Unraveling the slopes of photoluminescence: Where calculus meets clusters

by

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B.S., Doane University, 2017 M.S., University of Glasgow, 2018

AN ABSTRACT OF A DISSERTATION

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Abstract

Noble metal nanoclusters are vital for advancing research in biology, electronics, catalysis, and several other fields, as they can produce different properties with a variety of geometric and electronic changes. A few properties that have garnered interest are absorption and photoluminescence. Atomically precise nanoclusters have large energetic gaps, rather than a more bulk-like structure which has small energy gaps between bands. As large energetic gaps promote radiative emission, understanding the electronic structure leads to the creation of more emissive materials for bioimaging, sensing, and other applications. As clusters continue to be synthesized with different sizes, shapes, and ligand shell structures, it is imperative to understand absorption and emission properties and be able to tune them for the advancement of nanomaterials. Thus, it is critical to be able to model the electronically excited states in these systems.

One of the most popular methods to model these clusters is time-dependent density functional theory (TDDFT). In this dissertation, DFT is used to model geometric and electronic structure, and TDDFT is used to model optical and photoluminescent properties to analyze the structure-property relationships as a result of a specific change to the system. Initially, ligand effects are analyzed through three examples: the ligand exchange mechanism of Ag₂₉(BDT)₁₂ to Ag₂₉(DHLA)₁₂, the influence of the chiral ligand structure in Au₁₈(S-Adm)₈(SbPh₃)₄Br₂, and the role of the stibine as a protecting ligand in $[Au_6(SbP_3)_2]^{2+}$ and how it differs from the phosphine protected $[Au_6(PPh_3)_6]^{2+}$ cluster. As heteroatom dopants have recently become a popular way to further tailor the structure-property relationships, the role of the Pt dopant on Au₂₄Pt(SR)₁₈ compared to the well-studied $[Au_{25}(SR)_{18}]^-$ cluster will be discussed, in addition to the role of Ni, Pt, Au and Cu dopants in Ag₂₉(BDT)₁₂ clusters. As theory becomes an essential tool in deciphering photoluminescent mechanisms in noble metal nanoclusters, the dual emission mechanism of Au₁₄Cd(S-Adm)₁₂ will be examined, as well as the unique emission mechanisms that arise from different ligand choices in small alkynyl protected Au₂₂ nanoclusters.

TDDFT has proved to be a great theoretical model as it is relatively accurate compared to experiments in a wide range of chemical species. Unfortunately, modelling photophysical and photochemical processes with TDDFT becomes substantially more computationally expensive in large molecular systems and nanoparticles when properties other than energy are required. It is therefore vital to develop methods that solve the scaling problem for excited state energy calculations in TDDFT but retain a similar accuracy. Time-dependent density functional theory plus tight binding (TDDFT+TB) uses a monopole approximation for the transition density in the excited states. As a result, TDDFT+TB reproduces linear response TDDFT results 100x faster than TDDFT in large plasmonic NCs, keeping the electronic excited states properties, however, no one had derived and implemented the analytical excited state gradient derivation to help chemists gain insights into the minimum points on the excited state potential energy surface for insight into photoluminescent mechanisms.

To acknowledge both the application and method development sides in understanding noble metal nanoclusters, this dissertation has two main research prongs. Initially, the role of geometry and electronic structure in optical and photoluminescent properties is ascertained for various nanoclusters with different sizes, shapes, ligand structures, charge states and heteroatom dopants. Second, the analytical gradients for TDDFT+TB will be discussed, which enables more efficient modelling.

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Chapter 1 - Introduction

1.1 – Light-matter interactions

Since the 1600s, when Isaac Newton observed colors from measuring sunlight with a prism, scientists have been captivated with the idea of 'light'. In modern times, it is well known that the meaning of light is really electromagnetic radiation, and the frequency of light scales much further than just the rainbow colors observed with a human eye.¹ Due to the complex physical and chemical behavior of light in different mediums, photochemistry revolves around understanding light-matter interactions. Light-matter interactions can be studied experimentally through techniques such as spectroscopy, or theoretically through quantum and classical mechanical methods. The classical description of electromagnetic radiation can be seen as an oscillating electric field that is in phase and mutually perpendicular to the magnetic field as demonstrated through Maxwell's equations.¹⁻³ Slightly different from the classical approach, the quantum mechanical description of light originates from the idea that photons (elementary particles of electromagnetic radiation) share quantum states, and hence the vector potential takes the form of a superposition of different allowed cavity modes.^{1,4} As the quantum mechanical description of light is very complex, theoretical methods commonly use a classical description of light with a quantum mechanical description of matter.^{1,5} The quantum mechanical description of matter is extremely important in this regard as electrons exhibit a diffraction pattern from interacting with light, just as light would experience a diffraction pattern when propagating through two different mediums.⁶ Diffraction is inherently described to a wave, and hence a wave-like form of matter is important in understanding photochemical processes.

Electronic structure is the most basic way to understand matter and can be understood as the way in which electrons are arranged in atoms or molecules.⁷ The quantum mechanical

methods used to model electronic structure in this dissertation will be described in detail in the next chapter; however, to introduce topics in photochemistry, a good description of energy must be discussed. In atoms, electronic energy levels are quantized and discrete and can be best described as an electrostatic interaction of the negatively charged electron with the positively charged nuclei.⁷ As electrons are added to the system there are more electron-nuclei interactions as well as electron-electron repulsion. To account for these interactions, multi-electron systems are best described by a specific electronic configuration in which electrons fill electronic energy levels from lowest energy to highest in pairs of two with opposite spins.⁸ Molecular energy levels are a result of interacting atomic contributions to form bonding and antibonding molecular orbitals, which also have discrete energy levels. In a similar way to atoms, the electrons fill the molecular energy levels from lowest to highest in pairs of two with opposite spins.⁹ If an atom or molecule is at its lowest possible energy level, or most stable configuration, the electrons are said to be in the ground state. An atom or molecule may access a higher excited state through a process called absorption or access the ground state from a higher excited state through a process called emission. A diagram of absorption and emission processes is summarized in the Jablonski diagram in figure 1.1.



Figure 1.1. Jablonski diagram for organic dyes (IC—internal conversion, ESA—excited state absorption, ISC—intersystem crossing). Reproduced from Ref.¹⁰ with permission from the Royal Society of Chemistry. Copyright 2003

Absorption is the process in which a chemical system (matter) absorbs a photon (elementary particle of light). By absorbing light, the chemical system gains energy. Through this process, an electron gets promoted from a lower energy shell to a higher one and therefore changes electronic configurations.¹⁰ An example of absorption in the visible spectrum can typically be demonstrated through the idea of complementary colors; for instance, a blue solution will absorb light that corresponds to the wavelength of light in its complementary color (i.e., orange). In this case, the blue solution would change electronic configurations when it absorbs the orange light. The molecule may gain energy by accessing a different vibrational mode; however, this does not change the electronic configuration of a molecule as there is not enough energy to promote an electron to a higher electronic energy state.

To access a higher excited state, a chemical system will absorb a photon; however, to relax back down to its lowest energy level, several different processes may occur through nonradiative or radiative mechanisms. Nonradiative relaxation includes all possible ways in which an excited state can lose energy without emitting a photon, such as exerting energy through vibrational modes or atomic collisions.^{1,10} Radiative processes such as fluorescence and phosphorescence release a photon and change electronic states.¹ In figure 1.1, ISC stands for intersystem crossing. This means that the chemical system is crossing from its open shell triplet state (two unpaired spin up electrons) to its closed shell singlet state (two unpaired opposite spin electrons), or vice versa. If a chemical system emits a photon from the triplet state, through the processes of phosphorescence, it must undergo a spin-flip process to get back to the singlet ground state. In this manner, it takes much longer for the molecule to relax, and hence phosphorescence has a longer radiative lifetime than fluorescence.¹¹ Fluorescence mechanisms emit a photon from an excited singlet state (most commonly S₁) back to the ground state (S₀), and hence have a smaller radiative lifetime compared to phosphorescence as the chemical system does not have to undergo a spin-flip process.

All in all, light-matter interactions are extremely important to understand as they have a plethora of applications from electronics and catalysis to biomedicine. Particularly in noble metal nanoclusters, understanding light-matter interactions paves the way to new biosensors, chemical sensors and photocatalysis.

1.2 – Ligand Protected Noble Metal Nanoclusters

Ligand protected noble metal nanoclusters (NC) are a class of highly stable nanomaterials that are atomically precise and composed of tens to hundreds of atoms.¹² These NCs consist of a noble metal core that is protected by an organic-inorganic ligand shell as seen in the example in figure 1.2, such that the Au₇ core is protected by alternating S-Au-S staple motifs, and the organic ligand would connect to the sulfur groups around the cluster to form the full Au₂₀(SR)₁₆ nanocluster.¹³



Figure 1.2. Anatomy of the structure of Au₂₀(TBBT)₁₆: Au₇ kernel and the octameric ring motif. Reprinted with permission from *J. Am. Chem. Soc.* 2014, 136, 34, 11922-11925. Copyright 2014 American Chemical Society

Several different organic ligands are used to protect the nanocluster such as an aromatic ligand, or a longer carbon chain aliphatic ligand. Thiolate-protected noble metal nanoclusters are one of the most popular types of ligand protected nanoclusters; however, there are several other types such as phosphine-protected, alkynyl-protected, stibine-protected, DNA-protected, and more. This makes noble metal nanoclusters extremely useful as their core-ligand structure can be tuned to different chemical environments, and thus different applications. Additionally, they have a strong quantum confinement effect,¹⁴ and therefore adding or removing an atom drastically changes the geometric structure of the nanocluster.¹⁵ Nanoclusters self-assemble with highly symmetric cores and a protecting metal-organic ligand shell that surrounds the core.¹⁶ The interfacial structures of the ligand shell are often dependent upon the shape and size of the core. A general trend in thiolate-protected nanoclusters, for example, is that a smaller nanocluster core requires a longer, more ring-type motif.¹³ Alkynyl ligands, on the other hand, connect through alternating sigma-sigma and sigma-pi type bonding motifs.¹⁷ Through extensive experimental and theoretical structural analysis, it is apparent that these small nanoclusters complete this selfassembly process with a certain amount of metal core to ligand-based pairs.¹² These size regimes correspond to highly stable nanoclusters and are therefore resistant to degradation in environmental conditions. Extensive work has been done trying to understand why the ratio of metal core atoms to ligand base pairs leads to "magic"-sized clusters,¹⁸⁻¹⁹ which eventually led to

one of the most adopted theories for atomically precise nanoclusters, called the superatom model.

1.2.1 – Superatom Theory

Based on the Jellium model, which is a quantum mechanical description of interacting negative and positive charges in a uniform space, superatom theory shows that the high stability of "magic" sized clusters originates from delocalized valence electrons that are dependent upon the size of the nanocluster core as well as the collective contribution from the stabilizing ligands.¹⁸ Described through a counting rule, the number of delocalized electrons can be seen in equation 1.2.1 such that N_{v_A} is the number of electrons from the core metal atoms, M is the number of electrons that are being withdrawn into the ligand shell, and z is the overall charge on the nanocluster complex.¹⁹

$$n^* = N_{\nu_A} - M - z \tag{1.2.1}$$

To calculate the number of delocalized electrons from the Au₂₀(SR)₁₆ nanocluster in figure 1.2, for example, the first step is to initially look at the electronic configuration of the metal. In this case, gold has an electron configuration of [Xe]4f¹⁴5d¹⁰6s¹, which has one unpaired electron, Au will therefore contribute one electron to the overall cluster resulting in a N_{v_A} value of 20 for this example as there are 20 Au atoms each contributing one electron. The thiolate ligands withdraw one electron each, i.e., M = 16. The cluster is overall neutral (z = 0), so the total number of delocalized electrons or the "superatomic" electron count is 4. Analogous to atomic theory, the number of delocalized electrons corresponds to a specific configuration in which the electrons occupy "superatomic" molecular orbitals in pairs of two with opposite spins. A cluster with 8 superatomic electrons, for example, corresponds to an S²P⁶ superatomic configuration in which one spherical S orbital and three dumbbell-shaped P orbitals are occupied from a collective atomic contribution from the Au atoms. As the Jellium model is based on a spherical coordinate system, "magic" clusters correspond to closed shell superatomic electronic counts (2, 8, 18, 20, ...).¹⁹ Superatomic electron counts such as 4 electrons in the example in figure 1.2, follow more prolate or ellipsoidal models such as the Clemenger-Nilsson shell model.²⁰ In 2013, Cheng and Yang proposed a different way to treat species that do not have a "magic" number of delocalized electrons by using superatom-superatom bonding, which has similar bonding patterns to that between atoms.²¹ Regardless of the model chosen, superatom theory is incredibly important as it allows an easy connection between atoms and noble metal nanoclusters.

1.3 – Structure-Property Relationships in Noble Metal Nanoclusters

As a result of the small size and atomically precise nature, ligand protected noble metal nanoclusters have discrete energy levels, like a molecule. This is different from larger nanoparticles (>2nm) and bulk metals in which the small energy differences between states leads to a more band like structure in which the states form almost a manifold of surfaces that are very close to each other as seen in figure 1.3.²²



Figure 1.3. Energy level diagram comparing a bulk semiconductor to its molecular analog and a quantum dot. The semi-conductor's electrons are in bands; the molecule's electrons are in molecular orbitals. The vertical arrow denotes the bandgap Eg. Reprinted from *Appl. Spectrosc.* 2002, 56, 1, 16A-27A with permission. Copyright 2002 SAGE Publications

This means that when light interacts with nanoclusters, discrete energetic transitions are made. Further, as noble metal nanoclusters can be tuned with respect to different sizes and ligand shells, the change in corresponding energy levels, or electronic structure, changes the optical and photoluminescent properties in the nanoclusters, i.e., the absorption and emission processes. This means that by simply changing the physical aspect of a noble metal nanocluster, the properties can be tuned to a specific application.

One of the most studied nanoclusters theoretically and experimentally is Au₂₅(SR)₁₈. This nanocluster can be tuned through isomerization, ligand exchange, surface modification, self-assembly mechanisms, etc. for a variety of applications in photothermal therapy, bioimaging, biosensing, and more.²³⁻²⁶ Further, this cluster is important as it was one of the first nanoclusters to be separated and identified, and therefore became the fundamental model in the field of atomically precise nanochemistry.²⁷ The basic skeleton structure of the cluster can be seen in

figure 1.4, such that the nanocluster has a 13-atom core that is protected by 6 S-Au-S 'V' shaped staple motifs.



Figure 1.4. Structure of Au₂₅SR₁₈ NCs. Au, yellow; S, red. Carbon and hydrogen atoms have been omitted for clarity. Reprinted from *Acc. Chem. Res.* 2021, 54, 4142-4153 with permission. Copyright 2021 American Chemical Society

The core has three perpendicular 2-fold axes and forms an approximate icosahedron made up of 20 triangle faces.²⁸ The overall cluster has a charge of -1 and possesses an approximate C₃ axis with nearly T_h group symmetry. According to the superatom model, this cluster has 8 superatomic electrons which correspond to a S²P⁶ configuration. This results in electronic density that forms three dumbbell P occupied orbitals, and 5 unoccupied (or virtual) molecular orbitals that take the form of a superatomic D orbital in the core of the nanocluster.²⁹⁻³⁰ Similar to atomic theory, the high symmetry of this cluster results in the occupied P orbitals forming a nearly triply degenerate set. Additionally, since the point group is nearly T_h , the D orbitals split into an approximately doubly degenerate and a nearly triply degenerate set.

Optically, $[Au_{25}(SR)_{18}]^{-}$ follows similar selection rules from molecular spectroscopy. The low energy peak, for example, is a result of P \rightarrow D electronic transitions.²⁸ As these molecular orbitals are dominated by sp atomic orbitals from the Au atoms, this results in intraband transitions (sp \rightarrow sp). The highest experimentally observed peak is a result of interband (d \rightarrow sp) transitions, and the middle peak has a mix of both types of transitions.²⁸ These peaks are dependent upon the charge state and ligand structure as the electronic structure changes when different charge states or ligands are applied. An example of the optical differences between different charge states can be seen in figure 1.5.



Figure 1.5. Absorption spectra of Au₂₅(S-PhC₂H₄)₁₈ nanoclusters with charge state of -1, 0, and +1. Reproduced from Ref.²⁷ with permission from the Royal Society of Chemistry. Copyright 2018.

As the cluster goes from an anion to a cation, electrons are removed from the superatomic P orbitals. This results in a large splitting between P orbitals as a result of the Jahn-Teller effect.³¹ As a result of the larger energetic gap between the occupied P and unoccupied D orbitals, the low energy peak in the absorption spectrum blue shifts to higher energy (figure 1.5 C). The charge state makes additional changes in the absorption spectrum, such that as the cluster loses electrons, the middle peak is redshifted, and the high energy peak is blue shifted. As touched upon earlier, changes in optical spectrum are not just a result of different charge states, but also the ligand structure. In fact, according to calculations by Tlahuice-Flores, et al., the more distorted the ligand structure in Au₂₅ clusters, the lower the HOMO-LUMO gap, and thus larger optical differences between ligands.³² TDDFT calculations have further shown that keeping the

symmetry and shape of Au₂₅ clusters but simply switching the S atoms to Se atoms has large optical differences.³³⁻³⁴ This means that not only is the charge state, ligand structure, core composition, etc. incredibly important in understanding optical properties, but these optical properties can be directly tuned by changing the chemical environment of noble metal nanoclusters.

As absorption properties change by altering the core-ligand structure or charge state, it can be presumed that the emission may also be tuned in noble metal nanoclusters by modelling different structure-property relationships. However, emission mechanisms are more difficult to predict because relaxation to the ground state can take both nonradiative and radiative pathways. Spectroscopy serves as an incredible tool for measuring the experimental emission in molecules and nanoclusters, but unfortunately, it cannot predict which excited state is emitting, which limits full understanding of the emission mechanism. Theoretical methods are therefore required in advancing the field of tunable emissive nanomaterials. Both quantum and classical mechanics play a role in obtaining the radiative and nonradiative pathways for photochemical processes. Larger systems, such as noble metal nanoclusters, however, are constrained to the level of theory and system size as modelling both electrons and nuclei becomes too computationally expensive. Considering the fact that atomically precise nanoclusters have discrete energy gaps, which promotes radiative emission, modelling the electronic states often suffices in obtaining a good picture of the photoluminescent mechanism for different nanoclusters.

Revisiting the well-known $[Au_{25}(SR)_{18}]^{-}$ cluster, it was found in 2002 that the watersoluble cluster with glutathione ligands shows dual emission at 1.15 eV and 1.55 eV.³⁵ Initially it was suggested that the lower emission could be coming from a phosphorescent mechanism, and the higher energy emission could be coming from fluorescence, though they were not certain,

and had a few different suggestions.³⁵ Several experimental studies were completed to try and deduce the dual emission mechanism with slightly different ligands and solvents. The predicted emission mechanism changed through these studies in which the higher energy emission was still a result of fluorescence, but the lower energy emission was predicted to be a result of some metal-ligand state.³⁶⁻³⁷ It was not until 2016 that Weerawardene et al. used time-dependent density functional theory (TDDFT) analytical gradients to optimize the excited state and find the emissive minimum points.³⁹ Excited state gradients are an important method as they can be used to find minimum points on excited state surfaces using optimization methods. Compared to the orbital energies in the ground state, optimizing the S₁ state results in the occupied superatomic P orbital being destabilized by 0.22 eV, and the unoccupied superatomic D being stabilized by 0.27 eV, which lowers the overall HOMO-LUMO gap and thus the S_1 emission energy.³⁹ Through their work, no charge-transfer states were found between the metal core and ligand shell. It was therefore concluded that the lower emission energy is a result of the vibrationally relaxed geometry in the first excited state, which proposed a core dominated fluorescent mechanism.³⁸ For the higher emission peak, it was suggested that emission may be from a state between the S₂ and S_{6} .³⁹ Through nonadiabatic dynamics calculations, however, it was shown that the S_2 - S_6 states would more likely nonradiatively decay via vibrational relaxation down to the S₁ state.⁴⁰ In the past few years, experimental work has suggested that the second emissive peak may be from the neutral Au₂₅ cluster mixing in with the anionic cluster, as the two charge states have different photochemical properties.^{27,41} The emission mechanism is still highly debated. In this regard, however, there is no doubt that the S_1 state is important.

Similar to absorption, emission from the S_1 state can be tuned to different applications by changing the physical aspects of the nanocluster. It was found that the HOMO and LUMO

orbitals are destabilized/stabilized respectively by different amounts depending on the different type of organic ligand used to protect the cluster.³⁹ This relationship can be seen in figure 1.6, such that the HOMO-LUMO gap in the optimized S_1 geometry gets smaller with the larger protecting ligand.



Figure 1.6. Comparison of energy levels of the frontier orbitals in S₀ and S₁ states of [Au₂₅(SR)₁₈]⁻ clusters. The S₁ state is shown in a cartoon representation with a single electron in one of the D orbitals. Dashed lines are drawn to show the splitting of triply degenerate HOMO/HOMO-1/HOMO-2, doubly degenerate LUMO+2/LUMO+3 and triply degenerate LUMO+2/LUMO+3/LUMO+4 orbitals of the ground state upon photoexcitation. Reprinted from *Acc. Chem. Res.* 2018, 51, 3065-3073 with permission. Copyright 2018 American Chemical Society.

Jin et al. showed that the photoluminescent intensities change with different charge states, and the center of the emission peak slightly blue shifts as the cluster loses electrons (i.e., goes from anionic cluster to cationic cluster).⁴¹ Additionally, it was found that the photoluminescent emission will red shift when the pH of the solution is increased (i.e. when the cluster is

introduced to a more basic solution).⁴² This means that the chemical environment around the nanocluster along with the ligand shell is critical in tuning the emission mechanism. The fact that the emission does change in these scenarios, however, proves that atomically precise nanoclusters, such as Au₂₅, are extremely tunable for potential applications, and a full understanding of their structure-property relationships must be understood.

Similar to the photoluminescent mechanism in Au₂₅ clusters, fluorescence from the S₁ state is critical in all noble metal nanoclusters. The reason can be traced back to 1950 when Michael Kasha came up with a rule that originated from spectroscopy experiments in molecules.⁴³ Kasha's rule states that large quantum yield originates from emission from the lowest electronic state of a certain multiplicity, i.e., the T₁ or S₁ state.⁴³ As noble metal nanoclusters have discrete energy gaps, like molecules, this rule translates well for understanding the photoluminescent mechanisms in Au and Ag clusters. Unfortunately, not all ligand protected noble metal nanoclusters follow this rule. An example of this is nanoclusters that show the rededge effect (REE). REE is related to fluorescence spectra that red shifts when the excitation energy is changed to lower energy (or the red side of the visible spectrum).⁴⁴ This process violates Kasha's rule as the emission energy should be independent of the excitation energy.⁴³ Glutathione coated gold nanoclusters introduced by Zhou et al. in 2010 additionally show that emission sometimes depends on the excitation energy.⁴⁵ It was found that these nanoclusters emit from the T_1 state when excited at 420 nm but emit from the S_1 state when excited at 530 nm.⁴⁵ This is a complicated emission mechanism as the T_1 and S_1 states are nearly degenerate, and the change in radiative lifetime is the main observable difference between the potential mechanisms. Aggregation induced emission and charge transfer from higher excited states are photoluminescent mechanisms in the literature that additionally contradict Kasha's rule.⁴⁶ Ligand

to metal charge transfer (LMCT) is a popular mechanism in Ag nanoclusters as the oxidationresistive Ag(I)-thiolate complex acts as a protective shell around an Ag center, and additionally enhances the PL mechanism by promoting LMCT states.⁴⁷ The photoluminescent quantum yield of LMCT has been studied in a variety of nanoclusters and can be enhanced by using electron donating ligands that increase intramolecular charge transfer.⁴⁸⁻⁵⁰ It is unknown why these photoluminescent mechanisms are often seen in Ag clusters; however, the fact that Au nanoclusters have a strong outer shell contraction and reduced 5d-6s energetic gap⁵¹ could hint that the hybridization in Au nanoclusters gives the cluster more outlets to nonradiatively decay to the lowest electronic state. In 2014, Chen et al. strived to piece together the connection between ligand shell and metal core transfer that had been previously seen as a possible PL mechanism in Ag nanoclusters.⁵² Through their work, they showed that the type of ligand shell is critical as the mechanism completely changes and quenches the high luminescence when replacing carboxylprotecting ligands with sulfonic acid groups but not changing the shape or size of the Ag core.⁵² In this cluster, they proposed that the photoluminescent mechanism is ligand to metal to metal charge transfer (LMMCT) as seen in figure 1.7.



Figure 1.7. Schematic illustration of the structures of the luminescent Ag-carboxylate with Ag⁺ -carboxylate complexes shell. Reprinted from *Phys. Rev. Lett.* 2004, 93, 9, 093401 with permission. Copyright 2014 American Physical Society.

In this case, electrons get absorbed into an excited state dominated by the oxygen atoms in the carboxyl ligand. Upon emission, the cluster shows ligand to metal charge transfer from the oxygen atoms to the Ag atoms in the protecting shell of the nanocluster. The cluster then relaxes via nonradiative mechanism to the Ag core atoms, and the Ag core atoms radiatively release a photon and relax the cluster back to its ground state configuration.⁵²⁻⁵³ This paper does not discuss electronic states as it is purely from an experimental point of view; however, the different spectra shows that the PL mechanism in these clusters can be quite complicated.

Overall, emission mechanisms can be as simple as radiative relaxation from the Fermi energy levels (S_1 state) or very complicated with electronic density transferring to higher electronic states due to intramolecular interactions. Theoretical methods are therefore imperative in piecing together the exact mechanism of photoluminescence in ligand protected gold nanoclusters to advance a plethora of fields in biology, electronics, and chemistry.

1.4 – Objectives

Noble metal nanoclusters are vital for advancing research in biology by showing efficient energy transformation for photodynamic therapy,⁵⁴ electronics by successfully modulating the flow of electrons,⁵⁵ catalysis by enhancing the reduction of CO₂⁵⁶ and several other energetic processes in a plethora of fields. These atomically precise nanoclusters are unique as they have discrete energy gaps, which can promote radiative emission, and therefore their optical and photoluminescent properties can be tuned with a variety of geometric and electronic changes. Experimental groups have used different techniques to analyze the absorption and emission processes, however, theoretical work is still needed to piece together the mechanisms. This dissertation will therefore focus on elucidating the structure-property relationships in ligand protected noble metal nanoclusters, particularly in the realm of photoluminescence. Unfortunately, theoretical studies with these nanoclusters are limited to system size and level of theory due to the extensive computational cost of excited state calculations, particularly with time-dependent density functional theory. This dissertation therefore has two main research objectives.

Initially, from an application point of view, the main objective is to unveil the structureproperty relationships in noble metal nanoclusters by looking at the geometric structure, electronic structure, optical and photoluminescent properties in noble metal nanoclusters with different core-ligand structures and heteroatom dopants. Chapters 3, 4 and 5 will discuss the effect of different core-ligand structures on these properties. Chapters 6 and 7 will elucidate the role of the heteroatom dopant in optical and photoluminescent properties compared to the parent cluster. Photoluminescence is the main focus in Chapters 8 and 9, as the dissertation will go more in depth about the unique emission mechanisms in Au₁₄Cd(S-Adm)₁₂ and Au₂₂(SR)₁₂.

Emission mechanisms are incredibly important to understand, especially from a theoretical perspective as experiments give a great initial picture but cannot specify exact states or electronic transitions.

The second main objective is to develop a relatively accurate method for the study of excited states at a smaller computational cost than TDDFT. While the idea for investigation is primarily to cut computational costs for noble metal nanoclusters, this method can be used for any chemical system of interest. Therefore, after a thorough discussion of structure-property relationships in noble metal nanoclusters, method development of the analytical excited state gradients for time-dependent density functional theory plus tight-binding (TDDFT+TB) will be discussed in Chapter 10 for more efficient potential energy surface exploration.

1.5 – References

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Chapter 2 - Methods

History professors have often signified the importance of the scientific revolution around the late 1500's. This revolution, arguably started by scientists such as Galilei, Newton and Leibniz, is important as it emphasized the scientific method and laid the foundation for legitimacy and fact-based knowledge.¹ This new way of thinking not only gained traction but led to many discoveries that are vital in understanding the modern world such as classical mechanics, thermodynamics, magnetism, and light. Unfortunately, starting in the 1800s, theorists were unable to capture the behavior observed by newly discovered experimental techniques, and it quickly became obvious that the methodology of classical mechanics, i.e., the study of motion and displacement of particles from the result of a force, could not hold up for extremely small systems such as atoms and molecules.² Physicists such as Max Planck and Albert Einstein were vital in making mandatory changes to classical mechanics suggesting theories such as a quantized form of light.³ These new theories kicked off the study of quantum mechanics, i.e., the study of light-matter interactions on the subatomic scale. Even with this advanced level of thinking, however, more advanced mathematical methods were required to continue forming these theories as numerical methods were limited. Scientists such as Bohr, Heisenberg, Schrödinger, Pauli, Dirac, and others were vital in advancing quantum mechanics.⁴ Arguably, quantum mechanics is one of the most notable interdisciplinary research fields as it perfectly encapsulates chemistry, physics, and mathematics. Unfortunately, it is not the easiest to interpret or derive as quantum mechanics is inherently a probabilistic theory; i.e., it cannot predict with certainty what will happen, but only gives probabilities.⁵ Despite this probabilistic nature of the method, it is undisputed that quantum mechanics not only provides an accurate model of the description of matter but succeeds in cases where other methods fail.⁶ While there has been

incredible advancement in this field since the 1920s, the work in this field is far from complete as there are several situations in which quantum mechanics cannot be applied to larger systems due to the resulting mathematic complexity combined with limited computational power.

This chapter will discuss electronic structure theory concepts that have been adopted from the 1920s along with more advanced methods that have been used to model the structureproperty relationships in noble metal nanoclusters. As this field advances more and more everyday as scientists, physicists and mathematicians continue to try and evolve the expertise needed to surpass these barriers, it is important to note that the methods discussed in this chapter are simply a subset of the large field that is quantum mechanics.

2.1 – Electronic Structure Theory

The field of quantum mechanics originates from theoretical methods that try to understand the basic electronic structure of atoms and molecules. As electrons are like glue, helping atoms cling together, it is important to understand how they interact. In 1913, Niels Bohr predicted that electrons travel around nuclei in fixed orbitals, like how a satellite would orbit planets.⁷ Slightly expanding on this idea, the quantum mechanical description of an atom suggests that rather than fixed orbits, electrons form a large cloud around the nuclei that is denser the closer the electrons are to the positively charged center. This new model was introduced by Erwin Schrödinger, when he applied the idea of a quantized form of light into the wave equation and created the time-independent Schrödinger equation.⁸

2.1.1 – Time-Independent Schrödinger Equation

The time-independent Schrödinger equation (TISE) fully describes the time-independent properties of a single nonrelativistic particle in terms of its wavefunction.⁹ This equation uses the kinetic, T, and potential energy, V, operators to quantize energy or angular momentum in a

specific atom or molecule.¹⁰ Schrödinger's partial differential equation for a particle mass in one dimension can be seen in equation (2.1.1),

$$T(x)\Psi(x) + V(x)\Psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$
(2.1.1)

such that \hbar is the reduced Planck constant, *m* is the mass of the particle, and if the particle is free to move parallel to the x-axis, the potential energy, V(x) is zero. The combination of kinetic and potential energy is called the Hamiltonian operator, and Ψ is the wavefunction of the system. To solve equation (2.1.1), $\Psi(x)$ must represent the wave like nature of the particle and solve both sides of the Schrödinger equation. The choice of wave function is very important in quantum mechanics because it signifies the complete description of a particle over time.

For molecules, equation (2.1.1) must be expanded to match the degrees of freedom in the system. In this case, adding just one electron into the system adds another three electronic degrees of freedom to the wavefunction for the corresponding x, y and z dimensions. Due to the high dimensionality, the TISE only has an exact analytical solution in systems in which there is one electron, and even then, this equation may only be solved exactly for multiple atom one electron systems in which the Born-Oppenheimer approximation is used.¹¹ Theoretical approaches therefore require numerical methods or approximations to get as close as possible to the exact solution.

One of the most common approximations to the wavefunction is the Born-Oppenheimer (BO) approximation. This approximation rewrites the wavefunction in terms of an electronic wavefunction for each position of the nuclei. The relationship stems from the movement of the different particles, i.e., because electrons are many orders of magnitude lighter than the nuclei, they move much faster. In a conceptual framework, this means that the electrons can be seen moving around in a field of fixed nuclei. This method is also called the adiabatic approximation

as the system will stay in its purely electronic energy eigenstate given a weak perturbation of nuclear movement.¹² To be more explicit, the general expanded version of equation (2.1.1) is demonstrated by equation (2.1.2).¹³ In this equation, the wavefunction represents both the electronic, **r**, and the nuclear, **R**, degrees of freedom of a molecule (Note: i, j, ... indices represent an electron, A, B, ... indices represent a nucleus, M_A is the mass of atom A, and Z_A is the charge on atom A).

$$\left(-\frac{1}{2}\sum_{i}\nabla_{i}^{2}-\sum_{A}\frac{1}{2M_{A}}\nabla_{A}^{2}-\sum_{iA}\frac{Z_{A}}{r_{i}A}+\sum_{i,j>i}\frac{1}{r_{ij}}+\sum_{A,B>A}\frac{Z_{A}Z_{B}}{R_{AB}}\right)\Psi(r,R)=E\Psi(r,R) \quad (2.1.2)$$

With the BO approximation, the kinetic energy of the nuclei (second term of equation (2.1.2)) will disappear, and the potential energy of interacting nuclei (term five in equation (2.1.2)) will be held as a constant or scalar term as it does not depend on the electronic coordinates. Allowing the wavefunction to have a parametric dependence on the nuclei therefore reduces the dimensionality of the wavefunction.

While the reduced dimensionality of the wavefunction is extremely important in analyzing electronic structure, the exact formulation of the electronic wavefunction is very difficult to produce. The reason for this is that the wavefunction is not an exact experimental observable, and therefore, it must be derived from theoretical equations.¹⁴ Considering the fact that the TISE is a wave equation, the electronic wavefunction should essentially behave like a wave. Notably, this is where one of the biggest differences comes in between classical and quantum mechanics. Max Born contributed the idea of probability, perpetuating that if an electron exists, it should be somewhere, i.e., there is 100% probability that an electron should exist in space.¹⁵ This deterministic nature of electrons led to the normalization condition of the wavefunction. Adding to the theory, Pauli discussed that fermions have +1/2 and -1/2 spin states,

and therefore the electronic wavefunction should have a spin contribution in addition to the spatial contribution of an electron.¹⁶ Considering these different interactions, a Slater determinant was proposed to form the electronic wavefunction. The Slater determinant for a system with *N* electrons is represented in equation (2.1.3), such that χ is the spin-orbital of electron *N*.¹⁷

$$\Psi(\mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{1}(\mathbf{x}_{1}) & \chi_{2}(\mathbf{x}_{1}) & \dots & \chi_{N}(\mathbf{x}_{1}) \\ \chi_{1}(\mathbf{x}_{2}) & \chi_{2}(\mathbf{x}_{2}) & \dots & \chi_{N}(\mathbf{x}_{2}) \\ \vdots & \vdots & \dots & \vdots \\ \chi_{1}(\mathbf{x}_{N}) & \chi_{2}(\mathbf{x}_{N}) & \dots & \chi_{N}(\mathbf{x}_{N}) \end{vmatrix}$$
(2.1.3)

As represented in equation (2.1.3), the normalization condition from Born and antisymmetric principle from Pauli are satisfied. This representation of the wavefunction satisfies the basic behavior of electrons and is commonly used to solve the Hartree-Fock equations.

2.1.2 – Hartree-Fock

Hartree-Fock aims to solve the TISE to find the energy and bond distances in multielectron, multi-nuclear systems, such as molecules. The basic idea behind this method is that as electron clouds are interacting between atoms, each individual electron should feel the repulsive effect from the other electrons as well as the attractive effect from the nuclei. The method models these interactions in an average way by using the variation principle.⁹ In other terms, the energy obtained from the method, ϵ , will always be an upper bound to the exact electronic energy, E_0 , such that equation (2.1.4) holds true.^{18,19}

$$\epsilon = \frac{\int \dots \int d^3 r_1 \dots r_N \ \Psi^* H \Psi}{\int \dots \int d^3 r_1 \dots r_N \ |\Psi|^2} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \ge \mathbf{E_0}$$
(2.1.4)

The full Hamiltonian in this case takes the form of a Fock operator. The Fock operator includes the core Hamiltonian (kinetic and potential energy of each nonrelativistic particle) with a Coulombic and exchange operator.²⁰ Coulomb is in reference to the electrostatic interactions

between electronic clouds, and exchange is in reference to the interaction of two identical particles.¹⁹ The exchange term can be thought of a large coulombic interaction between particles that share an identical spin state, and hence it is often correlated to the antisymmetric nature of the wavefunction.¹⁹ Since the expectation value is used in equation (2.1.4), the interaction of electron 1 for instance with electron 2 is averaged over all positions of electron 2 as represented in the expectation value of the Coulomb and exchange operators. Unfortunately, the expectation value of electron 2 cannot be known without knowing the expectation value of electron 2 in terms of all the positions of electron 3 (and so on and so forth...). This essentially means that the answer must be known, to know the answer.¹⁹ This method therefore uses a self-consistent field (SCF) approach to solve the equations. To a certain degree, this method can be seen as a guess and check method. An initial guess is made for the spatial orbitals, the Fock operator is then used to produce new spatial orbitals by adjusting a specific parameter in the trial wavefunction, and the cycle is completed over and over until there is minimal change between the old and new spatial orbitals and energy.²¹ When the SCF cycle has acceptably converged, the energy it produces is the lowest, or ground state energy for a chemical system.

2.1.3 – Basis Functions

A common theme in this chapter has been that the exact formulation of the electronic wavefunction is unknown. As implemented with the Hartree-Fock method, it is vital to have an adjustable parameter for the trial wavefunction to find the optimal spatial function that lowers the energy of the system. For this reason, the spatial function is often written as a linear combination of specific basis functions as demonstrated through equation (2.1.5)

$$\Psi_i = \sum_{j=1}^N c_j \psi_j \tag{2.1.5}$$

such that ψ_j is a set of basis functions with specific coefficients c_j .^{9,19} There are several different functions that can represent ψ_j such as Slater-type orbitals (STO) and Gaussian-type orbitals (GTO). Note: basis functions with respect to building a molecular spatial orbital are in general called atomic orbitals (AO).

STOs make use of spherical harmonics because atoms are inherently spherically shaped. The functional form of an STO can be seen in equation (2.1.6) such that *N* is the normalization constant, $Y_{l,m}$ is a spherical harmonic, and the exponential function models the decay behavior of an electron as exhibited by the hydrogen atom.^{9,22}

$$\psi_{n,l,m}(r,\theta,\phi) = NY_{l,m}(\theta,\phi)r^{n-1}e^{-\zeta r}$$
(2.1.6)

The basis is no longer in terms of the spatial coordinates x,y,z of an electron, but rather spherical coordinates r, θ , ϕ . Unfortunately, STOs do not have a radial node, and hence are usually implemented by using a linear combination of STOs to form an atomic orbital. As an alternative to STOs, Gaussian-type orbitals have a Gaussian functional form as seen in equation (2.1.7), such that $r^2 = x^2 + y^2 + z^2$. ^{9,23}

$$\psi_{i,j,k}(x,y,z) = N x^{i} y^{j} z^{k} e^{-\alpha r^{2}}$$
(2.1.7)

The form of the exponential in the GTO no longer follows the decay behavior of an electron as the r value is squared, which does not fit the decay represented by an electron in the hydrogen atom. This means that the slater-type orbitals are more accurate; however, due to mathematical tricks that can be used with Gaussian functions, GTOs are cheaper computationally. Both forms of the basis function, however, are critical to understand in order to best model a specific chemical system of interest based on a good cost to accuracy relationship. GTOs and STOs are atom-centered basis functions; however, just one basis function per spatial orbital is often not enough to correctly demonstrate the behavior in atoms and molecules. Basis sets are therefore not only classified by type, but also by quantity. A double zeta (DZ) basis set, for instance, means that two atom centered STOs or GTOs are used for each spatial orbital. Similarly, triple zeta (TZ), quadruple zeta (QZ), quintuple zeta (5Z), etc. basis sets exist in which a number (3, 4, 5, ...) of atom-centered basis functions is used to describe one spatial orbital.²⁴ Additionally, there are extra basis functions that are added into the set. An example of this would be polarization functions. Polarization functions add an additional function for the next higher angular momentum spatial orbital in the electron configuration.²⁴ For example, a double zeta polarized (DZP) basis set for carbon would have 15 basis functions total (two functions for each spatial orbital 1s, 2s, $2p_x$, $2p_y$, $2p_z = 10$ basis functions + 5 d-orbital polarization functions). The polarization functions help account for different types of bonding in molecules as different atomic orbitals get mixed together.

All in all, the choice of basis set is very important as the calculation gets more accurate when more basis functions are included. Unfortunately, this also results in a higher computational cost. In all quantum mechanical calculations, a good balance between accuracy and computational cost must be deduced depending on the specific chemical system of interest and what property of interest is being obtained from modelling that system.

2.1.4 – Relativistic Effects

The methods introduced in this chapter so far have been in reference to single nonrelativistic particles. The later chapters of this dissertation will discuss noble metal nanoclusters, which makes relativistic effects vital to discuss. Relativistic effects technically

apply to all electrons in all quantum shells; however, the delocalization of the energy due to relativistic effects increases drastically in bigger atoms with larger electronic shells.²⁵

In the simplest sense of the term, the term relativistic effect refers to the discrepancies between a model that includes special relativity (defined by Einstein in 1905) vs. models that do not. Special relativity states that the laws of physics hold true in all inertial frames.²⁶ To put this into simple terms, imagine that there is a group of baseball players travelling to a tournament on a bus. Two of the baseball players decide to throw a baseball back and forth at a constant pace to start warming up their arms before getting to their destination. A little boy happens to be on the street as they pass by. To the little boy, the baseball seems to be going much faster, as from his perspective, there is motion of the baseball in addition to motion of the bus.

In chemistry terms, as an electron gets much further away from the nucleus, it feels less of an attractive pull from the positive charge. From electronic structure theory, it is known that the radial coordinate scales ~ 1/Z where Z is the nuclear charge.²⁷ This means that as the atom gets bigger (larger Z value), the radial coordinate is much smaller. This essentially "confines" electrons to a much smaller radial component. According to the Heisenberg uncertainty principle, when an electron is confined to a smaller space, it increases in radial velocity.²⁸ As special relativity is defined such that the law of physics do not change between the different electrons even though they have increased velocity, theoretically, the energy levels are destabilized, and are observed differently.²⁶ Therefore, just as the little boy would have to essentially correct for the increased velocity of the bus to understand the true velocity of the baseball, theorists must correct for the increased velocity of the delocalized electrons.

In quantum mechanics, relativistic effects may be added as an additional term in the Hamiltonian or as a corrective term. In this dissertation, the relativistic effects are included by using the ZORA approach. ZORA stands for the zero-order regular approximation.^{29,30} In this method, the scalar relativistic effects are added into the Hamiltonian. This method additionally compensates for the additional kinetic energy of the electrons by including steeper core-like functions into the calculations.²⁹

2.2 – Density Functional Theory

While the Hartree-Fock method is an essential starting point to understanding electronic structure in atoms and molecules, as well as being one of the most used methods well into the 1950s, it has some major drawbacks. Initially, the Hartree-Fock method assumes that the many electron wavefunction may be written as a single Slater determinant. Second, the method does not incorporate all electron correlation. Third, Hartree-Fock calculations are quite costly, scaling as N^4 , where *N* is the number of basis functions in the system.³¹ Several methods have worked to combat some of these drawbacks, and of those methods, density functional theory (DFT) has become one of the most preferred methods to use for deciphering the electronic structure of different chemical systems.³² In principle, DFT bypasses the need for a many electron wavefunction by analyzing the total energy of the system as a function of electronic density.³³ In reality, however, Kohn-Sham wavefunctions are needed to fully implement the method. The idea of density functional theory can be traced back to theorems from Hohenberg and Kohn.

