Electronic Structures of Perfunctionalized Dodecaborate Clusters

Thesis by

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To my father

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Finally, I am eternally grateful to my amazing girlfriend Courtney who has supported and pushed me through the final stages of my graduate studies. Having her by my side allowed me to approach my work with confidence and stay calm during stressful periods. The structure and motivation she has brought to my life has been invaluable—without her I would have undoubtedly needed an additional year (or two) to finish this thesis.

ABSTRACT

This thesis summaries my exploration of hypoelectronic aryloxy-perfunctionalized dodecaborate clusters ([$B_{12}(OR)_{12}$]). *Closo*-dodecaborate (*closo*-[$B_{12}H_{12}$]$^{2-}$) is only stable as a dianionic closed-shell species. However, some perfunctionalized dodecaborate clusters can be isolated in hypoelectronic oxidation states, such as *hypocloso*-[$B_{12}(OR)_{12}$]$^{1-}$ and *hypercloso*-$B_{12}(OR)_{12}$ (R = alkyl or aryl). Depopulation of the [$B_{12}(OR)_{12}$] highest occupied molecular orbital (HOMO) give rise to strong visible absorption bands, which has opened up for their use as photoredox reagents. Furthermore, their inert nature and highly reversible redox behavior has inspired applications in charge–storage devices and as dopants in conducting polymers.

The work presented in Chapters 2–4 were part of a broad collaborative effort lead by Professor Alexander M. Spokoyny (University of California, Los Angeles). Chapter 2 discusses my early contributions, which aimed to spectroscopically investigate the photoredox properties of aryloxy-perfunctionalized *hypercloso*-$B_{12}(OR)_{12}$ clusters. Obtaining reliable photophysical data proved exceedingly difficult, due to formation of *hypercloso*-[$B_{12}(OR)_{12}$]$^{1-}$, disproportionation and solvent-cluster interactions. Chapter 2 summarizes discoveries made while attempting to understand these issues, as well as the final luminescence data collected for *hypercloso*-$B_{12}(OR)_{12}$ and *hypercloso*-[$B_{12}(OR)_{12}$]$^{1-}$ clusters. Much of the discussion is speculative, but we felt it should be published here so that other researchers can learn from our struggles.

Given the issues we had with photophysical characterization of the aryloxy-perfunctionalized clusters discussed in Chapter 2, we turned our attention to the alkyloxy-perfunctionalized analogues, which we hoped would be more amenable to spectroscopic characterization. These clusters did not help our investigation of the photoredox behavior, however, while electrochemically characterizing [$B_{12}(OEt)_{12}$] (Et = C_2H_5) we discovered a third reversible oxidation wave, corresponding to the [$B_{12}(OEt)_{12}$]$^{1+/0}$ couple. Chapter 3 discusses this discovery and the characterization of super-oxidized [$B_{12}(OR)$]$^{1+}$ clusters.

Up until now, electronic structure descriptions of hypoelectronic dodecaborate clusters have been largely limited to computational work. Attempts to access the distribution of the frontier orbitals through electron paramagnetic resonance (EPR) spectroscopy had been hindered by the lack of resolution in the continuous wave (CW) spectra of *hypocloso*-$[B_{12}]^{1-}$ species. In chapter 4, we present Q-band pulsed EPR results that give a quantitative measure of the spin distribution of both *hypocloso*-$[B_{12}(OR)_{12}]^{1-}$ and super-oxidized $[B_{12}(OR)_{12}]^{1+}$ clusters. This is to our knowledge the first time pulsed EPR techniques have been applied to hypoelectronic dodecaborate clusters. Our results indicate that the frontier orbitals of *hypocloso*-$[B_{12}(OR)_{12}]$ clusters are confined to the cluster core and delocalized evenly across the B_{12} pseudo-icosahedron. The data for the super-oxidized $[B_{12}(OR)_{12}]^{1+}$ indicate a somewhat more localized spin distribution, which we suggest stems from increased elongation along the z-axis resulting in a concentration of spin density around the equatorial boron atoms. Furthermore, we provide UV–vis–NIR evidence indicating that visible and NIR electronic transitions in $[B_{12}(OR)_{12}]$ occur between orbitals that are largely confined to the cluster core.

PUBLISHED CONTENT AND CONTRIBUTIONS

Axtell, J. C.; Messina, M. S.; Liu, J.-Y.; Galaktionova, D.; Schwan, J.; Porter, T. M.; Savage, M. D.; Wixtrom, A. I.; Rheingold, A. L.; Kubiak, C. P.; Winkler J. R.; Gray H. B.; Král P.; Alexandrova A. N.; Spokoyny A. M. Photooxidative Generation of Dodecaborate-Based Weakly Coordinating Anions. *Inorg. Chem.* **2019**, *58* (16), 10516–10526. DOI: 10.1021/acs.inorgchem.9b00935.

