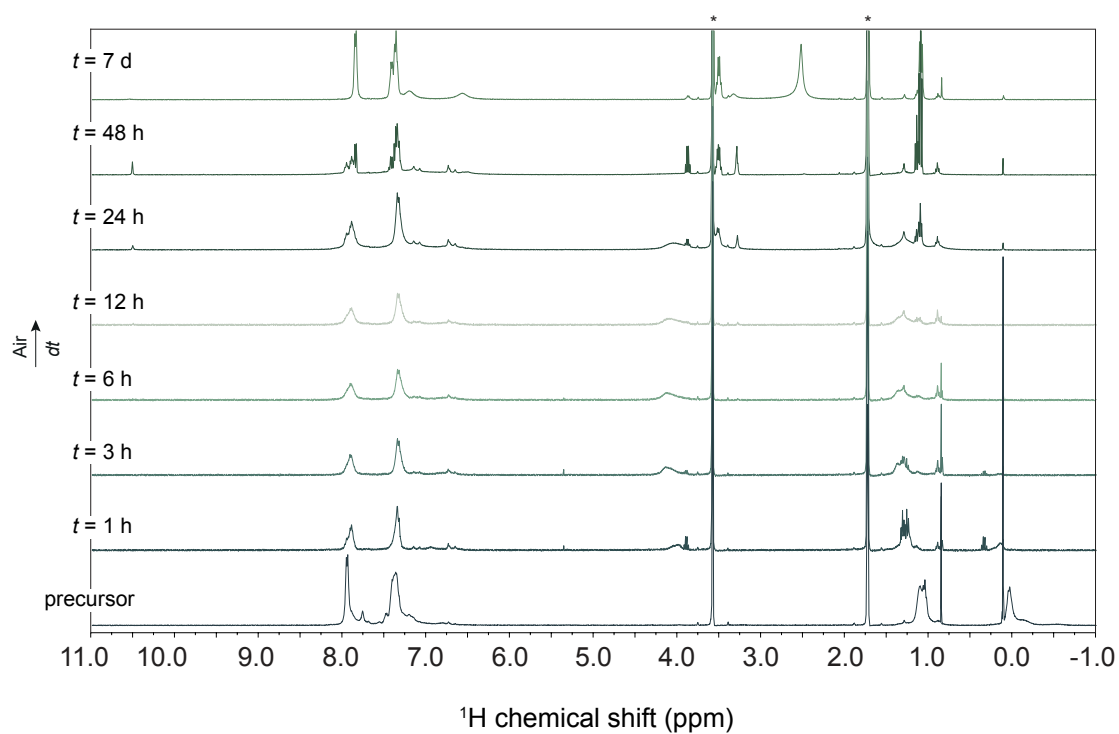


Figure 9.7: In situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_4$ reactivity in THF-d_8 during air exposure.