2.2.1 – Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem states that there is a unique one-to-one mapping of external potential to an electronic density.³⁴ In other terms, an external force resulting from the nuclear attraction on an electron will result in a specific electronic density that is unique to that force. As the density is unique to a specific external potential, the ground state density uniquely
determines the Hamiltonian and therefore, determines all ground state properties from the ground state density.³⁴ Due to this, the complete ground state energy may be written as a functional of the ground state electron density as seen in equation (2.2.1)

$$E_{\nu(r)}[n(r)] = \int n(r)\nu(r) \, d^3r + F[n(r)]$$
(2.2.1)

such that *F* contains a broad form of the Hamiltonian with a kinetic energy and electron-electron repulsion energy, v is an arbitrary external potential, and n(r) is the ground state density.³³ Unfortunately, this theorem is simply an existence theorem, i.e., there exists a unique ground state electronic density that solves all ground state properties. It is important to note that the exact form of the density is unknown.

The second Hohenberg-Kohn theorem states that there is a ground state density functional such that the energy of this functional is the true ground state energy.³⁵ This theorem is often called the Hohenberg-Kohn variational theorem as the energy obtained from a trial density is always an upper bound to the true electronic density of the system.³⁶ In principle, the true electronic ground state density would give the true ground state energy and solve the TISE exactly.³³ As stated above, however, the exact true ground state electronic density is unknown. This brings in the idea of the Kohn-Sham (KS) formulation of density functional theory.

2.2.2 – Density Functional Theory

Considering that the ground state electronic density may be difficult to figure out due to the complexity of the interacting electrons, Kohn and Sham decided to map a system of interacting electrons to a system of non-interacting electrons.³⁷ The Kohn Sham (KS) equations are shown in equation (2.2.2) such that the Hamiltonian has a similar form to the single particle Schrödinger equation demonstrated through non-interacting single particle KS spatial

orbitals.^{33,37} The potential is represented by v(r), n(r) is the electron probability density, v_{XC} is the exchange-correlation potential, and ϵ_i is the Kohn-Sham energy.

$$\hat{h}\phi_{i}^{KS} = \left[-\frac{\nabla^{2}}{2} + \nu(r) + \int \frac{n(r')}{|r-r'|} dr' + \nu_{XC}(r)\right]\phi_{i}^{KS} = \epsilon_{i}\phi_{i}^{KS}$$
(2.2.2)

The overall ground state density can then be found by calculating the square of the absolute value of the KS spatial orbitals, summed over all the electrons. Similar to the Hartree-Fock method which essentially guesses the exact form of the spatial wavefunction and uses a parameter to adjust the trial function until the wavefunction has converged, the KS formulation of DFT does this with KS spatial orbitals to obtain the non-interacting electronic density. DFT is therefore an SCF method.

After the ground state electronic density is obtained, the density can be plugged into equation (2.2.1) for a system of non-interacting particles to obtain an equation for the ground state energy. The overall energy equation is represented by equation (2.2.3) where T_s is the total kinetic energy of non-interacting particles, V_{ne} is the nuclear-electron interaction, V_{ee} is the electron-electron repulsion, ΔT is the correction term to the kinetic energy from the interacting system, and ΔV_{ee} is the non-classical electron-electron repulsive correction from the interacting system.³⁸ It is important to note that the terms relating to the correction in response to the interacting system are lumped together into one term called the exchange-correlation energy functional.

$$E[n] = T_{s}[n(r)] + V_{ne}[n(r)] + V_{ee}[n(r)] + \Delta T[n(r)] + \Delta V_{ee}[n(r)]$$
(2.2.3)

The method works very well, and since the form of the Coulomb and exchange terms are different due to the dependence on the electronic density, rather than the spatial coordinates, the scaling is lowered from the Hartree-Fock method. Additionally, as the method strives to use the exact ground state electronic density, static electron correlation is accounted within the fifth term in equation 2.2.3.³³ Note that DFT is an exact theory as shown through the different theorems represented in this chapter; however, some of the equations must be solved approximately because even though the exchange-correlation term that solves the method exactly exists, it is unknown. To this point, however, many scientists have come up with formulations of the exchange-correlation functional that give fairly accurate results compared to experiments.

2.2.3 – Exchange-Correlation Functionals

As briefly mentioned in the above section, the exact form of the exchange-correlation energy functional is unknown, and therefore must be approximated. The exchange-correlation functional is important as the exchange term is used to treat electrons that have the same or opposite spin, and the correlation term is used to account for the local spatial movement of an electron. Recall that the Hartree-Fock method does not account for all electron correlation. This is because each electron is treated with an average potential of the other electrons. In DFT, the instantaneous, or local dependence of two electrons coming together due to this interaction of spin and spatial coordinates is accounted for in the exchange-correlation term.^{33,35,38} Several approximations to the exchange-correlation functional have been derived to get more accurate results. Unfortunately, just like most things in quantum mechanics, as the functional gets more accurate, it gets more computationally expensive.

The simplest exchange-correlation functional is the local density approximation (LDA). This functional, ϵ_x , is based on the uniform electron gas in which the variations to the electron spin density are minimal, and therefore the functional depends on the electronic density (n(r)) alone.^{38,39} One example is the X α functional in which the correlation energy is neglected completely, and the exchange energy is simply represented by a scalar of the Slater exchange energy as seen in equation (2.2.4).³⁸

$$\epsilon_{x}[\mathbf{n}(r)] = -\frac{9\alpha}{8} \frac{3^{1/3}}{\pi} \mathbf{n}^{1/3}(r)$$
(2.2.4)

The next best exchange-correlation functional is constructed with the generalized gradient approximation (GGA). GGA functionals include the gradient of the electronic spin density in addition to the density itself, which improves the local nature of the functional.⁴⁰⁻⁴¹ By this point, a pattern has emerged. Mathematically, more information about a function can be extracted when higher derivatives are considered. Example: A parabola can be described as some sort of polynomial to the second order; with the first derivative of a specific spatial coordinate, the slope at that point is deduced. Further, the concavity is understood when the second derivative is considered. Hence one can view the more accurate exchange-correlation functionals as essentially adding another derivative of the electronic spin density to better understand the topology of the local spin density due to electron exchange. In a similar way, meta-GGA exchange-correlation functionals can improve this local nature by adding a term that depends on the Laplacian, or second derivative, of the electronic spin density to obtain the appropriate asymptotic nature of the exchange potential in finite limits.⁴²⁻⁴³ Further, many meta-GGA functionals will include a term that depends on the derivative of the kinetic energy density for the same reason.⁴²⁻⁴³ Unfortunately, the LDA and GGA exchange-correlation functionals are too focused on the locality of the electronic spin density. In most cases, the functionals are too local in nature as they consider more of the spatial interaction (correlation term) opposed to the actual exchange energy. In addition, by incorporating a self-exchange and self-correlation term, these functionals give unphysical behavior.³² To improve these functionals, a certain amount of exact

Hartree-Fock exchange must be added into the functional. The addition of exact Hartree-Fock exchange is called a hybrid exchange-correlation functional. One example of adding exact Hartree-Fock exchange can be seen in equation (2.2.5) such that the coefficient *a* can be varied between 0 and 1 to determine how much exact Hartree-Fock exchange (E_X^{HF}) should be considered in addition to the exchange-correlation obtained from DFT (E_{XC}^{DFT}).^{33,38}

$$E_{XC} = (1-a)E_{XC}^{DFT} + aE_X^{HF}$$
(2.2.5)

The last type of functional that is important to mention in this section is the long-range corrected functionals (LRCF). As mentioned above, the LDA and GGA functionals can be too local in nature such that the asymptotic relation of the electronic spin density in the long range leads to an incorrect relationship with the nuclear distance R.⁴⁴⁻⁴⁵ Meta-GGAs improve upon this behavior, but still only retain the asymptotic behavior to finite limits and hence do not include long range interactions.^{42,44} Instead of correcting this by simply adding a certain amount of the exact Hartree-Fock exchange term, like a hybrid functional, LRCF removes a certain amount of local exchange and replaces it with a short range exact HF exchange term while simultaneously splitting the screened coulombic interactions into a long range and short range part as seen in the general form in equation (2.2.6) such that α , β_i , and ε_j are constants, and ω_i is a continuous function that goes to 1 as r_{12} approaches zero, but additionally goes to 0 as r_{12} approaches large distances.⁴⁵

$$\frac{1}{r_{12}} = DFT + HF = \frac{\alpha + \sum_{i} \beta_{i} \omega_{i}(\gamma_{i}, r_{12})}{r_{12}} + \frac{\delta + \sum_{j} \varepsilon_{j} \omega_{j}(\gamma_{j}, r_{12})}{r_{12}}$$
(2.2.6)

As a result of these corrections, LRCF tends to improve results over hybrid functionals in comparison to experiments, particularly with reaction barriers and excitation energies.⁴⁶ A big advantage to LRCF is that the long-range character more accurately predicts charge transfer

reactions, which DFT on its own has trouble with as the exchange is too local in nature.⁴⁷ It is important to note that this type of functional, while extremely promising, is very computationally expensive.

2.3 – Time-dependent Density Functional Theory

Ground state properties in themselves are extremely important in understanding low energy structures for chemical reactions and modelling different types of bonding. For modelling photophysical and photochemical systems, however, it is imperative to expand on the ground state and model excited state properties. For excited state properties, it is ideal to theoretically model how the chemical system reacts in response to an electronic field from a laser, such as would be done in experiment. As a first basic idea, one could solve the many-body Schrödinger equation by including energy terms into the Hamiltonian that describe the energy field of the laser. Unfortunately, while this may sound simple in words, it is extremely computationally expensive (keep in mind that the Schrödinger equation cannot be solved exactly with the current Hamiltonian past the hydrogen atom, let alone in response to an electric field).

In 1984, Runge and Gross decided to use ground state DFT and form an analogue to model time-dependent behavior based on electronic density.⁴⁸ Through their work, they showed that there is a one-to-one unique correspondence between a time-dependent external potential, and time-dependent electronic density, and therefore the time-dependent density of an interacting system can be mapped to the time-dependent density of a system that is not interacting.⁴⁸ The KS equations can then be solved through DFT processes with a local density as described in section 2.2.2. To simulate the electronic density in response to a laser field, several different types of calculations may be performed; however, for the purpose of this work, linear response

TDDFT and linear response TDDFT+TB will be the only methods discussed in this chapter as other methods are outside the scope of this work.

2.3.1 – Linear Response Time-dependent Density Functional Theory

To get excited state properties, the time-dependent density can be expanded as a reference density, n_0 , and a perturbation to the electronic density, δn , as a result of the electronic density interacting with the laser field as shown in equation (2.3.1).⁴⁹

$$n(r,t) = n_0(r) + \delta n(r,t)$$
(2.3.1)

From here, a Taylor expansion of the electronic density is made around the external potential, v. As this is linear response, the first order term is the only one evaluated. This leads to a densitydensity response function, χ , for the interacting system as shown in equation (2.3.2)

$$\chi_{s(r,t,r',t')} = \frac{\delta n[\nu](r,t)}{\delta \nu(r',t')} |_{V_0[n_0]}$$
(2.3.2)

such that

$$n_1(r,t) = \int \chi(r,t,r',t') v_1(r',t') d^3 r' dt'$$
(2.3.3)

where n_1 is the first order density response with respect to the external potential. The goal from here is to therefore find a way to calculate the first order density response (equation (2.3.3)) without explicitly calculating the response function of the interacting system (equation (2.3.2)).⁵⁰ Once again by using theorems from ground state DFT, a mathematical mapping is formed between the interacting and non-interacting system using the KS equations. This leads to a new response function within the KS approximation such that the poles of the response function give single orbital excitation energies.⁵⁰⁻⁵¹ This is the starting point for the Casida equations.

2.3.2 – The Casida Equations

Considering the equation of motion formulation (EOM) and acknowledging that the solution of EOM has an excitation and de-excitation function, Mark Casida introduced a one particle/one hole (occupied/virtual orbital) solution to the KS application to the linear response functions to obtain equations (2.3.4) and (2.3.5) such that the first function represents the excitation, and the second function represents a de-excitation with respect to a particular external potential.⁵²⁻⁵⁴ The notation used in this section will be i, j, ... for occupied molecular orbitals, and a, b, ... for virtual (unoccupied) molecular orbitals. Further, Δ_I is the vertical excitation energy, and $\Delta_{ia} = (\epsilon_a - \epsilon_i)$ is the single orbital transition energy difference. For simplicity, the spin orbital indices are not included.

$$\sum_{jb} \left[\delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i + \widetilde{\omega}) + K_{ia,jb} \right] X_{jb} + \sum_{jb} K_{ia,bj} Y_{jb} = -\delta V_{ia}^{ext}$$
(2.3.4)

$$\sum_{jb} \left[\delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i - \widetilde{\omega}) + K_{ai,bj} \right] Y_{jb} + \sum_{jb} K_{ai,jb} X_{jb} = -\delta V_{ai}^{ext}$$
(2.3.5)

In these equations, there is a specific amount of coupling, $K_{ia,jb}$, between the possible single particle transitions that make up a specific vertical excitation energy represented by equation (2.3.6) as a result of the external potential V_{ai}^{ext} .

$$K_{ia,jb} = K_{ia,jb}^{H} + K_{ia,jb}^{XC} =$$

$$\int \int d^{3}r d^{3}r' \phi_{i}^{*}(r) \phi_{a}(r) \frac{1}{|r-r'|} \phi_{b}^{*}(r') \phi_{j}(r')$$

$$+ \int \int d^{3}r d^{3}r' \phi_{i}^{*}(r) \phi_{a}(r) f^{XC}(r,r') \phi_{b}^{*}(r') \phi_{j}(r')$$
(2.3.6)

Introducing equations (2.3.7) and (2.3.8), the equation may be simplified into a matrix form of the EOM, or a combined system of equations.⁵²⁻⁵⁴

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + K_{ia,jb}$$
(2.3.7)

$$B_{ia,jb} = K_{ia,bj} \tag{2.3.8}$$

Assuming that the molecular orbitals from DFT are real, excitation and de-excitation vectors, (X + Y) and (X - Y), may be added together to obtain an alternate matrix form of the system of equations as demonstrated by equation (2.3.9).

$$\begin{pmatrix} A+B & 0\\ 0 & A+B \end{pmatrix} \begin{pmatrix} X+Y\\ X-Y \end{pmatrix} = \Delta_I \begin{pmatrix} 0 & -1\\ -1 & 0 \end{pmatrix} \begin{pmatrix} X+Y\\ X-Y \end{pmatrix}$$
(2.3.9)

Solving the system of linear equations exhibited in the matrices in equation (2.3.9), and applying specific symmetry constraints, the final form of the Casida equations is obtained as shown in equation (2.3.10) such that the operator is demonstrated in equation (2.3.11).^{53,54}

$$\Omega F = \Delta_I^2 F \tag{2.3.10}$$

$$\Omega_{ia,jb} = \delta_{ij} \delta_{ab} \Delta_{ia}^2 + 2 \sqrt{\Delta_{ia}} K_{ia,jb} \sqrt{\Delta_{jb}}$$
(2.3.11)

The benefit of the Casida equations is that the time-dependent KS equations from linear response theory are simplified down to an eigenvalue equation that can be solved by almost all linear algebra codes. Further, the eigenvalues that result from solving the eigenvalue equation are the square of the vertical excitation energy which allow for easy access to information about the excited states in a specific chemical system. These energies may then be used to find the oscillator strength of different vertical excitations in a system to get a full theoretical absorption spectrum. As a result of using mathematical techniques to convert a very complicated response equation to a simple system of linear equations, the Casida equations has become arguably one of the most popular methods to obtain theoretical optical absorption spectrum for a wide variety of systems.

2.4 – Time-dependent Density Functional Theory plus Tight-Binding

Time-dependent density functional theory plus tight binding (TDDFT+TB) is extremely similar to TDDFT. The main purpose of the method is to target the computationally expensive coupling matrix in linear response TDDFT by applying a first order monopole approximation to the transition density.⁵⁵⁻⁵⁶ To be more specific, TDDFT+TB uses DFT ground state molecular orbitals, and simply changes the coupling matrix in equation (2.3.6) to equation (2.4.1) by using an approximation that introduces a partial charge analysis, $q_{ia,A}$, and a chemical hardness parameter, γ_{AB} .

$$K_{ia,jb} = \sum_{AB} q_{ia,A} \gamma_{AB} q_{jb,B}$$
(2.4.1)

The Löwdin partial charge analysis is chosen as it is more suitable with larger basis set size and it is less sensitive to diffuse basis functions, meaning that it can better model ionic compounds, Rydberg states, and rich electronegative atoms that possess a lot of electron density.^{54-55,58} As the two-electron integrals are the computational bottle neck of classic TDDFT calculations, this approximation drastically improves the computational time while retaining the accuracy of vertical excitation energies within 0.10 eV of TDDFT for large plasmonic nanoclusters.⁵⁷⁻⁵⁸

2.5 – Excited State Potential Energy Surfaces

To actively apply theoretical methods to experiments and advance science by predicting and modelling chemical reactions, a variety of quantum mechanical methods have been used to calculate the total energy of atoms and molecules given relative positions of atoms in space. To this end, it is vital to consider not just one set of coordinates, but all possible structures, or in other terms, distinguish the potential energy surface of a specific chemical compound. As all possible structures are considered, one can visualize the potential energy surface of a chemical

system as a surface that exhibits all possible reaction pathways from one isomer to another.^{38,59-60} The topology of these potential energy surfaces (PES) can therefore elucidate energetic pathways, transition and equilibrium structures, relaxation characteristics, and many more properties and chemical insights.⁶⁰ These physical insights are obtained from solving the TISE, or other quantum mechanical equivalent, such as (TD)DFT, at several different structures, and then analyzing the topology of the surface. The topology can be analyzed by calculating stationary points as they can find local minima, saddle points, etc. A local minimum point physically represents the lowest energy structure for a specific reaction pathway, or an equilibrium structure, and a transition state structure can be found by analyzing a saddle point.⁶⁰ Stationary points are found when a gradient calculation, or derivative of energy with respect to the position of nuclear coordinates, is equal to zero. In an excited state, the local minimum point would provide an excited state equilibrium geometry, which is where the molecule or compound would have a high probability to fluoresce or emit a photon. Gradients are therefore incredibly important as they can be used to obtain a full picture of photochemical and photophysical properties from analyzing different electronically excited states in different chemical systems. The exact methodology of calculating analytical gradients for excited state systems will be discussed in chapter 10.

2.6 – Radiative Lifetime

As mentioned in Chapter 1, photoluminescent mechanisms are difficult to understand as an electron can relax back to the ground state through radiative and nonradiative pathways. Further, some mechanisms give nearly degenerate emission energy between T_1 and S_1 states, which limits the understanding of the emission mechanism to the difference in radiative lifetime. Recall that if a chemical system emits a photon from the triplet state, it must undergo a spin-flip

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process to get back to the singlet ground state. This means that phosphorescence has a longer radiative lifetime than fluorescence.⁶¹ With this knowledge, radiative lifetimes can provide insight into the photoluminescent mechanism of the system of interest. Thus, it is important to be able to predict the radiative lifetime of the emission process.

Initially, the PL average lifetime (τ_{AV}) has a relationship with the quantum yield (QY) Φ and can be calculated by equation 2.6.1.⁶²

$$\Phi = \tau_{\rm AV} \times K_{\rm R} \tag{2.6.1}$$

where K_R is the radiative decay rate. From the experimentally determined quantum yield and K_R , the nonradiative decay rate (K_{NR}) can be calculated by equation 2.6.2 as given below,

$$\Phi = \frac{K_R}{K_R + K_{NR}} \tag{2.6.2}$$

The equations can then be rearranged to solve for the average PL lifetime.

Theoretically, the photoluminescent quantum yield is unknown, and there is no emission spectrum to obtain a radiative decay rate. Fermi's Golden Rule is therefore used to calculate the radiative lifetime (shown in equation 2.6.3) where τ is the radiative lifetime, α_0 is the fine structure constant, ΔE is the vertical excitation energy, and M_{α} is the transition dipole moment in the $\alpha = x, y, z$ direction.⁶³

$$\frac{1}{\tau} = \frac{4}{3t_0} a_0^3 (\Delta E)^3 \sum_{\alpha \in (x, y, z)} |M_{\alpha}|^2$$
(2.6.3)

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Chapter 3 - Impact of Ligands on Structural and Optical Properties of Ag₂₉ Nanoclusters

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3.1 – Abstract

A ligand exchange strategy has been employed to understand the role of ligands on the structural and optical properties of atomically precise 29 atom silver nanoclusters (NCs). By ligand optimization, ~ 44-fold quantum yield (QY) enhancement of $Ag_{29}(BDT)_{12-x}(DHLA)_x$ NCs (x = 1-6) was achieved, where BDT and DHLA refer to 1,3-benzene-dithiol and dihydrolipoic acid, respectively. High-resolution mass spectrometry was used to monitor ligand exchange, and structures of the different NCs were obtained through density functional theory (DFT). The DFT results from $Ag_{29}(BDT)_{11}(DHLA)$ NCs were further experimentally verified through collisional cross-section (CCS) analysis using ion mobility mass spectrometry (IM MS). An excellent match in predicted CCS values and optical properties with the respective experimental data lead to a likely structure of $Ag_{29}(DHLA)_{12}$ NCs consisting of an icosahedral core with an $Ag_{16}S_{24}$ shell. Combining the experimental observation with DFT structural analysis of a series of atomically precise NCs, $Ag_{29-y}Au_y(BDT)_{12-x}(DHLA)_x$ (where y, x = 0,0; 0,1; 0,12 and 1,12; respectively) it was found that while the metal core is responsible for the origin of photoluminescence (PL), ligands play vital roles in determining their resultant PLQY.

3.2 – Introduction

Noble metal nanoclusters (NCs) are composed of metal atoms and organic ligands (in general thiols) with distinct optical properties.¹⁻² High photostability and ultrasmall sizes are the primary features of these metal NCs.³⁻⁶ The significant disadvantage of these metal NCs in terms of their vis-nIR photoluminescence is their low quantum yield (PLQY) compared to semiconductor quantum dots (QDs).⁷ Research strategies on improving the PLQY are in high demand, particularly for any PL-based application of metal NCs. Tuning the PLQY of metal NCs requires a fundamental understanding of their PL mechanism.⁷ Questions such as the origin of PL, PL kinetics, the role of metal cores, ligands, etc. need careful consideration. Several reports exist on understanding the PL mechanisms of AuNCs. For example, Jin et al. reported that functional groups in the side chain of thiol ligands strongly influence the PL intensity of Au₂₅(SR)₁₈ NCs.⁸ They inferred that thiol ligands with electron-rich atoms, such as O or N in the side chain, can promote the PL intensity through ligand to metal charge transfer (LMCT) or ligand to metal to metal charge transfer (LMMCT).⁸ On the other hand, a "kernel-origin" based PL mechanism was proposed by Aikens et al. through computational analysis.⁹ It is conceivable that the kernel-structure relaxation is primarily responsible for the NIR emission of $Au_{25}(SR)_{18}$ NCs, rather than kernel-to-shell relaxation (i.e., Au(0) to Au(I)).⁹ In another recent report, Jin et al. have supported such a "kernel-origin" mechanism by carefully choosing a correlated series of "mono-cuboctahedral kernel" AuNCs.¹⁰ Results from such examples are summarized in a review article by Zhu et al.⁷ The aggregation-induced emission (AIE) concept was proposed by the Xie group to explain the PL mechanism of AuNCs.¹¹⁻¹² Considering these results, it is yet unclear whether the metal core (e.g., kernel-origin mechanism) or the 'ligand' (e.g., LMCT mechanism) is playing the dominant role in the PL properties of structurally known AuNCs. Furthermore, it

has remained unclear whether these types of PL mechanism are general for all coinage-metalbased NCs or very specific to individual AuNCs only. In contrast to the latter, most of the coinage metal NCs with high QY are water-soluble,¹³⁻¹⁴ and their structural details have not been elucidated to date.

 $Ag_{29}(S_2R)_{12}$ NCs are one of the most studied fluorescent NCs from the silver family.¹⁵⁻¹⁷ It is reported that by enhancing the structural rigidity¹⁸ (which decreases the probability of nonradiative relaxation of the excited states) or by doping,¹⁹ the PLQY of Ag₂₉(BDT)₁₂ NCs (BDT: 1,3-benzene-dithiol) can be significantly improved. For example, Zhu et al. reported that by lowering the temperature, ~20-fold enhancement in PLQY is achievable due to reduced nonradiative relaxation from excited states.¹⁸ Bakr et al. showed 26-fold and 2.3-fold enhancement in the PLQY due to Au and Pt doping, respectively.¹⁹ Zhu et al. have demonstrated 13-fold enhancement of the PLQY by adding excess triphenylphosphine (TPP), and aggregationinduced emission (AIE) was proposed as the prime reason for the enhancement. Pradeep et al. showed a nearly 30-fold enhancement of the PLQY by replacing such secondary TPP ligands with diphosphines of increasing chain length.²⁰ From DFT analysis, they proposed a LMCT mechanism to be responsible for the PLQY enhancement.²⁰ On the contrary, Ag₂₉(DHLA)₁₂ NCs (having the same chemical formula; DHLA: dihydrolipoic acid) do not have any such secondary ligands, but they are reported to have a higher PLQY than corresponding Ag₂₉(BDT)₁₂ NCs.^{15, 21} The change of the PLQY could be due to structural differences or due to the effect of ligands. Notably, the presence of carboxyl groups in the thiol side chain (e.g., DHLA,^{15, 22} mercaptosuccinic acid (MSA),²³ 11-mercaptoundecanoic acid (MUA),^{14, 24} glutathione (GSH),^{12,} ²⁵⁻²⁶ etc.) is common in most of the water-soluble metal NCs with highest PLQY. The question arises if the carboxyl group promotes the PL, making LMMCT/LMCT the most dominant PL

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mechanism for the case of $Ag_{29}(DHLA)_{12}$ NCs? Since the crystal structure of $Ag_{29}(DHLA)_{12}$ NCs has not been solved yet, a different approach was taken here to characterize the structure of $Ag_{29}(DHLA)_{12}$ NCs, which can help to solve the puzzle of their PL mechanism.

In this work, a ligand exchange strategy is employed starting with the structurally known $Ag_{29}(BDT)_{12} NCs^{16}$ to understand the effect of ligands on the structure and optical properties of $Ag_{29}(DHLA)_{12} NCs$. High-resolution electrospray ionization (HRESI) and ion mobility (IM) mass spectrometry (MS) confirmed the ligand exchange, leading to the formation of $Ag_{29}(BDT)_{12-x}(DHLA)_x NCs$ (x=1-6). This ligand exchange showed significant enhancement (-44 fold) in PLQY. Consequently, density functional theory (DFT) has been implemented to determine the most stable structure of single ligand exchanged $Ag_{29}(BDT)_{11}(DHLA)^{3-}$ (i.e., trianion species where only one BDT ligand had been exchanged by one DHLA ligand), which was further verified using ion size analysis by collisional cross-sections (CCS) determined via IM-MS experiments. This inference of the most stable isomer in $Ag_{29}(BDT)_{11}(DHLA) NCs$ led us to a likely structure of $Ag_{29}(DHLA)_{12} NCs$, which has an icosahedral core with an $Ag_{16}S_{24}$ shell. Structural analysis of a series of atomically precise NCs, $Ag_{29-y}Au_y(BDT)_{12-x}(DHLA)_x$ (where y, x = 0,0; 0,1; 0,12 and 1,12; respectively) and experimental observations suggest that both ligand and core contribute to the PL properties of $Ag_{29}(DHLA)_{12} NCs$.

3.3 – Theoretical Analysis

To obtain the molecular structure, the coordinates of Ag₂₉(BDT)₁₂ were taken from Abdul et al.¹⁶ There are 12 BDT ligands that consist of six symmetry equivalent pairs in the NC, giving two possible thiol sites for the addition of DHLA. As each BDT ligand has two thiol groups, this allows one doubly deprotonated (protons from -SH group) DHLA ligand to replace a single BDT group. The TPP ligands also present in the solid were removed as they are not present in the Ag₂₉(DHLA)₁₂ NCs. Four possible isomers were created for Ag₂₉(BDT)₁₂. $_x(DHLA)_x^{3-}(x=1)$ using the MacMolPlt visualization tool, and the connectivity to the thiol groups can be seen in Figure 3.1.²⁷ The thiol groups guide the construction of the ligand, so the distance between thiol sites was measured, as well as the distance between the same thiol site on the neighboring ligand (6 ligand pairs or 'neighbors' making 12 total ligands in the cluster).



Figure 3.1. Molecular structures of the four isomers created for Ag₂₉(BDT)₁₁DHLA³⁻. The green, yellow, grey, red, and white atoms represent silver, sulfur, carbon, oxygen, and hydrogen. All four isomers kept the thiol group locations from the crystal structure in place (atoms 1 and 2). (A) The trans A structure sticks out with 180 dihedral angles ~14.20 Å away from the center of the icosahedral core. The DHLA ligand was constructed by starting at thiol group 2 and connecting atoms 2-5-4-3-6 with thiol group 1 connecting to carbon atom 3. (B) The trans B structure also sticks out with 180 dihedrals, with the same distance away from the core. The DHLA ligand was constructed by starting at thiol group 1 and connecting atoms 1-3-4-5-6 with thiol group 2 connecting to carbon atom 5. (C) The curled A structure has the same connectivity as Trans A; however, it is curled around the NC to observe the interaction between the carboxyl group and outer shell Ag motif. (D) The curled B structure has the same connectivity as Trans B, and it is also curled around the NC like the Curled A structure. The calculated most stable isomer (Trans B) is in agreement with the corresponding experimental data, as revealed by a close match between CCS values (exp and cal). All the CCS were calculated using trajectory method as implemented in IMOS 1.09 taking the different isomeric DFT optimized structures and assuming the 3- charge was distributed following Natural Population Analysis (NPA). The quadrupole moment of N₂ was included in the CCS calculation.

The average bond lengths calculated at the BP86/DZ level of the theory of the ground

state structure upon the addition of ligands are shown in Table 3.1. As the DHLA ligands are

added, the Ag₁₃ icosahedral core and the Ag-Ag shell bonds elongate. Elongation in the core specifically happens in the outer part of the icosahedron, where bonds not involving the center atom can get up to ~0.040 Å longer and others ~0.035 Å shorter as seen in Figure A-1. Elongation in the core and shell is generally consistent as each DHLA ligand is added. Eventually, the average difference between Ag₂₉(BDT)₁₂ and Ag₂₉(DHLA)₁₂ is 0.003 Å in the core and 0.054 Å in the shell. The Ag-S bonds (both crown and motif positions, Figure 3.2C) shorten by ~0.005 Å between Ag₂₉(BDT)₁₂ and Ag₂₉(DHLA)₁₂ NCs. The distance between thiol sites ('1' and '2', Figure 3.1) gets slightly larger with the addition of DHLA. The thiol sites between neighboring ligands (site '1' compared with site '1' on the closest neighboring ligand) do not show a common trend, however this distance does increase when all 12 DHLA ligands are added as compared to 12 BDT ligands. Therefore, the surface configuration does change in conjunction with the thiol groups.

[Å]	Ag core-	Ag shell-	Ag shell-S	Ag shell-S	S thiol-S	S group-S
	Ag core	Ag shell	crown	motif	thiol	group
Ag ₂₉ (BDT) ₁₂	2.959 ±	2.984 ±	2.564 ±	2.619 ±	5.680 ±	4.389 ±
	0.106	0.021	0.015	0.040	0.015	0.043
Ag ₂₉ (BDT) ₁₁ DHLA	2.959 ±	2.992 ±	2.563 ±	2.621 ±	5.684 ±	4.391 ±
	0.105	0.025	0.016	0.044	0.023	0.038
Ag29(BDT)10(DHLA)2	2.960 ±	2.994 ±	2.563 ±	2.621 ±	5.689 ±	4.388 ±
	0.106	0.027	0.017	0.051	0.030	0.051
Ag29(BDT)9(DHLA)3	2.961 ±	2.990 ±	2.563 ±	2.619 ±	5.697 ±	4.374 ±
	0.103	0.032	0.019	0.049	0.034	0.048
Ag ₂₉ (BDT) ₈ (DHLA) ₄	2.961 ±	2.994 ±	2.563 ±	2.618 ±	5.699 ±	4.388 ±
	0.103	0.029	0.020	0.049	0.030	0.058
Ag29(DHLA)12	2.963 ±	3.038 ±	2.56 ±	2.615 ±	5.736 ±	4.480 ±
	0.102	0.038	0.021	0.043	0.017	0.032

Table 3.1. Average bond lengths of the optimized structures upon the addition of DHLA.



Figure 3.2. (A) Molecular structures of the lowest energy isomers of Ag₂₉(BDT)₁₁DHLA³⁻ (a) and Ag₂₉(DHLA)₁₂³⁻(e). The green atoms (deep green are in the core and olive green are in the shell) are silver, yellow atoms are sulfur, grey atoms are carbon, white atoms are hydrogen, and red atoms are oxygen. (a) The entire 187-atom NC with one BDT ligand replaced by one DHLA ligand. (b) The structure without the organic part containing an icosahedral core with an Ag₁₆S₂₄ shell. (c) Ag₁₆S₂₄ shell made of four Ag₃S₆ crowns with four Ag₁S₃ motifs. (d) The 13-atom icosahedral core. (e) The entire 341-atom Ag₂₉(DHLA)₁₂ NC. Each BDT group has now been replaced by the corresponding DHLA group. (B) Absorption spectra calculated for Ag₂₉(BDT)_{12-x}(DHLA)_x³⁻(x=0-4,12) together with the experimental spectra of Ag₂₉(BDT)₁₂ (black dotted line) and Ag₂₉(DHLA)₁₂ NCs (red dotted line), respectively. I (E) is proportional to [Absorbance/(Energy)²].

The ground state (S₀) geometry optimization was run for each trianion isomer with x=0-4 and 12. The most stable energy isomer is Trans B, which can be seen in Figure 3.2A (labelled a). For further confirmation, CCS values have been measured using IM-MS²⁸ and were compared with the corresponding calculated values (Figure 3.1) (details of the CCS calculations are mentioned in SI). The close match of the experimental CCS values with the calculated ones for Trans B isomer strengthens the theory-experimental correlation. While the theory and experiment agree that the lowest energy isomer is the Trans B structure, and hence it is used for further

computational study. The possibility that other isomers may exist in solution cannot be excluded. The relative energies vary between isomers from 0.03 eV - 0.5 eV depending upon the level of theory and are reported in the tables A1-A3. However, to understand exactly how the alkane chain in DHLA transforms in solution, dynamics calculations would be required.

Predicted absorption spectra for Ag₂₉(BDT)_{12-x}(DHLA)_x NCs are in good agreement with the experimental results (Figure 3.2B). When x=0, the higher energy peak appears at 2.80 eV, which corresponds to the experimentally observed peak at 2.76 eV. The lower energy peak appears at 2.52 eV, which corresponds to the experimentally observed shoulder at 2.43 eV. Upon the addition of DHLA, both peaks blue shift. The higher energy peak appears at 3.02 eV, and the lower energy peak appears at 2.68 eV. This blue shift of both peaks upon the addition of DHLA also appears in the experimental spectrum (Figure A-2). The PL of $Ag_{29}(BDT)_{12-x}(DHLA)_x$ NCs are analyzed by running an excited singlet state geometry optimization from the optimized ground state (S_0) geometry (for trianions). The emission energy is calculated by taking the difference between the excited and ground-state energies at the optimized excited state geometry. Triplet states could not be accessed as there were SCF convergences issues at the BP86/DZ level of theory. The theoretical emission energy, 0.84 eV, is significantly underestimated compared to the experimental PL spectrum centered at 1.91 eV. The geometry and HL gaps of our optimized S₁ state are shown in tables A4 and A5, however, due to the neglect of spin orbit coupling and only analyzing stationary points on adiabatic states, there are limitations to understanding the PL mechanism from a theoretical perspective. Consequently, the calculations with long-range exchange-correlation functional, presented in figure A-3, hint that the PL mechanism may primarily arise from metal-to-metal transitions.

To reveal the metal kernel's role on the optical properties, the Ag₂₉(DHLA)₁₂ NCs were doped with Au via a post-synthesis modification route with different doping percentage. A 4-fold increase in the PLQY of Au_yAg_{29-y}(DHLA)₁₂ was observed in comparison to Ag₂₉(DHLA)₁₂ NCs. The average lifetime decreased from 3.7 μ s (in Ag₂₉(DHLA)₁₂ NCs) to 1.5 μ s (in Au_vAg₂₉. $_{v}$ (DHLA)₁₂ NCs) upon doping. Hence, the results suggest that even single Au atom doping can result in an enhancement in PLQY of Ag₂₉(DHLA) 12 NCs, and hence the contribution of the metal core in the PL mechanism cannot be ignored. DFT structural analysis (figures A-4, A-5, and A-6) suggests that a single Au atom doping in Ag₂₉(DHLA)₁₂ NCs can change the HOMO-LUMO gap significantly (table A-6) from 1.24 to 1.37 eV (a similar trend has been observed upon doping Ag₂₉(BDT)₁₂ NCs); on the other hand, a single ligand exchange does not affect the HOMO-LUMO gap (Figure 3.3A). Ag₂₉(BDT)_{12-x}(DHLA)_x NCs have structural similarities (table A-7), but the increase in experimental PLQY shares specific patterns with the theoretical ground state analysis. Both gold mono-doping and exchanging the ligands to DHLA increase the Ag-Ag shell bond lengths while simultaneously shortening the Ag-S bonds. The average core bond lengths change less than ~0.006 Å, which hints that the core's average structural differences may not be the only contribution to the enhanced experimental PLQY. Still, a consistent blue shift in both absorption (Figure A-7) and emission peaks upon doping suggests the core structure is responsible for the origin of PL in $Ag_{29}(DHLA)_{12}$ NCs. The transitions that are responsible for the theoretical absorption spectrum are presented for all clusters in figures A-8 – A-10.



Figure 3.3. (A) The HOMO-LUMO energy gaps of a series of $Ag_{29-y}Au_y(BDT)_{12-x}(DHLA)_x^{3-}$ (where y, x = 0,0; 0,1; 0,11; 0,12 and 1,12; respectively). Blue column (right axis) represents the energy gap via LRCF calculation, whereas the other color column represents the energy gap via BP86 calculation, together with their corresponding representative HOMO (downside) and LUMO structures (upper side), respectively. (B) DFT optimized dimer structure of $(Ag_{29}(BDT)_{11}DHLA)_2^{6-}$ with a calculated HOMO-LUMO gap of 1.16 eV. Dimers were identified from IM-MS as shown in B. Extracted MS from the 10-11 ms region in the mobilogram (labeled as dimer 4-) is shown in the inset, which shows an exact match with the isotopologue distribution expected for the 4- dimer of $Ag_{29}(BDT)_{11}DHLA$ NC with a few solvent molecules. (C) Jablonski diagram illustrating the proposed dominating relaxation mechanism for each $Ag_{29-y}Au_y(BDT)_{12-x}(DHLA)_x^{3-}$ NC cases (marked as (y, x)). The energy levels are drawn in a qualitative way and does not reflect their accurate energies.

While the excitations within the core might be the origin of the PL, ligands play a vital role in the PLQY especially for the case of $Ag_{29}(BDT)_{12-x}DHLA_x$ NCs. Experimentally, the PLQY can be enhanced in two ways, either by increasing the radiative contribution or by decreasing the nonradiative contribution (i.e., surface vibration and ultrafast structural relaxation).⁷ In this case, the ligand exchange leads to a considerable decrease in nonradiative relaxation (~100-fold decrease in the qualitative K_{NR} value as revealed from their lifetime data,

Table A-8). A decreasing contribution of nonradiative relaxation in $Ag_{29}(BDT)_{12-x}DHLA_x NCs$ could be due to additional intra-NC ligand interaction (between BDT and DHLA) or due to intra-NC interaction via dimer formation (please note that polymer formation or the possibility of aggregation has already been excluded - see above). Using IM-MS, dimer formation in the solution is confirmed and corresponding MS data representing dimers of Ag₂₉(BDT)₁₁DHLA NCs (Figure 3.3B). The existence of proton and Na ion bound dimers has been reported for Ag₂₉(BDT)₁₂ NCs.²⁹ The DFT optimized structure of the dimer multianions revealed a smaller HOMO-LUMO gap (1.16 eV) than the parent NC (1.42 eV). The concentration-depended shift in their PL emission maxima (Figure A-2) further confirms dimers' existence in the solution. The formation of dimers leads to a decrease in molecular flexibility, minimizing the nonradiative relaxation and, hence, the increase in PLQY. However, that alone might not explain 44-fold PLQY enhancement in the ligand-exchanged NCs. Understanding the PL mechanism would be needed to explain this high PLQY. The lifetime dynamics for Ag₂₉(BDT)₁₂ NCs show the highest contribution (93%) from τ_2 , whereas for ligand exchanged NC, Ag₂₉(DHLA)₁₂ and Au-doped NC cases, it comes from τ_3 . The longer lifetime (in the range of μ s) indicates triplet states' involvement via intersystem crossing, which supports the major contribution of phosphorescence (which involves LMCT) in their PL mechanism. In contrast, fluorescence is dominating for the case of Ag₂₉(BDT)₁₂ NC (Figure 3.3C). Solvent induced shift confirms the charge transfer³⁰⁻³⁴ in the excited states and O₂-induced PL quenching confirms the involvement of triplet states and provides a strong proof of LMCT.¹⁷ The differences in ligands backbone structure play an important role in facilitating the charge transfer process in the following two ways.

Firstly, the electron-donating capacity of the DHLA ligand is more than the BDT ligand (due to delocalization and involvement in additional π - π inter-ligand interactions), which

facilitates the charge transfer via Ag-S bonds to the metal core. The addition of ligands with multiple electrons donating groups results in enhancing the PL intensity, supporting the above statement. Secondly, the free carboxyl group can be further involved in intra-NC (when one of the thiols ends is not attached to Ag) and inter NC (for dimers) charge transfer via carboxyl group as seen for glutathione protected Au₂₅ NCs.⁸ This is supported by the pH-dependent experiment where deprotonation enhances the PL intensity.

3.4 – Conclusions

In summary, this chapter has shown how ligand exchange can tune the structure, and optical properties of $Ag_{29}(S_2R)_{12}$ NCs. Ligand exchange with DHLA ligands on $Ag_{29}(BDT)_{12}$ NCs showed ~ 40-fold enhancement in PLQY. Extensive DFT calculation predicts the structure, optical, and photo-physical properties of $Ag_{29}(BDT)_{12-x}$ DHLA_x³⁻ (x=1, 12). CCS comparison based on IM-MS and trajectory calculations confirms a good match of the DFT-predicted structure with the experimental one. The photoluminescence mechanism involves both the fluorescence and phosphorescence processes. However, based on the lifetime dynamics analysis, fluorescence is a major contributor in Ag_{29} NCs with x=0, whereas phosphorescence dominates in x=1-12 and even for Au doped NCs. The involvement of the triplet state suggests that the PLQY enhancement is due to LMCT. Ligand's structure and orientation play a major role in the LMCT process. DHLA being more electron-donating than BDT, facilitates the charge transfer via Ag-S bond to metal core.

