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PhD thesis / Review

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

Litwin Jacob

Currently, there is a strong demand in novel functional materials for energy storage and energy conversion. Boron clusters are very unique and interesting compounds in that respect. These 3D σ -aromatic cage compounds can be synthetically functionalized in multiple ways and the resulting compounds have been used already in various applications ranging from boron neutron capture therapy for treatment of tumors to material science. The Kaszyński group has developed a large diversity of boron cluster based liquid crystals. However, the tailored synthesis and application of boron clusters for energy storage and conversion has only been little explored. This challenge has been taken up by Litwin Jacob in his doctoral thesis.

The written thesis contains 4 parts, i.e. a general introduction, goals and objectives, part A and part B. The general introduction gives a good overview over the current challenges in the development of battery, energy storage and space exploration materials. Boron clusters, their biomedical, material science and liquid crystal applications are discussed.

The doctoral thesis focused on two main goals. One aim (part A) was to investigate bisphenyliodonium [*c*loso-B₁₀H₁₀] Zwitterion as synthetic intermediate to obtain various 1,10-difunctionalized boron clusters. These compounds were designed as charge transfer materials for photovoltaics. The second aim (part B) was to develop a polymer electrolyte based on [*c*loso-1-CB₁₁H₁₂] anion as Li⁺-ion battery materials.

Part A of the thesis contains a detailed introduction into the chemistry of 1,10-disubstituted *closo*-decaborate anion. This chapter gives the reader an excellent overview of the current state of art and might serve as the basis for a review article or account. In the results section the synthesis of novel *closo*-decaborate anions carrying various substituents in the 1,10-position of the boron cluster is described. The compounds are well characterized including solid state structures and complementary DFT calculations, which provide a detailed insight into the structure and reactivity of the boron clusters. This work has been published in *Eur. J. Inorg. Chem.* **2020**, 32, 3083-3093.

Next, tunable intermolecular charge transfer of *closo*-decaborate anion ILCs was investigated. Although ILCs based on boron clusters have been previously described by the Kaszyński group, this paper focuses on the highly original aspect of intermolecular charge transfer between mesogenic *closo*-decaborate anion and mesogenic pyridinium cation. A library of novel congruent ion pairs was synthesized and characterized. The resulting ILCs showed SmA mesophases. Charge transfer between anion and cation was studied by absorption and solvetochemical experiments and DFT calculation of the frontier molecular orbitals. These studies revealed that the HOMO, LUMO energies could be nicely tuned by choice of anion and cation. The results were published in *Chem. Mater.* **2022**, 34, 6476-6491.

Part B of the thesis gives first a detailed introduction into electrolytes for Li⁺ ion batteries and the relevance of boron clusters in solid-state electrolytes. Furthermore, the impedance spectroscopy, a very useful method to determine charge transport and electrical conductivity studies were performed. In the results section, the synthesis of liquid crystalline electrolytes based on the 1,2-disubstituted [*closo*-CB₁₁H₁₂] anion is described. Examination of the liquid crystalline properties of neat compounds and mixtures showed SmC, SmA, SmI and N phases, which were fully characterized by POM, DSC and XRD. The conductivity was found to be strongly dependent on the phase, i.e. it decreased from Cr via SmI to SmC. More importantly, the conductivity could be significantly enhanced by alignment of the sample. Complementary voltammetric experiments provided information on the electrochemical window. These results were published in *J. Mol. Liq.* **2023**, 377, 121525.

The following chapter takes the results from the *J. Mol. Liq.* paper a step further towards liquid crystalline electrolytes and deals with the synthesis and characterization of Li⁺ salts of [*closo*-CB₁₁H₁₂] anions and investigation of their anisotropic charge transport. Laterally fluorinated monomeric and dimeric biphenyl benzoates carrying oligoethylenoxide side chains were designed for this purpose. The phase behaviour depended on the chain lengths of the oligoethylenoxides, longer chains favored the N phase over the SmA phase. Most importantly,

the conductivity perpendicular was much higher than in parallel direction, rendering these boron cluster containing electrolytes as suitable alternatives for current Li⁺ ion electrolytes.

The final chapter of the thesis deals with liquid crystalline polymer electrolytes based on [*c*/*o*-CB₁₁H₁₂]⁻ anion for Li⁺ ion battery application. For this purpose, the mesogenic boron clusters developed in the previous chapter were mixed with a main chain LC resulting in smectic mesophases for the mixture polystyrene. Good alignment was achieved for the LC polymer mixture and the nanosegregation of ionic and non-ionic parts into lamellar mesophase gave rise to Li⁺ ion conducting channels. The materials were incorporated into prototype coin batteries. Although the prototype batteries did not show the expected charging / uncharging behavior, these experiments are a very important step towards novel Li⁺ ion battery materials.

Overall, this is a well written, clearly structured doctoral thesis. The topic and aim are very challenging and the approaches to solve the goals are unique and highly original. The organization into different chapters makes it even for the more distant reader easy to follow the storyline of the thesis. The aims, methods, results and conclusions were clearly and concisely addressed. All experiments were carried out with great care and nicely complemented by theoretical calculations to support mechanistic hypotheses.

There are no points of criticism within this thesis. I just have some open questions out of my curiosity which might be addressed in the discussion during the oral PhD defense.

- (1) As I am not familiar with the boron cluster chemistry and the general reactivity of the *c*/*o*-decaborate anion and the corresponding *c*/*o*-carbaborate anion, I would like to know whether it is possible to functionalize both apical and equatorial positions of the boron cluster at the same time. Is it possible to introduce both nucleophiles and electrophiles? E.g. in scheme 1: why is the equatorial position never attacked?
- (2) Scheme 23: The reaction mechanism for the conversion of compound **66** to **67** might be discussed in more detail.
- (3) How flexible is the cation exchange with regard to LC properties?
- (4) On page 41-42 in Fig. 3 and Fig. 6 the smectic I (Sml) phase is discussed. As the hexatic Sml phase is not so common among ILCs, details of the packing behavior for this mesophase type might be discussed. Parameters (POM, DSC, XRD) should be discussed, how Sml is differentiated from SmA or SmC.

Overall, I strongly recommend the excellent doctoral thesis by Litwin Jacob to the Scientific Council of the Centre of Molecular and Macromolecular Studies of the Polish Academy of

Sciences. Upon comparison of this thesis with other theses from our Department of Chemistry, I would like to recommend the grade with distinction (summa cum laude).

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