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Report on the PhD Thesis of Mr. Litwin Jacob entitled,

Development of functional materials based on boron clusters for energy storage and conversion

Mr. Litwin carried out the work in his thesis under the supervision of Professor Piotr Kaszyński at the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź, Poland.

The work comprises a combination of chemical synthesis, careful purification, and detailed characterization including extensive physicochemical studies of a variety of boron cluster-containing compounds and materials. Some of the physicochemical studies have been performed in collaboration with other researchers from different institutions in Poland, Europe, and the US. Mr. Jacob's thesis is divided into two main parts A and B that are preceded by an introduction and a chapter that describes the goals and objectives. The two main chapters A and B are organized into subchapters. The experimental details and references are included separately at the end of the introduction and at the end of each subchapter, respectively. The last section of the thesis is an appendix that contains the declaratory statements from the co-authors of the published results.

After a very brief section on batteries, energy storage, and space exploration Mr. Jacob introduces the reader to the relevant aspects of boron cluster chemistry. The introduction provides a concise and clear overview about different types of boron cluster chemistry and their application in biomedicine and different fields of materials sciences. The last section of the introduction deals with liquid crystals and boron clusters in the design of liquid crystalline materials.

The topic of Part A of the thesis is the development of novel functional materials based on 1,10-disubstituted [*closo*-$B_{10}H_{10}]^{2-}$ derivatives. The subchapter A1 entitled "Chemistry of the 1,10-disubstituted derivatives of the *closo*-decaborate anion ([*closo*-$B_{10}H_{10}]^{2-}$)" provides a detailed review on the chemistry of the 10-vertex *closo*-dianion with two substituents at the B1 and B10 atom. After general aspects, e.g. electronic properties, of the {*closo*-B_{10}} cage, the

focus is on synthetic strategies and methods that provide access to these unique difunctionalized boron cages. The main section of the review is organized according to the different types of B–X bonds (X = C, O, N, S, halogen) and 1,10-heterodisubstituted derivatives. These synthetic sections are followed by brief chapters on applications of these 1,10-difunctionalized {*closo*-B_{10}} clusters, for example liquid crystals and metal complexes. Chapter A2 “Synthesis, structural analysis, and functional group interconversion in the [*closo*-$B_{10}H_8$-1,10-X_2]$^{2-}$ (X = CN, [OCRNMe$_2$]$^+$, OCOR, and [OH_2]$^+$) derivatives.” contains a series of excellent results on 1,10-difunctionalized {*closo*-B_{10}} cages that have been published (*Inorg. Chem.* **2020**, *32*, 3083–3093). The key synthetic method relies on a strategy developed in the Kaszyński group, earlier. It is the exchange of iodonium substituents against nucleophiles, for example CN^- or DMF. Some of these initial products were successfully converted into further valuable {*closo*-B_{10}} derivatives. However, the study shows the unique chemical properties of anionic boron clusters and the different behavior compared to related benzene derivatives, e.g. it was not possible to convert dianion [1,10-$(NC)_2$-*closo*-$B_{10}H_8$]$^{2-}$ into the dicarboxylate derivative [1,10-$(HOOC)_2$-*closo*-$B_{10}H_8$]$^{2-}$ using conventional organic methods. A further important aspect are the electronic properties of the boron cages that reveal communication between the substituents attached to the 1 and 10 position of the cluster, which are in agreement to earlier reports. The last chapter of Part A entitled “Tunable intermolecular charge transfer in ionic liquid crystalline derivatives of the [*closo*-$B_{10}H_{10}$]$^{2-}$ anion.” has been published in advance, as well (*Chem. Mater.* **2022**, *34*, 6476–6491). Mr. Jacob reports on a series of salts of 1,10-difunctionalized dianionic {*closo*-B_{10}} clusters with pyridinium countercations. The salts reveal unprecedented stepwise melting and formation of SmA phases. In addition, the photophysical properties have been studied by spectroscopic methods and the data have been analyzed using results from quantum chemical calculations. Most noteworthy, anions and cations show intermolecular charge transfer bands that mirror the electronic properties of both ions. This latter study is a highly valuable example for the potential of 1,10-difunctionalized {*closo*-B_{10}} clusters in special and (anionic) boron clusters in general.

In Part B, Mr. Jacob describes his results on new electrolytes based on [*closo*-1-$CB_{11}H_{12}$]$^-$ for Li-ion battery applications. The chapter is divided into four subchapters the first of which is a well-written introduction into electrolytes used in Li-ion batteries (LIBs). This introductorily chapter covers general aspects on electrolytes for LIBs, focuses on liquid crystalline electrolytes, which are of potential for specialized battery applications, describes the state-of-the-art of applications of anionic boron clusters as component of (solid-state) battery electrolytes, and provides a brief description of the principles of electrochemical impedance spectroscopy (EIS). In summary, the introduction of Part B nicely prepares the reader for the following three subchapters. In Chapter B2 entitled “Liquid crystalline electrolytes derived from the 1,12-disubstituted [*closo*-$CB_{11}H_{12}$]$^-$ anion.” Mr. Jacob presents a new concept for the use

of liquid crystalline materials for electrolyte design (*J. Mol. Liq.* **2023**, *377*, 121525). A neutral LC host is doped with an ionic additive. The anion is closely related to the neutral host, *i.e.* a neutral benzene ring is formally exchanged by an anionic {*closo*-1-CB_{11}} cage, and the countercation is Li^+. In Chapter B3 the concept described in Part B2 has been extended to further liquid crystalline host matrices doped with a Li^+ salt containing anionic {*closo*-1-CB_{11}} units that are structurally similar to the LC matrix. The last subchapter B4 is closely related to the preceding sections B2 and B3. However, the partially aligned LC phases that have been doped with Li^+ salts of anions that are similar to the LC host molecules but contain a {*closo*-1-CB_{11}} cluster were fixed by polymerization. The potential of these polymeric designer electrolytes was demonstrated by Mr. Jacob by fabrication and testing of CR2032 type coin cells.

Overall, the thesis is extremely well organized and very well written, including plenty of relevant references. The results are without any doubts thus, leaving no obvious open questions with respect to the interpretation of the data. Excerpts of the thesis have been published in three contributions in high-ranking journals (*Inorganic Chemistry*, *Chemistry of Materials*, *Journal of Molecular Liquids*). New compounds were synthesized, carefully purified, and fully characterized. In addition, the work involves extensive and very detailed physicochemical studies. The comprehensive dissertation describes a considerable body of research work performed on a very high level, which is a sign of the target-oriented work and productivity of Mr. Jacob. In summary, Mr. Jacob has clearly demonstrated his ability to work independently, and to draft scientific papers for publication. Thus, I strongly recommend acceptation of the thesis.

Würzburg, 17.10.2023

(Prof. Dr. Maik Finze)