Furthermore, the carboxyl group of the DHLA can also promote inter-NC and intra-NC charge transfer. Additionally, nonradiative relaxation is relatively less significant in $Ag_{29}(BDT)_{12}$. xDHLAx³⁻ (x=1-6) due to the dimer formation, enhancing the structural rigidity and thus the resulting enhancement in the PLQY. Hence, although the core might be responsible for photoluminescence's origin, the ligand plays a vital role in determining their PLQY. Surface engineering on ligands or doping in the core can affect the PL intensity and the PLQY, but tunability in emission wavelength is achievable via doping for Ag₂₉(DHLA)₁₂ NCs. This result also suggests that the PL mechanism is specific to individual NCs, where 'every metal atom and ligand matters', unlike semiconductor QDs. The ligand's structure and functionality in NCs could be a potential key in solving the mystery of the PL of metal NCs.

3.5 – Computational Details

All calculations were done using the Amsterdam Density Functional (ADF) 2017.110 and 2018.105 packages.³⁵ All geometry optimizations (ground and excited state) were calculated with the generalized gradient approximation (GGA) BP86 exchange-correlation functional³⁶⁻³⁷ and a double zeta (DZ) basis set. All structures were optimized in the gas phase. Scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).³⁸⁻³⁹ Any dispersion calculations were completed by adding the Grimme1 dispersion correction to the exchange- correlation functional.⁴⁰⁻⁴¹ The energy and gradient convergence criteria were tightened to 1×10^{-4} and 1×10^{-3} respectively for geometric accuracy. After the initial ground state geometry optimization, a linear response time-dependent density functional theory plus tight binding⁴² (TDDFT+TB) calculation was run to obtain vertical (singlet) excitation energies which are then convolved into the optical absorption spectrum with a Gaussian fit with a 0.20 eV full width half maximum. This method is very similar to TDDFT; however, it allows us to reach higher energies of the absorption spectrum at a lower computational cost (Figure A-11). After obtaining the ground state structure and absorption spectrum, TDDFT excited-state gradients⁴³ were used to optimize the structure of the first singlet excited state.

3.6 – Acknowledgements

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Chapter 4 - Crystal Structure and Optical Properties of a Chiral Mixed Thiolate/Stibine-Protected Au₁₈ Cluster

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4.1 – Abstract

The first example of a chiral mixed thiolate/stibine-protected gold cluster is reported, formulated as $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ (where S-Adm = 1-adamantanethiolate). Single crystal X-ray crystallography reveals the origin of chirality in the cluster to be the introduction of the rotating arrangement of $Au_2(S-Adm)_3$ and $Au(S-Adm)_2$ staple motifs on an achiral Au_{13} core, and the subsequent capping of the remaining gold atoms by SbPh₃ and Br⁻ ligands. Interestingly, the structure and properties of this new Au_{18} cluster are found to be different from other reported achiral Au_{18} clusters and the only other stibine-protected [$Au_{13}(SbPh_3)_8Cl_4$]⁺ cluster. Detailed analyses on the geometric and electronic structures of the new cluster are carried out to gain insights into its optical properties as well as reactivity and stability of such mixed-monolayer protected clusters.

4.2 – Introduction

Monolayer-protected metal clusters, consisting of a precise number of metal atoms and ligands, lie at the interface of small molecules and bulk metal and have recently emerged as a new frontier in colloidal nanoscience. Gold clusters, in particular, act as paradigm systems due to their extraordinary stability, unique geometric structures and physicochemical properties, and hence are commonly referred to as superatoms or "magic-sized" clusters.¹⁻³ Since the pioneering crystal structure determination of a $Au_{102}(SR)_{44}$ cluster by Kornberg in 2007,⁴ several thiolate- and alkynyl-protected Au cluster superatoms, containing tens to hundreds of Au atoms, have been reported.⁵⁻¹⁰ In parallel, phosphine-protected Au clusters have attracted renewed interest since the early reports dating back to the late 1960s.¹¹⁻¹⁵

Among the various structurally-resolved Au clusters, the Au₁₁ and Au₁₃ icosahedral superatom structural motifs are frequently encountered,² both as (1) structures of standalone clusters directly protected by ligands, e.g., $[Au_{13}(dppe)_5Cl_2]^{2+}$ (where dppe = 1,2bis(diphenylphosphino)ethane),¹² Au₁₁(PPh₃)₇Cl₃,¹³ etc.; or by the staple motifs exhibited by thiolate- and alkyne-protected clusters (e.g., core-shell Au₂₅ clusters)¹⁶⁻¹⁸, and (2) structural segments for the growth of larger clusters. For example, a "cluster of clusters" motif has been generated in biicosahedral Au₂₅,¹⁹ triicosahedral Au₃₇²⁰ and pentaicosahedral Au₆₀ clusters²¹ (coprotected by phosphines and thiolates/selenolates/alkynes) through the sharing of vertex Au atoms in the icosahedral Au₁₃ structure. While the Au₁₃ core cannot be seen as a 'building block', as it is composed of 20 tetrahedra that can distort in different clusters,²² edge- and face-sharing modes of cluster growth have been identified using this core.²³⁻²⁶ Very recently, N-heterocyclic carbenes (NHCs), with stronger s-donor properties as compared to analogous phosphines, have been used to synthesize stable Au₁₃ and Au₂₅ clusters based on the icosahedral Au₁₃ core.²⁷⁻²⁹ On the other hand, Au clusters protected by heavier phosphine-analogues such as stibines are severely underdeveloped, despite these ligands exhibiting unique coordination and reactivity features in Au(I) complexes at the molecular scale.³⁰ Given these attractive characteristics, it is surprising to note that stibines have not been widely used for making materials at the nanoscale and to the best of our knowledge, even to make materials at larger length scales such as self-assembled

monolayers (SAMs). With the lone exception of a $[Au_{13}(SbPh_3)_8Cl_4]^+$ cluster reported in 2018, no other reports on stibine-based gold clusters currently exist.³¹ A major reason for this is believed to be the weaker coordinating ability of stibines as compared to phosphines due to their diffuse donor orbitals.

In this work, the first example of a mixed thiolate/stibine-protected Au cluster is reported containing 18 Au atoms. The crystal structure of the new charge-neutral, chiral cluster formulated as $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$, (S-Adm = 1-adamantanethiolate), features an icosahedral Au_{13} core protected by a pair of $Au_2(S-Adm)_3$ dimeric and one $Au(S-Adm)_2$ monomeric staple motifs, in addition to four coordinated SbPh₃ ligands and two Br^- ions (Figure 4.1). By comparing this new cluster's properties with previously reported stibine-protected [$Au_{13}(SbPh_3)_8Cl_4$]⁺ and thiolate-protected $Au_{18}(SC_6H_{11})_{14}$ clusters,³² it is demonstrated for the first time that the properties and stability of stibine-based Au clusters can be tailored at the atomic level by employing a mixed-ligand approach. These insights are not only expected to broadly expand the use of stibine-based ligands at larger length scales, but also provide key design rules in mixed ligand-mediated tuning of surface properties of nanomaterials.



Figure 4.1. Crystal packing in the unit cell of the $[Au_{18}(S-Adm)_8(SbPh_3)_4Br_2]^0$ structure. The unit cell contains a pair of left- and right-handed isomers, as the structure is centrosymmetric. (Color labels: Brown = Au; yellow = S; blue = Sb, pink = Br, grey = C, H are omitted for clarity).

4.3 – Structure Determination

The crystal structure of the $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster is best described in the centrosymmetric triclinic space group $P\overline{1}$, with the unit cell comprising a pair of enantiomers exhibiting quasi-C₂ symmetry (Figure 4.1). The kernel of the cluster is a Au_{13} icosahedron (Figure 4.3.1A), like the core of the previously reported stibine-protected [$Au_{13}(SbPh_3)_8Cl_4$]⁺ cluster,³¹ which, in turn, is protected by three kinds of ligands. Starting with thiolates, a pair of closely-



Figure 4.2. Anatomy of the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster, starting with the icosahedral Au₁₃ kernel (A); addition of two dimeric staggered staple motifs and one monomeric staple motif gives rise to (B) and (C) respectively, followed by the addition of stibine and bromide ligands to remaining Au atoms, yielding the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster (D). (Color labels: brown/green = Au; yellow = S; blue = Sb, pink = Br, carbon tails of triphenylstibine and 1-adamantanethiolate ligands are omitted for clarity).

spaced, staggered Au₂(S-Adm)₃ dimeric staple motifs (closest Au-Au distance between the dimers is 2.963 Å, Figure 4.2B) and one Au(S-Adm)₂ monomeric staple motif were found, directly opposite to the pair of dimers (Figure 4.2C). The remaining 6 exposed Au atoms are further capped by 4 triphenylstibine and 2 bromide ions (Figure 4.2D). Electrospray ionization mass spectrometric analysis (ESI-MS) and NMR spectroscopy was further performed to confirm the mass and surface ligand composition of the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster, respectively.

Interestingly, the pair of staggered dimers and a monomeric staple motif in the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster structure are reminiscent of the widely studied chiral Au₃₈(SR)₂₄ clusters, the structure of which features staggered dimeric staple motifs on a face-fused biicosahedral-based Au core, leading to its chiral nature.^{24,33-35} Apart from using chiral protecting ligands, chirality in NCs can be typically induced in two ways: (1) presence of an inherent chiral Au core,^{36,37} and (2) chiral arrangement of ligand-binding modes or "staple motifs" around an achiral Au core.^{18,24} Additionally, it has been observed that chirality predominantly originates from the rotating arrangement of multiple staple motifs in chiral thiolate-protected Au clusters.³⁵ Hence, the introduction of Au-thiolate staple motifs and subsequent capping of the remaining Au atoms by SbPh₃ and Br⁻ ligands is the key to breaking the symmetry of the achiral Au₁₃ core in the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster (Figure 4.3).



Figure 4.3. Total structures of triphenylstibine-based Au clusters in different orientations; (A) $[Au_{13}(SbPh_3)_8X_4]^+(X=Cl/Br)$; (B) the two enantiomers of $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ (Color labels: brown/green = Au; yellow = S; blue = Sb, pink = Br/Cl, carbon tails of triphenylstibine and 1-adamantanethiolate are omitted for clarity).

It is also worthy to comment on the crystal structures of the other reported ligand protected Au₁₈ clusters. Unlike the icosahedral Au₁₃ core in the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster (Figure 4.4A), the Au core of a diphosphine-protected $[Au_{18}(dppm)_6X_4]^{2+/4+}$ (X=Cl/Br) cluster can be envisioned as a bi-capped bioctahedral Au₁₈ core (Figure 4.4B),²⁵ or the fusion of two distorted Au₁₁ incomplete icosahedra by sharing a common Au₄ face.²⁶ On the other hand, a fully thiolate-protected Au₁₈(SC₆H₁₁)₁₄ was found to contain a face-fused bioctahedral Au₉ core, where two distorted Au₆ octahedra were assembled together by sharing a common Au₃ face (Figure 4.4C).^{32,38,39} This indicates the critical role of different kinds of ligands in determining and stabilizing the highly diverse Au cores of clusters in this size regime.^{1-2, 22, 32, 40}



Figure 4.4. Experimentally determined Au cores and total structures of ligand protected Au₁₈ clusters: (A) Au₁₈(S-Adm)₈(SbPh₃)₄Br₂, (B) [Au₁₈(dppm)₆X₄]^{2+/4} (X=Cl/Br), and (C) Au₁₈(SC₆H₁₁)₁₄. (Color labels: brown/mustard = Au; yellow = S; blue = Sb, pink = Br/Cl, orange = P; gray = C).

4.4 – Theoretical Analysis of Optical and Chiroptical Properties

To achieve insights into the electronic structure of the $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster, density functional theory (DFT) calculations were carried out at the B3LYP/DZ level of theory (see Supplementary Information for details), where the bond distances were maintained at the geometry indicated by the crystal structure. The Right isomer (Figure 4.3B) of the cluster was also optimized at the BP86-D3/DZ and X α /TZP levels of theory. As there are no notable differences in the absorption spectra between the optimized and unoptimized clusters, the analysis was done with the bond distances maintained by the average length represented in the crystal structure of the cluster. The crystal structure of Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ demonstrates that the average Au-Sb bond is 2.549 ± 0.027 Å and the average Au-Br bond is 2.437 ± 0.001 Å. These bonds are slightly larger than the average Au-S bonds in the cluster which are 2.338 ± 0.072 Å. To understand how the electronic density distribution changes in terms of atomic charges (due to Au-ligand interactions) within the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster, a Hirschfield charge analysis was carried out. Herein, all the Sb atoms are found to possess an approximate +0.47 partial charge, while Br atoms possess partial charges of approximately -0.17. The sulfur atoms stay neutral in all except two positions, where the partial charge increases to +0.02.

Figures 4.5 and 4.6A show the experimental and theoretical optical absorption spectra of the $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster, respectively. The theoretical absorption spectrum of the cluster at the B3LYP/DZ level of theory shows a broad peak at 363 nm (3.41 eV) with an oscillator strength of 0.1027 a.u. In addition to the main peak, there is a shoulder at 3.10 eV with an oscillator strength of 0.0721 a.u.



Figure 4.5. Experimental UV-visible absorption spectrum of the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster. The most prominent peak appears at 372 nm (3.33 eV) and 481 nm (2.58 eV).

Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ possesses a set of unique optical properties that slightly differs from that of pure thiolate-protected Au₁₈ clusters and $[Au_{18}(dppm)_6Cl_4]^{4+}$.^{25, 38-39} In the low energy region, three peaks are seen in the theoretical spectrum at 512 nm, 558 nm and 600 nm; these peaks have oscillator strengths below 0.002 a.u. The transitions responsible for these three peaks take place in the core of the nanoparticle, all showing superatomic P \rightarrow D nature where the main transitions occur between HOMO \rightarrow LUMO+4, HOMO \rightarrow LUMO+3 and HOMO \rightarrow LUMO, respectively. These peaks, however, have much lower oscillator strengths than the most prominent absorption peak in the spectrum, which are found to arise from ligand-based transitions.

The main peak of interest occurs at 3.41 eV in the calculations and only slightly overestimates the experimental peak at 372 nm (3.33 eV). This peak is made up of two dominant transitions, HOMO-10 \rightarrow LUMO+2 and HOMO-1 \rightarrow LUMO+11; the orbitals involved in these transitions are provided in Figure 4.6B. The first transition is HOMO-1 \rightarrow LUMO+11, which arises



Figure 4.6. (A) Theoretical optical spectrum of the $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster (Inset: zoomed-in optical spectrum of the $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster in the low energy region); (B) Molecular orbitals (MOs) of $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ at the B3LYP/DZ level of theory that contribute to the peak at 363 nm (3.42 eV). (Color labels: brown = Au; yellow = S; blue = Sb, pink = Br, grey = C, white = H) (C) Molecular orbital diagram and contributing atomic orbitals of $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ at the B3LYP/DZ level of theory. The number of degenerate MOs at a specific energy is in parenthesis.

from an electronic transition out of an occupied superatomic P shaped orbital in the icosahedral core of the cluster to an antibonding orbital comprised of the π^* orbitals on the phenyl rings of the SbPh₃ ligands. The second dominant transition, HOMO-10 \rightarrow LUMO+2, arises from an occupied orbital that primarily consists of individual p_x and p_y orbitals residing mostly around the bromine atoms, with little contribution from the sulfur p orbitals across the -S-Au-S- staple motifs. The electronic transition occurs into a superatomic D_z^2 shaped orbital in the icosahedral core of the Au₁₈ cluster. These transitions show that the electronic density corresponding to the main absorption peak includes both core \rightarrow ligand and ligand \rightarrow core contributions. Other levels of theory have been analyzed, and the qualitative results of the transitions that correspond to the main

absorption peak remain the same. The molecular orbital (MO) diagram for this nanocluster is shown in Figure 4.6C. At the B3LYP/DZ level of theory, the HOMO-LUMO gap of the nanocluster at the crystal structure geometry is 2.82 eV. It is important to note that the HOMO-LUMO gap and the first excited state energy (i.e., the optical gap) can differ. Although the first excited state is often dominated by the HOMO to LUMO transition, it is not always the principal transition (in this case, the peak at 2.02 eV arises from HOMO-LUMO+1, with contributions from the HOMO-LUMO and HOMO-LUMO+2). Most importantly, several transitions mix together to yield an excited state, and this can reduce the energy of the state due to configuration interaction.

As shown in figure B-1, the HOMO, HOMO-1 and HOMO-2 MOs show superatomic P type character in the core of the nanoparticle. These orbitals have relative energies of 0.00 eV, -0.16 eV and -0.53 eV respectively. The frontier orbitals of this cluster are highly delocalized from s contributions in the gold core. However, it is further noted that different cluster geometries have been shown to lead to different orbital morphologies with different energy separations due to broken spherical symmetry, but they are still classified as superatomic orbitals.⁴¹ As an example, in clusters such as $Au_{11}(dpb)_4Cl_2^+$, the HOMO-2 orbital is 0.44 eV lower in energy than the HOMO, but still shows superatomic P type nature. As an additional comparison, the superatomic P orbitals in thiolated clusters are much closer to degeneracy, differing only around 0.03 eV.^{17,42} The HOMO-3 and HOMO-4 orbitals are primarily based around the two Au₂(S-Adm)₃ staple motifs with minimal contribution from the third Au(S-Adm)₂ monomeric motif on the other side of the Au₁₈ cluster. HOMO-5 through HOMO-8 are primarily ligand-based, arising from the p orbitals on Br as well as the p orbitals from Au and S that are concentrated around the dimeric and monomeric Au-thiolate staple motifs, with no contribution from the Sb atoms. Small contributions start to appear from the Sb atoms in the HOMO-9 orbital. Further, LUMO through LUMO+4

corresponds to superatomic D orbitals in the core of the Au₁₈ cluster. The antibonding character in the ligands starts to show in the LUMO+6, which is comprised of π^* orbitals on the phenyl rings of the SbPh₃ ligands.

To probe the chirality of the $Au_{18}(S-Adm)_8(SbPh_3)_8Br_2$ cluster, the computed circular dichroism (CD) spectra of the Au_{13} core as well as the total $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ are shown in figure 4.7. As Au atoms in the core are not in their most symmetric locations due to their interactions with the ligands, there is still a small intensity from the Au_{13} core (blue curve, figure 4.7). However, the signal from the full Au_{18} cluster is significantly more intense (red curve, figure 4.7), confirming the chirality of the $Au_{18}(S-Adm)_8(SbPh_3)_8Br_2$ originates from the ligand shell of the cluster.



Figure 4.7. Calculated CD spectra of both the full Au₁₈ cluster (right isomer) as well as the Au₁₃ core alone at the BP86/DZ level of theory.

4.5 – Conclusion

The crystal structure of a new mixed thiolate/stibine-protected Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster was synthesized and experimentally determined, the properties of which are found to be

very different from the only previous stibine-protected [Au₁₃(SbPh₃)₈Cl₄]⁺ cluster. Specifically, the incorporation of dimeric and monomeric Au-thiolate staple motifs in the Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ structure is found to (1) induce chirality by breaking the symmetry of the achiral Au₁₃ core, thereby indicating that chirality can be engendered in achiral clusters protected by electroneutral ligands such as PPh₃ and SbPh₃, through generation of Au-thiolate staple motifs on their surfaces, and (2) enhance the stability of clusters by resisting ligand exchange in the presence of excess glutathione. Our results not only underscore the importance of the ligand shell in tailoring the observed properties of closely related clusters but also inform that a mixed-ligand strategy may be used to synthesize stable metal clusters with weakly coordinating ligands such as SbPh₃. This knowledge is expected to spur the development of such mixed ligand protected metal clusters with new properties and help gain critical insights into the effects of mixed-monolayer ligand shells on the stability and reactivity of metal nanoparticles.

4.6 – Acknowledgements

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Chapter 5 - A First Glance into Mixed Phosphine-Stibine Moieties as Protecting Ligands for Gold Clusters

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5.1 – Abstract

Atomically precise gold clusters have attracted considerable research interest as their tunable structure-property relationships have resulted in widespread applications, from sensing and biomedicine to energetic materials and catalysis. In this article, the synthesis and optical properties of a novel $[Au_6(SbP_3)_2][PF_6]_2$ cluster are reported. Despite the lack of spherical symmetry in the core, the cluster shows exceptional thermal and chemical stability. Detailed structural attributes and optical properties are evaluated experimentally and theoretically. This, to the best of our knowledge, is the first report of a gold cluster protected via synergistic multidentate coordination of stibine (Sb) and phosphine moieties (P). To further show that the latter moieties give a set of unique properties that differs from monodentate phosphine-protected $[Au_6(PPh_3)_6]^{2+}$, geometric structure, electronic structure, and optical properties are analyzed theoretically. In addition, this report also demonstrates the critical role of overall-ligand architecture in stabilizing mixed ligand-protected gold clusters.

5.2 – Introduction

Metal clusters, containing tens to hundreds of metal atoms and exhibiting strong metalmetal bonds, show unique quantum confinement effects and are generally considered a bridge

between small molecules and bulk-materials. In recent years, ligand protected gold clusters have attracted significant interest owing to their unique geometric structures and physicochemical properties which make these clusters suitable for a wide range of applications including catalysis, sensing, luminescence, and biomedicine.²⁻³ Thiolate-, alkyne-, and phosphine-protected clusters, in particular, have dominated this realm of gold-cluster chemistry,⁴⁻¹¹ although heavier thiolateanalogues such as selenolates have also been explored to synthesize stable gold clusters.¹² On the other hand, heavier phosphine-analogues such as stibines are severely underexplored and have only recently garnered interest as potential ligands to stabilize gold clusters. In 2018, Leong et al., reported the first stibine-protected gold cluster viz. [Au₁₃(SbPh₃)₈Cl₄]⁺.¹³ Very recently, Das *et al.*, reported the first mixed stibine-thiolate gold cluster formulated as Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ (S-Adm=1-adamantanethiolate).¹⁴ These two are the only reports of stibine-protected gold clusters to date. The underutilization of stibines as ligands is typically ascribed to their weaker coordinating ability from the diffuse donor orbitals.¹⁵⁻¹⁶ However, it has been experimentally observed that the mixed stibine-thiolate-protected Au₁₈(S-Adm)₈(SbPh₃)₄Br₂ cluster exhibits enhanced stability compared to the *only-stibine*-protected [Au₁₃(SbPh₃)₈Cl₄]⁺ cluster.¹⁴ This opens up the possibility that suitable multidentate ligand design involving stibines alongside strongly coordinating groups such as thiolates or phosphines, will lead to synergistic coordination modes, yielding robust clusters with unique structural attributes and optical properties.

In this work, properties of a Au₆ cluster stabilized by a multidentate ligand containing one stibine (Sb) and three phosphine (P) moieties are synthesized and illustrated, in which the Au₆ core can be envisioned as comprising of two Au₄ tetrahedra which assemble together by sharing a common Au₂ edge (highlighted in green in figure 5.1). This, to the best of our knowledge, is the first report where a ligand containing both stibine and phosphine coordinating sites has been

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utilized as a protecting group for gold cluster synthesis. It is worthwhile to note that bidentate diphosphine ligands have been previously used to synthesize Au₆ clusters exhibiting "core+exo" structures comprising of a Au₄ tetrahedral core and 2 exo Au atoms, in sharp contrast to the edge-sharing bitetrahedral Au₆ core in the newly synthesized [Au₆(SbP₃)₂][PF₆]₂ cluster.¹⁶⁻¹⁷ On the other hand, a similar bitetrahedral Au₆ core was observed in the case of monodentate phosphine-protected [Au₆(PPh₃)₆]²⁺ clusters.¹⁸⁻¹⁹ Comparison of our results with [Au₆(PPh₃)₆]²⁺ re-affirmed the role of ligand architecture in stabilizing these "rarely-reported" cluster-geometries. The role of ligand architecture was illustrated using another mixed stibine-phosphine ligand: ((phenylstibinediyl)bis(2,1-phenylene))bis(diphenylphosphine), abbreviated as SbP₂. It was observed that while cluster synthesis with SbP₃ results in a robust Au₆ cluster, analogous synthetic efforts with SbP₂ resulted in unstable clusters under similar experimental conditions. Thus, our report not only highlights the necessity of synergistic interactions of Sb and P moieties but also sheds light on the importance of overall-ligand architecture to achieve stable gold clusters.

5.3 – Computational Details

All calculations were completed using the Amsterdam Modeling Suite (AMS) 2021.1 package.²⁰ The initial unrefined crystal structure was used as an input structure for all calculations, which can be described as a single monomer isolated from the packed crystal structure. Scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).^{21,22} All calculations were completed at the BP86-D3/DZP level of theory, where BP86 is a generalized gradient approximation (GGA) exchange-correlation functional,^{23,24} -D3 refers to the dispersion effects added to the exchange-correlation functional via the Grimme3 model,²⁵ and a double-zeta polarized (DZP) basis set is used.²⁶ The theoretical absorption spectrum was calculated with linear

response time-dependent density-functional theory plus tight binding (TDDFT+TB)²⁷ where the vertical excitation energies were convolved into the optical absorption spectrum with a gaussian fit with a full width half maximum (FWHM) of 30 nm (for plots shown in wavelength) or 0.20 eV (for plots shown in eV). The structure was optimized in the gas phase and the gradient convergence criteria was tightened to 1×10^{-3} Hartree for geometric accuracy. All calculations had a tightened SCF convergence requirement of 1×10^{-8} . Due to the locality of the GGA functional, as well as charge transfer character from the molecular orbital transitions, additional results are calculated with simplified time-dependent density-functional theory (sTDDFT)²⁸ with a Yukawa long-range separated hybrid functional with a gamma value of 0.75 on the optimized BP86-D3/DZP S₀ state.²⁹ For the circular dichroism (CD) spectrum, the isolated Au₆²⁺ core was optimized at the BP86-D3/DZP level of theory in addition to the full cluster.

5.4 – Results and Discussion

Magic clusters, i.e. clusters that have fully filled superatomic orbitals, analogous to those of a noble gas, show high stability from the energetics between the spherically symmetric superatomic orbitals.^{30,31} Both $[Au_{13}(SbPh_3)_8Cl_4]^+$ and $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ are examples of this with a superatomic electron count of 8 that yields a S²P⁶ configuration.^{13,14} Unlike these clusters, however, $[Au_6(SbP_3)_2]^{2+}$ has a superatomic electron count of 4, corresponding to a S²P² configuration. The structure of the ligand SbP₃ and the crystal structure of $[Au_6(SbP_3)_2]^{2+}$ are shown in figure 5.1.



Figure. 5.1. (A) Chemical structure of the mixed phosphine-stibine ligand (SbP₃); (B) Total structure of $[Au_6(SbP_3)_2]^{2+}$ cluster; (C) Structure of the Au₆ core comprised of two Au₄ tetrahedra which assemble together by sharing a common Au₂ edge (highlighted in green). (Color labels: brown/green = Au; orange = P; blue = Sb, grey = C; H atoms are not shown for clarity).

As the P orbitals are not fully filled, the cluster is less spherically symmetric and more prolate. Because of this, the cluster follows the ellipsoidal Clemenger-Nilsson shell model rather than the spherical shell (or superatomic) model. $[Au_6(SbP_3)_2]^{2+}$, the monodentate phosphine-protected species, also has a superatomic electron count of 4 resulting in a more prolate geometry. Herein, to understand the exact role of ligands in dictating the core geometric and electronic structure, calculations were performed on monodentate phosphine-protected $[Au_6(PPh_3)_6]^{2+}$ clusters in addition to the mixed phosphine-stibine protected $[Au_6(SbP_3)_2]^{2+}$.

The crystal structure of $[Au_6(SbP_3)_2]^{2+}$ is best described in the triclinic space group $\overline{P1}$, with six gold atoms, two SbP₃ ligands, and two PF⁶⁻ ions (figure 5.1 B). $[Au_6(SbP_3)_2]^{2+}$ has a Au₆ core composed of two edge-sharing tetrahedra (figure 5.1 C), protected by two SbP₃ ligands via multidentate coordination, where each Au atom bonds with one Sb atom and one P atom. The unit cell is comprised of two $[Au_6(SbP_3)_2][PF_6]_2$ monomers that slightly differ in average bond lengths, and the average bond lengths of both monomers are reported in Table C-1. The average Au-Au bond distance in the crystal structure is 2.760 ± 0.048 Å, which is 4.2% shorter than bulk gold, 2.88 Å, and is essentially identical to the experimental Au-Au average bond distance of 2.759 Å in [Au₇(dppp)₄](BF₄)₃ which also has a bitetrahedron gold core and a S²P² configuration from the superatom electron count of 4. Further, the Au-Au bond distance in [Au₆(SbP₃)₂][PF₆]₂ is found to be similar to the Au-Au bond distances reported for [Au₆(PPh₃)₆]²⁺. This finding is of quintessential importance as it is well-established that the bitetrahedral geometry is a result of strong Au-Au interaction for [Au₆(PPh₃)₆]²⁺, which in turn, is determined by the optimum-ligand architecture (or more specifically the cone-angle). Thus, it can be safely argued that our ligand SbP₃ has an optimum-architecture to stabilize bi-tetrahedral gold(VI) geometry. This also illustrates the importance of ligand-design for exploring nanocluster-chemistry.

The average Au-P bond distance in $[Au_6(SbP_3)_2][PF_6]_2$ is ca. 2.3 Å, comparable to Au-P bond distances previously reported for other nanoclusters. The average Au-Sb bond distances were found to be 3.095 ± 0.137 Å, where one of the Au-Sb bonds on each side of each cluster is ~10% longer than the other two bonds. These Au-Sb bond distances are much greater than the Au-Sb bond distance of 2.48 ± 0.02 Å obtained for $[Au_{13}(SbPh_3)_8Cl_4]^+$ cluster as well as the Au-Sb distance of 2.549 ± 0.027 Å in $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$. This demonstrates that Au-Sb bond lengths, and thus the geometric aspects of gold nanoclusters, can be tuned using novel stibinebased ligands. Further, even though a longer bond suggests a weaker interaction, the formation of a stable-nanocluster indicates that the overall interaction between the metal-center and ligands are re-enforced via the synergistic effect of mixed-ligands.

To obtain further insight into the geometric and optical properties of this cluster, theoretical calculations were performed as described in the computational details. At the BP86-D3/DZP level of theory, the Au-Au and Sb-C bonds are ~0.02 Å larger than the crystal structures as seen in Table

C-1. The average Au-Sb bond lengths are 0.017 Å shorter than the average distance between the two monomers in the crystal structure, and the Au-P and P-C bonds remain essentially the same, with a variation of less than 0.009 Å. The bitetrahedron core of the nanocluster is essentially achiral, and the addition of the ligands makes the entire cluster chiral as shown by the theoretical circular dichroism spectrum in figure C-1. The average bond distances in $[Au_6(PPh_3)_6]^{2+}$ are essentially negligible different compared to $[Au_6(SbP_3)_2]^{2+}$ with Au - Au, Au - P, and P - C bond distances of 2.774 ± 0.045 Å, 2.307 ± 0.009 Å, and 1.818 ± 0.004 Å, respectively.

 $[Au_6(SbP_3)_2]^{2+}$ and $[Au_6(PPh_3)_6]^{2+}$ only have one occupied P molecular orbital, which breaks the spherical symmetry of the superatom model. This gives a large energetic gap between the P' HOMO and P' LUMO of 1.94 eV and 1.97 eV respectively at the BP86-D3/DZP level of theory. Further, there are no degeneracies between the HOMO and HOMO-1, as shown in the molecular orbital (MO) diagrams in figures C-2 and C-3. (To quantitively compare between the ellipsoid and spherical basis, P' and D' refer to the elongated equivalents of the P and D superatomic orbitals.) Despite the incredibly similar Au-Au geometric structure in the Au₆ clusters, as well as a similar atomic contribution in the HOMO, the p orbitals from Sb atoms directly mix into the frontier orbitals of $[Au_6(SbP_3)_2]^{2+}$. This causes smaller energetic gaps between the frontier orbitals.



Figure 5.2. Absorption spectrum of [Au₆(SbP₃)₂]²⁺. (A) Experiment (B) LRCF-D3/DZP//BP86-D3/DZP spectrum in nm. (C) BP86-D3/DZP//BP86-D3/DZP in eV. (D) LRCF-D3/DZP//BP86-D3/DZP spectrum in eV.

The theoretical optical absorption spectrum of $[Au_6(SbP_3)_2]^{2+}$ at the BP86-D3/DZP level of theory matches well with experiment with peaks at 3.30 eV (368 nm) and 2.81 eV (442 nm) (figure 5.2 A); however, as a result of the Sb mixing, the vertical excitation energies are closer together, which forms more of a manifold rather than discrete electronic states, as seen in figure 5.2 C. Investigation of the MOs involved in these transitions show charge transfer character where there is little to no overlap in electronic density between the occupied MOs, dominated by s and p atomic orbitals from the Au, P, and Sb atoms, and the virtual MOs, which primarily arise from carbon contributions in the aromatic groups (figures C-4 and C-5). Exchange-correlation functionals at the generalized gradient approximation (GGA) level, such as BP86, do not account for charge transfer;³⁷ therefore, to further distinguish the optical properties of this cluster, a long range corrected hybrid functional (LRCF) was used in a linear response calculation at the BP86D3/DZP S₀ geometry. The vertical excitation energies of the peaks with this functional, compared to BP86, can be seen in Table C-2. The LRCF-D3/DZP//BP86-D3/DZP level of theory (figure 5.2 B) shows good spectral similarity with experiment, and the dominant excitation can be seen at 395 nm (3.14 eV). Due to the long-range interactions, the vertical excitations show more discrete transitions than with BP86 as seen in the vertical excitation energies (figure 5.2 D). It is important to note that despite the better energetic treatment, the long-range interactions overestimate the experimental energy, as well as the energetic gaps between orbitals; this overestimation, however, is a common artifact of this type of functional.³⁸⁻⁴⁰ In this cluster, there is an intraband transition originating from the S₂ state dominated by the HOMO \rightarrow LUMO+1 transition, and S₁ state dominated by the HOMO \rightarrow LUMO transition at 2.93 eV. As an atomically precise gold cluster that is less than 2 nm, these gold core \rightarrow gold core transitions are expected to dominate the low energy optical peak(s), which is precisely what happens at this level of theory.

The second peak occurs at 3.14 eV and originates from the S₃ state dominated by a HOMO \rightarrow LUMO+2 transition and an S₂ state dominated by a HOMO \rightarrow LUMO+2. The molecular orbitals responsible for the transition of this peak can be seen in figure 5.3. Due to the geometric distortion in the core, the P' HOMO has large atomic orbital contributions from the sp orbitals on the gold atoms, but it is lengthened from the prolate geometric nature. This leads to an orbital that may better be described as a cluster π orbital rather than as an atomic p (or superatomic P) orbital. Furthermore, the slight mixing of p orbitals from the Sb atoms in the L+2 MO pulls the electronic density away from the Au atoms, essentially flattening the once spherically symmetric four-lobed D orbital. This distortion in the D' orbital results in a lack of overlap of electronic density with the occupied orbital. As the Sb atoms are already mixing into [Au₆(SbP₃)₂]²⁺, the stretched nature of

the electronic density is exaggerated. The electronic density elongating due to the Sb atoms is not just an artifact seen in theoretical calculations, but it is also seen in experiment. The NMR analysis, for instance, showed a downfield shift of ca. 12 ppm in the phosphorous signal upon cluster formation which reveals that Au-atoms interact strongly with SbP₃, withdrawing significant amount of electron density upon cluster formation. The molecular orbitals at the BP86-D3/DZP and LRCF-D3/DZP//BP86-D3/DZP level of theory in the first 12 frontier orbitals are displayed in figures C-6 – C-8.



Figure 5.3: Molecular orbital details at the LRCF-D3/DZP level of theory at the BP86-D3/DZP S₀ geometry for $[Au_6(SbP_3)_2]^{2+}$. (A) Atomic orbital contributions to molecular orbitals and (B) Molecular orbitals responsible for the 3.14 eV peak.

The optical absorption spectra of $[Au_6(PPh_3)_6]^{2+}$ at the BP86-D3/DZP level of theory is very different from that of $[Au_6(SbP_3)_2]^{2+}$ despite the similar geometric structure and same amount of superatomic electrons as seen in figure C-9. Of note, there is a much smaller energetic gaps between the frontier orbitals, which drastically changes the single orbital transitions in the theoretical absorption spectrum. Specifically, $[Au_6(SbP_3)_2]^{2+}$ has a lot more mixing of single orbital transitions underneath the peaks, whereas $[Au_6(PPh_3)_6]^{2+}$ has one dominant excitation in the low energy regime. Analyzing these clusters at the LRCF-D3/DZP//BP86-D3/DZP, they share more spectral similarities as $[Au_6(PPh_3)_6]^{2+}$ also has an intraband transition originating from the S₂ state dominated by the HOMO \rightarrow LUMO+1 transition, and S₁ state dominated by the HOMO \rightarrow LUMO transition at 2.88 eV as well as a second peak that originates from the S₃ state dominated by a HOMO \rightarrow LUMO+2 transition and an S₂ state dominated by a HOMO \rightarrow LUMO+2 at 3.44 eV as seen in figure C-10. Despite the similar electronic transitions, however, the electronic density of these transitions is very different between the two clusters as seen in figures C-11 and C-12.

Despite the lack of spherically symmetric orbitals in the core, $[Au_6(SbP_3)_2][PF_6]_2$ shows remarkable thermal stability. At 70°C, the cluster shows little to no decomposition for 16 hours. Further, the stability and reactivity of the $[Au_6(SbP_3)_2][PF_6]_2$ cluster was compared between monodentate stibine-protected Au_{13} and phosphine-protected Au_{11} nanoclusters to study the effects of multidentate SbP₃ ligand coordination in the presence of excess glutathione (GSH) in a previously reported two-phase reaction.^{10,13} Unlike both the monodentate ligand protected Au_{13} and Au_{11} clusters which convert to a water-soluble $Au_{25}(SG)_{18}$ cluster with 8 superatomic electrons, it is observed that the $[Au_6(SbP_3)_2][PF_6]_2$ cluster does not react or decompose when treated with excess glutathione and remains intact in the organic phase. These thermal stability and reactivity studies unequivocally underscore the importance of multidentate and synergistic stibinephosphine coordination in generating robust metal nanoclusters.

5.5 – Conclusion

In summary, a new gold cluster formulated as $[Au_6(SbP_3)_2][PF_6]_2$ stabilized by a multidentate ligand containing both stibine and phosphine moieties has been synthesized and structurally determined using single-crystal X-ray crystallography. This, to the best of our knowledge, is the first report of a gold-nanocluster stabilized by synergistic stibine-phosphine coordination. This cluster demonstrates an edge-sharing bi-tetrahedral Au₆-core, that has been rarely reported in literature. The $[Au_6(SbP_3)_2][PF_6]_2$ cluster demonstrates excellent thermal stability. The chemical stability of the synthesized cluster in presence of excess thiol (glutathione) has been compared to monodentate stibine- and phosphine-protected gold nanoclusters. It is observed that despite the break of spherical symmetry, as determined from theoretical calculations, $[Au_6(SbP_3)_2][PF_6]_2$ shows no signs of decomposition in presence of excess thiol in sharp contrast to the control systems. In addition, no cluster formation is observed in presence of another mixed phosphine-stibine ligand (SbP₂) under similar experimental conditions in which formation of $[Au_6(SbP_3)_2][PF_6]_2$ occurs. This demonstrates that the ligand SbP₃ has unique characteristics and structural attributes that change the optical properties of Au_6 clusters. These results are expected to spur the design of new multidentate ligands which, in turn, should lead to the development of robust nanoclusters with yet-unknown properties.

5.6 – Acknowledgements

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Chapter 6 - Characterization of Pt-doping effects on nanoparticle emission: A theoretical look at Au₂₄Pt(SH)₁₈ and Au₂₄Pt(SC₃H₇)₁₈

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6.1 - Abstract

Developments in nanotechnology have made the creation of functionalized materials with atomic precision possible. Thiolate-protected gold nanoclusters, in particular, have become the focus of study in literature as they possess high stability and have tunable structure-property relationships. In addition to adjustments in properties due to differences in size and shape, heteroatom doping has become an exciting way to tune the properties of these systems by mixing different atomic d character from transition metal atoms. Au₂₄Pt(SR)₁₈ clusters, notably, have shown incredible catalytic properties, but fall short in the field of photochemistry. The influence of the Pt dopant on the photoluminescence mechanism and excited state dynamics has been investigated by a few experimental groups, but the origin of the differences that arise due to doping has not been clarified thoroughly. In this paper, density functional theory methods are used to analyze the geometry, optical and photoluminescent properties of Au₂₄Pt(SR)₁₈ in comparison with [Au₂₅(SR)₁₈]¹. Further, as these clusters have shown slightly different geometric and optical properties for different ligands, the analysis is completed with both hydrogen and propyl ligands in order to ascertain the role of the passivating ligands.

6.2 - Introduction

Atomically precise nanoclusters have excited the science community in part because they possess specific geometric,²⁻⁴ optical,⁵⁻⁶ and photoluminescent⁷⁻⁹ properties that depend

sensitively on the various sizes and shapes of the nanoclusters (NCs). The demand for these NCs is increasing, as they can be controlled with atomic precision, and therefore, they provide an alternative to bulk materials or larger nanomaterials because they have precise electronic and geometric structure.¹⁰⁻¹³ A well-known example of this is $[Au_{25}(SR)_{18}]^{1-}$, which was structurally determined by the Murray and Jin groups in 2008.¹⁴⁻¹⁵ Since 2008, experimental and theoretical groups have showed that the properties of this cluster can be tuned for different applications such as photodynamic therapy,¹⁶⁻¹⁷ small molecule activation,¹⁸⁻²⁰ biosensing,²¹⁻²² and more. The immense applicability of $[Au_{25}(SR)_{18}]^{1-}$ has further trigged a variety of theoretical and experimental studies benchmarking the properties of thiolate-protected nanoclusters with different sizes, shapes, ligands, and charge states.²³⁻²⁷

In addition to changing the ligand shell or surface structure of the nanocluster, controlled modification of the metal core via doping has become an exciting new progression of this work. Au₂₄M(SR)₁₈ clusters (M = dopant) have become star models in understanding the role of the dopant in thiolate-protected clusters,²⁸ largely because the parent cluster, $[Au_{25}(SR)_{18}]^{1-}$, has been thoroughly studied.²⁹⁻³³ Out of the immense number of transition metal dopants, Au₂₄Pt(SR)₁₈ stands out, as it is an exceptional catalyst³⁴ as well as a robust oxidizer.³⁵ Despite initial difficulties to structurally characterize this cluster, which arises in part due to the similarities between Pt and Au,³⁵⁻³⁶ the crystal structure was accomplished by Jin and coworkers in 2012.³⁷ Since that time, several structures of Au₂₄Pt(SR)₁₈ have been used to theoretically and experimentally describe the Au-Pt bonding,³⁸ the cluster stability,³² the large catalytic activity,³⁵ the optical properties, and more. As the electronic structure of a doped cluster is dictated by the type of dopant, the precise dopant location, and synthetically, by the dopant concentration,³⁹⁻⁴¹ Au₂₄Pt(SR)₁₈ is a perfect model to examine how the properties change with a heteroatom dopant.