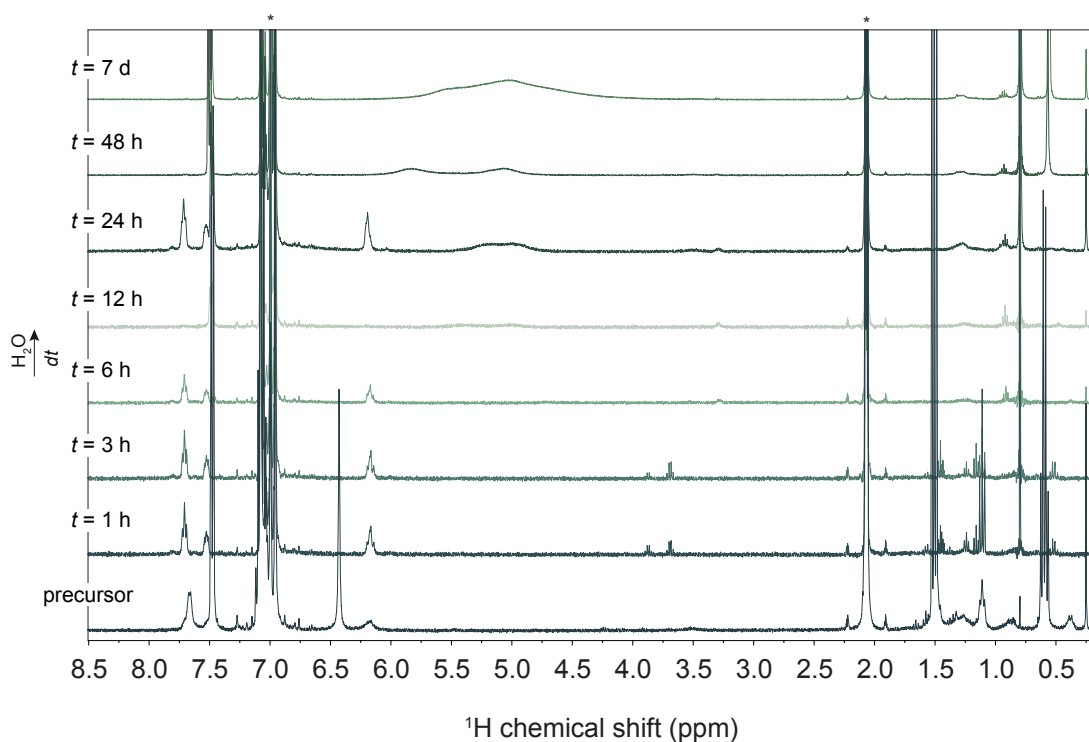


Figure 9.8: In situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_4$ reactivity in toluene-d_8 during air hydrolysis.

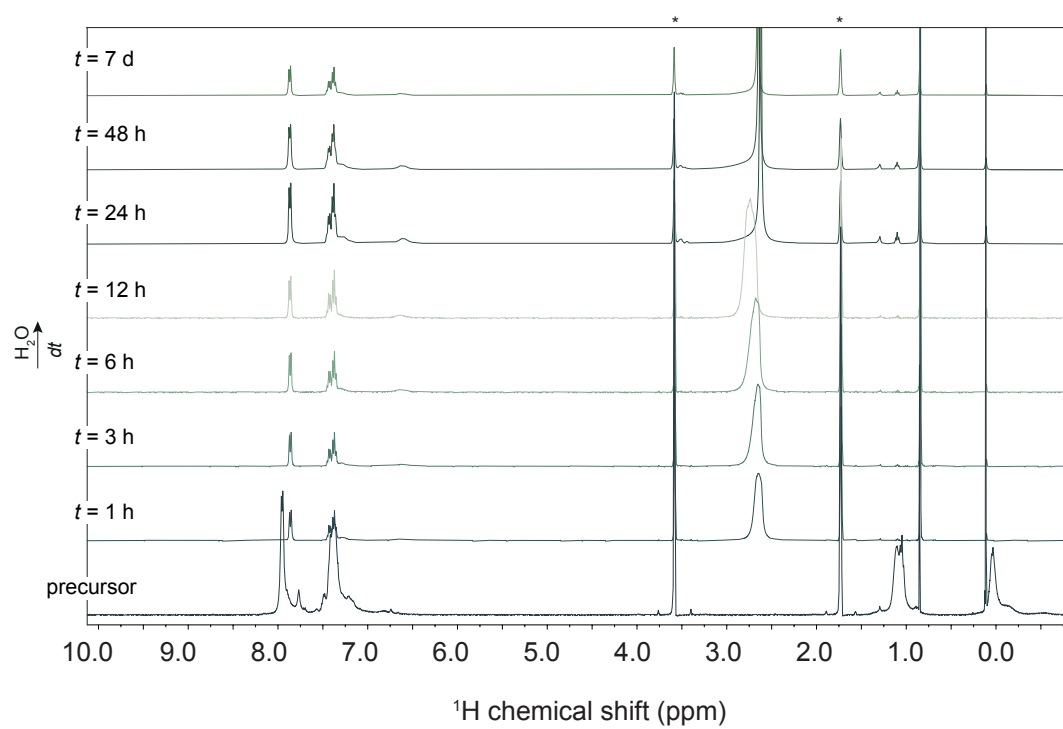


Figure 9.9: In situ ^1H NMR studies of $[(\text{BA})\text{ZnEt}]_4$ reactivity in THF-d_8 during hydrolysis.

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