Understanding the reactivity of molecular precursors to colloidal nanocrystals

by

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DEDICATION

To the memory of my distant cousin, Clifford E. Berry, PhD, Iowa State College, 1948 (1918 – 1963). Digital computers were central to the completion of this work. If only he could see how mass spectrometers and computers are interfaced today.

TABLE OF CONTENTS

ACKNOWLEDGMENTS

I could not tell over the multitude of them nor name them,

not if I had ten tongues and ten mouths, not if I had

a voice never to be broken and a heart of bronze within me…

-Homer's *Iliad,* Book II. Translation by Richmond Lattimore.

As Homer listed the ships, the captains, and the multitudes who took part in the Trojan War he called upon the Muses to aid his memory with the hope that no one be left out. So, too, I list those who helped me with science, composition of this thesis, and my education.

My earliest inclinations to attend graduate school occurred while pursuing a chemistry degree at Augustana College in Rock Island, Illinois – a seven mile journey that crossed the Mississippi River in a rusty 1989 Toyota Camry from my home in Davenport, Iowa. While each member of the faculty there had a hand in "getting me into this mess," I credit several of them specifically here: Dave DeWitt, my first inorganic professor who also gave me a very early research opportunity to look at some cobalt ethylenediamine complexes by NMR for inclusion in a teaching lab; Kurt Christoffel's physical chemistry lab course presented my first window into computational chemistry – my finest hour engaged in such activity was spent running a Fortran 77 program that calculated the electronic energy of the He atom, all the while eating a Subway sandwich one spring evening; and Pamela Trotter, who showed me the unusual ways that chemists combine their passions by bringing me as an assistant to her renaissance fair alchemy demos because my long hair "looked the part." Most

culpable of all is Greg Domski, who started as a professor in the summer of 2008. No doubt our first meeting was a startling affair as I accosted this new stranger that very summer in his office while he unpacked his books. As he had the freshest perspective on graduate research at the time, I sought his advice on all things surrounding my next step beyond Augustana. This was also the beginning of my formal research training in synthesis, where I worked on phosphine-functionalized n-heterocyclic carbene binuclear ruthenium complexes.

My education then continued at Iowa State University, where the number of influential people I met increased, as did their impacts on my scientific career. Javier Vela was a one-of-a-kind adviser who gave me the opportunity to supplement this young group's growing body of synthetic work with computational data. I am grateful for him providing opportunities, feedback, and keeping a "scientific roof" over my head. It was under his guidance that I developed a curiosity for all things nanosized and saw that this emerging discipline was a rigorous and interdisciplinary pursuit, valuable not only as a pure science but also for its immediate applications.

All the members of the Vela group also provided an environment of constant fun, support, and cultural enrichment. While the foods that I sampled, the music that I heard, and the discussions that we had exposed small differences, they better illustrated common characteristics held by all humans. I thank them all for the opportunity to learn, even if their customs originated from the far-reaches of Minnesota and Wisconsin.

I also thank my thesis committee for their guidance, input and even hard questions over the years. This group initially consisted of Gordon Miller, Arthur Winter, Keith Woo and Andreja Bakac. Following Andreja Bakac's retirement, Jim Evans officially took her

place, and I thank him for being willing to enter the fray so late in the proceedings. I also apologize to the entire committee for holding my defense at 8 am.

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I also feel the need to acknowledge Anthony Stender, who called me out in his acknowledgments section (yes, I actually read it), so I should return the favor. Over the years since his graduation, we managed to stay in regular contact despite living in different

locations. I benefitted much from his experience and insight into all manner of problems, both chemical and not.

The total support of my family cannot be understated. They have all been at the receiving end of harangues about chemistry, even during my years as an undergraduate, and kindly smiled and nodded at the details that they heard. My parents, especially, held no grudges over my late night arrivals as a commuter from Augustana, fresh from another physical chemistry study session or orchestra rehearsal.

Finally, I thank you, dear reader, for what is an author without an audience? Do not fret if your name does not appear on these pages, for your deeds are beyond the scope of such a technical document, and your names are not meant to be sullied by its content. The muses recount your actions in a different medium that is altogether bigger than ink on paper or packets of electrons in circuits.

ABSTRACT

Colloidal semiconductor nanocrystals are materials with intriguing properties that make them useful for a diverse array of applications such as photocatalysts, light-absorbing materials in solar cells, light emitting diodes and luminescent biological tags, to name only a few. Performance of nanomaterials in these applications is directly related to the size, shape and stoichiometry of the nanocrystals. Strategies exist to control these characteristics during colloidal synthesis, but they tend to rely on certain surfactants, additives, or multi-step procedures to achieve desirable properties. This thesis describes new directions in the synthesis of colloidal nanomaterials that use computational chemistry as a guide. Using new and efficient methods in density functional theory (DFT) to reliably calculate bond dissociation energies (BDEs) of organodichalcogenide (sulfide or selenide) precursors enables the rational synthesis of dot, rod and tetrapod morphology cadmium chalcogenide nanocrystals. Precursors with weaker C-E (E = S, Se) bonds and stronger E-E bonds yielded dot-shaped nanocrystals, while precursors with stronger C-E and weaker E-E bonds afforded rod or tetrapod shapes. This methodology readily extends to the BDE calculation of tertiary phosphine chalcogenides with substituted phenyl, alkyl, perfluoroalkyl moieties or Verkade-type cage structures. In these systems the BDE of a series of P—S or P—Se bonds increases with slightly increasing bond distance, although the BDE of P—Se bonds is significantly lower than P—S bonds.

Another promising method in colloidal nanocrystal synthesis is photochemical decomposition of precursors to access unusual phases or shapes. This thesis also describes

the photochemical synthesis of cobalt(III) oxyhydroxide, Co(O)OH, nanocrystals from chloropentaamminecobalt(III) salts in aqueous solution. Compared to the thermal decomposition of the starting material in the absence of light, the photochemically-synthesized material exhibits a smaller size with a lower-temperature phase transition to cobalt(II,III) oxide, Co_3O_4.