One of the reasons that thiolate-protected clusters stand out is their high stability, which can be traced back to geometric and electronic effects that can be understood from the superatom model.⁴²⁻⁴³ Analogous to atomic theory, superatomic electrons occupy a set of delocalized superatomic orbitals that possess the symmetries of spherical harmonic functions.⁴⁴ For instance, similar to an atomic p orbital, there would be a set of three superatomic P molecular orbitals (MOs) that would be energetically degenerate if the nanocluster has perfect spherical symmetry.⁴⁵ These molecular orbitals are usually comprised of 6s contributions from the gold atoms in the core of the nanocluster. In the case of $[Au_{25}(SR)_{18}]^{1-}$, there are eight superatomic electrons that create a S²P⁶ configuration.⁴⁶ This configuration is equivalent to the atomic configuration of a noble gas, which is one reason why the cluster is so stable. Neutral $Au_{24}Pt(SR)_{18}$, on the other hand, has a S^2P^4 configuration as a result of the six superatomic electrons present in this system, which results in one empty superatomic P orbital.^{20,47} Because that first unoccupied orbital is empty, the first two excited state transitions $(P \rightarrow P)$ are dipoleforbidden, and hence, Au₂₄Pt(SR)₁₈ clusters have shown to have similar absorption trends to $[Au_{25}(SR)_{18}]^{1+}$, as well as similar electron dynamics to the open shell neutral $Au_{25}(SR)_{18}$ cluster.⁴⁸ The Pt dopant is thought to accelerate the core-shell coupling, which results in a faster relaxation to the ground state as compared to $[Au_{25}(SR)_{18}]^{1-.49-50}$

While there is some literature on how the Pt dopant changes the electron dynamics mechanisms compared to the parent cluster based on 2DES and TA measurements, no experimental photoluminescence (PL) emission peak is present in the range of 600-1600 nm.⁵¹ The reason for the missing emission in Pt-doped clusters is unclear, perpetuating the need for theoretical studies. Further, among the Au₂₄Pt(SR)₁₈ literature, several different ligands have been used. Negishi and coworkers showed in 2019 that there is a large difference in geometry as

well as optical absorption spectra when R=PET (PET = 2-phenylethanethiolate) and R=TBBT (TBBT = 4-tert-butylbenzenethiolate) in Au₂₄Pt(SR)₁₈.³⁶ While some gold nanoclusters with the same core size have shown similar optical properties between ligands,⁵² small nanoclusters such as Au₂₄Pt(SR)₁₈ experience a larger influence from the bulkiness of the ligand shell.⁴¹ This paper will therefore provide a theoretical look into the electronic structure, optical, and photoluminescent properties of Au₂₄Pt(SH)₁₈ and Au₂₄Pt(SC₃H₇)₁₈ and examine how the dopant changes the properties compared to $[Au_{25}(SR)_{18}]^{1-}$.

6.3 - Computational Details

All calculations with Au₂₄Pt(SH)₁₈ were performed using the Amsterdam Density Functional (ADF) 2016.101 package, and all calculations of Au₂₄Pt(SC₃H₇)₁₈ and $[Au_{25}(SC_{3}H_{7})_{18}]^{1-}$ were completed using the ADF 2018.105 package.⁵³ Several experimental crystal structures of $[Au_{25}(PET)_{18}]^{1-}$ (Refs.^{14,15,30,54,55}) with removed phenyl groups were used as initial input structures for the theoretical calculations of $[Au_{25}(SC_3H_7)_{18}]^{1-}$. The lowest energy isomer was initially used with single atom Pt replacements as initial input structures to optimize Au₂₄Pt(SC₃H₇)₁₈. The core structure was later edited with a more flattened-oblate structure to help the calculation converge. For Au₂₄Pt(SH)₁₈, the crystal structure of $[Au_{25}(SR)_{18}]^{1-}$ (Refs. ^{4,14}) with single atom Pt replacements was used as an input structure for all calculations. The $Au_{24}Pt(SR)_{18}$ results are obtained with a neutral charge state to match the experiment. Scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).⁵⁶⁻ ⁵⁷ All calculations were completed at the BP86/DZ level of theory. BP86 is a generalized gradient approximation (GGA) exchange-correlation functional,⁵⁸⁻⁵⁹ and DZ refers to a doublezeta basis set. Additional calculations are performed at the BP86/TZP level of theory for benchmark purposes, where TZP is a triple-zeta polarized basis set. The structure was optimized
in the gas phase for all calculations, and the energy and gradient convergence criteria were tightened to 1×10^{-4} Hartree and 1×10^{-3} Hartree respectively for geometric accuracy. All calculations had a tightened SCF convergence requirement of 1×10^{-8} . The theoretical absorption spectrum was calculated with linear response time-dependent density functional theory (TDDFT),⁶⁰ where the vertical excitation energies were convolved with a gaussian fit with a fullwidth half-maximum (FWHM) of 0.15 eV. TDDFT analytical excited state gradients⁶¹ were used to optimize the S₁-S₂₁ states for R=H and R=C₃H₇ using the same convergence criteria and level of theory as the ground state. All pictures of the molecular orbitals were created with the ADF graphical user interface (GUI) and presented with a contour value of 0.015.

6.4 – Geometric Structure

Au₂₄Pt(SR)₁₈ has the same general shape as $[Au_{25}(SR)_{18}]^{1-}$ and is composed of a 13 atom 'icosahedron' core with 6 Au₂S₃ motifs that protect the core by forming rigid V-shaped S-Au-S-Au-S staples that are further protected by organic ligands. It has been shown that the Pt dopant prefers the center position in the core of the nanocluster.^{28,36,38,46} This paper additionally supports the conclusion that the Pt dopant prefers the center of the core; energies at the BP86/DZ and BP86/TZP levels of theory are provided in table D-1 for various isomers with R=C₃H₇. For simplicity, the term 'icosahedron' refers to the general shape of the core, even though the core of Au₂₄Pt(SR)₁₈ is not made up of 20 equivalent equilateral triangles but more of a flattened triangle base, as seen by figure D-1. This breaking of spherical symmetry creates a distorted oblate ellipsoid⁶² and is a direct result of the Jahn-Teller effect, which occurs because the P orbitals are not completely filled.⁶³ The core distortion from the dopant is more prominent with the larger ligand, and in fact, this geometric change between ligands can be qualitatively observed in pictures (figure 6.1). The optimized ground state (S₀) structures in both clusters experience an elongation of two specific Au core – Pt center bonds that have an average distance of 2.850 Å in Au₂₄Pt(SH)₁₈ and 2.940 Å in Au₂₄Pt(SC₃H₇)₁₈. With the larger C₃H₇ ligand these two bonds are ~0.11 Å larger than the rest of the Au core – Pt center bonds, whereas in Au₂₄Pt(SH)₁₈, the elongated bonds are only 0.03 Å larger than the rest of the Au center – Pt bonds.



Figure 6.1. Optimized ground state geometry of $Au_{24}Pt(SR)_{18}$ with R = H (left) and $R = C_{3}H_{7}$ (right). Color scheme: black = Pt, green = Au core atoms, brown = Au shell atoms, yellow = S, grey = C, and white = H. (A) Distorted 'icosahedron' Au_{12}Pt core. (B) Au_{12}Pt core protected by six Au_{2}S_{3} staples. (C) Full $Au_{24}Pt(SR)_{18}$ cluster with the different ligands.

Despite the almost identical average Au-S-C angle of 103.7° for $[Au_{25}(SC_3H_7)_{18}]^{1-}$ and $Au_{24}Pt(SC_3H_7)_{18}$ at the BP86/DZ level of theory, the orientation of the propyl groups changes in one S-Au-S staple. To be more specific, in the lowest energy isomer of $[Au_{25}(SC_3H_7)_{18}]^{1-}$, the propyl groups attach to the Au₂S₃ staples in alternating cis/trans configurations, exhibited in figure D-2.⁶⁴ In Au₂₄Pt(SC₃H₇)₁₈, one of the Au₂S₆ staples has a trans/trans orientation rather than a cis/trans orientation. As a consequence of this change, the propyl groups attached to two

nearby staples create gauche/gauche/anti and gauche/anti/anti configurations, which is quite different from the all-anti configuration that is present in the propyl groups of the $[Au_{25}(SC_3H_7)_{18}]^{1}$ cluster. This shows that not only does the Pt atom distort the core, but also the shell of the nanocluster, the attachment of the propyl groups to the shell, and the configurations of the propyl groups themselves. In 2019, it was found that the interaction between phenyl groups in the TBBT ligand leads to a higher symmetry as compared to the PET ligand.³⁶ The work demonstrated that with that higher symmetry ligand (TBBT), the metal core shrinks. This same relationship is seen between hydrogen and propyl groups as the Pt center-Au core and Au core-Au core bonds both shrink ~0.03 Å with the more symmetric ligand (R=H). Despite the difference in electronic structure, the average bond distances in $Au_{24}Pt(SH)_{18}$ and $[Au_{25}(SR)_{18}]^{1-}$ are very similar, differing less than 0.006 Å in the core/shell as seen in table 6.1.

in the core and ~0.02 Å in the Au-S and S-S bonds. While the Jahn-Teller effects are still present in Au₂₄Pt(SH)₁₈, the symmetry distortion is more exaggerated with the larger ligand.

	0	0		0	0	
(Å)	Au/Pt Center-	Au Core-	Au Core-	Au Core-	Au Shell-	S-S
(A)	Au Core	Au Core	Au Shell	S Terminal	S Staple	Distance
$[Au_{25}(SC_{3}H_{7})_{18}]^{1-}$	2.830	2.973	3.121	2.539	2.430	4.821
	0.014	0.100	0.130	0.005	0.009	0.008
Au ₂₄ Pt(SH) ₁₈	2.827	2.974	3.115	2.516	2.422	4.809
	0.016	0.189	0.119	0.023	0.005	0.006
$Au_{24}Pt(SC_{3}H_{7})_{18}$	2.853	3.003	3.133	2.523	2.424	4.817
	0.054	0.256	0.157	0.030	0.008	0.009

Table 6.1. Average bond distances (Å) and standard deviation (Å) of the core and shell atoms at the BP86/DZ ground state geometry. The atom labels are given in figure D-3.

6.5 – Electronic Structure

These large geometric changes between the parent and the doped cluster originate from the breaking of spherical symmetry of the superatomic orbitals. As illustrated through the molecular orbital (MO) diagram in figure D-4, the HOMO and HOMO-1 MOs are essentially degenerate in Au₂₄Pt(SH)₁₈, only differing by 0.03 eV. The larger symmetry distortion in Au₂₄Pt(SC₃H₇)₁₈ results in a larger splitting of the HOMO and HOMO-1 MOs, which have a difference in energy of 0.11 eV. The empty superatomic P MO differs significantly in energy from the two other P MOs that are occupied. Au₂₄Pt(SR)₁₈ clusters have a completely different electronic structure than $[Au_{25}(SR)_{18}]^{1-}$ because of this difference in P superatomic MO occupation. This results in much smaller HOMO (H) – LUMO (L) gaps of 0.37 eV and 0.42 eV for Au₂₄Pt(SR)₁₈ with R=H and R=C₃H₇, respectively, compared to a H-L gap of 1.11 eV in $[Au_{25}(SC_3H_7)_{18}]^{1-}$. Images of the first six frontier MOs for the Pt-doped systems (H-2 through L+2) can be seen in figure D-5.

6.6 – Optical Absorption Spectra

In the literature, the energy of the main peak for Au₂₄Pt(SR)₁₈ clusters has ranged from 2.07 - 2.12 eV,^{34-36,65} with two other optical features of note: one broad band in the IR range, and one high energy shoulder on the edge of the UV spectrum. These three spectral features are similar to those seen in $[Au_{25}(SR)_{18}]^q$ clusters (q = -1, 0, +1), where the anionic cluster has a high energy shoulder around 403 nm (3.08 eV), a peak at 450 nm (2.76 eV) and a broad peak around 680 nm (1.81 eV).⁶³ When the cluster starts to lose electrons, i.e. goes from the anionic to cationic cluster, and hence goes from a fully filled P shell to an empty P shell, the shoulder has slightly higher energy at 3.15 eV, the main peak redshifts to about 2.58 eV, and the broad band blue-shifts to ~1.88 eV.³⁰ Similar optical shifts are also seen with the Pt atom as Au₂₄Pt(SR)₁₈ clusters have an experimental high energy shoulder at 400 nm (3.10 eV) that slightly blueshifts compared to $[Au_{25}(SR)_{18}]^1$, and the main peak is redshifted to 2.10 eV.^{37,62} At the BP86/DZ level of theory, the spectral shape between the experimental absorption spectrum and theory matches almost identically as seen in figure D-6. Depending on the ligand, the high energy

shoulder is around 420 or 450 nm (2.76 or 2.95 eV), the main peak is around 550-590 nm (2.1-2.25 eV) and the broad peak at the lower energy part of the spectrum is in the 700-900 nm range (1.37-1.77 eV).

The low energy peak attributed to the band from 770-870 nm is a combination of two dominant excitations for each nanocluster. The two strongest transitions in this energy range lie at 1.62 eV and 1.66 eV for R=H (table 6.2), which are S₂₀ and S₂₁ for this system (table D-2). The two strongest transitions for R=C₃H₇, are a little more split, with excitation energies of 1.43 and 1.54 eV (table 6.2), which are S₁₄ and S₁₇ for this system. For both ligands, the lower energy peak arises as a result of an excitation between an occupied superatomic P MO (H or H-1) to one of the two lowest energy superatomic D virtual MOs (L+1 or L+2). In the propyl ligand, an additional transition from a MO with large d-atomic orbital contributions from the gold atoms (H-13) transitions into the empty P LUMO which starts to mix with the P→D transition. This mixing is only present with the larger ligand. In general, the propyl system exhibits more mixing and splitting, which is likely due to its greater geometrical distortion from an idealized icosahedral core.

The dominant peak observed in the spectrum, corresponding to the ~600 nm experimental peak, is very different between the two ligands (figure 6.2). For the propyl ligand, there is one dominant excitation at 2.17 eV that makes up the peak with mixed $P \rightarrow D$ and $d \rightarrow P$ character, whereas for hydrogen, there are several excitations around 2.20 eV that make up the peak. The excitation with the largest oscillator strength lies at 2.30 eV and is made up of a dominant $P \rightarrow D$ transition. To observe the differences from the Pt dopant, the absorption energies for S_1 - S_{21} were calculated at the BP86/DZ level of theory, along with the type of transitions responsible for each excitation (table D-2). Only the first 21 states were analyzed in detail;

however, the first 1500 excitations were calculated to create the full theoretical spectrum (figure
D-6). It is worth noting that the first two excitations, S_1 and S_2 , for $Au_{24}Pt(SR)_{18}$ originate from
dipole-forbidden transitions (P \rightarrow P). These transitions are present in the theoretical spectrum at
0.42 eV and 0.45 eV or 0.47 eV and 0.59 eV for the hydrogen and propyl groups, respectively. In
comparison, $[Au_{25}(SC_3H_7)_{18}]^{1-}$ has three vertical excitations that make up the first peak, and all
of these excitations arise from $P \rightarrow D$ transitions. The excitation with the largest oscillator
strength is at 1.36 eV, which is a slightly lower absorption energy than the first peak with the Pt
dopant. Other density functional theory (DFT) studies resulted in an absorption energy of 1.32
eV for $[Au_{25}(SC_{3}H_{7})_{18}]^{1-}$ at the same level of theory, which matches well with our work. ⁶⁴

Table 6.2. Absorption details of the vertical excitation energies that make up the dominant peaks in the absorption spectrum (figure 6.2) at the BP86/DZ level of theory in Au₂₄Pt(SR)₁₈ for R = H and R = C₃H₇.

Peak	Peak Energy (eV)	Oscillator Strength (a.u.)	Major Transitions	Transition Type
R = Hydrogen (a)	1.62	2.19 x 10 ⁻²	H→L+2 H-1→L+1	P→D P→D
R = Hydrogen (b)	1.66	2.20 x 10 ⁻²	H-1 → L+2	P→D
R = Hydrogen (c)	2.30	1.22 x 10 ⁻²	H-1 → L+4	P→D
R = Propyl (a)	1.43	2.31 x 10 ⁻²	H-1→L+1 H→L+2	P→D P→D
R = Propyl (b)	1.54	2.12 x 10 ⁻²	H-1→L+2 H-13→L	P→D d→P
R = Propyl (c)	2.17	2.89 x 10 ⁻²	H-1→L+4 H-30→ L	P→D d→P



Figure 6.2. TDDFT absorption spectrum at the BP86/DZ level of theory for $Au_{24}Pt(SR)_{18}$ with R = H (solid purple) and $R = C_3H_7$ (dotted red).

6.7 – Emission

In 2016, the S₁ state of $[Au_{25}(SR)_{18}]^{1-}$ was reported to be the emissive state originating from a superatomic P→D transition in the core of the nanocluster.⁶⁴ Because the S₁ state arises from P→P transitions in $Au_{24}Pt(SR)_{18}$ clusters, these clusters will undergo a very different PL mechanism from the $[Au_{25}(SR)_{18}]^{1-}$ cluster. Excited state optimization calculations on the S₁ and S₂ excited states of the $Au_{24}Pt(SR)_{18}$ clusters failed due to near-degeneracies with the ground state, which indicate that a conical intersection is nearby. Nonradiative relaxation occurs quickly near conical intersections, so these findings indicate that the S₁ and S₂ states are unlikely to yield emission with an appreciable quantum yield. This conical intersection likely occurs because the P orbitals that provided the HOMO and LUMO in the ground state can become degenerate once the nanocluster has appropriately distorted during the excited state relaxation process. To examine the PL mechanism further, higher excited state geometry optimizations were completed. Two states (S₃, S₁₉) in $Au_{24}Pt(SC_3H_7)_{18}$ and three states (S₁₅, S₁₈, S₂₁) out of the first 21 in Au₂₄Pt(SH)₁₈ converged geometrically to our chosen criteria, rather than failing due to quasidegeneracies with the next lower energy excited state. Out of the five minima found for the two clusters, three of the excited states originate from $d \rightarrow P$ transitions (S₃, S₁₅, S₁₈, S₁₉). Some of these excited states have optimized HOMO-LUMO gaps that are less than 0.10 eV (table 6.3). Of note, the S₁₅, S₁₈ and S₁₉ states have very small energy gaps between the optimized excited state geometries and the state below (denoted as *n*-1, where *n* is the optimized excited state). A smaller energetic gap between orbitals leads to more efficient coupling of the excited state with the ground state, promoting a nonradiative transition over the emission of a photon.⁴⁹ Thus, the system is unlikely to remain in these geometries for any significant amount of time. The S_n – S_{n-1} gap is a little larger for the S₃ state, at 0.28 eV. Even though the S₃ geometry was unable to fully converge when R=H, a similar energy gap is observed between S₃ and S₂ with that ligand. The separation between the S₃ and the S₂ state could potentially be large enough to observe emission; however, this emission is predicted to be very low in energy (< 0.51 eV) and may be outside of typical experimental windows.

The S₂₁ state is unique, originating from a dipole allowed P \rightarrow D transition with a predicted emission energy of 1.52 eV. At the optimized S₂₁ geometry, the nanocluster has a relatively large HOMO-LUMO gap of 0.23 eV. This value is not as large as the optimized H-L gap in the S₁ state of [Au₂₅(SR)₁₈]¹⁻ (0.83 eV);⁶⁴ however, the energy gap could be large enough to potentially emit a photon. At the optimized S₂₁ state, however, the S₂₀ energy only differs by 0.002 eV from the S₂₁ energy. As the energy difference is negligible between the two states, it is likely that a system in the S₂₁ state would quickly cross to the S₂₀ state. While likely not an emissive minimum, the S₂₁ state does have a more unique electronic structure than the other excited state minima. The purely radiative lifetime of the S₂₁ state is predicted to be 0.42 µs, which is ~45x faster than the radiative lifetime value of 19.36 μ s from the S₁ state in [Au₂₅(SR)₁₈]¹⁻, predicted by the Fermi-Golden rule. Geometrically, there is no notable difference between the S₀ and S₂₁ states, as each type of bond changes less than 0.005 Å (table D-3).

Overall, this work shows that all the minima found from the first 21 excited singlet states would likely exhibit nonradiative relaxation rather than the emission of a photon, and therefore, these findings indicate that there is not an emissive state for the $Au_{24}Pt(SR)_{18}$ cluster in the 600-1600 nm energy range. Transient absorption and other pump/probe experiments have been used to try and gain insights into the excited state relaxation mechanism by exciting higher energy states. These studies have concluded that excited state deactivation includes ultrafast (~0.6 ps) relaxation within the core states, several picoseconds of core relaxation to surface states, followed by slow relaxation (>1 ns) back to the ground state.⁴⁸ Further, it was shown that the core states should not contribute to the TA signal after 30 ps.⁵⁰ The present theoretical work indicates that there are no charge transfer surface or 'trap' states between the superatomic core states, but there are no likely candidates for singlet states that would undergo radiative relaxation. The full picture of electronic relaxation in the $Au_{24}Pt(SR)_{18}$ nanocluster is not complete without a nonradiative analysis, which would require nonadiabatic calculations that are outside the scope of this work.

Table 6.3. Emission information for Au₂₄Pt(SR)₁₈ with R = H and R = C₃H₇ from converged minima on different excited state potential energy surfaces as calculated by TDDFT at the BP86/DZ level of theory. $S_n - S_{n-1}$ gap refers to the difference in emission energy of the state with the state below it at the optimized geometry in the table. The calculated Stokes shift is reported with respect to the vertical excitation energy of the main peak (i.e., 2.30 eV and 2.17 eV for R = H and R = C₃H₇, respectively) for consistency.

Sn	S ₃	S ₁₅	S ₁₈	S ₁₉	S ₂₁
Ligand	R=Propyl	R=H	R=H	R = Propyl	R=H
Emission energy (eV)	0.51	1.25	1.34	1.41	1.52
Stokes shift (eV)	1.66	1.05	0.96	0.76	0.78
Lifetime (µs)	51.4	1.46	45.5	0.38	0.42
$S_n - S_{n-1}$ Gaps (eV)	0.278	0.030	0.025	0.000	0.002
H-L Gap (eV)	0.08	0.04	0.02	0.28	0.23
Transition Origin	d→P	d→P	d→P	d→P	P→D

6.8 – Conclusion

Heteroatom dopants have provided a new way to tune the geometric, optical and photoluminescent properties of atomically precise thiolate-protected gold nanoclusters for several different applications. Known for their large catalytic ability, Au₂₄Pt(SR)₁₈ clusters provide a good example of how the distortion from a different superatomic electron count directly changes the properties of [Au₂₅(SR)₁₈]¹⁻. (TD)DFT calculations were performed to investigate these changes in the gas phase. Geometrically, the dopant distorts the parent cluster from an icosahedron to an ellipsoid, redshifts the absorption energy of the main peak and quenches the photoluminescence. Replacing the small hydrogen groups with a bulkier ligand, such as propyl, creates more distortion in the core/shell structure both geometrically and electronically, and redshifts the absorption energy. Higher excited state calculations suggest that there is not an emissive electronic state due to the small energy gaps between orbitals, but instead, nonradiative relaxation mechanisms are expected to dominate in the excited state dynamics mechanism. No charge-transfer or surface states are observed in this work, which

suggests that the change in the superatomic P electron count in the electronic structure of the core is the primary origin for the change in photoluminescence properties observed between the doped and parent cluster.

6.9 – Acknowledgments

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Chapter 7 - Open d Shells Acting as "Glue" for the Creation of Superatomic Occupied Orbitals: A Study on the Optical and PL Properties of Doped Ag₂₉ Systems

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7.1 – Introduction

Numerous reports have highlighted the ability of a dopant to change the optical and photoluminescent properties of noble metal nanoclusters.¹⁻³ The ability to tune these properties, particularly with different transition metals, arises as the d orbitals between the noble metal and transition metal mix, which leads to a change in atomic contribution and therefore a change in the overall electronic structure of the system. Experimental studies have revealed complicated metal migration in different metal dopant experiments, which has posed questions about the number of incorporated dopant atoms, their exact position within the nanocluster, as well as the nature of the dopant itself.⁴ As theory can provide detailed information into geometric and electronic structure on the optical and photoluminescent properties of noble metal nanoclusters, it is vital to study the effect of a transition metal dopant for continued application.

Different transition metals share common themes when they are used as a heteroatom dopant. Pd-doped and Pt-doped nanoclusters, for example, have shown to be favorable catalysts,⁵⁻⁷ while the integration of Au into Ag nanoclusters has shown enhanced fluorescent activity.⁸⁻⁹ Recently, scientific interest has shifted to Ni as a heteroatom dopant. The reason for this is that ferromagnetic metals, such as Ni, may provide a way to introduce stronger magnetic properties into noble metal nanoclusters.¹⁰

In 2020, it was shown that $[NiAg_{28}(BDT)_{12}]^{4-}$ and $[NiAg_{28}(BDT)_{12}]^{3-}$ both exist in solution, however the low stability compared to the parent cluster yielded further questions into the use of this dopant, as well as the charge state in these nanoclusters.¹¹ Unfortunately, Ni doped nanoclusters, particularly with Ag, are not thoroughly studied due to the lack of crystal structures,¹² which naturally puts a gap in understanding the structure-property relationships. This chapter therefore aims to study the geometric and electronic structure, optical and photoluminescent properties of Ni doped Ag₂₉ nanoclusters from a theoretical perspective, and additionally compare them to the parent cluster, and other transition metal dopants such as Au, Cu, and Pt.

7.2 – Computational Details

All calculations were done using the Amsterdam Modeling Suite (AMS) 2021.1 package.¹³ The crystal structure of [Ag₂₉(BDT)₁₂]³⁻ was used as an input structure for all calculations with the TPP groups removed.¹⁴ Scalar relativistic effects were included in all calculations by utilizing the zeroth-order regular approximation (ZORA).¹⁵⁻¹⁶ All calculations were completed at the BP86-D3/DZP level of theory, where BP86 is a generalized gradient approximation (GGA) exchange-correlation functional,¹⁷⁻¹⁸ -D3 refers to the dispersion effects added to the exchange-correlation functional via the Grimme3 model,¹⁹ and a double-zeta polarized (DZP) basis set.²⁰ [Ag₂₈Ni(BDT)₁₂]⁴⁻ cluster was optimized with restricted and unrestricted wavefunctions at different charge states ranging from -4 to +1 with a frozen core basis set, as it is the default in AMS calculations. Clusters that fully converged at that level of theory with -3 and -4 charge states were then rerun with all-electron basis set calculations. All other dopant calculations were calculated with an all-electron basis set. The theoretical absorption spectrum was calculated with linear response time-dependent density functional theory plus tight binding (TDDFT+TB)²¹ where the vertical excitation energies were convolved into the optical absorption spectrum with a gaussian fit with either a 0.20 eV FWHM (if an energy axis is used) or a 20 nm FWHM (wavelength axis). The structure was optimized in the gas phase for these calculations, and the energy and gradient convergence criteria were tightened to $1x10^{-4}$ Hartree and $1x10^{-3}$ Hartree respectively for geometric accuracy. All calculations had a tightened SCF convergence requirement of $1x10^{-8}$. Due to the locality of the GGA functional, as well as charge transfer character from the molecular orbital transitions, additional results are calculated with simplified time-dependent density functional theory (sTDDFT)²² with a Yukawa long-range separated hybrid functional with a gamma value of 0.75^{23} on the optimized BP86-D3/DZP S₀ state.

7.3 - Geometric Structure

 $[Ag_{28}Ni(BDT)_{12}]^{4-}$, similar to the parent cluster $[Ag_{29}(BDT)_{12}]^{3-}$, is best described as a quasi-spherical cluster with four tetrahedral symmetric positions as seen in figure 7.1.²⁴ This cluster has a $Ag_{12}Ni$ icosahedron core, which is covered by four tetrameric Ag shell atoms, as well as four tetrameric Ag₃ shell atoms that form four symmetric triangles around the cluster. The BDT ligand contributes two sulfurs that connect to the shell creating a crown-like structure around the Ag triangles in the shell, which connect to the Ag tetra atoms forming S-Ag-S motifs.



Figure 7.1. Structure of $[Ag_{28}Ni(BDT)_{12}]^{4-}$. Color scheme: silver core = dark green, silver shell = light green, nickel = blue, sulfur = yellow, carbon = grey, hydrogen = white. (A) Icosahedral Ag_{12}Ni core (B) Ag_{12}Ni core with added silver shell atoms. (C) Ag_{12}Ni core with added silver and sulfur shell atoms. (D) Full $[Ag_{28}Ni(BDT)_{12}]^{4-}$ cluster

The four TPP groups that connect to the Ag tetra atoms in the crystal structure²⁴ were removed for computational efficiency. Theoretically, the absorption spectrum has similar peak positions with and without TPP groups as seen in figure E-1, and the S₁ emission energy is within 0.01 eV between the two clusters. An illustration of the individual core-ligand structure of $[Ag_{28}Ni(BDT)_{12}]^{4}$ can be seen in figure 7.1. To decipher the correct position of the monodopant into the parent cluster, the Ni atom was placed in the center, core, 'tetra' (referring to the tetrameric Ag connections) and 'tri' positions (referring to the tetrameric Ag atoms in the Ag₃ triangles connected to the core) (figure E-2). These different optimized structures were compared, and the lowest energy structure was deemed most stable. Different structures converged with -3 and -4 charge states with unrestricted and restricted wavefunctions respectively. Through these calculations it was found that the dopant prefers the center position with a charge state of -4, whereas it prefers the 'tri' shell position with a charge state of -3 as seen in table E-1. While different structural isomers could exist in solution, the theoretical analysis reported in the manuscript will be for the -4 charged cluster as it exists in a closed shell singlet in its ground state. The Ni dopant shrinks the core somewhat as shown from the Ni center – Ag core bonds compared to the Ag center – Ag core bonds observed in the parent cluster, with average bond distances of 2.709 ± 0.044 Å and 2.811 ± 0.101 Å, respectively. In addition to the center bonds, the Ag core – Ag core bonds in the icosahedron core are smaller than the parent cluster with an average bond distance of 2.848 ± 0.065 Å. In the shell of the nanocluster, the addition of the Ni dopant expands the tetrameric Ag shell – Ag core 'tri' bonds, pushing the shell a little further away from the center. The Ag shell – S crown, S crown – S crown, S crown – S motif average bond distances do not change with the addition of the Ni dopant as seen in table E-2, with atom labels shown in figure E-2.

7.4 - Electronic Structure

Both $[Ag_{29}BDT_{12}]^{3-}$ and $[Ag_{28}NiBDT_{12}]^{4-}$ have a superatom electron count of 8, giving rise to a S²P⁶ configuration. This naturally causes splitting between the different types of supermolecular orbitals in the cluster. This behavior can be seen in the molecular orbital diagram in figure E-3, where there is set of six virtual molecular orbitals that are lower in energy compared to the rest of the virtual orbitals. These orbitals are the five D orbitals mixing in with the S orbital. Unfortunately, due to the heavy contribution of the p orbitals on the sulfur atoms in the BDT ligands, $[Ag_{29}BDT_{12}]^{3-}$ does not show any superatomic P nature in the occupied MOs. In $[Ag_{28}NiBDT_{12}]^{4-}$, however, while there is a lot of electronic density of the sulfur atoms, the contribution from the d orbitals in Ni collectively come together with the sp orbitals on the Ag core atoms to create a supermolecular P orbital in the HOMO (H), H-1 and H-2 that is not observed in the parent cluster at this level of theory. The HOMO-LUMO (H-L) gaps in $[Ag_{29}BDT_{12}]^{3-}$ and $[Ag_{28}NiBDT_{12}]^{4-}$ are 1.48 eV and 1.62 eV respectively, and the gap between

the highest energy D orbital to the next set virtual molecular orbitals (LUMO+5-LUMO+6) is 0.99 eV and 0.84 eV respectively. In $[Ag_{28}NiBDT_{12}]^{4-}$, the L and L+1 are low energy 4-lobed D orbitals, the L+2 is a low-energy S, L+3 is the D_z^2 orbital, and the L+4, L+5 orbitals are the other high energy 4-lobed D orbitals. This is different from the parent cluster in which the L+2 is the D_z^2 orbital and L+3 is the S orbital. Further, the D orbitals split into a doubly degenerate and triply degenerate set in the parent cluster, but this is not seen with the Ni dopant due to the slight break in symmetry of the core. As briefly mentioned, the atomic contributions to the occupied frontier orbital are quite different between the two clusters. Atomic p contributions from the sulfur and carbon atoms are dominant in both clusters, however, the d orbitals on Ni atoms help stabilize the occupied MOs and hence there is more mixing between the ligands and the superatomic core with the Ni dopant. Additionally, there is a contribution of Ni that mixes into the superatomic virtual orbitals; however, the mixing is very minimal and the major contributions to these superatomic orbitals are the sp orbitals on the Ag core atoms. The lower energy occupied, and higher energy virtual orbitals form almost a manifold of states with very small energetic gaps between states. This creates more of a band-like structure in which several states have similar atomic character contributing to nearly degenerate molecular orbitals.

7.5 - Optical Properties

The theoretical absorption spectrum of $[Ag_{28}NiBDT_{12}]^{4-}$ matches the experimental spectrum shape very well with peaks at 482 nm (2.57 eV), 424 nm (2.92 eV) and 312 nm (3.97 eV) as shown in figure E-4. In both the parent and doped cluster, there are a lot of single vertical excitations mixing into all the peaks. This is due to the small energy gaps between molecular orbitals. In the lower energy region, the absorption spectrum has a very broad weak peak across 1.5-2.5 eV as seen in figure E-5(A). The first dominant peak is made up of several vertical excitations; the one with the highest oscillator strength is at 2.57 eV with a value of 2.85×10^{-2} a.u. as documented in tables E-3 and E-4. This excitation is dominated by a transition from H-32 to L+1, or an interband transition from a molecular orbital containing large contributions on the p atomic orbitals on sulfur transitioning to a superatomic D orbital created from a collective contribution from sp orbitals on Ag atoms in the core. The dominant transition that makes up the second peak at 2.92 eV is incredibly similar to the lower energy transition. The H-36 molecular orbital is primarily made up of p atomic contributions coming from the sulfur atoms in the ligands. This orbital transitions into a superatomic D orbital in the core of the nanocluster. As the electronic density in the occupied and virtual orbitals involved in both transitions do not overlap, there is ligand to metal charge transfer character as shown in figure 7.2. DFT methodology does not model charge transfer well at this level of theory as the exchange-correlation functional chosen is too local in nature. Due to this, a long-range corrected exchange-correlation functional (LRCF) was used to try to model these excitations better. As shown in figure E-5(B), the results with the LRCF still have a large number of vertical excitations mixing underneath the peaks, and therefore, the change of functional does not improve the charge transfer behavior observed in the cluster. The peaks in the doped and parent cluster absorb in the same part of the visible region between 2.5 - 3.5 eV. $[Ag_{28}NiBDT_{12}]^{4-}$ has three peaks, the parent cluster has two main peaks and a very small high energy shoulder. The two peaks are at 2.49 eV and 2.85 eV in the parent cluster also have ligand to metal charge transfer character from an interband transition between the p orbitals on the sulfur atoms in the ligands, to a superatomic D orbital in the core of the cluster. This means that even though there is superatomic P nature with the Ni dopant, it does not change the behavior in the main absorption peak as the transitions do not originate from the occupied frontier orbitals.



Figure 7.2. (A) Atomic orbital contribution in selected Kohn-Sham molecular orbitals at the BP86-D3/DZP level of theory for $[Ag_{28}NiBDT_{12}]^{4-}$ (B) Molecular orbitals that make up the dominant transition in the first two peaks of the theoretical absorption spectrum at the BP86-D3/DZP level of theory for $[Ag_{28}NiBDT_{12}]^{4-}$ (contour = 0.0135).

7.6 - Photoluminescent Properties

Both $[Ag_{28}NiBDT_{12}]^{4-}$ and $[Ag_{29}BDT_{12}]^{3-}$ underestimate the experimentally observed emission energy of 1.90 eV (653 nm). The theoretical emission energies from the S₁ state are at 1.18 eV and 1.08 eV for the dopant and parent cluster respectively, with roughly the same radiative lifetime value of 12.65 µs. The theoretical emission from the T₁ state is higher than S₁ state in $[Ag_{28}NiBDT_{12}]^{4-}$ with a value of 1.36 eV. Both the parent cluster and the doped cluster change in the same way both geometrically and electronically upon excitation. The Ag shell – Ag core and Ag shell – Ag shell average bond distances get smaller, the Ag core - S motif average bond distances get larger, and the other bond distances do not change by a notable amount as seen in table E-5. Electronically, the HOMO gains 0.16 eV in energy upon excitation and the LUMO decreases by ~0.30 eV as seen in figure E-6. Both clusters shown ligand to metal charge transfer character in the electronic transitions; however, emission from the S₁ state originates from a dominant HOMO \rightarrow LUMO transition in both clusters. This hints that the PL mechanism would be slightly different between the two clusters if emission originates from the S₁ state. As discussed above, the Ni dopant has superatomic P nature in the HOMO in addition to the large p contribution from the sulfur atoms, whereas the parent cluster has no contribution from the core in the HOMO orbital. If emission does happen from this state, it is likely that the parent cluster will show ligand to metal charge transfer mechanism, while the Ni dopant would show core-based emission.

7.7 - Ni, Pt, Au, Cu Dopants

Considering the distinct differences between the parent cluster and the Ni dopant in the electronic structure, optical absorption spectrum, and first electronically excited state, it is important to analyze other dopants and find trends. Monodopants Pt, Au and Cu are analyzed in addition to Ni and compared with the parent cluster. To properly model these clusters, the first step was to find the most stable dopant position in the ground electronic state. In a similar way to the Ni dopant, Au was examined in the center, core, 'tri' shell and 'tetra' shell positions. Cu and Pt have been studied experimentally and it has been shown that Pt prefers the center position²⁵⁻²⁶ and Cu prefers a position in the shell.²⁷ Pt was therefore evaluated in the center position, and Cu was analyzed in the core, 'tri' shell and 'tetra' shell positions to determine the preferred position. All in all, Ni, Au and Pt prefer the center position of the core and Cu prefers the 'tetra' position in the shell of the nanocluster; the relative energies at the BP86-D3/DZP level of theory can be seen in table E-6. In the optimized ground state structure, the X center – Ag core bonds and Ag core – Ag core bonds are much smaller than the Ag center – Ag core and Ag core – Ag core bonds observed in the parent cluster in all the doped clusters, even where the dopant is not in the center position. This means that the addition of a monodopant into this cluster will result in a

smaller icosahedral core regardless of the dopant chosen. With the Au dopant, both the Ag shell – Ag core 'tri' and 'tetra' bonds get larger than the parent cluster, and the opposite happens with the Cu dopant. In Ni and Pt, the 'tri' bonds get much larger, but the 'tetra' bonds get smaller. The overall size of the ligand shell has negligible changes with the different dopants, showing that the dopant changes the core but not the overall structure. The average bond distances in the ground state are shown in table E-7 and E-8.

All clusters have a superatomic electron count of 8 leading to a S²P⁶ configuration. The only clusters that collectively form three occupied superatomic P orbitals in the core, however, are the Ni and Pt dopants. In these cases, there is still a large contribution from the p orbitals on the sulfur atoms, but the atomic d contribution from the dopant that is simultaneously mixing with the Ag to form the P orbitals in the HOMO, HOMO-1 and HOMO-2. The parent cluster, Au dopant and Cu dopant have hardly any contribution in the core of the icosahedron, and the occupied frontier orbitals are dominated by atomic p orbitals on the sulfur atoms. The virtual frontier orbitals in all clusters are core dominated with D-like superatomic orbitals mixing in with an energetically lowered S orbital. The splitting of the D orbitals as well as the molecular orbital responsible for the superatomic S is different between clusters. Further, the atomic contributions to these orbitals are slightly different as seen in figure E-7. There is hardly any contribution from the Au and Cu dopants in the frontier orbitals, which is different from Ni and Pt dopants which have very large contributions from the dopant integrating into the frontier orbitals. Ni and Pt have the largest HOMO-LUMO gaps at 1.62 eV and 1.68 eV respectively, but the smallest energetic gap between the L+5 and L+6 orbitals at 0.84 eV and 0.59 eV respectively. The Au dopant has essentially the same HOMO-LUMO gap to the parent cluster at 1.48 eV, and the Cu dopant has a HOMO-LUMO gap of 1.41 eV. The energetic gap between the

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L+5 and L+6 orbitals are very similar in Cu and Ag at 0.99 eV, while the Au dopant has a slightly smaller gap of 0.85 eV between the L+5 and L+6 orbitals. The difference in the electronic density between the different dopants in the HOMO and LUMO molecular orbitals can be seen in figure 7.3. There is a difference between the transition metals that have an open d shell and those that do not. Further down the row of the periodic table, the HOMO-LUMO gap increases. It is worth noting that the LUMO is a 4-lobed D orbital in the parent cluster, Ni doped and Cu doped clusters, a Dz^2 type orbital in the Au doped cluster, and an S orbital in the Pt doped cluster.



Figure 7.3. HOMO-LUMO gaps (in eV) from the optimized ground state geometry at the BP86-D3/DZP level of theory where the electronic density of the HOMO is shown at the bottom of the graph, and the LUMO is shown at the top of the graph for each doped cluster and the parent cluster.

Optically, all the clusters absorb light between 2.0-3.5 eV as seen in figure E-8. Similar to the Ni dopant, the Pt dopant has three strong peaks opposed to just two in Au, Cu and the parent cluster. Unlike the Ni dopant where the three peaks are all within 1 eV interval, Pt spaces out the three peaks across the entire spectrum. All clusters have large mixing of vertical excitation energies under the peaks. The vertical excitation with the highest oscillator strength in the first peak happens around 2.5 eV in every cluster except Pt in which there is a lower energy shoulder at 2.36 eV before the first dominant peak at 2.81 eV. All the clusters, regardless of dopant choice, have a dominant transition that has ligand to metal charge transfer character in the first two peaks which is comprised of an orbital primarily dominated by the p orbitals on the sulfur atoms transitioning into a superatomic D orbital in the core of the nanocluster. Despite the observed P orbitals in Ni and Pt, the electronics do not change much in the transitions of the main peaks as the occupied P orbitals are not involved in the electronic transitions in the doped and parent clusters. The optical data at this level of theory can be seen in tables E-9 and E-10. Unfortunately, even with a long range corrected functional, the energy levels involved in the transitions form almost a manifold of states rather than the more discrete electronic state structure in all clusters. It is important to note that the while the long range corrected functional strives to account for long range exchange interaction between electrons, this functional could be altered further to include more global exact Hartree-Fock exchange which may improve the theoretical results. Unfortunately, adding exact Hartree-Fock exchange adds additional computational cost to the already expensive excited state optimizations.

The emission energy and radiative lifetime value from the optimized S_1 state for each doped cluster at the BP86-D3/DZP level of theory is shown in table E-11. All doped clusters underestimate the experimental emission energy just like the parent cluster. This could be an

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artifact of using DFT due to the charge transfer character in all the clusters. The largest emission energy is in the Pt doped cluster, followed by Ni, Au, Ag, and Cu clusters with values of 1.23 eV, 1.18 eV, 1.11 eV, 1.08 eV and 1.06 eV respectively. The differences between the optimized S_1 geometry and the ground state geometry are below 0.05 Å except in the Ag core – Ag shell 'tri' bonds in the Pt doped cluster in which the average bonds get 0.06 Å smaller upon excitation. In every doped cluster, the S₁ state has smaller average Ag shell – Ag core bonds (both 'tri' and 'tetra'), Ag shell – Ag shell bonds, and S crown – S crown bonds. Further, the Ag core – S motif average bond distances get larger, and the X center- Ag core, Ag core – Ag core, Ag shell – S crown, S crown - S motif bond distances do not change upon excitation. The average bond distances in the optimized S_0 and S_1 state can be seen in tables E-12 and E-13. In all the doped clusters, the HOMO-LUMO gaps get smaller as seen in figure E-9. All clusters show ligand to metal charge transfer in the HOMO \rightarrow LUMO transition. In the Ni and Pt doped clusters, the superatomic P nature that was in the frontier orbitals of the optimized ground state change to frontier orbitals that are completely dependent upon the contribution from the s and p orbitals in the sulfur and carbon atoms. This means that despite having superatomic P nature in the ground state upon excited state optimization, the superatomic nature is lost. The emission mechanism is therefore similar in all clusters, which is dominated by a charge transfer mechanism from the ligands into the core of the Ag cluster.

7.8 – Conclusion

In summary, this chapter studied the geometric and electronic structure, optical and photoluminescent properties of Ni doped Ag_{29} nanoclusters from a theoretical perspective, and compared them to the parent cluster, as well as other transition metal dopants such as Au, Cu, and Pt. It was found that in Pt and Ni, the open atomic d orbital contribution from the dopant aids in creating superatomic P-like HOMO – HOMO-2 molecular orbitals. Regardless of the dopant chosen, the icosahedral core gets smaller, and the cluster has a dominant transition with ligand to metal charge transfer character in the first two absorption peaks. Pt has the highest S_1 emission energy, followed by Ni, Au, and Cu. Unfortunately, however, emission from the S_1 state in all dopants underestimates the experimental emission energy. In the Ni and Pt doped clusters, the superatomic P nature in the is lost upon S_1 optimization. The emission mechanism is therefore similar in all clusters, which is likely a result of ligand to metal charge transfer.

