

DANIEL M. CHEVRIER
BSc (Honors Chemistry), Dalhousie University, 2011

DEPARTMENT OF CHEMISTRY

TITLE OF THESIS: STUDIES ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF THIOLATE-PROTECTED GOLD NANOCCLUSERS BY X-RAY SPECTROSCOPY

TIME/DATE: 1:30 pm, Tuesday, December 13, 2016

PLACE: Room 3107, The Mona Campbell Building, 1459 Lemarchant Street

EXAMINING COMMITTEE:

Dr. Zhifeng Ding, Department of Chemistry, Western University (External Examiner)

Dr. Robert L. White, Department of Chemistry, Dalhousie University (Reader)

Dr. Jan K. Rainey, Department of Biochemistry, Dalhousie University (Reader)

Dr. Erin R. Johnson, Department of Chemistry, Dalhousie University (Reader)

Dr. Peng Zhang, Department of Chemistry, Dalhousie University (Co-Supervisor)

Dr. Amares Chatt, Department of Chemistry, Dalhousie University (Co-Supervisor)

DEPARTMENTAL REPRESENTATIVE: Dr. Josef W Zwanziger, Department of Chemistry, Dalhousie University

CHAIR: Dr. Elizabeth Cowley, PhD Defence Panel, Faculty of Graduate Studies

ABSTRACT

Thiolate-protected gold nanoclusters (Au(SR) NCs) exhibit molecule-like properties that are both remarkable and unusual for metal-based nanoparticles. The ultra-small particle size and high stability enables Au(SR) NCs to be synthesized with atomic precision, where distinct particles have an exact composition of Au atoms and thiolate ligands. Recently, crystal structures of atomically-precise Au(SR) NCs (*e.g.*, Au₂₅(SR)₁₈ and Au₁₀₂(SR)₄₄) have been elucidated. This structural information enables their fascinating structure and properties to be examined in great detail, allowing for the effect of structural components (*e.g.*, core, surface, ligand) on the molecule-like properties to be addressed. Working towards this remaining challenge, experimental X-ray absorption spectroscopy and supporting techniques were utilized as a suitable means to study the structure and electronic properties of Au(SR) NCs from an element- and site-specific perspective.

Herein, studies were devoted to understanding the effect of core structure and protecting ligands on the structure and properties of Au(SR) NCs and related metal NC systems. The influence of core size and geometry is first examined for icosahedral-based and face-centred cubic (FCC)-based Au(SR) NCs. It is shown that a difference of only a few Au atoms in the core can modulate the valence electronic structure and restructure the surface of icosahedral-based Au(SR) NCs. Au(SR) NCs with FCC core geometry are found to have a common Au₄ core structural component that directs the molecule-like electronic properties and temperature-dependent bonding properties that are unique to FCC-based Au(SR) NCs. Examining the effect of ligand head group, structurally analogous selenolate-protected Au NCs reveal the predominate effect of Se on the electronic and bonding properties of Au NCs through more covalent Au-ligand interactions. The role of water-soluble glutathione ligands on the structure and photoluminescence of Au(SR) NCs were then investigated along with a comparison to organo-soluble Au(SR) NCs of the same composition. Finally, experimental and investigative techniques developed throughout this work were extended to study the structure and properties of Au NCs stabilized by proteins and the thiolate-protected Ag NC analog, Ag₄₄(SR)₃₀ NCs.