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**Review of the doctoral dissertation of Aleksandra Borkenhagen, M.Sc., Eng., entitled
„Controlled transformations of organozinc precursor systems towards semiconductor
nanocrystals”**

The doctoral dissertation submitted to me for review was carried out at the Institute of Physical Chemistry of the Polish Academy of Sciences under the supervision of Prof. Janusz Lewiński. The dissertation focuses mainly on the methodology for the synthesis and characterization of nanocrystalline semiconductor materials based on zinc(II) oxide and sulfide. Research in this field is currently being pursued in many laboratories due to the broad range of potential applications of these materials. The present work constitutes a logical continuation of the highly productive research that has been conducted for many years in Prof. Lewiński's group.

The reviewed dissertation is written in English, comprises more than 160 typescript pages, and is organized in a classical manner: it includes a literature review, a multi-part discussion of the Author's own research accompanied by a summary, an experimental section, and a bibliography. The dissertation opens with a brief introduction in which the Author presents the aim of the work—namely, the development of a solid-state synthesis methodology for semiconductor ZnO and ZnS nanocrystals based on an appropriate organozinc precursor, the cluster $[(BA)ZnEt]_4$ (BA = benzamidate). This compound contains reactive Zn–C and Zn–N bonds that are susceptible, among other processes, to hydrolysis under ambient conditions.

In the literature review, the Author discusses the topic of quantum dots, i.e., inorganic semiconductor nanocrystals, with particular emphasis on comparing different synthetic approaches. I evaluate this section positively, as it provides a coherent introduction to the subject of the Author's own research and demonstrates her solid command of the field. As expected, given her research focus, the Candidate presents in greatest detail the methods for obtaining ZnO nanocrystals from various organozinc compounds, which have been extensively examined for this purpose in Prof. Lewiński's group. A major advantage of such precursors is

their ability to transform into nanocrystalline ZnO phases under mild ambient conditions due to the presence of Zn–C bonds susceptible to oxidation and hydrolysis. In Fig. 1.9 (p. 23), this approach is compared with the widely used hot-injection method for the synthesis of inorganic semiconductor nanocrystals developed by Bawendi and co-workers. However, since this method also employs organometallic precursors such as dimethylcadmium (as the Author notes on p. 18), one may ask what the corresponding energy profile of their conversion into nanocrystals would be. Another comment concerns the statement on p. 19 that bonds in cadmium and lead chalcogenides possess a predominantly ionic or strongly polarized covalent character, whereas the bonds in ZnO and InP are more covalent.

Chapter 3 provides a concise introduction to the discussion of the Author's own results. Its first section concerns the synthesis and characterization of the cluster $[(BA)ZnEt]_4$, for which the appealing acronym HOPE was adopted. To characterize this compound, the Candidate employed several analytical techniques, including single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), $^{13}C\{^1H\}$ and ^{15}N CP-MAS solid-state NMR spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). In my view, the interpretation of these data is generally correct. Nevertheless, the statement on p. 65 that the ^{13}C CP-MAS NMR spectrum exhibits ethyl-group resonances at 13.4 and -0.82 ppm raises doubts, as Fig. 3.7 clearly shows four distinct signals in the 10–15 ppm range rather than a single resonance at 13.4 ppm—an observation that may indicate structural inequivalence. Similarly, the interpretation of the ^{15}N CP-MAS NMR spectrum, which is said to show a sharp signal at around -225 ppm, appears debatable. I am also not fully convinced by the interpretation of the TGA data. While I agree that the first decomposition step corresponds to ethane elimination, the suggestion that the second step involves sublimation or decomposition of benzamide is not chemically plausible. This conclusion seems to stem from the reported mass loss of 56%, but according to Fig. 3.9, this value is measured relative to the initial mass, not relative to the mass after the first decomposition step. It may therefore be worthwhile to identify the actual decomposition products to resolve this discrepancy.