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Chapter 8 - Deciphering the Dual Emission in the Photoluminescence of Au₁₄Cd(SR)₁₂: A Theoretical Study using TDDFT and TDDFT+TB

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8.1 – Abstract

Determining excited state processes for small nanoclusters (NCs), specifically gold, aids in our ability to fine-tune luminescent materials and optical devices. Using TDDFT and TDDFT+TB, a detailed theoretical explanation for the dual emission peaks displayed in Au₁₄Cd(S-Adm)₁₂ (Adm = Adamantane) is presented. As dual emission is relatively rare, we decipher whether the mechanism originates from two different excited states, or from two different minima on the same excited state surface. This unique mechanism, which proposes that the dual emission results from two minima on the first excited state, stems from geometrical changes in the bi-tetrahedron core during the emission process.

8.2 – Introduction

Understanding photoactive biomolecules, large nanoparticles (NPs) and photoluminescent (PL) species has important applications ranging from solar energy conversion to biosensing.¹⁻⁵ In particular, heavy atom transition metals, such as gold, have garnered attention in the physical chemistry community due to the nanoclusters' (NCs) ability to be efficient, selective and easily tuned.⁶⁻⁹ These NCs also show enhanced PL properties¹⁰⁻¹¹ which give unique mechanisms and thereby a deeper understanding into functional materials. Several gold

NCs have been synthesized in the past decade providing pathways to tune the emission for extensive physical applications. Specific emission can be tuned by changing the particle size, surface ligands and valence states for NCs.¹² Specific examples of tuning photoluminescent properties with surface ligands can be seen through the work of Hui et al. where they discovered that PL enhancement is governed by the formation of smaller Au species etched by thiol groups in AuCyt (Cyt = Cytidine), which is usually quenched due to the close adsorption of the thiol groups to the surface of the gold NC.¹³ Wu et al. further studied the effect of surface ligands in thiolate-protected gold NCs and found out that longer Au^I-SR motifs can be used to sustain a strong aggregation induced emission pathway, while shorter Au^I-SR motifs lead to a larger Au⁰ core allowing the fluorescence from the core of the NC to dominate the PL mechanism.¹⁴ Many groups have also successfully doped their nanoclusters with Cd as a way to tailor the chemical and physical properties such as photoluminescence and surface flexibility.¹⁵⁻¹⁷ Cd doping has been shown to lead to unique mechanisms; for example, Au₂₄Cd(SC₂H₄Ph)₁₈ undergoes a S_{N1}like ligand exchange mechanism due to its stability.¹⁸ Further, it has been shown that by introducing a Cd–Br bond on the surface of gold NCs, large dipole moments can be achieved.¹⁹

In 2013, Jiang et al. used DFT to predict the geometry of the smallest stable thiolatestabilized gold nanocluster, $Au_{15}(SR)_{13}$, for the experimentally observed $Au_{15}(SG)_{13}$ (SG = glutathionate) system.²⁰ This Au_{15} thiolate-protected NC and its derivatives have since been synthesized and studied rigorously; however, due to the flexibility of the SG ligand, it is difficult to obtain the crystal structure.²¹ In 2018, Yang et al. tried to obtain the crystal structure of $Au_{15}(SR)_{13}$ via two routes: (1) direct ligand exchange of $Au_{15}(SG)_{13}$, and (2) Cd doping of $[Au_{15}(SG)_{12}]^{-}$. Through the latter method, $Au_{14}Cd(S-Adm)_{12}$ (Adm = Adamantane) was found and classified through single crystal X-ray diffraction.²¹ $Au_{14}Cd(S-Adm)_{12}$ has a Au_5Cd bitetrahedron core with one shared Au-Cd 'bridging' bond, two tetrameric Au₄S₅ staple motifs and one AuS₂ motif connected to the core. The framework of the tetrameric motifs (figure 8.1 (c)) gives the NC a boxed four-quadrant appearance from two tetrahedrons sharing an edge, while the AuS₂ motif (figure 8.1 (d)) caps the core of the NC. Further experimental investigation from Li et al. showed that this NC exhibits rare dual emission behavior, which they attributed to a predicted 'restrained'-type distortion in the core due to one tetrahedron growing/folding up and the other shrinking/folding down upon relaxation.²² While the experiments hypothesize a photoinduced structural distortion and electronic redistribution, the exact geometric differences and origin of electronic states are unknown. Herein, we directly suggest a PL mechanism for this Au₁₄Cd thiolate-protected NC by exploring the excited state potential energy surfaces from a theoretical perspective.



Figure 8.1. Crystal structure of Au₁₄Cd NC. Reprinted with permission from *J. Am. Chem. Soc.* 2018, 140 (35), 10988-10994. Copyright 2018 American Chemical Society. (a) Thiolateprotected framework; (b) Au₅Cd bi-tetrahedron core; (c) Two Au₄S₅ tetrameric motifs (i) connected to core; (d) AuS₂ staple motif (ii) capping the core. The gold atoms are blue, sulfur atoms are red, and the Cd atom is orange. No carbon or hydrogen atoms are shown.

8.3 – Computational Details

All calculations were done using the Amsterdam Density Functional (ADF) 2018.105 package.²³ The crystal structure from Yang et al.²¹ was used as an initial input structure for the geometry optimization of $Au_{14}Cd(S-Adm)_{12}$. $Au_{14}Cd(SR)_{12}$ NCs with R = H and CH_3 were also created by editing the ligands in the crystal structure using the MacMolPlt visualization tool.²⁴ All geometry optimizations (ground and excited state) were calculated with the local density approximation (LDA) X α exchange-correlation functional²⁵ and a double zeta (DZ) basis set.²⁶ All structures were optimized in the gas phase. Scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).²⁷⁻²⁸ The energy and gradient convergence criteria were tightened to 1×10^{-4} and 1×10^{-3} Hartree respectively for geometric accuracy in closed shell calculations, and the gradient convergence criteria was loosened to $2x10^{-3}$ Hartree for open shell calculations. After the initial ground state geometry optimization, a linear response time-dependent density functional theory plus tight binding²⁹ (TDDFT+TB) calculation was run to obtain vertical excitation energies, which were then convolved into the optical absorption spectrum with a Gaussian fit and a 0.20 eV full width half maximum (FWHM). Similar results were obtained through TDDFT³⁰ as a comparison for excited state methodology. Further details about TDDFT+TB are provided in the supporting information. After obtaining the ground state structure and absorption spectrum, TDDFT analytical excited state gradients³¹ were used to optimize the minimum energy structures of the excited states.

8.4 – Results and Discussion

An important component of excited state potential energy surface (PES) exploration is finding a level of theory that accurately represents the system, while trying to save computational cost. In this work, it is first considered whether model ligands are reasonable substitutes for the
full S-Adm ligand. In some situations, optical spectra have been found to be similar regardless of ligand;³²⁻³⁴ in other cases, large optical changes between different ligands can be expected as small gold NCs are more sensitive to the length of the S-Au-S staple motifs.³⁵ Using the crystal structure from Yang et al.,²¹ two model ligands were created by replacing adamantane with hydrogen and methyl groups, respectively. As demonstrated in figure 8.2, the absorption spectrum is highly dependent on the ligand. Thus, the full S-Adm ligand was used for further computational study.



Figure 8.2. Theoretical absorption spectrum of Au₁₄Cd(SR)₁₂ NCs where R = H (blue dotted), CH₃ (orange dashed) and S-Adm (green solid) with the X α /DZ level of theory.

Au₁₄Cd(S-Adm)₁₂ is a chiral compound with C₂ symmetry; the C₂ axis runs through the gold atom in the AuS₂ motif that caps the core. The ground and excited state structures of Au₁₄Cd(S-Adm)₁₂ were studied for the two enantiomers that differ in the positions of the Au and Cd atoms in the Au-Cd 'bridging' bond in the bi-tetrahedron core. Both enantiomers are examined because they are present experimentally and the crystal structure reveals that the Au-Cd 'bridging' bond possesses 50% partial occupancy of both atoms;²¹ as expected, both enantiomers yield the same linear optical absorption and emission properties as shown in the supplementary material (figures F-2-F-4 and table F-1). Figure 8.3 shows the molecular structure

of both $Au_{14}Cd(S-Adm)_{12}$ enantiomers and illustrates the atom switch in the core. As seen in Figure 8.3, the optimized ground state structures of both isomers are similar to the crystal structure with 12 Adm ligands providing structural rigidity around the shell, a Au₅Cd bitetrahedron core with a one shared 'bridging' bond, two tetrameric Au₄S₅ staple motifs and one AuS₂ motif connected to the Au/Cd core. The average bond distances of the optimized ground state structure (S₀) at the X α /DZ level of theory can be seen in table 8.1, where the atom definitions are illustrated in figure 8.4. It is important to note that LDA functionals are not the greatest for excited state energies.³⁶⁻³⁷ However, LDA functionals are good for geometric parameters, such as bond lengths.³⁸ Au-Au bond lengths, in particular, have been shown to match well with experiment;³⁹ for example, the average Au-Au distance from central atom to shell is 2.784 Å at the X α /DZ level of theory, which is very close to the experimental value of 2.782 Å in [Au₂₅(SH)₁₈]^{-,40} This average distance obtained from theory is only 0.86% larger than the Au-Au bond distances between the core atoms of Au₁₄Cd(S-Adm)₁₂, which is 2.760 ± 0.076 Å. As an additional point of comparison, compared to the Au-Au distance of 2.88 Å in bulk gold,⁴¹ the Au-Au core distances in Au₁₄Cd(S-Adm)₁₂ are 4.2% shorter. The average Au-Cd bond distance between atoms in the core is 2.833 ± 0.063 Å. The Au-Cd distances in this NC are 1.7% shorter than the Au-Cd distance of 2.88 Å calculated by the relationship between dopant-Au bond length and metallic radii.⁴² The M-M bonds (M = Au/Cd) provided in the core of the crystal structure are 2.856 Å on average.²¹ The combined average between Au-Cd and Au-Au bonds with theory underestimates this length by 2.2% with an average value of 2.793 ± 0.074 Å.



Figure 8.3. Optimized ground state geometric structures for the Au₁₄Cd(S-Adm)₁₂ enantiomers. The gold, cadmium, sulfur, carbon, and hydrogen atoms are green, orange, red, black, and white respectively. (A) The entire 327-atom nanocluster with the full S-Adm ligand. (B) The Au₄Cd core with one shared 'bridging' bond between the separate tetrahedrons. (C) Tetrameric framework originating from the Au atoms and thiolateprotected shell.



Figure 8.4. Atom definitions for table 8.1.

Table 8.1. The average bond lengths of the ground state geometry at the X α /DZ level of theory.

Average Bond Length (Å)				
Bond	So			
Au core - Au core	2.760 ± 0.076			
Au shell - Au shell	2.941 ± 0.101			
Au core - Cd core	2.833 ± 0.063			
Au shell - S terminal	2.469 ± 0.021			
Cd core - S terminal	2.530 ± 0.000			
Au shell - S staple	2.401 ± 0.035			
S staple - S staple	4.739 ± 0.037			

Au₁₄Cd(S-Adm)₁₂ has a HOMO (H)-LUMO (L) gap of 1.48 eV (figure F-5). Upon excitation, the absorption spectrum of the NC exhibits a strong S₁ state that is dominated by the H-L transition, and no other singlet-singlet excitations are present near the energy of the main peak. The molecular orbitals show a superatomic P to D transition in the core of the NC (figure 8.5A) from the 1.59 eV peak with an oscillator strength of 0.0387; there is also a shoulder that occurs at 2.15 eV. The experimentally observed peak is seen at 2.25 eV (550 nm) with a slight shoulder at 2.95 eV (420 nm).²² The shape resulting from the convolution of the vertical excitation energies from theory is quite comparable to the experimental absorption spectrum despite the ~0.7 eV underestimation. This underestimation in energy is an expected result for LDA exchange-correlation functionals.⁴³



Figure 8.5. (A) HOMO and LUMO molecular orbitals from the X α /DZ level of theory. The HOMO forms a superatomic P shape in the core and the LUMO forms a superatomic D_z^2 shape in the core. Additional views of the HOMO and LUMO are provided in Figure F-6. (B) Theoretical absorption spectrum obtained from TDDFT+TB using the X α /DZ level of theory (a comparison between TDDFT+TB and TDDFT spectra is shown in Figure F-1). (C) Experimental absorption spectrum (data adapted with permission from Nat. Commun. 11 2897 (2020).

The PL mechanism can further be pieced together by looking at the theoretical emission energies. Exploration of the first excited state potential energy surface shows that the dual emission results from two different minima (which we call S_1 and S_1 ') on the first electronically excited state. The first minimum point, S_1 , was obtained by a geometry optimization of the S_1 state starting from the S_0 optimized geometry. This point has an emission energy of 1.09 eV. The second minimum point, S_1 ', was obtained by starting the geometry optimization of the S_1 state from a converged point on the S_2 PES (resulting from an S_2 optimization) as illustrated in figure 8.5A. S₁ is 0.29 eV lower in energy than S₁', and both minima originate from the transitions from the P \rightarrow D superatomic orbitals due to the prominent HOMO-LUMO excitation in the core. The initial input geometry was chosen differently to see if the same minimum point on the S₁ surface would be obtained. As the optimization did not result in the same minimum point, it can be concluded that the S₁ state has at least two different minimum points. The emission energy at this point (S₁') is 0.86 eV which is 0.23 eV lower than the emission energy from S₁ (figure 8.6B). This energy gap is essentially the same as the 0.24 eV gap that was observed between the dual emission peaks in the experimental spectrum;²² hence, it can be concluded the dual emission is a result of these two points on the S₁ surface. The theoretical Stokes shifts are 0.50 eV and 0.73 eV for S₁ and S₁', respectively. This only slightly underestimates the experimental Stokes shifts of 0.64 and 0.87 eV.²² This underestimation is likely an artifact of the functional used but may also be attributed to experimental factors such as solvent effects, counter ions, or intermolecular interactions. Some of these factors may be examined theoretically using solvent corrections or running dynamics; however, that is outside the scope of this current work.



Figure 8.6. (A) Proposed scheme of the origin of the dual emission (ems) peaks in Au₁₄Cd(S-Adm)₁₂. (B) Graphical image of the excitation/relaxation process in the first enantiomer of Au₁₄Cd(S-Adm)₁₂. The first emissive point occurs at 1.09 eV with a radiative lifetime of 1.00 µs and the second emissive point occurs at 0.86 eV with a radiative lifetime of 3.71 µs.

The average bond lengths are reported in table 8.2 for the ground state (S₀), first emissive geometry (S₁) and second emissive geometry (S₁'). The placement of the mono-dopant, Cd, in the core is involved in the PL mechanism as the Au-Cd bridging bond guides the structural change responsible for the second emissive peak. Excitation to S₁ from the S₀ state leads to a large change in the core where the Au-Cd bond grows up to 0.16 Å. This bond continues to enlarge by more than 0.1 Å upon conversion from the S₁ to S₁' minima as seen in figure 8.7. The same restrained type of behavior that was predicted between the emission peaks experimentally is seen with theory; however, the core shape changes very little overall as the average Au-Au bond lengths in the core only vary by 0.007 Å as seen in table 8.2. In addition, the Cd placement distorts the terminal bond on the tetrametric motif structure, giving large structural differences in the S-Au-S staple bonds. The length of the S-S staple that defines the motif structure becomes

larger upon excitation from $S_0 \rightarrow S_1$ by 0.017 Å and shorter upon the conversion from $S_1 \rightarrow S_1$ ' by 0.057 Å.

There are additional differences between the two minima. Between S_1 and S_1 ', the HOMO level increases in energy from -4.14 eV to -4.07 eV and the LUMO level decreases in energy from -3.15 eV to -3.28 eV (figure F-5). This decreases the HOMO-LUMO gap from 0.99 eV to 0.79 eV for the conversion from S_1 to S_1 '. The orbitals themselves also look different. The HOMO and LUMO orbitals are essentially identical for S_0 and S_1 , but upon conversion, the S_1 ' HOMO orbital differs. The S_1 HOMO has primarily superatomic P nature, while the HOMO from S_1 ' does not have a superatomic nature, and instead the major contributor to this orbital is the d atomic orbitals from the gold atoms. The LUMO orbitals are much more similar, with large s contributions from Cd, sp contributions from gold, and p contributions from the sulfur atoms.



Figure 8.7. Bond changes during excitation or conversion. The blue/pink solid lines represent the specific bond enlarging, while the red/orange dotted lines represent the specific bond shortening.

Table 8.2. Average bond lengths of the ground state and both emissive geometries in $Au_{14}Cd(S-Adm)_{12}$ at the X α /DZ level of theory.

Average Bond Length (Å)					
Bond	So	S_1	S ₁ '		
Au core - Au core	2.760 ± 0.076	2.753 ± 0.089	2.780 ± 0.098		
Au shell - Au shell	2.941 ± 0.101	2.901 ± 0.079	2.855 ± 0.102		
Au core - Cd core	2.833 ± 0.063	2.896 ± 0.109	2.949 ± 0.147		
Au shell - S terminal	2.469 ± 0.021	2.471 ± 0.016	2.514 ± 0.069		
Cd core - S terminal	2.530 ± 0.000	2.592 ± 0.000	2.594 ± 0.000		
Au shell - S staple	2.401 ± 0.035	2.414 ± 0.040	2.429 ± 0.048		
S staple - S staple	4.739 ± 0.037	4.756 ± 0.024	4.710 ± 0.081		

The radiative lifetimes of S_1 and S_1 ' are found to be 1.00 µs and 3.71 µs, respectively. The theoretical radiative lifetime of the two emissive minima are calculated using equation 8.4.1 by the ADF program²

$$\frac{1}{\tau} = \frac{4}{3t_0} a_0^3 (\Delta E)^3 \sum_{\alpha \in (x, y, z)} |M_{\alpha}|^2$$
(8.4.1)

where τ is the radiative lifetime, α_0 is the fine structure constant, ΔE is the vertical excitation energy, and M_{α} is the transition dipole moment in the $\alpha = x, y, z$ direction. The experiments find a dominant lifetime decay of 334 ps from the second emissive peak but are not able to distinctly fit the decay of the first emissive peak due to the overlap of the two excited-state absorptions.²² The theoretical radiative lifetime value does not account for nonradiative transitions and dynamics between the emission peaks; hence, it cannot be directly compared to the experimental results. It can be concluded that the S₁'s minimum emits with a longer lifetime than the S₁ and both S₁ structures are predicted to have microsecond radiative lifetimes.

8.5 – Conclusion

The photoluminescent mechanism for $Au_{14}Cd(S-Adm)_{12}$ was analyzed using TDDFT gradients. The results show that dual emission is present and originates from two minimum

points on the first electronically excited state, emitting 0.23 eV apart. The first emissive point was accessed via excitation to the S₁ state from the optimized ground state geometry, while the second emissive point was accessed via excitation to the S₂ state, followed by additional relaxation from the S₂ to the S₁. The average geometric differences between the minimum structures are quite large, which is a result from the Au-Cd 'bridging' bond enlarging more than 0.10 Å upon both excitation to the S₁ state (from S₀) and conversion to the S₁' minimum (as measured from S₁). Both S₁ and S₁' originate from the P \rightarrow D superatomic orbitals due to the prominent HOMO-LUMO excitation in the core, however, as the HOMO changes between the two states after optimization, the PL mechanism does not entirely arise from emission between core-based orbitals. Both lifetimes are predicted to lie in the microsecond timescale, which are long lifetimes for a singlet state. As dual emission is relatively rare, this paper serves as a theoretical basis for understanding the dual emission phenomenon in small emissive gold nanoclusters.

8.6 – Acknowledgements

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Chapter 9 - Understanding the Ligand-Dependent Photoluminescent Mechanism in Small Alkynyl Protected Gold Nanoclusters

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9.1 – Abstract

Alkynyl-protected gold clusters have recently gained attention because they have shown to be more structurally versatile compared to their thiolate-protected counterparts. Despite their flexibility, a higher PLQY has been observed experimentally compared to that of organic soluble thiolate-protected clusters. Experiments further concluded through spectral similarity that changing the R group in these clusters does not affect the geometric or electronic properties of the core. This paper serves as a follow-up to those experiments in which the geometric, optical, and PL properties for $Au_{22}(ETP)_{18}$ are pieced together to find the photoluminescent mechanism. These properties are then compared between $Au_{22}(C \equiv CR)_{18}$ clusters where the ligand is changed from R = ETP to PA and ET respectively (ETP = 3-ethynylthiophene, PA = phenylacetylene, ET = 3-ethynyltoluene, EA = 3-ethynylanisole). The results show that with the ETP ligand, there is ligand to metal-to-metal charge transfer (LMMCT), while PA and ET are likely a result of core dominated fluorescence. The changes are result of the Au(I) ring atoms as well as how the aromatic groups are connected to the cluster. The results do not reproduce experimental results and hence this paper also presents a supplementary benchmark of these properties between ligands for different levels of theory. Dispersion, solvent, and polarization functions in the basis set are all important to creating an accurate chemical environment, but the most useful tool in these calculations is using a long range corrected exchange-correlation functional.

9.2 – Introduction

With incredible stability,¹ simplistic synthesis,² and multiple surface functionalities,³ gold proves to be one of the most versatile and useful transition metals. Atomically precise gold nanoclusters (NCs) in particular can create enhanced activity as a catalyst,⁴ work to kill cancer cells through processes like photodynamic therapy,⁵ and act as electrochemical sensors.⁶ One promising property of gold is that some clusters have an increased photoluminescent quantum yield (PLQY) based on a ligand exchange or by changing the size of the particle.⁷⁻⁹ As gold nanoclusters have tunable structure-property relationships, examination of the photoluminescent properties opens a door to being able to tune the PLQY via changes in the size, geometry, charge state, dopant, ligands, etc.. This creates an extended array of applications from bioimaging and biosensing,¹⁰⁻¹¹ to electronics,¹²⁻¹³ and many more. Specifically, gold nanoclusters are advantageous for material applications in respect to the optical and geometric trends they share between ligands. This is why the NCs are usually classified by their ligand type (thiolate, alkynyl, phosphine, etc.) as there are reasonable assumptions that one can make based on the patterns shown with different cluster sizes of the same ligand type. To this end, clusters with the same core sizes also share patterns, and have actually been known to share geometric and optical properties between different ligand types.¹⁴ However, with smaller clusters it can be expected that the properties are more susceptible to change as the ligand shell is smaller.¹⁵

Alkynyl protected gold NCs have attracted the physical chemistry community since their first appearance by Maity et al. in 2011.¹⁶ Similar to thiolate-protected clusters, most alkynyl protected clusters are composed of a neutral gold core surrounded by interactions with Au(I)-R staples or oligomers.¹⁶⁻¹⁸ Alkynyl protected clusters further have the ability to couple the electronic structure of the R group through π -Au- π units. These units allow the motifs to twist

around each other depending on the preferred orientation of the aromatic ligands.¹⁹⁻²⁰ The ability to twist means that these type of clusters possess more diversity in the oligomers compared to their thiolate-protected counterparts. One might think that this flexibility would actually quench the PLQY due to the reduced rigidity of the ligands in the gold shell.²¹ Clusters such as Au₂₂(SG)₁₈, for example, show a PLQY of over 60% when the ligands are rigidified in the gold shell with tetraoctylammonium cations.²² However, in clusters such as Au₂₂(tBuC=C)₁₈, a large PLQY can still be achieved.²³ In fact, the experimental PLQY of Au₂₂(C=CR)₁₈ clusters are larger than those of organic-soluble thiolate-protected clusters.²⁴ As alkynyl-protected gold clusters have not been studied as prominently as their thiolated counterparts and very few structures have been structurally determined,²⁰ it is imperative to understand their optical and PL properties for the continued study of tunable nanomaterials.

In a recent paper by Ito et al., the authors outline how the interfacial structure of the terminal alkynyls influence the optical and PL properties with different R groups in $Au_{22}(C=CR)_{18}$.²⁴ Their work showed that the electronic and geometric structure in the ground state does not change with the R group; however, differences in PL properties arise from geometric changes in the first photoexcited state, thus leading to changes in the PLQY. This is an incredible result as differences in radiative and nonradiative PL mechanisms usually come from an altered electronic ground state that originates from geometric differences in the NC due to different ligands.²¹ Even with the same ligand, gold nanoclusters have shown to exhibit different optical and PL properties depending on the isomerization of the cluster.²⁵

In this paper, a theoretical insight into $Au_{22}(C \equiv CR)_{18}$ clusters will be analyzed by looking at the ground state, optical and PL properties of $Au_{22}(ETP)_{18}$ (ETP = 3-ethynylthiophene). The adaptation of these properties with respect to changing the ligand from ETP to PA (PA =

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phenylacetylene) and ET (ET = 3-ethynyltoluene) will be discussed after, and a final benchmark of the theoretical results will be examined last.

9.3 – Computational Details

All calculations were completed with the Amsterdam Density Functional (ADF) 2018.105 package.²⁶ The initial input geometry used for ground state geometry optimizations was the crystal structure of ETP.²⁴ The crystal structures for PA and ET were not crystalized, however, the clusters were verified by ¹H NMR spectroscopy and matrix-assisted laser desorption ionization mass spectrometry (MALDI MS).²⁴ In order to theoretically look at the cluster with the other ligands, the ETP ligand was replaced with PA or ET in MacMolPlt,²⁷ and all other atoms remained in the same positions as the ETP crystal structure. The cluster was then optimized with energy and gradient convergence criteria tightened to 1×10^{-4} and 1×10^{-3} Hartree respectively for geometric accuracy. As gold is a heavy transition metal, scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).²⁸⁻²⁹ To obtain the optical absorption profile of these clusters, vertical excitation energies were calculated using TDDFT+TB³⁰ or sTDDFT³¹ and convolved with a Gaussian fit, 0.15 eV full width half maximum (FWHM). For excited state method comparison, TDDFT³² calculations were ran at the same level of theory as TDDFT+TB, and as documented by the computational details in table G-1 and absorption spectrum in figure G-1, TDDFT+TB essentially duplicates the spectrum achieved with TDDFT at a much lower cost. In order to obtain PL properties, TDDFT analytical excited state gradients were utilized.³³ The level of theory ranges from utilizing solvent effects with COSMO,³⁴ dispersion effects with Grimme1³⁵ and Grimme3³⁶ parameters, changing the basis set between double zeta (DZ) and triple zeta polarized (TZP),³⁷ implementing frozen core (FC), constrained core (CC) calculations or all gold constrained (CC-AllGold) calculations,³⁸ and changing the exchange-correlation functional between LDA $X\alpha$,³⁹ GGA BP86,⁴⁰⁻⁴¹ Hybrid B3LYP,⁴² and a Yukawa long-range separated hybrid functional with a gamma value of 0.75.⁴³ For the benchmark results, the clusters were optimized at 13 different level of theories: BP86/DZ, $X\alpha$ /DZ, BP86-D1/DZ, BP86-D3/DZ, B3LYP-D3/DZ, BP86/TZP, BP86-D3-COSMO/DZ, BP86-D3-COSMO/TZP, CC-BP86/DZ, CC- $X\alpha$ -D3/TZP, CC-BP86-D3-COSMO/DZ, FC-BP86/DZ, and LRCF/DZ. Unfortunately, B3LYP-D3/DZ and LRCF/DZ did not fully converge due to computational restraints. Additional levels of theory were performed where the ground state optimized structure was calculated at a different level of theory than the linear response calculation; these include: B3LYP-D3/DZ on BP86-D3/DZ S₀, B3LYP-D3-COSMO/TZP on BP86-D3-COSMO/TZP S₀, SAOP-D3-COSMO/TZP on CC-BP86/DZ S₀, LRCF/DZ on CC-BP86/DZ S₀, and LRCF/DZ on CC-BP86/DZ S₀.

9.4 – Properties of Au₂₂(ETP)₁₈

The crystal structure of $Au_{22}(ETP)_{18}$,²⁴ given in figure 9.1, shows a bitetrahedral Au_7 core with one $Au_6(ETP)_6$ ring that coats the core. This cluster is further protected by three bidentate $Au_3(ETP)_4$ oligomers. The gold atoms in the figure are color coded to represent their particular position and bonding type in the units. Au sigma, for instance, represents the two sigma bonded Au atoms in the $Au_3(ETP)_4$ oligomers and Au pi represents the pi bonded Au atom. It is important to keep in mind that the initial predicted geometry of $Au_{22}(ETP)_{18}$ had a cuboctahedral Au_{13} core protected by six ETP ligands and three bidentate $Au_3(ETP)_4$ oligomers; however, due to the stability of the contorted Au_{13} core, this geometry is unlikely.²⁴ It turns out that the crystal structure (verified through single crystal X-ray diffraction) made by Ito et al., along with the initial proposed structure of the thiolate-protected species $Au_{22}(SG)_{18}$ by Pei et al. in 2015,⁴⁴

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(further verified by density functional theory)⁴⁵ is the same proposed shape to the structure of $Au_{22}(tBuC\equiv C)_{18}$ obtained by Han et al.²³ This shape is stable,⁴⁶ and the crystal structure formulates to have four valence electrons, giving a superatom configuration of S²P².⁴⁷



Figure 9.1: Crystal structure of $Au_{22}(ETP)_{18}$.²⁵ (A) Au₇ bitetrahedral core at two different orientations. (B) Isolated atoms to show the orientation of the gold in the cluster. (C) Full alkynyl-protected Au₂₂ NC. Atoms are colored by their bonding type or position within the cluster. Color key: green: Au core; pink: Au ring; red: Au sigma; blue: Au pi; yellow: sulfur; grey: carbon; white: hydrogen.

In this work, 11 fully optimized geometries were achieved with different levels of theory.

Of these, the BP86-D3-COSMO/TZP ground state structure (S₀) best reproduces the experimental crystal structure getting the best overall Au core – Au core, Au sigma – Au pi, and Au pi – C cusp bond distances as seen in table 9.1. This level of theory slightly overestimates the Au center – Au core, and Au sigma – Au ring bonds, and underestimates the Au core – Au ring, Au ring – Au ring and Au pi – Au ring bonds. The optimized S₀ structure slightly underestimates the Au core – Au core and Au center – Au core bond distances compared to the bulk gold Au-Au bond distance of 2.88 Å; however it matches well with other gold clusters that have a bitetrahedral core, such as $Au_{14}Cd(S-Adm)_{12}$ and $Au_{22}(SR)_{18}$ with Au core-Au core average bond

lengths of 2.760 \pm 0.076 Å⁴⁴ and 2.779 \pm 0.047 Å,⁴⁵ respectively. As an additional comparison,

the Au ring – Au ring bonds in the optimized structure fall in the range of the reported Au ring –

Au ring values of 3.130–3.304 Å in alkynyl protected clusters.^{23,49}

Table 9.1: Average bond distances of the crystal structure and ground state optimized geometry at the BP86-D3-COSMO/TZP, BP86/DZ and BP86/TZP levels of theory. Atom types are shown in figure 9.1, and the average bond distance that best reproduces the crystal structure out of 11 different levels of theory is shown in bold.

(Å)	Crystal	BP86-D3- COSMO/TZP	BP86/TZP	BP86/DZ
Au Center - Au Core	2.702	2.731	2.813	2.771
Au Core - Au Core	2.750	2.750	2.798	2.800
Au Core - Au Ring	3.095	3.076	3.084	2.981
Au Sigma - Au Ring	3.109	3.237	3.147	3.094
Au Ring - Au Ring	3.446	3.207	3.242	3.150
Au Sigma - Au Pi	3.432	3.465	3.231	3.139
Au Pi - Au Ring	3.429	3.024	3.251	2.940
Au Pi - C	2.184	2.290	2.445	2.537

One of the unique tailoring abilities in Au₂₂(C≡CR)₁₈ clusters is that the π -Au- π type bonding from the terminal alkynyls allows the Au₃(ETP)₄ oligomers to twist, giving a flexible motion in the vertex between the sigma motifs.²⁴ This previously unprecedented Au- π attractive interaction has also been seen in tandem with sigma bonding in several other gold clusters such as Au₈, Au₁₉, Au₂₃, Au₂₄ and others.^{19-20, 49-50} To document the twisting of the oligomers in Au₂₂(C≡CR)₁₈ clusters, the average angles from the three 'Au pi' joint/vertices on the NC were calculated. The atom definitions for the angles are displayed in figure 9.2. Even though the BP86-D3-COSMO/TZP S₀ state gives the closest average bond distances to the crystal structure, it is apparent from table 9.2 that this is not the case for the bond angles. The A-B-E and D-F-H angles get ~12° larger than the crystal structure, which elongates the distance between the two Au sigma units as a result of the shorter Au ring – Au pi bonds. The E-F-G angle gets ~20° smaller than the crystal structure, bringing the R groups closer together. This angle is smaller in all levels of theory when the atoms are allowed to move freely, and hence it is not an artifact of the level of theory being used. This therefore hints that the rigidity of this angle is required in the crystal structure. The S₀ optimization further restricts the alkynyl-R group attachment from twisting, not allowing the R group to bend away from the ligand as much as it does in the crystal structure as seen through the enlargement of the D-F-H bond. Due to π stacking from the aromatic ligands, which directly affects the alkynyl-R group twist, these angles are highly susceptible to change, which makes the ligand exchange in these clusters critical to further understand.

(°)	Crystal	BP86-D3-COSMO/TZP	BP86/DZ	BP86/TZP
A-B-C	126.2	133.4	125.4	121.0
A-B-D	96.2	103.6	95.6	91.5
A-B-E	84.8	96.4	94.1	88.2
A-B-F	63.1	69.0	65.2	60.5
A-B-G	44.3	44.9	38.9	33.8
A-B-H	32.0	32.5	32.6	29.7
E-F-G	145.2	126.1	128.1	124.9
D-F-H	160.7	174.1	161.3	157.8
D-E-I	163.7	171.0	178.4	173.6
H-G-J	160.2	161.5	170.3	172.8

 Table 9.2: Average angles between different atoms inside the three oligomers at the

 BP86/DZ level of theory.



Figure 9.2: Part of the Au₃(ETP)₄ oligomer such that the corresponding atom definitions are colored in table 9.2. Color key: green: Au core; pink: Au ring; red: Au sigma; blue: Au pi; yellow: sulfur; grey: carbon; white: hydrogen.

At this point, the next logical step would be to move on to optical and photoluminescent (PL) properties using the BP86-D3-COSMO/TZP level of theory. There is no question that using a more robust level of theory would give more accurate results; however, the system size puts constraints on what can be feasibly done. In this case, an S₁ optimization was not feasible using BP86-D3-COSMO/TZP, and the next best level of theory to reproduce the experimental results, BP86/TZP, is feasible; however, it is still extensively computationally expensive. Therefore, BP86/DZ will be used to further piece together the optical and PL properties. While BP86/DZ best reproduces the Au sigma - Au ring bond distance out of the 11 different levels of theory fully optimized, the bond lengths still change quite dramatically compared to the crystal structure. Three of the four triangular faces in the individual tetrahedrons expand away from the center atom, as the average Au center – Au core bond increases by 0.07 Å. The last triangular face in the back also expands slightly, on average by 0.05 Å between the two tetrahedra. This expansion is compensated by a closer Au-Au connection between the core and the gold atoms in the Au₆(ETP)₆ ring that coats the core, as well as the Au-Au connection between the ring atoms

and the 'Au sigma' and 'Au pi' atoms on the oligomers. Similar to the BP86-D3-COSMO/TZP level of theory, the D-E-I bond increases, and the E-F-G bond decreases, further highlighting the closer Au sigma – Au ring connection as well as the pi-stacking in the aromatic ligands. At the BP86/DZ level of theory, Au₂₂(ETP)₁₈ has a HOMO (H) – LUMO (L) gap of 1.66 eV in its ground electronic state. The core is achiral, and the protecting ligands make the full NC chiral as seen by the calculated circular dichroism spectrum in figure G-2. Chiral gold clusters from achiral ligands have been reported in several other alkynyl and thiolate-protected species.⁵¹⁻⁵⁴ The discovery of two enantiomers were documented in the experimental paper,²⁴ and while the optical and PL properties of enantiomers should be the same, theoretical calculations were only performed with the right-handed enantiomer.

At the BP86/DZ level of theory, the theoretical absorption of Au₂₂(ETP)₁₈ almost identically matches the shape of the experimental spectrum with a shoulder at 2.40 eV (517 nm) and a peak at 2.63 eV (471 nm) as seen in figure 9.3. This cluster is similar to Au₂₂(^BBuC=C)₁₈ as it shows an absorption peak around 2.60 eV; however, the weak shoulder peak in Au₂₂(ETP)₁₈ appears lower in energy to the main peak, rather than higher energy.²³ This cluster is different from other alkynyl protected clusters such as $[Au_{25}(C=CAr)_{18}]^{1-}$ because $Au_{22}(ETP)_{18}$ shows fewer spectral bands in the lower energy range compared to the Au_{25} cluster.⁵¹ The most notable observation of $Au_{22}(ETP)_{18}$ is that even though there is a large H-L gap (calculated at 1.66 eV), there is no spectral behavior in the 1-2 eV range of the experimental spectrum which would be expected with small gold clusters. There is a little behavior from the low energy range in the theoretical spectrum that can be analyzed; however, with the spectral shape matching well with experiment, the primary focus is on the higher energy peaks.



Figure 9.3: Absorption spectrum for Au₂₂(ETP)₁₈. (A) Experimental spectrum reprinted with permission from J. Phys. Chem. Lett. 2019, 10, 6892-6896. (B) Theoretical absorption spectrum for Au₂₂(ETP)₁₈ from the S₀ geometry at the BP86/DZ level of theory.

The shoulder at 2.40 eV has a large contribution from the H-5 \rightarrow L+5 transition with little contribution from an additional H-8 \rightarrow L+4 transition. The molecular orbitals that make up this transition can be seen in figure G-3. The H-5 molecular orbital (MO) has large contributions from the π bonds on the aromatic rings and p-type orbitals on the sulfur atoms in the ETP ligand. The L+5 MO has large contribution from the s atomic orbitals on the gold ring atoms as well as a little π character contribution from the carbon aromatic rings. The L+5 electronic density is adjacent to the H-5 density, lying along the Au ring rather than the oligomer. As the electronic density lacks overlap between the occupied and virtual MOs, this excitation has charge transfer character. This charge transfer character occurs from a ligand based occupied orbital to delocalized s-type virtual orbital in the gold ring atoms. The peak at 2.60 eV further shows this charge transfer character because the first two dominant transitions that make up this peak, H-10 \rightarrow L+6 and H-3 \rightarrow L+9, have essentially no spatial overlap in electronic density from the occupied to the virtual MOs as seen in figure G-4 and G-5. The third dominant transition in the main peak, H-22 \rightarrow L, has a larger overlap between the d contributions from the gold atoms in the core. H-10, H-3, and H-22 all possess electronic density with π character as well as p-type atomic orbital contributions on the sulfur atoms in the aromatic rings, with very minor contribution from the d atomic orbitals on the gold atoms in the core. L+6 and L+9 have strong contributions from the s and p atomic orbitals on the gold ring atoms, as well as π density on the aromatic rings at adjacent spots to the occupied densities.

The theoretical and experimental peak are within 0.1 eV as shown in the absorption spectrum (figure 9.3); hence the electronic state responsible for the emission should be around the experimental emission energy of 1.90 eV (650 nm).²⁴ The S_{15} state has an emission energy of 1.86 eV, as documented in table 9.3; however, there are no large energy breaks between the electronic states (all emission energies are within 0.08 eV of each other). With small differences in energy between excited electronic states, it is likely that the cluster will nonradiatively transition down to the S_1 state, with subsequent radiative relaxation from that geometry. Kasha's rule states that the lowest excited state of a specific multiplicity is responsible for the emission,⁵⁵ and this appears to be reasonable for this system. Multiplicity, however, is an important point, as other alkynyl protected gold clusters have shown to have intense phosphorescence.⁵⁶ The S₁ emission energy is 1.31 eV, and the T₁ emission energy is 1.27 eV, only 0.05 eV lower than the S_1 emission energy. These emission energies underestimate the experimental emission by ~0.60 eV, which is commonly seen with GGA functionals.⁵⁷⁻⁵⁸ Further, in a recent paper by Wang et al. they found that DFT ground state geometries are more accurate than excited state geometries obtained with TDDFT.⁵⁹ Hence, even though the vertical excitation energy at the BP86/DZ level of theory reproduces the experimental peaks almost identically, due to the errors in excited state geometry optimizations with TDDFT, there is an expected underestimation in emission energies.

Table 9.3: Au₂₂(ETP)₁₈ emission energies and lifetimes from the optimized S_n geometry, where n is the electronic state. These calculations all started from the geometry of the S₀ state at the BP86/DZ level of theory. The states not listed are ones that became nearly degenerate with the state below and thus struggled to converge geometrically.

State (S _n)	Energy (eV)	<u>Lifetime (µs)</u>
S_1	1.31	1.46
S_5	1.61	1.02
S_8	1.68	0.52
S 9	1.72	0.73
S ₁₀	1.77	1.19
S ₁₂	1.76	1.94
S ₁₅	1.86	0.57

The S₁ state in Au₂₂(ETP)₁₈ is dominated by a H \rightarrow L transition, which originates from superatomic P \rightarrow D character in the core of the nanocluster; the T₁ state also has spin density in the core of the nanocluster as seen in figure G-6. The movement of the bitetrahedron core is therefore vital in understanding the emission in this cluster. From S₀ \rightarrow S₁ and S₀ \rightarrow T₁ both of the back faces on the individual tetrahedra in the core distort slightly, as seen in figure G-7. The triplet state changes almost exactly the same as the singlet state upon excitation, and shares a similar optimized geometry as seen in table G-2, with corresponding angle differences in table G-3. Due to the close energy and geometry between the singlet and triplet states, the PL mechanism may incorporate fluorescence or phosphorescence.

In the structurally similar $Au_{22}(SG)_{18}$ cluster, Yu et al. established that the origin of PL greatly involved contributions from the Au(I) atoms in the shell, with a predicted aggregation induced emission pathway (AIE).⁶⁰ While AIE is possible, terminal alkynes with aromatic groups, such as PA and EPT (9-ethynyl-phenanthrene) have actually shown to be quite stable with no noticeable degradation compared to terminal alkynyl binding motifs such as OC (1- octyne).⁶¹ The PL mechanism attributed to $Au_{22}(ETP)_{18}$ is therefore ligand to metal metal charge transfer (LMMCT). Chen et al. described this mechanism for water soluble silver nanoclusters,

where it is attributed to three processes: (1) Charge transfer from the oxygen atom in the carboxylate ligands to the Ag(I) ions, (2) nonradiative electronic energy transfer from the Ag(I) atoms to the Ag(0) core, and (3) radiative relaxation from the core of the silver nanocluster.⁶² In $Au_{22}(ETP)_{18}$, three phenomena occur: (1) $Au_{22}(ETP)_{18}$ shows charge transfer behavior from occupied MOs dominated by π character on the aromatic groups to virtual MOs dominated by the s orbitals In the Au(I) ring atoms, (2) nonradiative relaxation occurs from the Au(I) ring atoms to the Au(0) core as depicted by the emission energies from the lowest 15 singlet states, and (3) the presence of almost identical energy and geometry between the T_1 and S_1 states which hints at (a) fluorescence in the core of the nanocluster originating from the S_1 state or (b) intersystem crossing followed by phosphorescence in the core from the T_1 state. A schematic of the proposed mechanism can be seen in figure G-8. Additionally, AIE from the Au(I) atoms in the ring and/or Au-pi or Au-sigma positions cannot be dismissed, and other gold clusters have been reported with an AIE mechanism.⁶³⁻⁶⁷ Regardless of whether the PL mechanism is LMMCT or AIE, however, the role of the Au(I) atoms in the protecting oligomers dominates the PL mechanism in these species. To complement the predicted PL mechanism, a spin-orbit coupling TDDFT calculation was completed at the ground state geometry. This resulted in a triply degenerate state at 1.52 eV, and a singly degenerate state at 1.56 eV.

