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Redox-Active Boron Clusters



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For the past decade, our group has been dedicated to exploring the unique redox behavior of boron cluster molecules, with the aim of understanding and harnessing their remarkable properties for molecular and materials applications. Boron clusters can be considered three-dimensional aromatic systems with redox and photophysical profiles that stand in sharp contrast to those of traditional planar organic aromatics. In particular, we have focused on functionalized *closo*-dodecaborate derivatives, such as $B_{12}(OR)_{12}$ clusters, which display highly tunable, multielectron redox processes. Through detailed spectroscopic and electrochemical studies, we have mapped out their accessible redox states and translated this knowledge into practical uses, including catholytes and anolytes for redox flow batteries, as well as chemical dopants for conjugated polymers.

Our investigations have also highlighted the visible-light absorbing and strongly oxidizing behavior of fluoroaryl-substituted $B_{12}(OR)_{12}$ clusters, which act as photoexcitable weakly coordinating anions capable of promoting photooxidation reactions. Building on these discoveries, we extended our studies from solution-phase systems to the solid state by leveraging $[B_{12}(OH)_{12}]^{2-}$ as a stable building block for hybrid metal oxide composites. In these materials, the boron cluster serves as a thermally robust cross-linker that enhances electron transfer between oxide nanoparticles, providing improved performance in photocatalysis and supercapacitor electrodes. Beyond the dodecaborate-based molecules, our group has begun investigating vertex-differentiated clusters that incorporate both alkoxy and halogen substituents to expand the accessible electrochemical potential window.

In addition, we have explored smaller boron clusters, such as *closo*-hexaborates and *closo*-decaborates, which show less reversible redox chemistry but reveal valuable reactivity under oxidative conditions. These systems have been transformed through selective oxidation into alkyl boronate esters or converted to electrophilic species capable of unique arene borylation, opening new pathways for small molecule synthesis.

Collectively, these efforts establish boron clusters as a versatile and underexplored family of redox-active molecules. Their distinctive electronic and structural properties offer a powerful platform for developing advanced materials with tunable physical and electrochemical behavior, as well as creating innovative reagents for organic transformations. This talk will highlight key recent advances from our group and lay out future directions in this exciting area with a focus on understanding fundamental structure function relationship between molecular bonding and physical properties of the boron clusters.