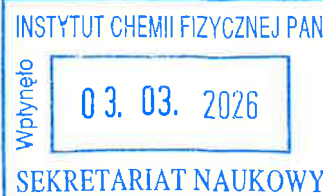




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**Reviewer's Report on the Thesis entitled Controlled transformations of organozinc precursor systems towards semiconductor nanocrystals
by Ms. Aleksandra Borkenhagen**

The doctoral dissertation by Ms. Aleksandra Borkenhagen has been carried out within the Warsaw PhD School in Natural and BioMedical Sciences at the Institute of Physical Chemistry Polish Academy of Sciences under the scientific supervision of prof. dr hab. Janusz Lewiński. The dissertation formally consists of nine principal chapters: i) Introduction, ii) Objectives and outline of the thesis, iii) Solid-state organometallic molecular systems for the synthesis of semiconductor nanocrystals, iv) Insights into nanocrystals formation upon chemical weathering of a single-crystal precursor, v) Vacuum-assisted formation of semiconductor aerogels, vi) Exploration the versatility of the HOPE system, vii) Reactivity of the model organozinc precursor in solution, viii) Conclusions and ix) Experimental section. The dissertation contains abstracts in both Polish and English, a list of acronyms, and a bibliography. The entire presentation is given on 164 pages.

The rapid progress of nanotechnology and the growing importance of nanoparticles have brought the development of sustainable synthetic strategies to the forefront of (nano)materials research. The first chapter, serving as an introduction, outlines recent advances and key achievements in the synthesis of semiconductor nanocrystals, with particular emphasis on molecular organozinc precursors and their solid-state conversion into nanocrystalline ZnO. The distinctive properties arising from quantum confinement in semiconductor nanostructures are discussed, followed by an overview of the principal classes of semiconductor nanoparticles. Particular attention is devoted to ZnO, which exhibits a unique combination of optical and electronic properties. Its three polymorphic forms are presented and their crystal structures described. Given that powder X-ray diffraction is one of the principal characterization techniques employed in this work, showing their

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PWXRD diffractograms would suit well. A subsequent section addresses the mechanisms of nanoparticle nucleation and growth, with emphasis on growth kinetics including Ostwald ripening and oriented attachment. The various synthetic approaches to nanostructured materials are then presented and critically evaluated in terms of the desired characteristics: crystallinity, uniform size and shape, and effective passivation to maintain well-defined electronic states free of surface defects. The discussed methods include vapor-phase approaches, liquid-phase routes - such as chemical precipitation, the hot-injection method, and the sol-gel process (hydrothermal and solvothermal synthesis, microwave assisted methods and microemulsion-based strategies were also mentioned), and, finally, solid-state synthetic strategies, which are intentionally highlighted as potentially superior, despite their typically slower reaction kinetics, which can result in longer synthesis times and scaling problems. Solid-state pathways are presented with particular attention to the principal factors influencing reactivity, namely temperature, mechanical activation, and, importantly, accelerated aging. The subsequent chapters focus on the wet-organometallic approach to the synthesis of colloidal semiconductor ZnO nanocrystals and on the solid-state preparation of ZnO nanocrystals from organic precursors. These sections describe a variety of synthetic strategies and highlight the significant achievements of the research group led by prof. Janusz Lewiński, what is highly appreciable. Of particular significance to the present study is the innovative development of a controlled organometallic precursor decomposition strategy, termed a one-pot, self-supporting organometallic (OSSOM) procedure. This approach offers a versatile, safe, and reproducible pathway to stable ZnO nanocrystals with tunable surface functionality. In my opinion, this introductory chapter is written in a highly comprehensive and accessible manner, enabling even non-specialists to benefit substantially from its content. I read it with great interest and consider it excellent. The literature part refers to 212 publications out of 281 presented in the bibliography section.

The concept and work plan are presented concisely. The primary objective of this dissertation is to develop new organozinc precursors for ZnO nanocrystals, including a well-defined solid-state system enabling ZnO formation under ambient conditions without thermal or mechanical activation. The ethylzinc benzamide complex $[(BA)ZnEt]_4$ was designed, synthesized, crystallized and structurally characterized with use of single crystal (SC-XRD) and powder diffraction (PWXRD) techniques. While the crystal and molecular structure is generally well presented and discussed, I have two critical remarks. The system crystallizes in the triclinic P-1 space group. According to the experimental section, there are four molecules in the unit cell, meaning that two moieties should constitute independent parts