The theoretical lifetime of the S₁ state calculated at the optimized S₁ geometry is 1.46 μ s. This is a long lifetime for a singlet state; however, the H→L transition that is responsible for the S₁ state is symmetry forbidden. Further, the spin-orbit coupling calculation showed that the triplet state lasts approximately 383x longer than the singlet with a lifetime value of 385 μ s. As depicted in the MOs that originate from the S₁ state in figure 9.4, the node between the lobes on the superatomic P orbital matches the axis that sits through the lobes on the superatomic D_z²

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orbital. This perpendicular nature of the MO transition corresponds to a symmetry forbidden state and is why there are no visible transitions in the low energy experimental absorption spectrum. A similar phenomena was seen in the alkynyl-protected cluster, Au₂₃(tBuC=C)₁₅, where the initial isomer showed a H→L transition that was optically forbidden; however this transition became allowed in a second isomer of the same cluster.²⁵ It is possible that there is another isomer of Au₂₂(ETP)₁₈ in which the H→L transition becomes optically active. Symmetry forbidden states correspond to long lifetimes;^{44,68} therefore, in this case, it is not unusual to see a theoretical radiative lifetime in the microsecond range. The S₁ lifetime is, however, much larger than the experimental lifetime of 0.14 μ s.²⁴ Fermi's equation is shown in equation (9.4.1), where τ is the radiative lifetime, α_0 is the fine structure constant, ΔE is the vertical excitation energy, and M_{α} is the transition dipole moment in the $\alpha = x,y,z$ direction.⁶⁹ If the transition dipole moment from the S₁ state is used, but the underestimation in energy is rectified to 1.90 eV (experimental value), the theoretical radiative lifetime would be predicted to be 0.48 μ s, which is more closely aligned with the experiment.

$$\frac{1}{\tau} = \frac{4}{3t_0} a_0^3 (\Delta E)^3 \sum_{\alpha \in (x, y, z)} |M_{\alpha}|^2$$
(9.4.1)

Hence, in addition to differences between experiment and theoretical chemical environments, the radiative lifetime differences between experiment and theory are also an artifact of the underestimation of the emission energy that arises from the XC functional.



Figure 9.4: Molecular orbitals responsible for the H \rightarrow L transition at the BP86/DZ level of theory. The pink line indicates the node between the lobes on the superatomic P HOMO, which is equivalent to the z axis along the superatomic D_z² LUMO.

9.5 – Comparison Between Ligands

As experimental conditions often change based on different applications, it is vital to discuss how replacing the ligands might affect the geometric, optical and PL properties. As discussed in the introduction, no notable differences between R groups were noted in the experimental absorption spectrum (figure 9.5), in addition to no geometric differences in the core.²⁴ However, the theoretical calculations do not reproduce this experimental result. This section will initially discuss electronic properties between ligands at the DFT level of theory that best reproduces the experiment, then it will discuss how the geometric, optical and PL properties change in general based on different levels of theory for these clusters.

In an effort to reproduce the experimental results, an immense number of calculations were performed to find the 'best level of theory'. The computational details are outlined in the supporting information. The two main criteria used to choose the best level of theory that reproduces experimental results are: (1) Similar vertical excitation energies and absorption shape between ligands, and (2) similar average bond distances between types of atoms in the clusters with different ligands. Theoretical emission energies are also important and will be briefly discussed in the next section; however, they are not as accessible due to the computational cost to compute analytical forces on systems of this size. The level of theory that shows the closest value for vertical excitation energies and most similar absorption shape between ligands is the long range corrected functional (LRCF) calculation with solvent effects, a DZ basis set, and Grimme3 dispersion (-D3) parameters from the CC-AllGold BP86-D3-COSMO/DZ S₀ state. 'CC-AllGold' refers to a constrained core calculation with all of the gold atoms constrained to the crystal structure geometry. Even though the gold atoms are constrained to the crystal structure, there are still changes in how the carbon atoms connect to the gold atoms upon optimization, as seen by the comparison between this level of theory and BP86/DZ in table G-4. With charge transfer character present in the transitions at the BP86/DZ level of theory, it is important to incorporate a long range corrected functional (LRCF) which gives better insight into the electronic transitions behind the optical peaks. Unfortunately, these functionals are too computationally expensive for ground state geometry optimizations with systems of this size. To rectify this issue, an sTDDFT calculation is performed, where the LRCF is only present in the linear response calculation. Figure 9.5 shows the theoretical absorption spectra at this level of theory between the three different ligands, with the vertical excitation energies in their corresponding colors. Unlike BP86/DZ, which reproduces the experimental absorption energy but does not correctly account for charge transfer (CT) excitations, the LRCF accounts for this CT character but overestimates the experimental excitation energy. The main electronic peak, ~3.75 eV, and corresponding low energy shoulder at ~3.50 eV match almost identically between the R groups of this cluster, varying only by 0.04 eV (table 9.4). Despite the similarity in peak

position, the electronic transition responsible for the peak in ETP is still different than that of ET and PA, i.e., for ETP the peak originates from a H-1→L+4 transition, while the peaks for PA and ET ligands originate from a H→L+2 transition. The MOs related to the peak transition for each R group can be seen in figures G-9 & G-10. It is important to note that even using a LRCF, the MOs responsible for the absorption peak in Au₂₂(ETP)₁₈ show a charge transfer excitation from the π groups in the aromatic rings to the Au(I) ring atoms, further verifying the LMMCT character from the proposed PL mechanism in the previous section. This is not seen with the other two R groups. While there are heavy contributions from the ring atoms in the virtual MOs, the PA and ET clusters show less contribution from the ligands and more contribution from the core in the occupied MOs. This hints that there may be a specific trend originating from the five membered ring with one sulfur atom, compared to six membered carbon rings. As one would expect, with differences apparent in the absorption spectrum, differences in the CD spectrum also occur. Figure G-11 shows these differences between ligands, as well as how the core of each NC contributes to the chirality of the cluster.

Au₂₂(ETP)₁₈ is not a highly emissive cluster; it has a lower PLQY compared to this NC with different R groups.²⁴ The excitations responsible for the peaks in Au₂₂(ETP)₁₈, on the other hand, have more contribution from the ligands compared to the electronic density with other R groups. More flexibility in the ligands decreases the radiative rate constant, decreasing the PLQY;⁷⁰ and in Au₂₂(ETP)₁₈, the ETP ligand decreases the proximity of the electronic density of the ligands to the core, which decreases the radiative rate constant. In Au₂₂(PA)₁₈, the nonradiative rate constant decreases, while the radiative rate constant increases, increasing the PLQY.²⁴ This shows that theoretically, there are indeed electronic changes that correspond to the different R groups.

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Figure 9.5: Theoretical absorption and stick spectrum at the LRCF-D3-COSMO/DZ level of theory from the optimized CC-AllGold BP86-D3-COSMO/DZ geometry. The ETP, PA, and ET ligands are in solid blue, dashed green, and red doubled lines respectively.

Table 9.4: Excitation energy and electronic transitions for Au₂₂(ETP)₁₈, Au₂₂(PA)₁₈ and Au₂₂(ET)₁₈ at the LRCF-D3-COSMO/DZ level of theory on the optimized CC-AllGold BP86-D3-COSMO/DZ S₀ geometry.

	Excitation Energy (eV)		Dominar	nt Transition
Ligand	Shoulder	Peak	Shoulder	Peak
ETP	3.50	3.73	$H-2 \rightarrow L$	H- $\overline{1 \rightarrow L}$ +4
PA	3.52	3.74	H → L	H→ L+2
ET	3.51	3.77	H → L	$H \rightarrow L+2$

In the theoretical calculations, the electronic changes mentioned in the paragraph above cannot correspond to different core geometries because the gold atoms are constrained to the crystal structure; however, a significant change between clusters can be noted in the angle differences between the oligomers in different R groups. As depicted in table 9.5, when all of the gold atoms are constrained, the angles between the gold atoms are also constrained. However, there are more drastic differences in the angles that involve the carbon atoms in the oligomers. One of the most notable observations is that in the crystal structure, the E-F-G angle is smaller than D-F-H; however, in the optimized cluster the E-F-G angle is larger than D-F-H. It is

possible that this change makes the D-E and H-G alkynyl bonds invert direction to each other as the aromatic rings point away from each other. The bending of the aromatic rings in connection to the alkynyl is largely due to the different π stacking between R groups, so even though all of the gold atoms are constrained, as the aromatic groups are different, these carbon angles change. This hints that the oligomer orientation with respect to the aromatic groups is crucial to understanding the physical phenomena in these clusters, and specifically in understanding the changes in the geometric and optical parameters.

Table 9.5. Average angles (°) between different atoms inside Au₂₂(ETP)₁₈, Au₂₂(PA)₁₈ and Au₂₂(ET)₁₈ at the crystal structure and the CC-AllGold BP86-D3-COSMO/DZ S₀. Atom definitions for this table are shown on the right. (Color key: green: Au core; pink: Au ring; red: Au sigma; blue: Au pi; yellow: sulfur; grey: carbon; white: hydrogen)

		CC-AllGold	AVERAGE		
Crystal	ETP	BP86-D3- COSMO/DZ	ЕТР	PA	ET
A-B-C	126.2	A-B-C	126.2	126.2	126.2
A-B-D	96.2	A-B-D	95.8	95.9	96
A-B-E	84.8	A-B-E	82.6	82.5	82.9
A-B-F	63.1	A-B-F	63.1	63.1	63.1
A-B-G	44.3	A-B-G	52.1	52.5	50.7
A-B-H	32	A-B-H	34.6	34.6	33.7
E-F-G	145.2	E-F-G	169.3	169.4	175.2
D-F-H	160.7	D-F-H	148.0	148.6	151.6
D-E-I	163.7	D-E-I	162.1	159.4	155.1
H-G-J	160.2	H-G-J	161.7	157.5	160.2



9.6 – Benchmark and Trends Between Ligands

Different levels of theory have different effects on the electronic and geometric structure with different R groups in these clusters. As briefly discussed above, several different levels of theory were used to model these clusters considering different specific parameters such as exchange-correlation functional, basis set, dispersion effects, solvent effects, and constrained core calculations. In order to document these changes, some of the following criteria were chosen for comparison: average bond distances, average angle distances in the oligomers, vertical excitation energies of the peak and shoulder, electronic density of the main transitions responsible for the absorption peak/shoulder, and S_1 emission energy when possible.

For DFT calculations, the choice of exchange-correlation functional is critical. The functional that most accurately represents the chemical system of interest while saving computational expense is usually the best choice. Unfortunately, in the clusters considered in this work, the XC functional that best reproduces the experimental spectrum differs between R groups. Figure 9.6 shows a comparison of the absorption spectrum calculated between LDA $X\alpha$, GGA BP86, and hybrid B3LYP functionals. In part A and B, it is apparent that the X α and BP86 XC functionals for ETP vary by less than 0.10 eV between peak positions at 2.72 eV and 2.63 eV respectively for the peak and 2.50 eV and 2.40 eV respectively for the shoulder. In the PA and ET ligands however, there is an immediate change in both absorption shape and vertical excitation energies between XC functionals. The results from the PA ligand shows a red shift in both the peak and shoulder by ~0.20 eV in BP86 compared to X α . The ET ligand shows concave down spectral behavior across the low energy range with a small peak at ~2.40 eV in BP86 and ~2.60 eV with X α . These spectral changes are associated with differences in the electronic ground state structure, as each R group was optimized with the corresponding functional. The geometric differences between X α and BP86 can be seen in table G-5, where it is apparent that BP86 is always predicts slightly longer bond lengths than $X\alpha$. Further, the S₁ state does not hold a trend between XC functionals in the clusters, as seen by a lowered emission energy in ET and ETP with X α , but a higher emission energy with X α for the PA ligand. To distinguish between spectral differences due to the XC functional vs. spectral differences from geometric effects, calculations with different functionals were also performed from an unaltered reference state.

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Figure 9.6 C and D depict this choice, where all absorption spectra calculations were performed at the optimized BP86-D3/DZ S₀ geometry. Hence, from part C to D, the only factor that is changing is the XC functional in the linear response calculation. It is apparent that the ET ligand retains the optical shape between functionals, but ETP and PA drastically change with the hybrid functional. The shape of the absorption spectrum matches experiment well in PA with the BP86 XC functional, but ETP shows the opposite trend. One of the most notable differences is that B3LYP blueshifts the optical gap ~0.50 eV to higher energy, which correlates well with experiment; however, that also blueshifts the main peak position in ET and PA. All in all, there is not one XC functional that matches well with experiment across all of the ligands. X α blueshifts the absorption spectrum while slightly underestimating the geometric parameters compared to BP86, and B3LYP makes the absorption peaks more prominent.


Figure 9.6: Theoretical absorption spectrum at different levels of theory. The ETP, PA, and ET ligands are in solid blue, dashed green, and red doubled lines respectively. (A) BP86/DZ level of theory at the BP86/DZ S₀ state geometry. (B) Xα/DZ level of theory at the Xα/DZ S₀ state geometry. (C) BP86-D3/DZ level of theory at the BP86-D3/DZ S₀ state geometry. (D) B3LYP-D3/DZ level of theory at the BP86-D3/DZ S₀ state geometry.

A second factor that can be considered in any quantum chemistry calculation is the choice of basis set. Optimizing the ground state geometry with a TZP basis rather than a DZ basis in these clusters increases the Au core – Au ring, Au sigma – Au pi, and Au pi – Au ring bonds, and decreases the Au pi-C cusp bonds. As one would expect, the bond angles also change between the two different basis sets. Table G-6 shows this comparison between bond angles in the oligomers. Most bond angles between the same R group and different levels of theory are similar, differing less than 10°, but there are a few exceptions. The E-F-G bond in ET increases by 27° and decreases by 12° in ETP with the TZP basis. While this bond slightly increases in PA, the more notable bond change for the PA ligand is in the A-B-G bond, which decreases by 17° with a TZP basis. Unfortunately, there is no dominant trend with the ground state

optimization between R groups when the polarization functions are added. Even between ET and PA, the six-membered carbon rings change in different ways. This means that even though the electronic density may act similar between six-membered carbon ring ligands, as discussed in the above section, the level of theory is still sensitive to how those ligands are arranged, as well as additional atoms, such as the methyl group in the meta position on the ET ligand. Unlike the geometric parameters, however, the optical properties show a few common trends between the ligands. With the added polarization functions, the absorption peak blue shifts, the optical gap increases, and the S_1 emission energy is increased in all clusters.

An additional factor to consider in DFT calculations is the addition of dispersion effects. Single reference methods, such as DFT, are unable to fully describe the instantaneous dipole moment in molecules or atoms due to the lack of connection with the local chemical environment.⁷¹ Dispersion parameters are therefore vital in theoretical calculations and are usually developed with semi-empirical parameters from experiments. While there are several options for dispersion parameters, the calculations in this work considered Grimme1 and Grimme3 dispersion. The absorption spectra calculated by including Grimme1 and Grimme3 parameters for the three clusters are shown in Figure G-12. Compared to the BP86/DZ level of theory, the absorption peak slightly red shifts ETP with Grimme1 and blue shifts the peaks in ETP with Grimme3. Both dispersion parameters blue shift the absorption peaks in PA and ET. Grimme1 lowers the optical gap, and Grimme3 increases the optical gap in all clusters. Since Grimme3 dispersion improves the description of metallic and heavy atom systems by using coordination number dispersion coefficients over atom connectivity,⁷² it is beneficial to further consider how the geometric parameters change with this choice. With the Grimme1 dispersion parameters, the Au core – Au core bond decreases, and the Au core – Au ring, Au ring – Au ring, Au sigma – Au ring and Au sigma – Au pi bonds increase. In opposition, the Grimme3 dispersion parameter decreases the Au center – Au core, Au core – Au ring, Au sigma – Au ring, and Au sigma – Au pi bond lengths while simultaneously increasing the Au pi ring bonds. Table G-7 shows the difference between the average bond distances when the clusters were optimized with the different dispersion parameters. For PL properties, Grimme3 dispersion increases the ET and PA emission energies to 1.41 eV and 1.69 eV respectively, but unfortunately lowers ET to 0.65 eV. Grimme1 dispersion lowers the emission energy with all ligands compared to BP86/DZ level of theory.

Theoretically modelling an experiment is often difficult as the experiment, likely taking place in a solution, possesses more intermolecular interactions with counter ions or solvent molecules. Counter ions and solvent molecules can be explicitly added into the geometry of the calculation, but the question then becomes where to add the atoms, and how many. Additionally, it is worth noting how many counter ions or an explicit solvent shell will raise the computational cost of the calculation. Alternatively, a dielectric background can be used to account for solvent effects. Solvent effects were addressed in this project by optimizing the geometry with COSMO in a water solvent. Using solvent effects in these clusters increases the Au center – Au core, Au sigma – Au ring and Au sigma – Au pi bonds. On the other side, it decreases the Au core – Au core bonds, Au ring-Au ring, and Au pi – Au ring bonds. Solvent effects decrease the optical gap in ETP and PA but increase the gap in ET. The theoretical absorption spectra, shown in figure G-13, shows that the peak of interest red shifts in energy in ET, while it blue shifts in ETP. The BP86-D3-COSMO/DZ level of theory is the closest to reproducing the experimental results with the main peak ~2.70 eV for all ligands and shoulder ~2.39 eV. The main issue with this level of

theory is the large influence of the core excitations as seen in the lower energy range of the spectrum for the ET ligand, but not PA and ETP.

In order to fully understand the effect of constrained core calculations, different calculations were performed with different gold layers constrained. Recall that the different color schemes are there to understand the different environment of different gold atoms, i.e., the core, the ring, the rigid sigma gold atoms as foundation for the oligomers, and the flexible pi gold atoms that lie at the vertex of the oligomers. The absorption spectrum after optimizing the constrained core layers at the BP86-D3-COSMO/DZ level of theory are seen in figure 9.7. Constraining the bitetrahedral core shows similarities between ETP and PA, but still results in different spectral behavior from the ET ligand. Constraining the gold core and gold ring atoms greatly lowers the intensity of the PA peak and shoulder but matches better with the spectral behavior of ET. The broad peak from (A) and (B) in ETP starts to split once the sigma atoms are also constrained, but the peaks between clusters line up the best when all of the gold atoms are constrained to the crystal structure, as shown in part (D). Given this information however, the spectral shape still changes dramatically between R groups when all the atoms are constrained. This further shows that the choice of R group affects the geometric and electronic structure of the system.

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Figure 9.7. Theoretical absorption spectrum with specific gold atoms constrained. The ETP, PA, and ET ligands are in solid blue, dashed green, and red doubled lines respectively. (A) BP86-D3-COSMO/DZ TDDFT+TB calculation at the core constrained BP86-D3-COSMO/DZ S₀ state (B) BP86-D3-COSMO/DZ TDDFT+TB calculation at the core & ring constrained BP86-D3-COSMO/DZ S₀ state (C) BP86-D3-COSMO/DZ TDDFT+TB calculation at the core, ring & sigma constrained BP86-D3-COSMO/DZ S₀ state (D) BP86-D3-COSMO/DZ TDDFT+TB calculation at the CC-AllGold BP86-D3-COSMO/DZ S₀ state.

9.7 – Conclusion

Au₂₂(ETP)₁₈ shows a LMMCT PL mechanism that originates from the charge transfer of the π orbitals in the aromatic ligands of the cluster transitioning into MOs that are dominated from the sp orbitals in the ring gold atoms, which then nonradiatively transition down to the core and then follow one of two pathways (1) radiative relaxation from the optically dark S₁ state or (2) intersystem crossing followed by radiative relaxation from the triplet state. Both the S₁ and T₁ states show movement in the bitetrahedral core with the same Au-Au bonds moving in the same ways. The PL mechanism does indeed change between the different R groups. Au₂₂(ETP)₁₈ is less emissive compared to PA and ET due to the decrease of the proximity of the electronic density from the ligands to the core as shown by the electronic density in the occupied and virtual MOs. PA and ET do not show charge transfer character, and hence do not have a LMMCT PL mechanism but rather hint that the radiative relaxation originates from core-based orbitals. All of the clusters are highly dependent upon the level of theory. Even with the levels of theory that best reproduce experimental results, BP86-D3-COSMO/DZ & LRCF-D3-COSMO/DZ sTDDFT on CC/BP86-D3-COSMO/DZ S₀, there are distinct differences in the absorption spectrum due to the change in geometric parameters from the different aromatic groups.

Dispersion, solvent, and polarization functions in the basis set are all important to creating an accurate chemical environment for these quantum chemistry calculations. One of the most important considerations however is using a long range corrected functional to give better insights into charge transfer excitations for these types of clusters. LRCF provides better CT character, which would give more reliable behavior in the MOs, but unfortunately it is not possible to run excited state geometry optimizations with this functional. Many theoretical groups have devoted their time to continuing development of (1) simplified methods to combat the cost of TDDFT, as well as (2) exchange-correlation development for energy functionals that demonstrate good behavior, as compared to experiment, that are computationally affordable. Until analytical forces are implemented, however, patterns arise in clusters that can be seen from lower class functionals and are used to further understand photophysical properties in gold clusters. In this case particularly, there are differences in optical and geometric properties between R groups, primarily taking place due to the strong dependence on the Au(I) ring atoms and how the pi-Au-pi intramolecular interactions organize the aromatic groups on the cluster.

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9.9 - References

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Chapter 10 - Analytical Excited State Gradients for TDDFT+TB

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10.1 – Abstract

Understanding photoluminescent mechanisms has become essential for photocatalytic, biological, and electronic applications. Unfortunately, analyzing excited state potential energy surfaces (PES) in large systems is computationally expensive, and hence limited with electronic structure methods, such as TDDFT. Inspired by the sTDDFT and sTDA methods, timedependent density functional theory plus tight binding (TDDFT+TB) has been shown to reproduce linear response TDDFT results much faster than TDDFT, particularly in large nanoparticles. For photochemical processes, however, methods must go beyond the calculation of excitation energies. Herein, this work outlines an analytical approach to the derivative of the vertical excitation energy in TDDFT+TB for more efficient excited state PES exploration. The gradient derivation is based on the Z-vector method, which utilizes an auxiliary Lagrangian to characterize the excitation energy. The gradient is obtained when the derivatives of the Fock matrix, the coupling matrix, and the overlap matrix are all plugged into the auxiliary Lagrangian, and the Lagrange multipliers are solved. This chapter outlines the derivation of the analytical gradient, discusses the implementation into Amsterdam Density Functional (ADF) software, and provides proof of concept by analyzing the emission energy and optimized excited state geometry calculated by TDDFT and TDDFT+TB for small organic molecules and nanoclusters.

10.2 – Introduction

Elucidating photophysical and photochemical processes requires some knowledge of excited state potential energy surfaces (PES). PES describe the energy and behavior of a molecule at a particular geometry, and therefore are useful for obtaining physical insights such as equilibrium structures and reaction dynamics.¹ In particular, analytical gradients and Hessians are used to understand the topology and stationary points of the system. Stationary points, such as minima or first order saddle points, are critical in obtaining physical insights, and for excited state surfaces, these points lead to excited state structures, emission, and excitation energies, and more. It can therefore be deduced that understanding stationary points in excited state PES leads to a range of applications in photochemistry, catalysis, biology, and electronics.²⁻⁶ Photoluminescent (PL) mechanisms in small atomically precise nanoclusters, in particular, has gained large scientific interest as small nanoclusters have discrete energy gaps, promoting radiative relaxation, opposed to materials in which the lack of energy gap between bands makes PL improbable.^{7,8} As clusters have tunable structure-property relationships with respect to different charge states, ligand structures, heteroatom dopants, and more,^{9–11} understanding the stationary points in the excited state PES of nanoclusters leads to highly luminescent materials, thus advancing fields in bioimaging, electronics and more.

One of the most popular quantum mechanical methods used to understand optical and PL properties in molecules and nanoclusters is time-dependent density functional theory (TDDFT).^{12–18} Unfortunately, the computational cost of TDDFT increases significantly when properties other than the energy are required, hindering the calculation of excited states on the level of theory and the system size. An example of this is Au₁₄Cd(S-Adm)₁₂, which exhibits a rare dual emission mechanism.¹⁹ TDDFT calculations were used to decipher the two emissive

points, but it took longer than 90 days to find and optimize both minima.¹⁴ Targeting the computational bottleneck of TDDFT, methods such as time-dependent density functional tight binding (TDDFTB) have been used to obtain excited state properties.^{20–22} Unfortunately, TDDFTB has shown large optical absorption red shifts (0.60 - 1.0 eV) in gold nanoclusters and nanowires as compared to TDDFT,^{23,24} which can be traced back to limited parameterization and the minimal basis set of the method.²⁵ It is therefore critical to develop inexpensive methods that maintain the accuracy of TDDFT for excited state PES exploration.

Inspired by the sTDDFT and sTDA methods by Stefan Grimme, time-dependent density functional theory plus tight binding (TDDFT+TB) was introduced in 2016.²⁵ TDDFT+TB has shown to reproduce linear response TDDFT results up to $100 \times$ faster than TDDFT in large plasmonic NCs, keeping electronic accuracy within 0.10 eV of TDDFT.²⁴ This method was created for pure exchange-correlation functionals, whereas sTDDFT and sTDA can be used with hybrid functionals. For large nanoparticles, however, this is not an issue as the level of theory is usually restricted to these functionals due to the large system size. TDDFT+TB uses a DFT ground state reference and targets the computationally expensive coupling matrix in TDDFT by applying a first order monopole approximation to the transition density in the linear response formulation.²⁵ Since the two-electron integrals are the computational bottleneck of classic TDDFT calculations, this approximation drastically improves the computational time. While TDDFT+TB has shown incredible accuracy with respect to TDDFT by maintaining the accurate DFT ground state geometry, the method has only been used to calculate excitation energies. Herein, the purpose of this paper is three-fold. Initially, using the Z-vector method, the analytical excited state gradients of TDDFT+TB are derived. Second, implementation of the gradients into ADF for closed shell excited state geometry optimizations for singlet-singlet transitions will be

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discussed. Finally, the paper will provide proof of concept by comparing emission energy and optimized excited state geometries between TDDFT and TDDFT+TB in small organic molecules and nanoclusters.

10.3 – Theory

In order to obtain excited state properties other than energy, such as local minima and first order saddle points on excited state surfaces, the analytical excited state gradients must be derived. Following the Lagrangian based approach, introduced by Furche and Ahlrichs,²⁶ the TDDFT+TB analytical gradients are derived by taking the derivative of excitation energy with respect to a real perturbation. The full derivation can be split into four main parts: defining an energy functional that is equivalent to the vertical excitation energy of that system, setting up an energy functional that is stationary with respect to the molecular orbital coefficients, solving the Lagrange multipliers after the constraints have been defined, and taking the full derivative of each term in the energy functional to obtain the full analytical gradient with respect to the position of the nuclear coordinates. The notation used in this paper is as follows. A molecular orbital will be denoted by the indices a, b, c, ... if it is unoccupied in the ground electronic state, and i, j, k, ... if it is occupied in the ground electronic state. Further, p, q, r, s, ... denotes a general molecular orbital; the derivation will later be separated into cases in which the general MO is occupied or unoccupied. Atomic basis functions will be denoted by the indices μ , ν , κ , ... which belong to a specific atom denoted by the capital letters A, B, C, ...

10.3.1 – Define an Energy Functional

The first step in calculating the derivative of the excitation energy with respect to the nuclear coordinates is to obtain an expression for the TDDFT+TB excitation energy. TDDFT+TB applies a first order monopole approximation to the transition density in the linear response formulation of TDDFT.²⁵ With this approximation, the two-electron integrals are no longer calculated, and $\varphi_i(r)\varphi_a(r)\approx\sum_a q_{ia,A}\zeta_A(r)$ where $\zeta_A(r)$ is a spherically symmetric function centered on atom A, and $q_{ia,A}$ is defined in equation (10.3.1)

$$q_{ia,A} = \sum_{\mu \in A} C'_{\mu i} C'_{\mu a}$$
(10.3.1)

where $\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C}$, \mathbf{C} is the molecular orbital coefficient matrix, and \mathbf{S} is the overlap matrix. Using the variational approach, the vertical excitation energy of TDDFT+TB is expressed in equation (10.3.2), where the excited state energies (Ω) are stationary points of the functional.

$$G[X,Y,\Omega] = \frac{1}{2} \left\langle \begin{matrix} X+Y\\ X-Y \end{matrix} | \Lambda | \begin{matrix} X+Y\\ X-Y \end{matrix} \right\rangle - \frac{1}{2} \Omega \left(\left\langle \begin{matrix} X+Y\\ X-Y \end{matrix} | \Delta | \begin{matrix} X+Y\\ X-Y \end{matrix} \right\rangle - 2 \right)$$
(10.3.2)

Such that

$$\Lambda = \begin{pmatrix} A+B & 0\\ 0 & A-B \end{pmatrix} \text{ and } \Delta = \begin{pmatrix} 0 & 1\\ 1 & 0 \end{pmatrix}$$

X and Y are the transition density vectors of single particle transitions defined on the Hilbert space $N_{virt}xN_{occ} \oplus N_{occ}xN_{virt}$, such that N_{occ} is the number of occupied molecular orbitals and N_{virt} is the number of virtual molecular orbitals. A and B are called rotational Hessians, where the matrix representation is shown in equations (10.3.3) and (10.3.4). Note that TDDFT+TB does not include any exact Hartree-Fock exchange. The coupling matrix is written in equation (5), and ε_p corresponds to the energy of the molecular orbital, p.

$$(A+B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 4K_{iajb}^{S/T} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 4\sum_{iajb}q_{ia,A}\gamma_{AB}q_{jb,B}$$
(10.3.3)

$$(A-B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$$
(10.3.4)

$$K_{iajb}^{S} = \sum_{AB} q_{ia,A} \gamma_{AB} q_{jb,B}$$
(10.3.5)

 γ_{AB} is a function of the internuclear distance and a chemical hardness parameter, which signifies the coulombic interaction between two point charges.²⁵ S refers to a singlet-singlet excitation; however, the method is also applicable to singlet-triplet excitations (T) in which a Hubbard parameter, W_A would replace the gamma function inside the coupling matrix as shown in equation (10.3.6).²⁵

$$K_{iajb}^{T} = \sum_{A} q_{ia,A} W_{A} q_{jb,A}$$
(10.3.6)

The analytical gradients for TDDFT+TB are currently only implemented for systems with a singlet ground state; hence, all spin indices are dropped for simplicity.

10.3.2 – Constrained Optimization Problem

If the derivative of equation (10.3.2) is simply taken as is, the calculation would be quite costly. The reason for this is that A depends on the molecular orbitals of the method. The derivation would therefore require an implicit calculation of the derivative of the molecular orbital coefficients, which would add a cost increase by the number of nuclear degrees of freedom in a molecule.²⁶ It is possible to circumvent this issue by using a common method in quantum chemistry called the 'Z-vector method'.²⁷ This method has been used to derive the analytical gradients for several methods including TDDFT²⁶ and TDDFTB²⁸. The Z-vector method uses a common mathematical way to solve constrained optimization problems, called the Lagrangian method. This method applies an equality constraint to the function of interest. For TDDFT+TB, the constraints should restrict the molecular orbital transformations. To do this, a new auxiliary functional is defined that is stationary with respect to all its parameter

$$L[X,Y,\Omega,C,Z,W] = G[X,Y,\Omega] + \sum_{ia} Z_{ia}F_{ia} - \sum_{pq,p \le q} W_{pq}(S_{pq} - \delta_{pq})$$

$$(10.3.7)$$

The functional, L, now represents a fully variational expression for the excitation energy under any external perturbation. The implicit dependence of the MO coefficients drops out in L by introducing Lagrange multipliers W and Z, which restrict the transformation of the molecular orbital coefficients. To be more explicit, the following restriction criteria is imposed:

$$\frac{\partial L}{\partial Z_{ia}} = F_{ia} = 0 \tag{10.3.8}$$

$$\frac{\partial L}{\partial W_{pq}} = S_{pq} - \delta_{pq} = 0 \tag{10.3.9}$$

The MOs are constrained to be orthonormal and satisfy the ground state DFT equations. This leads to equation (10.3.10), which will then be used to determine Z and W.

$$\frac{\partial L}{\partial C_{\mu p}} = 0 \tag{10.3.10}$$

As the MO coefficients are now stationary, the diagonal elements of the rotational Hessians are replaced by equations (10.3.11) & (10.3.12),²⁶

$$(A+B)_{iajb} = F_{ab}\delta_{ij} - F_{ij}\delta_{ab} + 4K_{iajb}^{S/T}$$
(10.3.11)

$$(A-B)_{iajb} = F_{ab}\delta_{ij} - F_{ij}\delta_{ab}$$
(10.3.12)

where

$$F_{pq} = h_{pq} + \sum_{i} [(pq|ii)] + V_{pq}^{XC}$$

such that h_{pq} and V^{XC}_{pq} have the usual form.²⁶

Before the formal derivative of equation (10.3.7) is taken, the Lagrange multipliers must be solved with respect to the constraints. To do this, equation (10.3.10) is expanded, summed over μ and right multiplied by the coefficient matrix to obtain equation (10.3.13).

$$Q_{pq} + \sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial F_{ia}}{\partial C_{\mu p}} C_{\mu q} = \sum_{rs, r \le s} W_{rs} \sum_{\mu} \frac{\partial S_{rs}}{\partial C_{\mu p}} C_{\mu q}$$
(10.3.13)

The constraint Q_{pq} is defined as the partial derivative of the initial G functional from equation (10.3.2) with respect to the molecular orbital coefficients, which has been right multiplied by the coefficient matrix.

$$Q_{pq} = \sum_{\mu} \frac{\partial G[X,Y,Z]}{\partial C_{\mu p}} C_{\mu q} = \sum_{\mu} \frac{1}{2} \left\langle \begin{matrix} X+Y\\ X-Y \end{matrix} \middle| \begin{pmatrix} \frac{\partial (A+B)}{\partial C_{\mu p}} C_{\mu q} & 0\\ 0 & \frac{\partial (A-B)}{\partial C_{\mu p}} C_{\mu q} \end{pmatrix} \middle| \begin{matrix} X+Y\\ X-Y \end{matrix} \right\rangle$$
$$= \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} \sum_{\mu} \frac{\partial (A+B)_{iajb}}{\partial C_{\mu p}} C_{\mu q} (X+Y)_{jb} + \frac{1}{2} \sum_{ia} \sum_{jb} (X-Y)_{ia} \sum_{\mu} \frac{\partial (A-B)_{iajb}}{\partial C_{\mu p}} C_{\mu q} (X-Y)_{jb}$$
(10.3.14)

From here, the definition of (A+B) and (A-B) from equations (10.3.11) and (10.3.12) are plugged into equation (10.3.14) to get the following form of Q_{pq} .

$$=\frac{1}{2}\sum_{ia}\sum_{jb}(X+Y)_{ia}\sum_{\mu}\frac{\partial(F_{ab}\delta_{ij}-F_{ij}\delta_{ab})}{\partial C_{\mu p}}C_{\mu q}(X+Y)_{jb}$$

$$+\frac{1}{2}\sum_{ia}\sum_{jb}(X+Y)_{ia}4\frac{\partial K_{iajb}^{S/T}}{\partial C_{\mu p}}C_{\mu q}(X+Y)_{jb}$$

$$+\frac{1}{2}\sum_{ia}\sum_{jb}(X-Y)_{ia}\sum_{\mu}\frac{\partial(F_{ab}\delta_{ij}-F_{ij}\delta_{ab})}{\partial C_{\mu p}}C_{\mu q}(X-Y)_{jb}$$

The first and third terms may look familiar as they produce the same terms from TDDFT gradients.²⁶ The reason for this is that the TDDFT+TB method uses ground state DFT molecular orbitals. The second term produces terms similar to TDDFTB gradients,²⁸ but with a different partial charge analysis. The reason for this is that the TDDFT+TB method uses the same monopole approximation as TDDFTB in the linear response formulation. The expanded derivation of each term can be seen in Appendix H. After expanding the terms, the following equation is obtained:

$$= \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} \left[\delta_{ij} (\delta_{pa}F_{qb} + \delta_{pb}F_{aq} + \delta_{p\in occ} 2(ab|pq) + \delta_{p\in occ} 2f_{abpq}^{XC}) \right] - \delta_{ab} (\delta_{pi}F_{qj} + \delta_{pj}F_{iq} + \delta_{p\in occ} 2(ij|pq) + \delta_{p\in occ} 2f_{ijpq}^{XC}) \right] (X+Y)_{jb} + \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} 4 \left[\delta_{pi}K_{qajb}^{S/T} + \delta_{pa}K_{iqjb}^{S/T} + \delta_{pj}K_{iaqb}^{S/T} + \delta_{pb}K_{iajq}^{S/T} \right] (X+Y)_{jb} + \frac{1}{2} \sum_{ia} \sum_{jb} (X-Y)_{ia} \left[\delta_{ij} (\delta_{pa}F_{qb} + \delta_{pb}F_{aq} + \delta_{p\in occ} 2(ab|pq) + \delta_{p\in occ} 2f_{abpq}^{XC}) \right] - \delta_{ab} (\delta_{pi}F_{qj} + \delta_{pj}F_{iq} + \delta_{p\in occ} 2(ij|pq) + \delta_{p\in occ} 2f_{ijpq}^{XC}) \right] (X-Y)_{jb}$$

$$(10.3.15)$$

such that f^{XC}_{pqrs} and (pq/rs) have the usual form.²⁹

For the occupied to occupied and virtual to virtual molecular orbital transitions, it is beneficial to incorporate symmetry. Similar to TDDFT and TDDFTB gradient methodology, terms are added to make use of symmetry, but then they must also be subtracted to hold equality. The terms added are underlined, and the terms removed are double underlined.

$$= \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} \left[\delta_{pi} (\underline{\delta_{qj}F_{ab}} - \delta_{ab}F_{qj} + 4K_{qajb}^{S/T}) + \delta_{pa} (\delta_{ij}F_{qb} - \underline{\delta_{qb}F_{ij}} + 4K_{iqjb}^{S/T}) \right] \\ + \delta_{pj} (\underline{\delta_{iq}F_{ab}} - \delta_{ab}F_{iq} + 4K_{iaqb}^{S/T}) + \delta_{pb} (\delta_{ij}F_{aq} - \underline{\delta_{aq}F_{ij}} + 4K_{iajq}^{S/T}) \\ \underline{-\delta_{pi}\delta_{qj}F_{ab}} + \underline{\delta_{pa}\delta_{qb}F_{ij}} - \underline{\delta_{pj}\delta_{iq}F_{ab}} + \underline{\delta_{pb}\delta_{aq}F_{ij}} \\ + \delta_{ij} (\delta_{p\in occ}2(ab|pq) + \delta_{p\in occ}2f_{abpq}^{XC}) - \delta_{ab} (\delta_{p\in occ}2(ij|pq) + \delta_{p\in occ}2f_{ijpq}^{XC})] (X+Y)_{jb} \\ + \frac{1}{2} \sum_{ia} \sum_{jb} (X-Y)_{ia} \left[\delta_{pi} (\underline{\delta_{qj}F_{ab}} - \delta_{ab}F_{qj}) + \delta_{pa} (\delta_{ij}F_{qb} - \underline{\delta_{qb}F_{ij}}) \\ + \delta_{pj} (\underline{\delta_{iq}F_{ab}} - \delta_{ab}F_{iq}) + \delta_{pb} (\delta_{ij}F_{aq} - \underline{\delta_{aq}F_{ij}}) \\ - \underline{\delta_{pi}\delta_{qj}F_{ab}} + \underline{\delta_{pa}\delta_{qb}F_{ij}} - \underline{\delta_{pj}\delta_{iq}F_{ab}} + \underline{\delta_{pb}\delta_{aq}F_{ij}} \\ + \delta_{ij} (\delta_{p\in occ}2(ab|pq) + \delta_{p\in occ}2f_{abpq}^{XC}) - \delta_{ab} (\delta_{p\in occ}2(ij|pq) + \delta_{p\in occ}2f_{ijpq}^{XC})] (X-Y)_{jb} \\$$
(10.3.16)

Making use of the definition of (A+B) and (A-B) from equations (10.3.11) and (10.3.12) results in equation (10.3.17):

$$= \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} \left[\delta_{pi} (A+B)_{qajb} + \delta_{pa} (A+B)_{iqjb} + \delta_{pj} (A+B)_{iaqb} + \delta_{pb} (A+B)_{iajq} \right]$$

$$= \frac{-\delta_{pi} \delta_{qj} \delta_{ab} \varepsilon_{a}}{-\delta_{pi} \delta_{qb} \delta_{ij} \varepsilon_{i}} - \frac{\delta_{pj} \delta_{iq} \delta_{ab} \varepsilon_{a}}{-\delta_{pj} \delta_{iq} \delta_{ab} \varepsilon_{a}} + \frac{\delta_{pb} \delta_{aq} \delta_{ij} \varepsilon_{i}}{-\delta_{pi} \delta_{aq} \delta_{ij} \varepsilon_{i}}$$

$$+ \delta_{ij} (\delta_{p \in occ} 2(ab|pq) + \delta_{p \in occ} 2f_{abpq}^{XC}) - \delta_{ab} (\delta_{p \in occ} 2(ij|pq) + \delta_{p \in occ} 2f_{ijpq}^{XC}) \left[(X+Y)_{jb} \right]$$

$$+ \frac{1}{2} \sum_{ia} \sum_{jb} (X-Y)_{ia} \left[\delta_{pi} (A-B)_{qajb} + \delta_{pa} (A-B)_{iqjb} + \delta_{pj} (A-B)_{iaqb} + \delta_{pb} (A-B)_{iajq} \right]$$

$$+ \delta_{ij} (\delta_{p \in occ} 2(ab|pq) + \delta_{p \in occ} 2f_{abpq}^{XC}) - \delta_{ab} (\delta_{p \in occ} 2(ij|pq) + \delta_{p \in occ} 2f_{ijpq}^{XC})$$

$$= \frac{-\delta_{pi} \delta_{qj} \delta_{ab} \varepsilon_{a}}{-\delta_{pi} \delta_{qb} \delta_{ij} \varepsilon_{i}} - \frac{\delta_{pj} \delta_{iq} \delta_{ab} \varepsilon_{a}}{-\delta_{pj} \delta_{iq} \delta_{ab} \varepsilon_{a}} + \frac{\delta_{pb} \delta_{aq} \delta_{ij} \varepsilon_{i}}{-\delta_{pj} \delta_{aq} \delta_{ij} \varepsilon_{i}} \right] (X-Y)_{jb}$$

$$(10.3.17)$$

Relations from linear response theory (equations (10.3.18)-(10.3.21)) are then used to further simplify Q_{pq}

$$(A+B)|(X+Y)\rangle = \Omega|(X-Y)\rangle$$
(10.3.18)

$$(A-B)|(X-Y)\rangle = \Omega|(X+Y)\rangle$$
(10.3.19)

$$\langle (X+Y)|(A+B) = \Omega \langle (X-Y)|$$
(10.3.20)

$$\langle (X-Y)|(A-B) = \Omega\langle (X+Y)|$$
(10.3.21)

and obtain equation (10.3.22)

$$= \frac{1}{2} \sum_{ia} \sum_{jb} (X+Y)_{ia} \Omega \left[(X-Y)_{jb} \delta_{pi} \delta_{qj} \delta_{ab} + (X-Y)_{jb} \delta_{pa} \delta_{ij} \delta_{qb} \right. \\ \left. + (X-Y)_{jb} \delta_{pj} \delta_{jq} \delta_{ab} + (X-Y)_{jb} \delta_{pb} \delta_{ij} \delta_{bq} \right] \\ \left. + \frac{1}{2} \sum_{ia} \sum_{jb} (X-Y)_{ia} \Omega \left[(X+Y)_{jb} \delta_{pj} \delta_{jq} \delta_{ab} + (X+Y)_{jb} \delta_{pb} \delta_{ij} \delta_{bq} \right. \\ \left. + (X+Y)_{jb} \delta_{pi} \delta_{qj} \delta_{ab} + (X+Y)_{jb} \delta_{pa} \delta_{ij} \delta_{qb} \right] \\ \left. + \frac{1}{2} \sum_{ia} \sum_{jb} \left((X+Y)_{ia} (X+Y)_{jb} + (X-Y)_{ia} (X-Y)_{jb} \right) \right. \\ \left. \left[\frac{-\delta_{pi} \delta_{qj} \delta_{ab} \varepsilon_{a}}{2} + \frac{\delta_{pa} \delta_{qb} \delta_{ij} \varepsilon_{i}}{- \frac{\delta_{pj} \delta_{iq} \delta_{ab} \varepsilon_{a}}{2}} + \frac{\delta_{pb} \delta_{aq} \delta_{ij} \varepsilon_{i}}{- \delta_{ab} (\delta_{p \in occ} 2(ij|pq) + \delta_{p \in occ} 2f_{ijpq}^{XC}) \right]$$

$$(10.3.22)$$

Plugging in the definition of relaxed difference density matrix T (equations (10.3.23) - (10.3.25)) as well as the linear transformation defined from TDDFT (equation (10.3.26)),²⁶

$$T_{ab} = \frac{1}{2} \sum_{i} ((X+Y)_{ia}(X+Y)_{ib} + (X-Y)_{ia}(X-Y)_{ib})$$
(10.3.23)

$$T_{ij} = -\frac{1}{2} \sum_{a} ((X+Y)_{ia}(X+Y)_{ja} + (X-Y)_{ia}(X-Y)_{ja})$$
(10.3.24)

$$T_{ia} = T_{ai} = 0$$
(10.3.25)
$$H_{pq}^{+}[T] = \sum_{rs} [2(pq|rs) + 2f_{pqrs}^{XC}]T_{rs}$$
(10.3.26)

the double summations are expanded, and the final equation for the constraint Q_{pq} is defined in equation (10.3.27).

$$Q_{pq} = \Omega \sum_{a} ((X+Y)_{pa}(X-Y)_{qa} + (X-Y)_{pa}(X+Y)_{qa}) -\sum_{a} \varepsilon_{a} ((X+Y)_{pa}(X+Y)_{qa} + (X-Y)_{pa}(X-Y)_{qa}) +\Omega \sum_{i} ((X+Y)_{ip}(X-Y)_{iq} + (X-Y)_{ip}(X+Y)_{iq}) +\sum_{i} \varepsilon_{i} ((X+Y)_{ip}(X+Y)_{iq} + (X-Y)_{ip}(X-Y)_{iq}) +\delta_{p\in occ} H_{pq}^{+}[T]$$
(10.3.27)

In order to clarify the constraints and start forming the Z-vector equation, cases are attributed to the four different MO transitions: occupied to occupied, virtual to virtual, occupied to virtual and virtual to occupied. The occupied to occupied and virtual to virtual case is seen in (28) and (29).