L. J. S. performed photophysical characterization and experimental investigation of intermolecular interactions. Additionally, L. J. S. assisted with data interpretation and development of the photooxidative mechanism.

Stauber, J. M.; Schwan, L. J.; Xhang, X.; Axtell, J. C.; Jung, D.; McNicholas, B. J.; Oyala, P. H.; Winkler, J. R.; Miller, T. F.; Gray H. B.; Spokoyny, A.M. Evidence for the Existence of Cationic Dodecaborate-based Clusters (*in preparation*).

L. J. S. performed electrochemical, spectroelectrochemical, EPR and chemical oxidation studies, including the initial discovery of the cationic dodecaborate.

Schwan, L. J.; Oyala P. H.; Axtell J. C.; McNicholas B. J.; Winkler, J. R.; Spokoyny A. M.; Gray H. B. Electronic Structures of Perfunctionalized Dodecaborates Clusters (*in preparation*).

L. J. S. participated in conception of the project, experiment design, collection and analysis of data, and writing of the manuscript.

Fajardo Jr. J.; Schwan, L. J.; Takase, M. K.; Winkler, J. R.; Gray, H. B. Third Generation W(CNAr)$_6$ Photosensitizers Featuring Fused-Ring and Alkynyl-Bridged Arylisocyanides (*in preparation).*

L. J. S. participated in conception of the project, synthesis and spectroscopic characterization.

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INTRODUCTORY REMARKS

My time at Caltech has been defined by a number of collaborations spanning a range of topics. My first main project was developing flash-quench techniques for mechanistic investigation of nitrogenase enzymes together with colleagues from the Rees lab (Caltech) and Tezcan lab (UCSD). At the same time, I was involved in researching organic electrooxidation using metal catalysts, and semiconductor photochemistry together with members of the Lewis Lab. During my third year at Caltech, I became interested in doing more synthetic inorganic chemistry and transitioned into one of the Gray group's current focus areas—Group 6 Metal Arylisocyanide complexes. Within that project I developed new classes of alkyne-bridged arylisocyanide ligands, along with mixed ligand carbonyl-arylisocyanide complexes. Additionally, I initiated a partnership with the Greer lab (Caltech) to use metal arylisocyanide complexes as absorbers for two-photon nanofabrication.

The research presented in this thesis started during my second year but was until recently a side project of mine. It was part of a broad collaboration initiated by Professor Alex Spokoyny at UCLA, who develops perfunctionalized dodecaborate clusters and investigates their reactivity and applications. Chapter 2 covers much of my early work. At that time, we were fumbling in the dark trying to understand dodecaborate photoredox mechanisms and photophysics. I truly enjoyed all the little experiments I performed to test various hypothesis' and trying to patch together large sets of seemingly unrelated data. However, I never thought that work would lead to anything significant, much less an entire thesis.

Two key advances drove the dodecaborate work to the forefront of my research. The first discovery was made using the newly acquired Q-band pulsed EPR system at Caltech. We found that Electron Nuclear Double Resonance (ENDOR) techniques could be applied to obtain information on hyperfine interactions in open shell dodecaborate clusters, which allowed us to experimentally describe the dodecaborate frontier orbitals. The second development was my electrochemical observation of a new super-oxidized cationic state in the electrochemistry of alkyloxy-perfunctionalized dodecaborate clusters. Both were major breakthroughs; the pulsed

EPR data provided experimental insights that had previously been inaccessible, and the discovery of cationic dodecaborates demonstrated that the clusters could reversibly reach oxidation states that were previously thought be highly unstable.

About a year ago Harry suggested that the dodecaborate data I had was enough for a thesis and that I should "*just write it up*". It was a difficult choice as I really enjoyed the metal arylisocyanide project, but I could not resist the draw of an earlier graduation date. Today, putting down the final words of this thesis, I am very happy about that decision. It has allowed me to finish my studies in good time and focus my energy toward future career goals. Additionally, I am excited about how the metal arylisocyanide project has evolved after I stepped away. Javier Fajardo has made amazing progress, both in continuing my work on alkyne-bridged isocyanides and in developing his own systems.

As I turn away from academia to pursue a career in consulting, I will surely miss Caltech and my time at the bench. It has been some of the most rewarding years of my life.

I hope you will enjoy reading this account of my Caltech experience!