In the subsequent chapter, the Candidate discusses detailed studies of the chemical transformation of HOPE precursor crystals under exposure to humid air, examined at both the molecular and nanometric scales using a broad set of spectroscopic, diffraction, microscopic, and thermal methods. These analyses captured the formation of nanocrystals and their aggregation within the crystalline precursor, as well as within the amorphous organic matrix formed by benzamide molecules. It was shown that hydrolysis of the Zn–C and Zn–N bonds produces hydroxo-zinc intermediates that ultimately condense into ZnO nanocrystals. For comparison, the precursor was also subjected to exposure in a dry oxygen–argon atmosphere. PXRD confirmed that under these conditions ZnO nanocrystals do not form. However, the diffractogram of the material obtained in this environment differs significantly from that of the original HOPE precursor including the positions of the peak with the highest intensity at the lowest 2θ value. Yet on p. 79, the Author suggests that the HOPE precursor is unreactive toward

oxygen because all four zinc atoms are four-coordinate. I believe this issue requires clarification given that the proposed mechanism for chemical weathering of the HOPE precursor in a humid air atmosphere relies solely on hydrolysis reactions.

In the following two chapters, the Candidate presents procedures for obtaining nanocrystalline ZnO and ZnS by removing benzamide generated during hydrolysis or, respectively, during the reaction of HOPE with H₂S. These transformations were achieved effectively through vacuum sublimation. Analysis of the resulting ZnO revealed the presence of surface-bound BA (benzamidate) ligands, with a surface coverage typical of this class of nanocrystalline materials.

The final results chapter addresses the transformation of the HOPE precursor in solution in the presence of water and molecular oxygen. ¹H NMR spectroscopy revealed significant differences between the processes occurring in toluene and in THF. In the latter donor solvent, the precursor exhibits dynamic structural behavior, as evidenced by substantial line broadening in the ¹H NMR spectrum, and the presence of a Schlenk equilibrium provides a reasonable explanation. The resulting diethylzinc species readily reacts not only with water but also with oxygen. The HOPE precursor dissolved in toluene is sensitive to water vapor but relatively resistant to oxygen, consistent with the ¹H NMR data, which indicate its structural stability under such conditions. At this point, I would like to return to my earlier doubts concerning the behavior of the HOPE precursor toward oxygen in the solid state.

The discussion of the Author's own results concludes with a concise and well-organized summary highlighting her most significant achievements and conclusions. I believe that the dissertation makes a valuable contribution to the development of innovative methods for the synthesis of nanocrystalline semiconductor materials, with particular emphasis on sustainable preparation strategies. The presented method is simple, economical, and energy-efficient. Moreover, the dissertation provides detailed molecular-level insight into the complex mechanisms of solid-state transformations, made possible by the use of a broad suite of modern analytical techniques. A slight disappointment arises from the absence of even a single demonstrative example illustrating the application potential of the obtained nanocrystalline materials, which would have further strengthened the case for the proposed synthetic methodology. The bibliography contains 281 references, most of them published within the past several years, attesting to the timeliness and future prospects of the research topic. Among these references, I identified one publication in the prestigious journal *ACS Applied Materials & Interfaces*, in which the Candidate is the first author. Another publication containing the most important research results on the transformation process of the HOPE precursor into ZnO nanocrystals was accepted in *Nature Communications* after submitting this dissertation. The dissertation is carefully edited and richly illustrated with numerous high-quality figures and schemes, including color graphics, which significantly facilitate comprehension.

Final conclusions

In summary, I conclude that the doubts and critical remarks presented above do not affect the final positive evaluation of the dissertation by Ms. Aleksandra Borkenhagen. I consider that the dissertation fully meets the requirements for doctoral theses as specified in the relevant provisions of the Act of 20 July 2018 – The Law on Higher Education and Science and I recommend that the Scientific Council of the Institute of Physical Chemistry admit the Candidate to the subsequent stages of the doctoral procedure.