1) p and q are both occupied

$$Q_{ij} = \Omega \sum_{a} ((X+Y)_{ia}(X-Y)_{ja} + (X-Y)_{ia}(X+Y)_{ja}) -\sum_{a} \varepsilon_{a} ((X+Y)_{ia}(X+Y)_{ja} + (X-Y)_{ia}(X-Y)_{ja}) + H^{+}_{ij}[T]$$
(10.3.28)

2) p and q are both virtual

$$Q_{ab} = \Omega \sum_{i} ((X+Y)_{ia}(X-Y)_{ib} + (X-Y)_{ia}(X+Y)_{ib}) + \sum_{i} \varepsilon_{i} ((X+Y)_{ia}(X+Y)_{ib} + (X-Y)_{ia}(X-Y)_{ib})$$
(10.3.29)

For the off-diagonal elements, it is beneficial to go back to equation (10.3.15) and then by using symmetries of the coupling matrix, the other two cases are simplified into equation (10.3.30) and (10.3.31).

3) p is occupied, q is virtual

$$Q_{pq} = 2 \sum_{ia} \sum_{jb} (X+Y)_{ia} [\delta_{pi} K_{aqjb}^{S/T} (X+Y)_{jb} + \delta_{pj} K_{iabq}^{S/T} (X+Y)_{jb}] + \frac{1}{2} \sum_{ia} \sum_{jb} [(X+Y)_{ia} (X+Y)_{jb} + (X-Y)_{ia} (X-Y)_{jb}] [\delta_{p \in occ} 2(ab|pq) + \delta_{p \in occ} 2f_{abpq}^{XC} - \delta_{p \in occ} 2(ij|pq) - \delta_{p \in occ} 2f_{ijpq}^{XC}] = 4 \sum_{b} (X+Y)_{ib} \sum_{jc} K_{abjc}^{S/T} (X+Y)_{jc} + H_{ia}^{+} [T]$$
(10.3.30)

4) p is virtual, q is occupied

$$Q_{pq} = 2\sum_{ia} \sum_{jb} (X+Y)_{ia} [\delta_{pa} K_{iqjb}^{S/T} + \delta_{pb} K_{iajq}^{S/T}] (X+Y)_{jb}$$
$$Q_{ai} = 4\sum_{j} (X+Y)_{ja} \sum_{kb} K_{jikb}^{S/T} (X+Y)_{kb}$$
(10.3.31)

Finally, Q_{pq} is plugged into the energy functional, equation (10.3.13), in addition to the partial derivative of the Fock matrix and the Overlap matrix with respect to the MO coefficients

(Appendix H). This gives equation (10.3.32) which solves the constrained optimization problem.

$$Q_{pq} + \sum_{ia} Z_{ia} (\delta_{pi} \delta_{qa} \varepsilon_a + \delta_{pa} \delta_{iq} \varepsilon_q) + H^+_{pq} [Z] = \sum_{rs,r \le s} W_{rs} \sum_{\mu} (\delta_{pr} \delta_{qs} + \delta_{ps} \delta_{qr})$$
(10.3.32)

10.3.3 – Solve Lagrange Multipliers

Now that the constraints have been clarified, the next step is to use equation (10.3.32) to find the Lagrange multipliers, Z and W. Analyzing the definition of W from the functional in equation (10.3.7), it is understood that the virtual MOs will never be lower in energy than the occupied MOs, and hence $W_{ai} = 0$. The constraint Q, however, still has virtual to occupied terms that are nonzero which leads to equations (10.3.33) and (10.3.34) for the occupied to virtual elements in the W matrix.

$$Q_{ia} + Z_{ia}\varepsilon_a + H^+_{ia}[Z] = W_{ia}$$
(10.3.33)

$$Q_{ai} + Z_{ia}\varepsilon_i = W_{ia} \tag{10.3.34}$$

Equation (10.3.34) is then subtracted from equation (10.3.33) to get rid of W and find an equation for Z.

$$0 = Q_{ia} + Z_{ia}\varepsilon_a + H_{ia}^+[Z] - (Q_{ai} + Z_{ia}\varepsilon_i)$$
$$-(Q_{ia} - Q_{ai}) = (\varepsilon_a - \varepsilon_i)Z_{ia} + H_{ia}^+[Z]$$
$$-R_{ia} = (\varepsilon_a - \varepsilon_i)Z_{ia} + \sum_{jb}H_{jb}^+[Z]$$

This leads to a system of linear equations that can be solved to obtain vector Z as shown in equation (10.3.35).

$$-R_{ia} = \sum_{jb} (A+B)_{iajb}^{TDDFT} Z_{jb}$$
(10.3.35)

such that equations (10.3.36) and (10.3.37) are defined below.

$$R_{ia} = Q_{ia} - Q_{ai}$$

$$\sum_{jb} (A+B)_{iajb}^{TDDFT} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 2(ia|jb) + 2f_{iajb}^{XC}$$

$$(10.3.37)$$

With knowledge of Z, cases are applied to equation (10.3.32) in order to find W. The four different cases are defined in equations (10.3.38)-(10.3.41).

1) p and q are both occupied

$$Q_{ij} + H_{ij}^{+}[Z] = W_{ij} + W_{ij}\delta_{ij}$$

$$W_{ij} = \frac{1}{1 + \delta_{ij}} \left(Q_{ij} + H_{ij}^{+}[Z] \right)$$

$$W_{ij} = \frac{1}{1 + \delta_{ij}} \left(\Omega \sum_{a} ((X + Y)_{ia}(X - Y)_{ja} + (X - Y)_{ia}(X + Y)_{ja}) - \sum_{a} \varepsilon_{a} ((X + Y)_{ia}(X + Y)_{ja} + (X - Y)_{ia}(X - Y)_{ja}) + H_{ij}^{+}[T] + H_{ij}^{+}[Z]) \right)$$

$$W_{ij} = \frac{1}{1 + \delta_{ij}} \left(\Omega \sum_{a} ((X + Y)_{ia}(X - Y)_{ja} + (X - Y)_{ia}(X + Y)_{ja}) - \sum_{a} \varepsilon_{a} ((X + Y)_{ia}(X - Y)_{ja} + (X - Y)_{ia}(X + Y)_{ja}) - \sum_{a} \varepsilon_{a} ((X + Y)_{ia}(X + Y)_{ja} + (X - Y)_{ia}(X - Y)_{ja}) + H_{ij}^{+}[P]) \right)$$
(10.3.38)

where the unrelaxed difference density matrix, P is defined as

$$P_{ij} = T_{ij}, P_{ab} = T_{ab}, P_{ia} = \frac{1}{2}Z_{ia}, P_{ai} = \frac{1}{2}Z_{ai}$$

2) p and q are both virtual

$$Q_{ab} = W_{ab} + W_{ab} \delta_{ab}$$

$$W_{ab} = \frac{1}{1 + \delta_{ab}} Q_{ab}$$

$$W_{ab} = \frac{1}{1 + \delta_{ab}} (\Omega \sum_{i} ((X + Y)_{ia} (X - Y)_{ib} + (X - Y)_{ia} (X + Y)_{ib})$$

$$+ \sum_{i} \varepsilon_i ((X + Y)_{ia} (X + Y)_{ib} + (X - Y)_{ia} (X - Y)_{ib}))$$

(10.3.39)

3) p is occupied, q is virtual

$$W_{ia} = Q_{ai} + \sum_{i} \varepsilon_{i} Z_{ia}$$
$$W_{ia} = 4 \sum_{j} (X+Y)_{ja} \sum_{kb} K_{jikb}^{S/T} (X+Y)_{kb} + \sum_{i} \varepsilon_{i} Z_{ia}$$
(10.3.40)

4) p is virtual, q is occupied

$$W_{ai} = 0$$
 (10.3.41)

10.3.4 – Full Derivative

After calculating the Lagrange multipliers, the derivative of the auxiliary functional,

L, is taken with respect to the position of the nuclear coordinates.

$$\frac{dL^{S/T}}{dR_A} = \frac{dG^{S/T}}{dR_A} + \sum_{ia} Z_{ia} \frac{dF_{ia}}{dR_A} - \sum_{pq,p \le q} W_{pq} \frac{dS_{pq}}{dR_A}$$
(10.3.42)

The functional G is then substituted into equation (10.3.42) to obtain (10.3.43).

$$\frac{1}{2} \sum_{iajb} \frac{d(A-B)_{iajb}}{dR_A} \left((X+Y)_{ia} (X+Y)_{jb} + (X-Y)_{ia} (X-Y)_{jb} \right) + 2 \sum_{iajb} \frac{K_{iajb}^{S/T}}{dR_A} (X+Y)_{ia} (X+Y)_{jb} + \sum_{ia} Z_{ia} \frac{dF_{ia}}{dR_A} - \sum_{pq,p \le q} W_{pq} \frac{dS_{pq}}{dR_A}$$
(10.3.43)

Rewriting the rotational Hessians in terms of the Fock matrix and using the definition of the relaxed difference density matrix, T, and its connection to the solution to the Lagrange multiplier, Z, the derivative of the functional G can be collapsed into derivatives of the Fock matrix of particular orbital transitions as seen in equation (10.3.44).

$$= \sum_{ab} \frac{dF_{ab}}{dR_A} T_{ab} + \sum_{ij} \frac{dF_{ij}}{dR_A} T_{ij} + \sum_{ia} \frac{dF_{ia}}{dR_A} Z_{ia}$$
$$+ 2\sum_{iajb} \frac{K_{iajb}^{S/T}}{dR_A} (X+Y)_{ia} (X+Y)_{jb} - \sum_{pq,p \le q} W_{pq} \frac{dS_{pq}}{dR_A}$$
(10.3.44)

The relaxed difference density matrix, P, helps simplify the equation further.

$$=\sum_{pq} \frac{dF_{pq}}{dR_A} P_{pq} + 2\sum_{iajb} \frac{K_{iajb}^{S/T}}{dR_A} (X+Y)_{ia} (X+Y)_{jb} - \sum_{pq,p \le q} W_{pq} \frac{dS_{pq}}{dR_A}$$
(10.3.45)

Finally, all of the terms can be plugged into equation (10.3.45) to obtain the full analytical gradient, which is shown below (equation (10.3.46)).

$$\begin{split} \sum_{pq} P_{pq} \sum_{\mu \in A, \nu \notin A} \frac{dh_{\mu\nu}}{dR_A} \left(C_{\mu p} C_{\nu q} + C_{\nu p} C_{\mu q} \right) + \sum_{pq} P_{pq} \sum_{\mu \in A, \nu \notin A} \frac{dV_{\mu\nu}^{XC}}{dR_A} \left(C_{\mu p} C_{\nu q} + C_{\nu p} C_{\mu q} \right) \\ &+ \sum_{pq} P_{pq} \sum_{\mu \in A, \nu \notin A} \frac{d(\mu\nu|rs)}{dR_A} \left(C_{\mu p} C_{\nu q} + C_{\nu p} C_{\mu q} \right) \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{B'} \gamma_{AB'} q_{B'}^{jb} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu i} S_{\mu\nu'}^{1/2} C_{\nu'a} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{B'} \gamma_{AB'} q_{B'}^{jb} \sum_{\mu \in A, \nu, \nu' \notin A} S_{\mu\nu}^{1/2} C_{\nu i} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu'a} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A',B'} \gamma_{A'B'} q_{B'}^{jb} \sum_{\mu \in A', \nu, \nu' \notin A} S_{\mu\nu}^{1/2} C_{\nu i} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu'a} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A',B'} \gamma_{A'B'} q_{B'}^{jb} \sum_{\mu \in A', \nu, \nu' \notin A} S_{\mu\nu}^{1/2} C_{\nu i} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu'a} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A',B'} \gamma_{A'B'} q_{B'}^{jb} \sum_{\mu \in A', \nu, \nu' \notin A} \frac{dS_{\mu\nu}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'a} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A',B'} \gamma_{A'A} q_{A'}^{ia} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'} \gamma_{A'A} q_{A'}^{ia} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'} \gamma_{A'A} q_{A'}^{ia} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'} \gamma_{A'A} q_{A'}^{ia} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'B'} \gamma_{A'B'} q_{A'B'}^{ia} \sum_{\mu \in A, \nu, \nu' \notin A} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'B'} \gamma_{A'B'} q_{A'B'}^{ia} \sum_{\mu \in B', \nu, \nu' \in B'} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'B'} \gamma_{A'B'} q_{A'B'}^{ia} \sum_{\mu \in B', \nu, \nu' \in B'} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu'b} \\ &+ 2 \sum_{ia,jb} U_{ia} U_{jb} \sum_{A'B'} \gamma_{A'B'} q_{A'B'}^{ia} \sum_{\mu \in B', \nu, \nu' \in B'} \frac{dS_{\mu\nu'}^{1/2}}{dR_A} C_{\nu j} S_{\mu\nu'}^{1/2} C_{\nu$$

$$+2\sum_{ia,jb} U_{ia}U_{jb}\sum_{A'B'}\gamma_{A'B'}q_{A'}^{ia}\sum_{\mu\in B',\nu,\nu'\in B'}S_{\mu\nu}^{1/2}C_{\nu j}\frac{dS_{\mu\nu'}^{1/2}}{dR_{A}}C_{\nu'b}$$

$$+2\sum_{ia,jb} U_{ia}U_{jb}\sum_{A'B'}\gamma_{A'B'}q_{A'}^{ia}\sum_{\mu\in B'\neq A',\nu,\nu'\in C'\neq B'\neq A'}\frac{dS_{\mu\nu}^{1/2}}{dR_{A}}C_{\nu j}S_{\mu\nu'}^{1/2}C_{\nu'b}$$

$$+2\sum_{ia,jb} U_{ia}U_{jb}\sum_{A'B'}\gamma_{A'B'}q_{A'}^{ia}\sum_{\mu\in B'\neq A',\nu,\nu'\in C'\neq B'\neq A'}S_{\mu\nu}^{1/2}C_{\nu j}\frac{dS_{\mu\nu'}^{1/2}}{dR_{A}}C_{\nu'b}$$

$$+4\sum_{ia,jb} U_{ia}U_{jb}\sum_{B'}\frac{d\gamma_{AB'}}{dR_{A}}\left(q_{A}^{ia}q_{B'}^{jb}+q_{A}^{jb}q_{B'}^{ia}\right)$$

$$-\sum_{pq,p\leqslant q} W_{pq}\frac{dS_{pq}}{dR_{A}}$$

(10.3.46)

1 10

Such that **U** is defined below.

$$U_{ia} = (X+Y)_{ia} \qquad U_{jb} = (X+Y)_{jb}$$

The first three terms in equation (10.3.46) represent the derivative of the Fock matrix without any Hartree-Fock exchange, which corresponds to the first term in equation (10.3.45). The next six terms represent the derivative of the coupling matrix, (term 2 in equation (10.3.45)) where the square root of the overlap matrix is brought in by the use of Löwdin partial charge analysis. The last term is based off of the Lagrange multiplier, W, which changes depending on the type of orbital transition as defined in the previous sections.

10.4 – Implementation

The implementation of the TDDFT+TB analytical gradients mimics the implementation of the spin-flip TDDFT Slater-type atomic orbital based analytical gradient code implemented in

the ADF engine of the Amsterdam Modelling Suite. The TDDFT+TB routines also share parts of the code with TDDFTB in the DFTB engine. Therefore, the implementation of TDDFT+TB gradients includes parts of the TDDFT analytical gradient implementation by Seth, Mazur and Ziegler³⁰ as well as the TDDFTB analytical gradients derived by Heringer, et al.²⁸ and implemented by Rüger,³¹ as well as parts from the TDDFT+TB method implemented into the ADF engine by Rüger, et al.²⁵

10.4.1 – General Strategy

The overall flow of the code is as follows:

- (1) Obtain the excitation energy and eigenvectors from linear response TDDFT+TB equations
- (2) Obtain the R vector from stationary requirement of molecular orbital coefficients
- (3) Solve the Coupled Perturbed Kohn-Sham equations (CPKS) to obtain Lagrange multiplier Z
- (4) Use R and Z to find Lagrange multiplier W

(5) Calculate gradient terms and evaluate overall gradient

10.4.2 – TDDFTB and TDDFT Contribution

Despite the derivation above in which the equations enforce the restriction that P = T + Zand $W_{ai} = 0$, the implementation of SF-TDDFT gradients into the ADF engine rearranges some of the matrices to take advantage of symmetric subroutines. More specifically, in the implemented code for TDDFT, $W_{ia} = W_{ai}$, and $P = T+Z+Z^*$. To apply this symmetry to the TDDFT+TB gradient derivation, the ai elements coming from the TDDFT+TB coupling matrix needed to be divided by a factor as the transformation of an upper triangular matrix to a full symmetric matrix requires all entries to be divided by two. The explicit changes are shown in equations (10.4.1)-(10.4.3).

$$R_{ia} = Q_{ia} - Q_{ai}$$

$$Q_{ia} = 2\sum_{b} (X+Y)_{ib} \sum_{jc} K_{abjc}^{S/T} (X+Y)_{jc} + H_{ia}^{+}[T]$$
(10.4.1)

$$Q_{ai} = 2\sum_{j} (X+Y)_{ja} \sum_{kb} K_{jikb}^{S/T} (X+Y)_{kb}$$
(10.4.2)

$$W_{ia} = W_{ai} = 2\sum_{j} (X+Y)_{ja} \sum_{kb} K_{jikb}^{S/T} (X+Y)_{kb} + \sum_{i} \varepsilon_{i} Z_{ia}$$
(10.4.3)

Implementing these changes leads to the final gradient form shown in equation (10.4.4).

$$2 \sum_{\mu \in A, \nu \notin A} \frac{dh_{\mu\nu}}{dR_A} P_{\mu\nu} + 2 \sum_{\mu \in A, \nu \notin A} \frac{d(\mu\nu|rs)}{dR_A} P_{\mu\nu} + 2 \sum_{\mu \in A, \nu \notin A} \frac{dV_{\mu\nu}^{XC}}{dR_A} P_{\mu\nu} + 2 \sum_{\mu \in A, \nu \notin A} \frac{dV_{\mu\nu}^{XC}}{dR_A} P_{\mu\nu} + 2 \sum_{\mu \in A, \nu \notin A} \frac{S_{\mu\nu}^{1/2}}{dR_A} (\Xi_A + \Xi_B) U_{\mu\nu} + 4 \sum_{\mu \in A, \nu \notin A} \frac{d\gamma_{AB}}{dR_A} U_A U_B - \sum_{\mu \in A, \nu \notin A} \frac{dS_{\mu\nu}}{dR_A} W_{\mu\nu}$$
(10.4.4)

Such that the following definitions are used from the implementation of TDDFTB gradients.³¹

$$U_A = \sum_{ia} (X+Y)_{ia} q_{ia,A}$$
 $\Xi_A = \sum_B \gamma_{AB} U_B$

It can be seen that the first three terms in equation (10.4.4) are exactly the same as TDDFT gradients without Hartree-Fock exchange.³⁰ These terms are implemented into the ADF

engine by transforming the matrices back into density integrals as shown in equation (10.4.5).³⁰ The linear response formulation of the density functional equations is modelling the energy with respect to a first order perturbation. For the gradients, it is therefore important to deduce the difference between a full straightforward derivative ζ , and a derivative with respect to a fixed stationary requirement, (ζ) .²⁶

$$2\sum_{\mu\in A, \nu\notin A} \frac{dh_{\mu\nu}}{dR_A} P_{\mu\nu} + 2\sum_{\mu\in A, \nu\notin A} \frac{d(\mu\nu|rs)}{dR_A} P_{\mu\nu}$$

+
$$2\sum_{\mu\in A, \nu\notin A} \frac{dV_{\mu\nu}^{XC}}{dR_A} P_{\mu\nu}$$

=
$$\sum_{\sigma} \int \rho_{\sigma}^{P(\zeta)} \left(T + V_{ext} + V_C + V_{\sigma}^{XC}\right)$$

+
$$\sum_{\sigma} \int \left(V_C^P \rho_{\sigma}^{(\zeta)} + V_{ext}^{\zeta} \rho_{\sigma}^P\right) + \sum_{\sigma\tau} \int \rho_{\sigma}^P f_{\sigma,\tau}^{XC,FULL} \rho_{\tau}^{(\zeta)}$$
(10.4.5)

In addition to parts from TDDFT and TDDFTB, the TDDFT+TB method has additional complexity in the gradient implementation. One example of this is through the use of Löwdin partial charge analysis. As the overlap matrix is a positive semi-definite matrix, there exists a square root that is a symmetric matrix by properties of semi-definite matrices. Hence, to implement the derivative of the square root of the coupling matrix into the ADF engine, the Sylvester equation can be used.³² The Sylvester equation is defined by equation (10.4.6).

$$XA + AX = B \tag{10.4.6}$$

Such that in this case,

$$A = S^{\frac{1}{2}}$$
$$B = \nabla_{\zeta} S$$
$$X = \nabla_{\zeta} S^{\frac{1}{2}}$$

As both A and B are known and calculated for other terms used in the gradient equation, these variables may be brought in and used in order to find the nuclear derivative of the square root of the overlap matrix.

10.5 – Results

To assess the accuracy of the TDDFT+TB gradients, the analytical results were compared to numerical results calculated using finite difference methods, and excited state geometry optimizations were then performed to compare the optimized geometry and emission energy between TDDFT and TDDFT+TB. It is important to note that as an approximate method, it is not expected that TDDFT+TB will be as accurate as the results from TDDFT.

10.5.1 – Computational Details

All of the test cases were completed in the development version of the Amsterdam Modelling Suite (AMS).³³ Numerical vs. analytical calculations were completed for test set 1, and excited state geometry optimizations for TDDFT and TDDFT+TB were completed for test set 2. As the TDDFT+TB method was created as an approximation to TDDFT, the results are focused on the comparison between the two methods rather than the comparison to experiment.

Test Set 1: The chosen test set for numerical vs. analytical gradients includes 37 total molecules consisting of 9 diatomic molecules and 28 small organic molecules from the Thiel test set.³⁴ The molecules in the Thiel test set include a range of different organic molecules from
aliphatic compounds and aromatic hydrocarbons to carbonyl compounds and more. A handful of compounds were tested with different basis sets and exchange-correlation functionals for proof of concept; however, the reported results are all completed at the BP86/DZ level of theory, where BP8635 is a GGA exchange-correlation functional, and DZ refers to a double zeta basis set. All calculations were calculated without symmetry, which is required for the TDDFT+TB method. Considering that the integrals in ADF are calculated on a numerical grid,³⁰ the numerical quality was set to VeryGood for diatomic molecules, and Good for the Thiel test set. All of the compounds were created in MacMolPlt³⁶ for the initial input geometry, where diatomic molecules, in particular, were tested on and off the axis. All reported numerical gradients were tested with a displacement of 0.001 Å in the x, y and z directions. Overall, the gradients give a vector of size $3 \times N$, where N is the number of atoms in the system. Ultimately, the goal is for that vector to match between the numerical and analytical gradients. In each molecule, the average numerical vs. analytical gradient difference is essentially zero, so it is advantageous to report the mean absolute deviation (MAD) between the analytical and numerical gradients for all atoms in all directions rather than reporting each individual difference. Recall that the mean absolute deviation (MAD) is defined in equation (10.5.1)

$$\frac{\sum_{i} |x_{i} - \bar{x}|}{n} \tag{10.5.1}$$

such that \overline{x} is the average numerical vs. analytical gradient difference in a chemical system in all directions, and x_i is the individual numerical vs. analytical gradient difference of a particular atom in a specific direction, and n is the total size of the gradient vector, which is 3×N.

Test Set 2: The chosen test set for excited state optimizations includes 39 total chemical systems consisting of 9 diatomic molecules, 26 small organic molecules from the Thiel test set,³⁴

1 gold nanocluster core, and 3 ligand protected gold nanoclusters. The gold nanoclusters were chosen from a range of application projects that are either published or ongoing in the Aikens lab and optimized with different electronically excited states.^{14,37,38} The reported results for the diatomic molecules, Thiel test set, and a few nanoclusters are completed at the BP86/DZ level of theory, where BP86³⁵ is a GGA exchange-correlation functional, and DZ refers to a double zeta basis set. The gold nanocluster core is calculated at the PBE/TZP level of theory such that PBE is a GGA exchange-correlation functional and TZP refers to a triple zeta polarized basis set. Further, for comparison with the published results, the two emissive points in $Au_{14}Cd(S-Adm)_{12}$ were calculated at the X α /DZ level of theory. For faster convergence, excited state optimizations for all nanoclusters were ran on 6 cores. All of the compounds were created in MacMolPlt³⁶ for the initial input geometry and were optimized to obtain the ground state geometry. All ground state and most excited state geometry optimizations were performed with an energy and gradient convergence criteria of 1×10^{-5} Hartree and 1×10^{-3} Hartree/Bohr respectively. Diatomic molecules were tightened to an energy and gradient convergence criteria of 1×10^{-5} Hartree and 1×10^{-4} Hartree/Bohr respectively. The calculations were calculated without symmetry, which is required for the TDDFT+TB method. Scalar relativistic effects were added into the excited state optimizations with gold using the zeroth-order regular approximation (ZORA).^{39,40} The method was additionally tested using the conductor-like screening model (COSMO) for solvent effects.⁴¹ As this method was created as an approximation to TDDFT, TDDFT was used to check the accuracy of the emission energy and geometry from the excited state geometry optimizations. For this purpose, the same AMS input file was created where the only change between the two methods was the keyword for TDDFT+TB in the EXCITATIONS block. The mean absolute deviation (MAD) and mean unsigned error (MUE) is reported for the difference in emission

energy between TDDFT and TDDFT+TB at the optimized excited state geometry for the diatomic molecules, Thiel test set, and gold nanoclusters. The equation for MAD is in (53), and the mean unsigned error (MUE) is defined in equation (10.5.2).

$$\frac{\sum_{i} |x_{i} - x|}{n} \tag{10.5.2}$$

In this case, \overline{x} is the average emission energy difference between TDDFT and TDDFT+TB for a specific set (i.e., diatomics, thiel test set, and nanoclusters), x_i is the individual emission energy difference of a particular molecule or nanoparticle, and n is the total size of the set (7, 26, and 6 respectively).

10.5.2 – Numerical vs. Analytical Gradients

To check the accuracy of the method, there are several different tests that can be completed. One of these is to check the numerical gradient value at different geometries and see if the analytical gradient is similar at that point. For this process, finite difference is used with a displacement of 0.001 Å for the numerical gradients. The results between the numerical and analytical gradients for TDDFT+TB are reported in table 10.1 for the S₁ states of diatomic molecules, and table 10.2 for the for the S₁ states of the Thiel test set. Recall that the MAD value is recorded for the numerical vs. analytical gradient differences in the molecule between all atoms in all directions.

Molecule	MAD
СО	7.12×10^{-5}
Cl_2	1.95×10^{-5}
Li ₂	8.77×10^{-5}
H_2	1.82×10^{-5}
HCl	1.14×10^{-5}
OH^-	6.97×10^{-5}
LiH	1.53×10^{-3}
NO^+	2.98×10^{-5}
N_2	4.16×10^{-5}

Table 10.1. Numerical vs. analytical gradient differences for diatomic molecules

Molecule	MAD
Acetamide	1.16×10^{-4}
Acetone	5.67×10^{-4}
Adenine	5.98×10^{-5}
Benzene	4.74×10^{-5}
Benzoquinone	9.51×10 ⁻⁵
Butadiene	3.22×10^{-4}
Cyclopentadiene	5.61×10 ⁻⁵
Cyclopropene	2.54×10^{-4}
Cytosine	9.36×10 ⁻⁵
Ethene	4.88×10^{-5}
Formaldehyde	9.28×10^{-5}
Formamide	9.91×10 ⁻⁵
Furan	8.12×10^{-5}
Hexatriene	4.79×10^{-5}
Imidazole	6.83×10 ⁻⁵
Naphthalene	6.76×10^{-5}
Norbornadiene	1.50×10^{-4}
Octatetraene	1.88×10^{-4}
Propanamide	7.34×10^{-5}
Pyrazine	3.02×10^{-5}
Pyridazine	5.77×10^{-5}
Pyridine	4.80×10^{-5}
Pyrimidine	3.93×10^{-5}
Pyrrole	5.31×10 ⁻⁵
Tetrazine	3.24×10^{-5}
Thymine	9.89×10 ⁻⁵
Triazine	5.44×10^{-5}
Uracil	8.77×10^{-5}

Table 10.2. Numerical vs. analytical gradient for organic molecules from the Thiel test set

Overall, the numerical vs. analytical gradients match very well where most molecules have a MAD value of less than 5.00×10^{-4} . The one molecule that seems to have the largest difference is LiH. At the initial input geometry implemented from MacMolPlt, the bond distance between Li and H is 2.43 Å. This distance is at a point on the dissociative wall of the potential energy surface for LiH where the gradient values are fairly large, and hence the numerical vs.

analytical gradient difference is actually relatively low in comparison. It is important to keep in mind that the numerical gradients are based on finite difference, and therefore may change depending on the displacement value. In this case, since the gradient values are so large, if the displacement is lowered to 0.0005 Å, then the new MAD value becomes 1.79×10^{-4} , which is well within the acceptable range. All in all, the numerical vs. analytical gradients serve as one test in which the TDDFT+TB analytical gradients provide accurate results.

10.5.3 – Excited State Geometry Optimization

Not only is the value of the derivative at a particular set of coordinates important to check, but the method should be able to complete a full excited state geometry optimization and find the minimum points on different excited state potential energy surfaces. In this section, the optimized excited state and emission energy difference at the minimum of that state between TDDFT and TDDFT+TB is reported in table 10.3 for diatomic molecules, table 10.4 for the Thiel test set, and table 10.5 for the gold nanoclusters.

Molecule	State	Energy Difference (eV)
СО	\mathbf{S}_1	0.89
H_2	S_2	2.28
Li ₂	\mathbf{S}_1	0.33
HeH ⁺	\mathbf{S}_1	0.05
HCl	\mathbf{S}_1	0.09
OH^-	\mathbf{S}_4	0.09
LiH	\mathbf{S}_1	0.07
\mathbf{NO}^+	S_3	-1.80
N2	\mathbf{S}_1	-0.62

Table 10.3. Emission energy differences between TDDFT and TDDFT+TB for diatomic molecules

Molecule	State	Energy Difference (eV)
Acetamide	\mathbf{S}_1	0.00
Acetone	\mathbf{S}_2	0.03
Adenine	\mathbf{S}_1	0.06
Benzene	\mathbf{S}_1	0.04
Benzoquinone	S_3	0.09
Butadiene	\mathbf{S}_2	0.04
Cyclopentadiene	\mathbf{S}_2	0.04
Cyclopropene	\mathbf{S}_1	0.35
Cytosine	\mathbf{S}_1	0.02
Ethene	\mathbf{S}_4	0.68
Formaldehyde	\mathbf{S}_2	0.12
Furan	\mathbf{S}_2	0.08
Hexatriene	\mathbf{S}_1	0.01
Imidazole	\mathbf{S}_2	-0.11
Naphthalene	\mathbf{S}_1	0.13
Norbornadiene	\mathbf{S}_1	0.13
Octatetraene	\mathbf{S}_1	-0.02
Propanamide	S_1a	0.09
Pyrazine	S_6	0.37
Pyridazine	\mathbf{S}_1	0.09
Pyridine	\mathbf{S}_1	-0.03
Pyrimidine	\mathbf{S}_1	0.02
Tetrazine	\mathbf{S}_1	0.48
Thymine	\mathbf{S}_1	0.14
Triazine	\mathbf{S}_1	0.10
Uracil	S_1	0.14

Table 10.4. Emission energy differences between TDDFT and TDDFT+TB for organic molecules from the Thiel test set

^a Reoptimized TDDFT from TDDFT+TB S₁ minimum

Table 10.5. Emission energy	differences betwe	en TDDFT and	TDDFT+TB for gold
nanoclusters			

Molecule	State	Energy Difference (eV)
Au_3^{7+}	\mathbf{S}_1	0.03
Au ₂₂ (PA) ₁₈	\mathbf{S}_1	0.02
$Au_{25}(SC_{3}H_{7})_{18}^{1-}$	$\mathbf{S}_1{}^{\mathrm{a}}$	0.02
$Au_{14}Cd(S-Adm)_{12}$	\mathbf{S}_1	-0.01
$Au_{14}Cd(S-Adm)_{12}$	S1'	0.00
Au ₁₄ Cd(S-Adm) ₁₂	S_2	-0.01

^a TDDFT geometry that converged to 1.32×10^{-3} constrained gradient max

It is important to note that some states are degenerate with the state below and therefore have issues fully converging to the optimization requirements outlined in the computational details. For this reason, the molecules were not all optimized at the S_1 state. The emission energy difference between TDDFT and TDDFT+TB has a MUE and MAD value of 1.53×10⁻¹ eV & 6.76×10^{-1} eV for diatomic molecules, 1.19×10^{-1} eV & 1.13×10^{-1} eV for the Thiel test set, and 8.33×10^{-3} eV & 1.50×10^{-2} eV for gold nanoclusters respectively. The method does not work as well for diatomic molecules, which is likely a result of the approximation in the coupling matrix. In addition, for cases such as hydrogen, the optimized S_2 energy is so large with TDDFT (19.80) eV) that the TDDFT+TB equivalent (17.52 eV) has a relatively small error when the magnitude of the excitation energy is considered. This issue, however, is inherent to the method and not the gradients. Further, it can be concluded that optimizing degenerate states do not work well for this method. This is a result of numerical inaccuracies in which the gradient may be using the wrong energy level upon displacing the starting geometry. Optimizing degenerate states is an issue with TDDFT as well and results in some states not being able to optimize at all, which is what happens with the S_1 state in pyrrole. In formamide, the S_1 state can be optimized with TDDFT but not with TDDFT+TB. This happens because the TDDFT+TB optimization misses the local minimum point and finds a lower energy geometry in which the molecule errors due to degeneracy with the state below. If the optimization with TDDFT+TB is started at the S₁ state of TDDFT, the method can obtain the minimum. In addition, TDDFT has issues optimizing excited states when the emission energy becomes lower than 0.50 eV. TDDFT+TB will still optimize these states as shown by the examples in chlorine and propanamide. If the optimization with TDDFT is started at the S₁ state of TDDFT+TB, the method can obtain the minimum in propanamide, but not chlorine. Overall, the TDDFT+TB emission energy obtained through the

analytical gradients match TDDFT very well in larger molecules and nanoclusters within 0.15 eV.

The benefit of using TDDFT+TB is that the accuracy has shown to match TDDFT well, but drastically cuts on cost. Therefore, it is imperative to not only compare the emission energy, but also the total run time of the calculation. A few examples are shown in tables 10.5.6-10.5.12 in which the run time is presented in 'days-hours:minutes:seconds'.

Table 10.6. S1 state of LiH

	TDDFT	TDDFT+TB
Runtime	00:01:00	'00:00:42
Emission Energy (eV)	2.31	2.24
Number of Geometry Steps	40	49

Table 10.7. S1 state of Octatetraene

	TDDFT	TDDFT+TB
Runtime	00:19:03	00:05:08
Emission Energy (eV)	3.63	3.65
Number of Geometry Steps	6	6

Table 10.8. S1 state of Cytosine

	TDDFT	TDDFT+TB
Runtime	00:15:55	00:04:59
Emission Energy (eV)	1.23	1.21
Number of Geometry Steps	9	9

Table 10.9. S₁ state of Au7³⁺

	TDDFT	TDDFT+TB
Runtime	01:10:13	00:17:00
Emission Energy (eV)	1.76	1.73
Number of Geometry Steps	13	10

Table 10.10. S1 state of Au₂₂(PA)₁₈

	TDDFT	TDDFT+TB
Runtime	17-06:40:45	6-13:20:19
Emission Energy (eV)	1.19	1.21
Number of Geometry Steps	193	153

The TDDFT+TB method takes approximately a third of the overall run time compared to TDDFT. While this difference is not as important for diatomic and small organic molecules, it really adds up when computing larger systems and nanoclusters. Au₂₂(PA)₁₈, for example, has 256 total atoms and takes 17 days to optimize the S₁ state with TDDFT. With TDDFT+TB, the calculation achieves essentially the same result in less than a week. Further, on a different type of node, the same calculation optimizes to a geometry that has an emission energy of 1.21 eV with TDDFT and 1.20 eV with TDDFT+TB. This means that the difference between TDDFT and TDDFT+TB is well within the error from the small fluctuations seen within the same calculation on different compute nodes.

In addition to run time and accuracy, it is important that this method can still obtain different emissive points. To double check that TDDFT+TB can achieve multiple minima, and not fall back into the same local minimum point, some calculations were performed from an intermediate geometry on $Au_{14}Cd(S-Adm)_{12}$, which has been shown to have dual emission from states S_1 and S_1 ^{',14} The results are displayed in tables 10.11 and 10.12.

Table 10.11. S ₁ state of Au ₁₄ Cd(S-Adm) ₁₂		
TDDFT	ТЪ	

	TDDFT	TDDFT+TB
Runtime	5-20:02:55	1-20:02:23
Emission Energy (eV)	1.11	1.10
Number of Geometry Steps	50	41

	TDDFT	TDDFT+TB
Runtime	5-07:50:17	3-17:14:54
Emission Energy (eV)	0.88	0.88
Number of Geometry Steps	51	108

Table 10.12. S₁' state of Au₁₄Cd(S-Adm)₁₂

10.5.4 – Discussion

Overall, the TDDFT+TB gradient code has shown to reproduce emission energies within 0.70 eV of diatomic molecules, 0.15 eV for organic molecules and 0.02 eV for nanoclusters. Of course, as an approximate method, TDDFT+TB gradients are not perfect and there exist test cases in which the TDDFT+TB results do not match as well with the results obtained from TDDFT. It is critical to keep in mind that the TDDFT+TB method has some problems modelling local transitions due to the atomic transition charges. This problem comes in with the definition of the TDDFT+TB method, specifically in the monopole approximation to the transition density. With this approximation, the basis functions that are on the same atom do not contribute to the atomic transition charges which underestimate vertical excitation energies for σ to π^* and n to π^* transitions.²⁵ This issue has been found to be less important as the system size increases and as the system becomes less symmetrical; thus, the method is ideal for larger systems.

The method currently cuts down about a third of the cost compared to TDDFT, but still uses the coupled perturbed Kohn-Sham (CPKS) equations from TDDFT to solve the Z-vector equation, i.e., to obtain the Lagrange multiplier, Z (equation (10.3.35)). If the TDDFT+TB approximation is made once more in the CPKS equations, the total run time of the calculation is expected to decrease dramatically. With this in mind, however, even the current state of the code is advantageous for larger chemical systems and plasmonic nanoparticles. As the

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chemical system gets bigger, the TDDFT+TB gradients seem to get more accurate compared to TDDFT, and the error is often significantly less than 0.30 eV. This is a good cost to accuracy relationship, especially for the continued study of photochemical systems.

10.6 – Conclusion

Tight binding approximations are extremely useful and can drastically cut the cost of excited state calculations. This work demonstrated the derivation and implementation of the analytical excited state gradients for TDDFT+TB. To derive the analytical excited state gradients, four steps were introduced: defining an energy functional that is equivalent to the vertical excitation energy of that system, setting up an energy functional that is stationary with respect to the molecular orbital coefficients, solving the Lagrange multipliers after the constraints have been defined, and taking the full derivative of each term in the energy functional to obtain the full analytical gradient with respect to the position of the nuclear coordinates. This method is currently implemented into Amsterdam Density Software and will be available for the 2023 release. The code works in serial and in parallel, with and without scalar relativistic effects, with and without COSMO, and produces emission energies for singlet-singlet and singlet-triplet excitations. Overall, the TDDFT+TB gradients have found to cut the overall cost of TDDFT gradients roughly by a factor of 3, while reproducing the TDDFT emission energy of different excited states within 0.15 eV for small organic molecules as well as larger nanoclusters. It is recommended that this method be used for chemical systems that are within hundreds of atoms in size.

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Chapter 11 - Conclusion and Outlook

The research presented in this dissertation outlines the importance of theory in modelling the structure-property relationships in noble metal nanoclusters for the continued study of tunable nanomaterials, which has a vast number of applications in biology, electronics, catalysis and more. Theoretical calculations provide information into the electronic energy levels, which serves as a great tool to decipher the electronic density in photophysical and photochemical processes and help explain experimentally observed behavior.

