

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

The 1,10-difunctional derivatives of the  $[closo-B_{10}H_{10}]^{2-}$  anion are attractive for the synthesis of self-organizing rod-like materials with controlled electronic properties, photophysical behavior, and the degree of intramolecular electronic interactions. Part A of the Dissertation investigated the fundamental chemistry of the 1,10-difunctionalized derivatives of the *closo*-decaborate anion  $[closo-B_{10}H_{10}]^{2-}$  in order to facilitate the development of new ionic functional materials.

Thus, nucleophilic substitution of  $[closo-B_{10}H_8-1,10-(IPh)_2]$  with  $CN^-$  and DMF yielded the dinitrile derivative  $[closo-B_{10}H_8-1,10-(CN)_2]^{2-}$  and the DMF adduct  $[closo-B_{10}H_8-1,10-(OCHNMe_2)_2]$ , respectively. These derivatives were envisioned as precursors for the diacid  $[closo-B_{10}H_8-1,10-(COOH)_2]^{2-}$  and the dihydroxy derivative  $[closo-B_{10}H_8-1,10-(OH)_2]^{2-}$ . Hydrolysis or reduction attempts on the dinitrile showed no reaction or formation of a complex mixture of products. On the other hand, the DMF adduct was hydrolyzed to produce diformate  $[closo-B_{10}H_8-1,10-(OCHO)_2]^{2-}$  and then protonated dihydroxy derivative  $[closo-B_{10}H_8-1,10-(OH_2)_2]$ . The latter was O-acylated with  $PhCOCl$ . The crystal and molecular structures of five derivatives were determined using single crystal XRD techniques and compared to those of other  $[closo-B_{10}H_8-1,10-X_2]^{2-}$  derivatives. DFT (B3LYP/TZVP) results were used to validate and correlate trends in the molecular geometry and reactivity of dinitrile and intermediate derivatives by analyzing bonding, charge distribution, and vibrational frequencies.

Furthermore, the recently developed chemistry in our laboratory for the apical functionalization of the  $[closo-B_{10}H_{10}]^{2-}$  anion was used to develop photoactive ionic liquid crystals with tunable intermolecular charge transfer. Thus, a new paradigm of ionic liquid crystals exhibiting low-energy charge transfer bands was demonstrated. Four series of ion pairs consisting of 1,10-disubstituted derivatives of the  $[closo-B_{10}H_{10}]^{2-}$  anion and substituted pyridinium cations were prepared, and their thermal and photophysical properties were analyzed. All pyridinium ion pairs form a smectic A (SmA) phase with clearing temperatures above 200 °C and an intermolecular charge transfer (CT) band in solid, liquid, and  $CH_2Cl_2$  solutions. The CT band maximum was between 320 and 510 nm, and its position correlated with the difference in frontier molecular orbital (FMO) energies of the ions (highest occupied molecular orbital (HOMO) of the

anions and lowest unoccupied molecular orbital (LUMO) of the cations), which, in turn, correlate well with the substituent  $\sigma_p$  parameters. Extensive density functional theory (DFT) calculations and X-ray diffraction (XRD) analyses augment the experimental results.

Part B of the Dissertation focused on the development of anisotropic ion-conductive materials based on the [*closo*-1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion for the use as an electrolyte material in Li-ion batteries. Efficient and safe electrolytes are bottleneck materials for the development of lithium-ion batteries and, thus, for sustainable mobility. Besides the hazard of explosions that emerges from the highly volatile and inflammable organic solvent, there are also environmental issues connected with toxic inorganic salt-solution based conventional electrolytes. Boron clusters are advantageous for use as lithium salts in electrolytes due to their excellent thermal and electrochemical stability and weakly coordinating nature.

Thus, a novel strategy for anisotropic liquid electrolytes was investigated in which the anion of the Li-salt is a 1,12-disubstituted [*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> derivative structurally similar to the molecules of the liquid crystalline host matrix exhibiting smectic C (SmC) and nematic (N) phases. The electrolyte samples were prepared by doping the lithium salt into the non-ionic liquid crystalline host matrix and investigated by optical, thermal, powder XRD, and impedance spectroscopy methods in a broad temperature range. Results demonstrated that increasing concentrations of ionic additives have little effect on mesophase stability but expand the lamellar SmA phase with ion-conducting channels. The ionic conductivity for the unaligned electrolyte sample was found to monotonically increase from 10<sup>-8</sup> to 10<sup>-4</sup> S cm<sup>-1</sup> with increase in temperature and Li-ion concentration. The Arrhenius analysis of the conductivity data revealed progressively decreasing activation energy  $E_{aIC}$  from crystalline (~102 kJ mol<sup>-1</sup>), to SmA (~70 kJ mol<sup>-1</sup>) and to nematic (~30 kJ mol<sup>-1</sup>) phases. The electrochemical stability window of the 15 mol% electrolyte was determined to be between 1.3 and 4.6 volts relative to the Li metal anode.

In addition, anisotropy in Li-ion transport in the aligned electrolyte sample was investigated, and the preliminary results showed that the ionic conductivity in the perpendicular direction is up to 0.09 mS cm<sup>-1</sup> at 120 °C, while it is only 0.04 mS cm<sup>-1</sup> at the same temperature in the parallel direction. Also, synthesis and testing of the first prototype of a solid polymer electrolyte designed for Li-ion battery applications were achieved. This involved several stages of development, including extensive synthesis and characterization of the liquid crystalline

electrolyte sample, parallel alignment of the electrolyte sample using different surface treatment methods, photopolymerization of the parallelly aligned liquid crystalline electrolytes to generate the solid polymer electrolyte films, and finally cell assembly and battery testing. EIS measurements conducted for the CR2032-type coin cells built using the partially aligned polymer electrolyte sample showed high internal resistance (k $\Omega$  range). This section of the dissertation also provides a summary of recent progress made toward the development of a completely aligned polymer electrolyte.