of the unit cell. In principle, they may slightly differ in geometry, and this should be taken into account in the discussion. The second objection concerns PXRD experimental pattern for $[(\text{BA})\text{ZnEt}]_4$ and the simulated pattern derived from SC-XRD data, shown in Figure 3.6. They are similar indeed, however, some additional peaks appear in the simulated pattern. It should be noted that the data were collected under different temperature conditions - PXRD at room temperature and SC-XRD at 100 K. This discrepancy raises the possibility that two different polymorphs might have been observed. From this perspective, it would be particularly interesting to perform a low-temperature thermogravimetric analysis. The single crystals of the $[(\text{BA})\text{ZnEt}]_4$ precursor served as a well-defined model for studying solid-state transformation into semiconductor nanocrystals. Although non-porous, these crystals are highly reactive toward water while maintaining their external morphology. Under ambient conditions high-quality ZnO nanocrystals on a multigram scale are obtained without solvents, reminiscent of natural chemical weathering. Through selective interactions with air components, the framework undergoes internal rearrangements that overcome typical solid-state mass transport limitations while maintaining the crystal's shape. The transformation, characterized by multiple advanced in situ techniques is scientifically remarkable and provides detailed insight into nucleation, growth, and aggregation at both molecular and nanoscale levels. It is both elegant and straightforward - congratulations! The development of an effective vacuum-assisted method for preparing semiconductor aerogels is another great achievement. Removal of the organic matrix transforms the embedded ZnO nanocrystals into a highly porous aerogel without solvents or complex chemical treatments. Compared to conventional methods, this sublimation process efficiently purifies the nanocrystals while preserving their structural integrity. Although characterized by PXRD, the patterns in Figure 5.4, in my opinion, deserves further discussion. Following vacuum sublimation, a strong peak appears below 10° , likely indicating a mesoporous scaffold of ZnO@BA nanocrystals, consistent with the TGA analysis. A brief comment addressing this interpretation would be appropriate. Another inspiring aspect of the work is the use of H_2S as an alternative hydrolytic agent to produce high-quality luminescent ZnS nanocrystals. Analytical techniques confirmed their successful formation, demonstrating that the hydrolytic mechanism established for ZnO nanocrystals can be extended to other semiconductors. Although studies with H_2Te and H_2Se were not conducted due to their high toxicity, they outline promising pathways for future research. Finally, complementary solution-phase studies were performed to clarify mechanistic differences, identify intermediates, and provide molecular-level insight into ZnO formation. Comparison of solid-

and solution-phase reactivity reveals notable differences. In the solid state, the precursor reacts selectively with water, while in solution both water and oxygen are involved, generating additional (undesired) byproducts.

The problems addressed and resolved by the Doctoral Student are highly significant, while the scope of the work, together with the analyses performed, is truly extensive. The use of a wide range of modern analytical methods is highly appreciated. Her research successfully bridges molecular precursor design and solid-state chemistry, showing that rationally engineered organozinc systems can enable controlled, mild, and sustainable synthesis of ZnO nanocrystals, with potential extension to ZnS and possibly H₂Te and H₂Se nanocrystals. This highly inspiring work represents a major achievement and in general opens great perspectives for the synthesis of novel functional materials.

The doctoral thesis demonstrates a high level of proficiency, both in terms of editing and graphics. The dissertation is written in a concise way, successfully balancing the literature review and novel experimental work: synthesis and physicochemical procedures/analyses. I highly appreciate the way the results are presented - all figures and graphs were prepared with great care. It is worth noting that a significant part related to the thesis has already been published in a leading journal: *Nature Communications* [2025, 16, 10254], where the Doctorate Student is the first author. She is likewise the first author of a thematically closely related article published in *ACS Applied Materials & Interfaces* [2025, 24, 36212–36225]. In addition, she is also a co-author of two further publications: *Chemistry of Materials* [2025, 37, 897–911] and *Small* [2024, 20, 2403685]. This demonstrates her dedication to Science. Minor imperfections in the thesis, such as the missing superscript formatting for ¹³C or ¹⁵N on page 142, are extremely rare and of negligible significance. The list of acronyms provided at the beginning of this dissertation is helpful, although it is not yet complete. Missing acronyms include: OR (page 14), OA (page 15), CVD, ACD and MBE, (page 16), TOP and TOPO (page 18), ZIF (page 30), OSSOM (44), SSP (page 47), DCM (page 61), SC-XRD (page 62), DLA and RLA (page 103), EA (page 103). To sum up: I am fully convinced that Ms. Aleksandra Borkenhagen's doctoral dissertation contains important elements of scientific novelty. The PhD student defined the research problem well, planned it well and performed quite excellent research.

The doctoral thesis by Ms. Aleksandra Borkenhagen meets all formal requirements specified in the current Act of the Law on Higher Education and Science of Republic of Poland. Therefore, it is with great pleasure that I recommend

to the Scientific Council of the Chemical Sciences Discipline of at the Institute of Physical Chemistry Polish Academy of Sciences that she be admitted to the next stages of the doctoral process. Furthermore, in view of the outstanding scientific quality of the conducted research, its novelty and originality, great significance to chemistry and materials science, as well as the candidate's evident scientific maturity, reflected in her exceptionally strong publication records, I further respectfully appeal the Scientific Council of the Chemical Sciences Discipline at the Institute of Physical Chemistry of the Polish Academy of Sciences to award her doctoral dissertation with distinction.

A handwritten signature in blue ink, appearing to read 'M.K. Cyrański', followed by a horizontal line.

Michał K. Cyrański