Changing the metal-organic ligand shell around the core in noble metal nanoclusters drastically changes the optical and photoluminescent properties as demonstrated in Chapters 3, 4 and 5. In Chapter 3, it was found that $Ag_{29}(BDT)_{12}$ NCs show ~40-fold enhancement in PLQY when the ligand is changed from BDT to DHLA. Theoretical analysis predicted the structure after ligand exchange, where the addition of DHLA makes the Ag₁₃ icosahedral core and the Ag-Ag shell bonds elongate, as well as the distance between the thiol groups. With the addition of DHLA, the absorption peaks blue shift, and the higher energy peak shows charge transfer character from the carboxyl group to the Ag shell atoms. Calculations with a long range corrected functional showed that the metal-to-metal transitions may be responsible for the emission; however, more calculations are needed as the S_1 emission energy is significantly less than the reported experimental emission. Similar to the Ag₂₉ NCs, the newly crystallized chiral $Au_{18}(S-Adm)_8(SbPh_3)_4Br_2$ cluster shows core to ligand and ligand to core contributions in the absorption peaks as demonstrated in Chapter 4. The superatomic $P \rightarrow D$ transitions are very low in oscillator strength, which results in different optical properties compared to other gold nanoclusters. Additionally, the cluster is unique as Sb mixes into almost all of the virtual molecular orbitals, and Br mixes into almost all of the occupied molecular orbitals. Chapter 5

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dove more into the role of Sb in gold nanoclusters through the comparison of $[Au_6(SbP_3)_2]^{2+}$ and $[Au_6(PPh_3)_6]^{2+}$. Despite the incredibly similar Au-Au geometric structure and the same superatomic configuration, the p orbitals from Sb atoms directly mix into the frontier orbitals of $[Au_6(SbP_3)_2]^{2+}$. This causes smaller energetic gaps between the frontier orbitals, which drastically changes the single orbital transitions in the theoretical absorption spectrum. Specifically, $[Au_6(SbP_3)_2]^{2+}$ has a lot more mixing of single orbital transitions underneath the peaks, whereas $[Au_6(PPh_3)_6]^{2+}$ has one dominant excitation in the low energy regime.

Heteroatom doping has become an efficient way to tune the structure-property relationships in noble metal nanoclusters to control synthesis, increase luminescence, enhance catalytic processes, and much more.¹⁻³ The oxidation state of the dopant will induce a different charge state of the cluster, which changes the superatomic electronic configuration, and therefore the overall electronic structure of the system. Chapters 6 and 7 elucidated the role of the heteroatom dopant in optical and photoluminescent properties compared to the parent cluster by looking at two examples. In $Au_{24}Pt(SR)_{18}$, it was found that the Pt dopant distorts the geometry of the core, the shell of the nanocluster, the attachment of the propyl groups to the shell and the configurations of the propyl groups themselves. Due to an empty superatomic P orbital, the HOMO-LUMO gap drastically decreases. Additionally, the Pt dopant redshifts the absorption energy of the main peak and completely quenches the photoluminescence. After a thorough investigation of the excited states, it is apparent that the addition of Pt increases the nonradiative contributions in the relaxation mechanism as the electronic energy levels become essentially degenerate with the state below after optimization. The Ag₂₉ cluster is revisited in Chapter 7, only from a dopant point of view rather than ligand exchange. An important observation is that the Pt and Ni dopants show superatomic P nature in the HOMO orbital (in addition to the large p

contribution from the sulfur atoms), whereas the Au and Cu dopants and the parent cluster have no contribution from the core. Regardless of the dopant chosen, the icosahedral core gets smaller, and the cluster has a dominant transition with ligand to metal charge transfer character in the first two absorption peaks. Pt has the highest S_1 emission energy, followed by Ni, Au, and Cu. Emission from the S_1 state in all dopants underestimates the experimental emission energy.

Emission mechanisms are incredibly important to understand, especially from a theoretical perspective as experiments give a great initial picture but cannot specify exact states or electronic transitions. Chapter 8 and 9 provided two examples of noble metal nanoclusters that show unique emission mechanisms that can be explained with theory. $Au_{14}Cd(S-Adm)_{12}$ exhibits a rare dual emission mechanism that originates from the dominant superatomic $P \rightarrow D$ transition in the absorption spectrum. Both emissive points were found to be a result of the S_1 state emitting 0.23 eV apart. The average geometric differences between the minimum structures are quite large, which is a result from the Au-Cd 'bridging' bond enlarging more than 0.10 Å upon both excitation to the S_1 state (from S_0) and conversion to the S_1 ' minimum (as measured from S_1). Both S₁ and S₁' originate from the prominent HOMO-LUMO excitation in the core, however, the HOMO changes between the two states upon optimization, meaning that the PL mechanism does not entirely arise between core-based orbitals. Chapter 9 emphasizes that the PL mechanism does indeed change between the different R groups. Au₂₂(ETP)₁₈, for example, shows a LMMCT PL mechanism that originates from the charge transfer of the π orbitals in the aromatic ligands of the cluster transitioning into MOs that are dominated by the sp orbitals in the ring gold atoms, which then nonradiatively transition down to the core and then follow one of two pathways: (1) radiative relaxation from the optically dark S_1 state or (2) intersystem crossing followed by radiative relaxation from the triplet state. PA and ET, however, do not show charge transfer

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character, and hence do not have a LMMCT PL mechanism but rather hint that the radiative relaxation originates from core-based orbitals.

The final chapter discussed a way to achieve insights into emission mechanisms at a cheaper computational cost through the method development of the analytical excited state gradients for TDDFT+TB. It was found that the TDDFT+TB gradients cut the overall cost of TDDFT gradients roughly by a factor of 3, while reproducing the TDDFT emission energy of different excited states within 0.20 eV. It is recommended that this method be used for larger nanoclusters and chemical systems that are within hundreds of atoms in size.

All in all, the work in this dissertation shows that the geometric and electronic structure is directly related to the changes in optical and photoluminescent properties. The continuation of noble metal nanocluster research is vital as these systems provide a plethora of opportunities in different fields. Unfortunately, as these are larger systems with hundreds of atoms, efficient and accurate theoretical methods are required. Method development in photochemistry is therefore essential, and simplified methods such as TDDFT+TB can allow for more efficient modelling.

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Appendix A - Supporting Information for "Impact of Ligands on Structural and Optical Properties of Ag₂₉ Nanoclusters"

Computational analysis:

Ground state (GS) analysis

The average bond lengths calculated at the BP86/DZ level of the theory of the ground state structure upon the addition of ligands are reported in the manuscript. The differences between NCs are also seen in the HOMO-LUMO (HL) gaps. The HL gap for $Ag_{29}(BDT)_{12}$ is 1.42 eV and drops to 1.24 eV when all 12 DHLA ligands have been appended.



Figure A-1. Bond distance changes from Ag₂₉(BDT)₁₂ and Ag₂₉(DHLA)₁₂ after an S₀ (ground state) geometry optimization. The silver atoms of interest are in green and the rest of the silver atoms are white for clarity. The yellow bonds are bonds that elongated upon the addition of DHLA, whereas the red dotted bonds are bonds that shortened upon the addition of DHLA.



Figure A-2. (A) Comparative UV-vis absorption and (B) normalized PL spectra of Ag₂₉(DHLA)₁₂ NCs (black trace), Ag₂₉(BDT)₁₂ NCs (red trace), and Ag₂₉(BDT)_{12-x}(DHLA)_x NCs (blue trace). (C-E) concentration-dependent PL spectra of three different NCs (a-e, represent lowest to highest concentrations).

Additional investigations were conducted on deprotonated isomers to understand the effect of pH

in solution, as well as the interaction between the carboxyl group and silver atoms.

Unfortunately, many of these isomers struggled to converge the self-consistent field (SCF)

iterations in the gas phase. To circumvent this issue, solvent effects were introduced using the

Conductor-like Screening Model (COSMO) for both, water and DMF.¹⁸. The relative energies of

these calculations can be seen in Table A-1 with their BP86/DZ counterparts.

Table A-1. Relative energies of the different isomers compared to the Trans B structure in different environments after an S_0 geometry optimization.

[eV]		BP86/DZ	with Solvent	Deprotonated with
				Solvent
Ag29(BDT)11(DHLA)	Trans A	0.16	0.08	0.30
	Trans B	0.00	0.00	0.00
	Curled A	0.19	0.16	0.54
	Curled B	0.11	0.08	0.57
Ag29(BDT)10(DHLA)2	Trans A	0.38	0.27	0.05
	Trans B	0.00	0.00	0.00
	Curled A	0.35	0.30	0.87
	Curled B	0.22	0.27	0.52
Ag ₂₉ (BDT) ₉ (DHLA) ₃	Trans A	0.11	0.03	0.16
	Trans B	0.00	0.00	0.00
	Curled A	0.41	0.49	1.28
	Curled B	0.35	0.41	0.93
Ag ₂₉ (BDT) ₈ (DHLA) ₄	Trans A	0.82	0.57	0.16
	Trans B	0.00	0.00	0.00
	Curled A	0.35	0.63	1.55
	Curled B	0.41	0.46	1.25
Ag ₂₉ (DHLA) ₁₂	Trans B	0.00		0.00
	Curled B	0.38		3.43

Table A-2. Relative energies in a.u. of the different isomers compared to the Trans B structure in different environments after an S_0 geometry optimization. It is observed that while the Trans B structure is the most stable isomer in most cases, the Curled B structure becomes ~0.066 a.u. (1.80 eV) more stable with Grimme 1 dispersion. This makes sense, as there is more interaction between the carboxyl group and the Ag or S atoms in the outer shell motifs in the Curled B isomer.

[a.u.]	BP86/DZ	with Grimme Dispersion
Ag ₂₉ (BDT) ₁₂	28.96	29.19
Ag ₂₉ (DHLA) ₁₂ _Trans B	0	0
Ag29(DHLA)12_Curled B	0.014	-0.066

Table A-3. Relative energies in a.u. of Ag₂₉(BDT)₁₂ after an S₀ geometry optimization. Theoretically, the energy to remove one electron from the system is ~0.053 a.u. (1.44 eV).

[a.u.]	BP86/DZ (Charge -3)	BP86/DZ (Charge -2)		
Ag ₂₉ (BDT) ₁₂	0	0.053		

Excited state analysis

The HL gap drops around ~0.62 eV upon photoexcitation $(S_0 \rightarrow S_1)$ between all of the NCs, and as

the emission energy decreases, the HL gap increases.

Table A-4. The HOMO LUMO energy gaps of $Ag_{29}(BDT)_{12-x}(DHLA)_x$ NCs upon photoexcitation.

		HL Energy [eV]	Energy Gap [eV]	Emission Energy [eV]
Ag29(BDT)12	\mathbf{S}_0	1.42		
	S_1	0.84	0.58	0.84
Ag ₂₉ (BDT) ₁₁ (DHLA)	\mathbf{S}_0	1.42		
	S ₁	0.79	0.63	0.79
Ag29(BDT)10(DHLA)2	\mathbf{S}_0	1.43		
	S_1	0.80	0.63	0.80
Ag29(BDT)9(DHLA)3	\mathbf{S}_0	1.41		
	S_1	0.78	0.63	0.78
Ag ₂₉ (BDT) ₈ (DHLA) ₄	\mathbf{S}_0	1.37		
	S_1	0.73	0.64	0.73

The average bond lengths calculated at the BP86/DZ level of theory of the ground (S_0) and first excited (S_1) state structures upon the addition of DHLA ligands are shown in Table A-5. After photoexcitation, the Ag-S bonds in both the crown and motif positions become longer, the Ag-Ag shell bonds become ~0.030 Å shorter, and the structure of the icosahedral core does not change by a notable amount. As the bond length changes are more prominent in the Ag-Ag shell and Ag-S motifs, the type of ligand and its corresponding functional groups, strongly affects the emission energy in part due to changes in these bond lengths.

Table A-5. Average bond lengths of the optimized ground (S_0) and first excited (S_1) state structures upon the addition of DHLA.

[Å]		Ag-Ag Core	Ag-Ag Shell	Ag Shell -S Crown	Ag Shell -S Motif
Ag29(BDT)12	\mathbf{S}_0	2.959	2.984	2.564	2.619
	\mathbf{S}_1	2.961	2.955	2.582	2.633
	Difference	-0.002	-0.028	0.018	0.013
Ag29(BDT)11DHLA	\mathbf{S}_0	2.959	2.992	2.563	2.621
	\mathbf{S}_1	2.959	2.957	2.580	2.631
	Difference	0.000	-0.035	0.017	0.009
Ag ₂₉ (BDT) ₁₀ (DHLA) ₂	\mathbf{S}_0	2.960	2.994	2.563	2.621
	\mathbf{S}_1	2.960	2.964	2.581	2.635
	Difference	0.000	-0.030	0.018	0.013
Ag ₂₉ (BDT) ₉ (DHLA) ₃	\mathbf{S}_0	2.961	2.990	2.563	2.619
	\mathbf{S}_1	2.960	2.956	2.582	2.632
	Difference	0.001	-0.034	0.019	0.013
Ag29(BDT)8(DHLA)4	\mathbf{S}_0	2.961	2.994	2.563	2.618
	\mathbf{S}_1	2.960	2.958	2.583	2.629
	Difference	0.001	-0.036	0.020	0.011

LRCF vs BP86 comparison

To better interpret the vertical excitations and corresponding transitions on a BP86/DZ level of theory, the HOMO and LUMO orbitals were compared to the LRCF/DZ level of theory. The long range corrected functional (LRCF) used was a Yukawa-range separated hybrid with a gamma value of 0.75.²² This type of functional sits high on the density functional theory Jacob's ladder as it accounts for the long-range van der Waals attraction between nonoverlapped electron densities.²³ Unfortunately, this method is too computationally expensive for TDDFT excited state gradients and therefore cannot be used to find emissive properties. The orbitals from the LRCF are more symmetrical as seen in Figure A-3. These orbitals show a super atomic P-D type of transition in the core which would correspond to a S₀ to S₁ transition and would likely be responsible for the PL emission. The HOMO orbital on a BP86/DZ level of theory is delocalized and has contributions from π orbitals in the aromatic rings of BDT and p orbitals from the crown sulfurs. The LUMO also shows a super atomic D shape.



Figure A-3. HOMO and LUMO orbitals compared between (A) BP86/DZ level of theory and (B) LRCF/DZ level of theory.

Dopant positions

Au-doped NC calculations were performed by replacing one silver atom with one gold atom in $Ag_{29}(S_2R)_{12}$ NCs. Three potential dopant positions were tested: at the center of the Ag icosahedral core, in the shell of the Ag icosahedral core, and in the Ag outer shell motifs. The most stable energy isomer reveals the dopant position at the center of the 13 Ag icosahedron core. It is common for a gold mono-dopant to prefer the center position of the NCs;¹⁹⁻²⁰ however, this is important to check as the location depends on the type of dopant.²¹ For comparison, the structure of AuAg₂₈(BDT)₁₂ was also calculated.



Figure A-4. Dopant positions that were tested (A) the center of the Ag icosahedral core (B) the shell of the Ag icosahedral core, and (C) the Ag outer shell motifs. The core silver atoms are green, shell silver atoms are olive green, yellow atoms are sulfur, and the gold atoms are orange.

Gold Doped Position	HL Gap [eV]	Relative Energy [eV]
Center of Core	1.50	0
Outer Core	1.37	0.39
Shell Motif	1.42	0.79

Table A-6. Relative energies, and HL gaps between the different dopant positions.

Structure of most stable doped AuAg₂₈(BDT)₁₂ NCs



Figure A-5. Geometric structure of AuAg₂₈(BDT)₁₂. The olive green atoms are silver shell, green are silver core, yellow atoms are sulfur, grey are carbon, and white are hydrogen. The gold atom is in orange. (A) The entire 173-atom nanocluster. (B) The 13-atom icosahedral core (C) Ag₁₆S₂₄ shell made of four Ag₃S₆ crowns with four Ag₁S₃ motifs.

Structure of most stable doped AuAg₂₈(DHLA)₁₂ NCs

The addition of the dopant increases the core and shell distances of Ag₂₉(DHLA)₁₂ by 0.003 and

0.045 Å, respectively. The Ag shell – S bonds shorten by ~0.005 Å.



Figure A-6. Geometric structure of AuAg₂₈(DHLA)₁₂ lowest energy isomer. The olive green atoms are silver shell, green are silver core, yellow atoms are sulfur, grey are carbon, white are hydrogen and red are oxygen. The gold atom is in orange. (A) The entire 341-atom nanocluster. (B) The 13-atom icosahedral core (C) Ag₁₆S₂₄ shell made of four Ag₃S₆ crowns with four Ag₁S₃ motifs.

[Å]	Ag-Ag Core	Ag-Ag Shell	Ag Shell- S Crown	Ag Shell- S Motif
Ag ₂₉ (BDT) ₁₂	2.959	2.983	2.564	2.619
AuAg ₂₈ (BDT) ₁₂	2.962	2.985	2.564	2.618
Ag29(DHLA)12	2.963	2.992	2.563	2.621
AuAg ₂₈ (DHLA) ₁₂	2.966	3.037	2.559	2.613

Table A-7. Average bond lengths of the optimized structures upon the addition of Au.

The quantum yield, average lifetime (τ_{AV}), and the calculated K_R and K_{NR} values of the four NCs are summarized in Table A-8.

Table A-8. Table of measured quantum yield Φ , average lifetime (τ_{AV}), and the corresponding calculated K_R and K_{NR} values of Ag₂₉(BDT)₁₂, Ag₂₉(BDT)_{12-x}(DHLA)_x NCs with 8.1 mM DHLA under excitation wavelength of 445 and emission wavelength of 655 nm and Ag₂₉(DHLA)₁₂, Au_yAg_{29-y}(DHLA)₁₂ NCs with 1.09% Au under excitation wavelength of 490 and emission wavelength of 655 nm.

NCs	Φ[%]	τ _{AV} [ns]	K _R [s ⁻¹]	K _{NR} [s ⁻¹]
Ag29(BDT)12	0.8	22.39	3.6x10 ⁵	4.4x10 ⁷
Ag29(BDT)12-x (DHLA)x	34.79	2969.16	1.2x10 ⁵	2.2x10 ⁵
Ag ₂₉ (DHLA) ₁₂	4.32	3752.74	1.2×10^4	2.5x10 ⁵
Ag29-yAuy(DHLA)12	17.97	1546.79	1.2x10 ⁵	5.3x10 ⁵

The shape of the calculated absorption spectra of AuAg₂₈(DHLA)₁₂ NCs matches quite well with the experimental spectrum, as seen in Figure A-7. The higher energy peak for AuAg₂₈(DHLA)₁₂ NCs appears at 3.03 eV and corresponds to a H-38 \rightarrow L+3 transition with 0.03927 oscillator strength. The lower energy peak appears at 2.50 eV, which corresponds to a H-21 \rightarrow L+12 transition with 0.01454 oscillator strength.



Figure A-7. (A, B) Absorption spectra of Ag₂₉(BDT)₁₂ and Ag₂₉(DHLA)₁₂ NCs before and after the addition of the Au dopant. (C) Experimental absorption spectrum of Au_yAg₂₉._y(DHLA)₁₂ NCs with 1.09% Au doped was plotted with the corresponding calculated spectrum of AuAg₂₈(DHLA)₁₂ NCs (re-plotted from B, red trace) showing excellent match in the peak positions. I (E) is proportional to [Absorbance/(Energy)²].

Occupied and virtual orbitals

The higher energy peak in Ag₂₉(BDT)₁₂ NCs has an oscillator strength of 0.05170, which corresponds to a HOMO (H) -7→LUMO (L) +7 transition. The lower energy peak in Ag₂₉(BDT)₁₂ NCs is broader and has a transitional range from H-26→L+3-4. The listed occupied orbitals are delocalized and have contributions from π orbitals in the aromatic rings of BDT and p orbitals from the crown sulfurs. The L+7 orbital has contributions from s and p orbitals in the Ag core, but it is mostly delocalized. The L+3 and the L+4 orbitals are degenerate, and both form super atomic D-like orbitals in the core.

The higher peak of $Ag_{29}(DHLA)_{12}$ NCs has an oscillator strength of 0.05173, which corresponds to a transitional range H-30/31 \rightarrow L+14, and the lower peak has an oscillator strength of 0.04279 with a corresponding transition from H-14 \rightarrow L+15. Similar to $Ag_{29}(BDT)_{12}$, the $Ag_{29}(DHLA)_{12}$ NCs have occupied orbitals, which mostly arise from the p orbitals in the sulfur crown positions in the shell. The L+14 orbital has contributions from s and p orbitals in the Ag core. Still, it is mostly delocalized, and the L+15 orbital centers around the carboxyl group at the end of the ligand with slight contributions from the Ag-Ag shell. The pictures of all occupied and virtual orbitals may be seen in Figure A-8 – A-10.



Figure A-8. Occupied and virtual orbitals at BP86/DZ level of theory of the transitions contributing to the higher energy peak in the absorption spectrum.



Figure A-9. Occupied and virtual orbitals at BP86/DZ level of theory of the transitions contributing to the lower energy peak in the absorption spectrum.



Figure A-10. HOMO (bottom) and LUMO (top) orbitals on the DZ/BP86 level of theory for $Ag_{29-y}Au_y(BDT)_{12-x}(DHLA)_x$ where $y_x = 0,0; 0,1; 0,11; 0,12$ and 1,12; respectively.





Figure A-11. Absorption spectrum comparing TDDFT and TDDFT+TB for Ag₂₉(BDT)₁₂ and the Trans B structure of Ag₂₉(BDT)₁₁(DHLA). I (E) is proportional to [Absorbance/(Energy)²]. The TDDFT calculation was run with 500 excitations, and the TDDFT+TB was run with 800 excitations. The excitation difference is visible in the figure with TDDFT only covering ~3.30 eV in the spectrum. For Ag₂₉(BDT)₁₂, the TDDFT calculation took 46 h with 16 cores and 17.68 GB memory whereas TDDFT+TB took 51 minutes with 16 cores and 5.99 GB memory. For Ag₂₉(BDT)₁₁(DHLA), the TDDFT calculation took 25 h with 22 cores and 21.08 GB memory whereas TDDFT+TB took 57 minutes with 16 cores and 6.23 GB memory.

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Appendix B - Supporting Information for "Crystal Structure and Optical Properties of a Chiral Mixed Thiolate/Stibine-Protected Au₁₈ Cluster"

Computational Details

All calculations were done using the Amsterdam Density Functional (ADF) 2018.105 package.¹ The crystal structure was used as an input structure for all calculations, and scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).²⁻³ The theoretical absorption spectrum presented in the main section was calculated with linear response simplified time-dependent density functional theory (sTDDFT)⁴ with the hybrid exchange-correlation functional B3LYP⁵ and a double zeta (DZ) basis set.⁶ The vertical excitation energies were then convolved into the optical absorption spectrum with a 20 nm full width half maximum (FWHM).

TDDFT⁷ and time-dependent density functional theory plus tight binding⁸ (TDDFT+TB) were also performed with other levels of theory including BP86/DZ, BP86-D3/DZ, BP86/TZP, X α /TZP, and X α -D3/TZP where BP86 is a generalized gradient approximation (GGA) exchange-correlation functional⁹, X α is a local density approximation (LDA) exchange-correlation functional,¹⁰ and -D3 refers to the dispersion effects added to the exchange-correlation functional via the Grimme3 model.¹¹ The crystal structure was optimized in the gas phase for these calculations, and the energy and gradient convergence criteria were tightened to 1×10^{-4} and 1×10^{-3} respectively for geometric accuracy. All calculations had a tightened SCF convergence requirement of 1×10^{-8} .

To probe the chirality of the Au₁₈(S-Adm)₈(SbPh₃)₈Br₂ cluster, the cluster was not optimized at the B3LYP/DZ level of theory, which is the main level of theory presented in the manuscript; however, the cluster was optimized at the BP86-D3/DZ and X α /TZP levels of theory. As there are no notable differences in the absorption spectra between the optimized and unoptimized clusters, analysis was continued with the bond distances maintained by the average length represented in the crystal structure.



Figure B-1. Occupied frontier molecular orbitals of Au₁₈(S-Adm)₈(SbPh₃)₄Br₂. Each MO shows superatomic P character in the core of the nanoparticle. The cluster has been converted to wireframe, and contour value lowered to 0.20 for clarity. The x, y, and z axis are thickened and shown in purple, yellow and teal respectively.

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Appendix C - Supporting Information for "A First Glance into

Mixed Phosphine-Stibine Moieties as Protecting Ligands for Gold

Clusters"

Table C-1. Average bond distances of the two [Au₆(SbP₃)₂]²⁺ monomers and [Au₆(PPh₃)₆]²⁺ in the crystal structure and optimized ground state geometry at the BP86-D3/DZP level of theory.

	Au-Au	Au-Sb	Au-P	Sb-C	P-C
Average Bolid Distance (A)	Bonds	Bonds	Bonds	Bonds	Bonds
Crystal	2.760	3.095	2.293	2.173	1.823
	0.048	0.137	0.004	0.018	0.011
BP86-D3/DZP S ₀	2.781	3.078	2.302	2.202	1.819
	0.064	0.018	0.011	0.008	0.007
Au ₆ (PPh ₃) ₆ Crystal	2.713		2.352		1.818
	0.141		0.119		0.004
Au ₆ (PPh ₃) ₆ BP86-D3/DZP S ₀	2.774		2.307		1.818
	0.045		0.009		0.004



Figure C-1. Theoretical circular dichroism spectrum at the BP86-D3/DZP level of theory.

Table C-2. Comparison of vertical energies between BP86-D3/DZP//BP86-D3/DZP and LRCF-D3/DZP//BP86-D3/DZP of the peaks displayed in the theoretical absorption spectra.

Peak	BP86-D3/DZP//BP86-D3/DZP	LRCF-D3/DZP//BP86-D3/DZP
(a)	2.34	2.93
(b)	2.83	3.14
(c)	3.06	3.62
(d)	3.30	3.89
(e)	3.67	4.16



Figure C-2. Molecular orbital details at the BP86-D3/DZP level of theory. Molecular orbital diagram (left) and atomic orbital contributions to molecular orbitals (right) of (A) [Au₆(SbP₃)₂]²⁺ and (B) [Au₆(PPh₃)₆]²⁺.



Figure C-3. Molecular orbital details at the LRCF-D3/DZP level of theory at the BP86-D3/DZP S₀ geometry. Molecular orbital diagram of (A) $[Au_6(SbP_3)_2]^{2+}$ and (B) $[Au_6(PPh_3)_6]^{2+}$.



Figure C-4. Molecular orbitals at the BP86-D3/DZP level of theory for the H-1 \rightarrow L+6 and H \rightarrow L+15 transitions in the 2.83 eV peak.



Figure C-5. Molecular orbitals at the BP86-D3/DZP level of theory for the H-3→L+7 and H-3→L+5 transitions in the 3.30 eV peak.



Figure C-6. Molecular orbitals at the BP86-D3/DZP//BP86-D3/DZP (left) and LRCF-D3/DZP//BP86-D3/DZP (right) levels of theory along with the corresponding orbital energy.



Figure C-7. Molecular orbitals at the BP86-D3/DZP//BP86-D3/DZP (left) and LRCF-D3/DZP//BP86-D3/DZP (right) levels of theory along with the corresponding orbital energy for LUMO+1 – HOMO-1.



Figure C-8. Molecular orbitals at the BP86-D3/DZP//BP86-D3/DZP (left) and LRCF-D3/DZP//BP86-D3/DZP (right) levels of theory along with the corresponding orbital energy for HOMO-2 – HOMO-5.



Figure C-9. Absorption spectrum of $[Au_6(SbP_3)_2]^{2+}$ at (A) BP86-D3/DZP//BP86-D3/DZP level of theory and (C) LRCF-D3/DZP//BP86-D3/DZP level of theory. Absorption spectrum of $[Au_6(PPh_3)_6]^{2+}$ at (B) BP86-D3/DZP//BP86-D3/DZP level of theory and (D) LRCF-D3/DZP//BP86-D3/DZP level of theory. (FWHM = 0.20 eV)



Figure C-10. Molecular orbital details at the LRCF-D3/DZP level of theory at the BP86-D3/DZP S₀ geometry for $[Au_6(PPh_3)_6]^{2+}$. (A) Atomic orbital contributions to molecular orbitals and (B) Molecular orbitals responsible for the 3.44 eV peak.



Figure C-11. Molecular orbitals at the LRCF-D3/DZP level of theory on the BP86-D3/DZP S₀ geometry for (A) the H \rightarrow L+2 transition in the 3.14 eV peak in [Au₆(SbP₃)₂]²⁺ and (B) the H \rightarrow L+2 transition in the 3.44 eV peak in [Au₆(PPh₃)₆]²⁺.



Figure C-12. Molecular orbitals at the LRCF-D3/DZP level of theory on the BP86-D3/DZP S₀ geometry for (A) the H \rightarrow L transition in the 2.93 eV peak in [Au₆(SbP₃)₂]²⁺ and (B) the H \rightarrow L+1 transition in the 2.88 eV peak in [Au₆(PPh₃)₆]²⁺.

Appendix D - Supporting Information for "Characterization of Pt-

doping effects on nanoparticle emission: A theoretical look at

Au₂₄Pt(SH)₁₈ and Au₂₄Pt(SC₃H₇)₁₈"

Table D-1. Relative energies of Au₂₄Pt(SC₃H₇)₁₈ isomers for different locations of the dopant. One BP86/TZP calculation was performed to check the relative energies in each location (center, outer shell of the core, staple).

Dopan	Dopant Position		Energy (eV)
Atom #	Location	BP86/DZ	BP86/TZP
P1	Center	0.00	0.00
P4	Core (Outer Shell)	0.38	
P5	Core (Outer Shell)	0.26	0.03
P7	Core (Outer Shell)	0.53	
P14	Core (Outer Shell)	0.63	
P15	Core (Outer Shell)	0.53	
P22	Core (Outer Shell)	0.28	
P24	Staple Motif	0.69	0.30



Figure D-1. Illustration of the flattened oblate Au₁₂Pt core as it appears in the optimized BP86/DZ ground state of Au₂₄Pt(SC₃H₇)₁₈. The two bonds that are ~0.11 Å larger than the rest of the Au core – Pt center bonds are colored in red.



Figure D-2. Illustration of the Au-S-C angles inside one Au₂S₃ staple in [Au₂₅(SC₃H₇)₁₈]¹⁻ outlined by the red, blue, and yellow circles. The S-C connection in red is directionally opposite from the S-C in blue, creating a trans configuration. The S-C connection in yellow is directionally the same as the one in blue, creating a cis configuration. Altogether, this forms an alternating trans/cis configuration across the staples. Further, the anti-configuration of the propyl groups can be seen in the propyl group connected to sulfur atom 33.



Figure D-3. Atom labels for bond distance analysis are shown in table 6.1.



Figure D-4. BP86/DZ molecular orbital diagram in eV for $Au_{24}Pt(SR)_{18}$ for R = H (left) and $R = C_3H_7$ (right).



Figure D-5. Images of the first six frontier MOs (H-2 through L+2) for $Au_{24}Pt(SR)_{18}$ for R = H (left), and $R = C_3H_7$ (right).



Figure D-6. Absorption spectrum of Au₂₄Pt(SR)₁₈ clusters. (A) Experimental results reprinted with permission from *J. Am. Chem. Soc.* 2008, 130, 5883-5885. Copyright 2008 American Chemical Society. (B) Theoretical spectrum calculated with TDDFT+TB^{*} at the BP86/DZ level of theory for R=H (solid purple) and R=C₃H₇ (dotted red).

*Note: The hydrogen results completed with TDDFT only included 100 vertical excitations. To achieve higher energy ranges at a cheaper computational cost, time-dependent density functional theory plus tight binding (TDDFT+TB) (Ref. 1) was used to calculate the first 1500 vertical excitation energies. These energies were then fitted with a 30 nm FWHM.

PtAu24(SH)18 ⁰ TDDFT			PtAu24(SC3H7)	18 ⁰ TDDFT	
State	Energy (eV)	Major transitions	State	Energy (eV)	Major transitions
S_1	0.423	ם \ ח	S_1	0.473	
S_2	0.454	P -7 P	S_2	0.585	P -7 P
S ₃	0.739		S_3	0.875	
S_4	0.796		S_4	0.941	
S_5	1.000		S_5	1.087	
S ₆	1.023	d→P	S_6	1.131	
S ₇	1.081		S_7	1.157	
S_8	1.088		S_8	1.205	
S 9	1.095		S 9	1.232	
S ₁₀	1.112		${f S}_{10}$	1.297	
S ₁₁	1.318		S_{11}	1.326	
S ₁₂	1.366		S ₁₂	1.365	P -7 D
S ₁₃	1.446		S ₁₃	1.407	d →P
S ₁₄	1.476		S_{14}	1.434	P→D
S ₁₅	1.494		S ₁₅	1.455	d 🗲 b
S ₁₆	1.563	P→D	S ₁₆	1.500	u→ P
S ₁₇	1.578	d→P	${f S}_{17}$	1.543	d D and D D minad
S ₁₈	1.580		S_{18}	1.548	
S19	1.598	$d \rightarrow P$ and $P \rightarrow D$ mixed	S ₁₉	1.551	
S ₂₀	1.615		S ₂₀	1.614	d→P
S ₂₁	1.661	P→D	S_{21}	1.654	

Table D-2. Absorption details (state, energy, transition type) of $Au_{24}Pt(SR)_{18}$ when R = H (left), and $R = C_{3}H_{7}$ (right)

State	Ligand	Pt Center –	Au Core-	Au Core –	Au Core –	Au Shell -	- S-S
State	Ligand	Au Core	Au Core	Au Shell	S Terminal	S Staple	Distance
So	R = Propyl	2.853	3.003	3.133	2.523	2.424	4.817
	SD	0.054	0.256	0.157	0.030	0.008	0.009
S ₃	$\mathbf{R} = \mathbf{Propyl}$	2.822	2.971	3.112	2.530	2.427	4.820
	SD	0.029	0.150	0.115	0.019	0.008	0.011
S19	$\mathbf{R} = \mathbf{Propyl}$	2.848	2.999	3.126	2.528	2.429	4.819
	SD	0.043	0.221	0.165	0.025	0.011	0.010
S ₀	R = Hydrogen	2.827	2.974	3.115	2.516	2.422	4.809
	SD	0.016	0.189	0.119	0.023	0.005	0.006
S ₁₅	R = Hydrogen	2.816	2.963	3.109	2.531	2.425	4.806
	SD	0.017	0.126	0.107	0.008	0.005	0.005
S ₁₈	R = Hydrogen	2.808	2.954	3.095	2.532	2.430	4.815
	SD	0.015	0.108	0.105	0.006	0.008	0.009
S ₂₁	R = Hydrogen	2.830	2.978	3.116	2.521	2.426	4.810
	SD	0.014	0.182	0.137	0.015	0.006	0.006

Table D-3. Average bond distances (Å) and standard deviation of the core and shell atoms at the BP86/DZ S₀, S₃, S₁₅, S₁₈ and S₂₁ minima.

Reference

1. Rüger, R.; van Lenthe, E.; Heine, T.; Visscher, L. Tight-binding approximations to time-dependent density functional theory — A fast approach for the calculation of electronically excited states. *J. Chem. Phys.* **2016**, 144, 184103.

Coordinates in angstroms

Au₂₄Pt(SH)₁₈ S₀

Pt	-0.002185	0.003993	0.003993
Au	-2.121659	1.527578	-1.075045
Au	-2.536522	-1.243027	-0.255114
Au	0.057064	-2.833653	-0.242455
Au	-0.779807	-1.188514	-2.410874
Au	-3.656018	-0.571270	-3.008225
Au	2.033871	-1.004752	-1.692732
Au	1.621753	-0.179875	-4.557285
Au	-2.362065	-3.782819	-2.015529
Au	1.011730	1.546944	-2.118314
Au	-3.997343	-1.573559	2.478594
Au	-2.932138	3.841441	0.819628
Au	-1.157848	4.158157	-2.250192
Au	2.122935	-1.516934	1.075095
Au	2.532880	1.254078	0.256705
Au	-0.059766	2.843583	0.251232
Au	0.780535	1.192017	2.418290
Au	3.658581	0.574059	3.006310
Au	-2.035384	1.022397	1.695393
Au	-1.629064	0.197242	4.561886
Au	2.359104	3.789011	2.018716
Au	-1.028545	-1.539520	2.121018
Au	3.987215	1.586659	-2.472205
Au	2.920723	-3.837924	-0.806508
Au	1.147722	-4.134646	2.267729
S	-3.871953	1.831066	-2.825623
S	-0.958106	-5.142738	-0.580704
S	-2.674856	5.498743	-0.930391
S	0.345807	3.187048	-3.871071
S	3.619389	1.164837	-4.824600
S	-0.384065	-1.498873	-4.856860
S	-3.954087	-2.902172	-3.613732
S	-4.860795	-2.110453	0.279872
S	3.660929	-2.609508	-2.770502
S	3.883951	-1.826773	2.814940
S	0.951098	5.154018	0.591709
S	2.644144	-5.492572	0.943214
S	-0.342343	-3.154532	3.893022
S	-3.635547	-1.137241	4.828462
S	0.388207	1.497341	4.865142
S	3.961125	2.905439	3.605202
S	4.859367	2.117278	-0.274291
S	-3.657643	2.618772	2.795025

Η	-3.032046	2.179841	-3.881839
Н	-1.781436	-5.107952	0.543297
Η	-3.844520	5.201044	-1.628782
Η	-0.560976	2.372681	-4.544938
Н	2.971629	2.366297	-5.113326
Н	0.207397	-2.759637	-4.791901
Н	-3.126181	-2.878920	-4.735836
Η	-4.565167	-3.472714	0.275165
Η	2.785565	-3.207564	-3.675682
Η	3.051228	-2.185909	3.873514
Η	1.774431	5.123803	-0.532395
Η	3.820693	-5.213748	1.638038
Η	0.565948	-2.326250	4.547595
Η	-2.994039	-2.339165	5.128994
Н	-0.190306	2.764186	4.803841
Н	3.144894	2.888211	4.735817
Η	4.568639	3.480513	-0.267318
Η	-2.772629	3.217657	3.690208

Au24Pt(C3H7)18 So

Pt	-0.053679	-0.006859	-0.182174
Au	-1.892125	1.649316	-1.596362
Au	-2.531068	-1.300742	-0.539691
Au	-0.110181	-2.807606	-0.623852
Au	-0.912940	-0.846609	-2.801564
Au	-4.035386	-0.550192	-2.982782
Au	1.832322	-1.055146	-1.968961
Au	1.504130	-0.471998	-4.906116
Au	-2.318773	-3.483774	-2.785123
Au	0.808355	1.483050	-2.465084
Au	-4.174445	-1.015267	2.310488
Au	-3.024566	3.894895	0.078691
Au	-0.551589	4.397482	-2.362764
Au	1.433881	-1.808113	1.493940
Au	2.249244	1.664802	0.009306
Au	-0.260904	2.883198	0.281999
Au	0.737673	0.924125	2.294980
Au	3.779592	0.742232	2.354535
Au	-2.088493	1.024996	1.471048
Au	-1.634977	0.308569	4.406045
Au	2.058472	3.727593	2.250787
Au	-1.254772	-1.554744	2.027238
Au	3.780629	1.125664	-3.010792
Au	2.602691	-3.975651	-0.190633
Au	0.031477	-4.483805	1.952955
S	-3.997100	1.867143	-2.911577

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S	1.257239	3.586182	-3.762600
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S	-4.632193	-2.900712	-3.205532
S	-4.829003	-1.983806	0.203598
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S	3.744196	-1.677121	2.412511
S	-0.105273	4.777111	2.006955
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С	4.736871	3.364552	4.429594
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С	5.339350	-4.550052	-2.488744
С	-0.267454	-4.015907	-7.968701
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С	5.060680	5.101877	6.255275
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С	1.565261	8.654052	1.285643
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Н	2.162703	-7.461678	2.547082
Н	2.364871	-5.187401	3.590051
Н	3.761271	-4.825246	2.554086
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Н	5.066635	-6.717250	3.632536
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Н	0.177624	-4.280699	5.231868
Н	0.505724	-2.605825	4.674867
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Н	-1.412312	-1.767104	6.040896
Н	0.531844	-3.506292	7.711892
Н	0.832836	-1.832533	7.159322
Н	-0.460465	-2.164390	8.337229
Н	-5.262820	5.680137	-1.187884
Н	-4.735475	7.361122	-1.424717
Н	-6.960359	6.964216	-2.529383
Н	-6.262089	5.657949	-3.516578
Н	-5.732120	7.345705	-3.762463
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Η	-3.772641	4.909077	-3.030071
Н	-3.244535	6.601842	-3.337089
Η	-2.949288	3.624753	3.390143
Η	-4.400891	2.764289	4.005926

Н	-4.412876	5.350993	2.321172
Η	-5.199104	4.906734	5.288313
Н	-5.350003	6.438148	4.389649
Н	-3.736060	5.763654	4.731334
Η	-5.868837	4.496632	2.874463
Н	1.010970	4.335501	7.696264
Н	-0.521424	4.712575	6.867159
Н	-0.542814	3.992474	8.497091
Н	0.449392	1.859745	7.594788
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Н	1.724236	2.842821	5.641431
Н	0.177988	3.200849	4.821518
Н	-6.162043	-2.098971	4.714669
Н	-3.960274	-1.173004	6.672495
Н	-5.763518	-2.818945	7.705051
Н	-3.723939	-2.326747	5.313688
Н	-6.400802	-0.979249	6.070201
Η	-5.524460	-3.941467	6.338742
Н	-7.148164	-3.299112	6.692787
Н	2.597765	-1.367400	4.605261
Н	6.333307	-2.014183	3.776748
Η	5.937195	-3.213471	5.034319
Н	6.844301	-1.741144	5.460831
Н	4.835895	-0.319452	4.922133
Н	4.459796	-1.504412	6.189745
Н	3.359603	-2.991300	4.460263
Н	4.920907	-5.913183	-4.156424
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Η	4.816230	-2.768969	-3.649128
Η	3.434693	-3.868489	-3.336681
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Н	2.737120	1.578218	-6.802368
Η	5.611643	0.686457	-6.157824
Η	4.449384	-0.192910	-7.204087
Η	3.833487	3.494987	-8.024732
Η	5.441516	2.813829	-7.683589
Η	4.313894	1.944206	-8.758625
Η	0.959863	2.547486	-5.970168
Η	-0.628216	2.996591	-5.297872
Η	-0.128524	5.430651	-5.727314
Η	1.459083	4.997728	-6.382944
Η	-0.180524	5.396651	-8.248019

Н	0.332916	3.690002	-8.253223
Η	-1.261295	4.138098	-7.597570
Н	-0.572251	-1.859978	-8.109368
Н	0.879933	-2.329040	-7.202574
Η	-1.312662	-4.293881	-8.180070
Н	0.298616	-4.084534	-8.910640
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Н	-1.450297	-5.856457	-0.035059
Н	-2.850763	-7.936040	0.222005
Н	-2.382282	-8.476118	-1.410970
Н	-2.684210	-5.942060	-1.311532
Н	0.256315	-6.806352	-1.652329
Н	-1.155838	-8.364281	-0.118077
Н	-1.000319	-6.813933	-2.934721
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[Au25(SR)18]¹⁻S0

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Н	-5.831384	-3.043813	-7.254281
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Н	-5.061600	-6.695554	3.096370
Н	-0.622669	4.199461	8.502128
Н	-0.652678	4.783542	6.817452
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Η	5.383072	-6.357467	-4.773502
Η	5.104190	-4.850240	-5.686208
Η	5.220285	3.108491	-7.987318
Η	6.630670	3.642635	-7.035454
Η	4.993753	4.179774	-6.578259
Η	-0.920958	-4.573532	-7.681443
Η	0.638849	-4.769233	-6.841921
Η	0.601008	-4.176437	-8.523368

Appendix E - Supporting Information for "Open d Shells Acting as "Glue" for the Creation of Superatomic Occupied Orbitals: A Study on the Optical and PL Properties of Doped Ag₂₉ Systems"



Figure E-1. Theoretical absorption spectrum calculated at the BP86-D3/DZP level of theory from the optimized ground state structures of $[Ag_{28}Ni(BDT)_{12}]^{4-}$ (solid purple line) and $[Ag_{28}Ni(BDT)_{12}(TPP)_4]^{4-}$ (dashed red line).



Figure E-2. Atom labels for the different bonds in Table E-2. Color scheme: silver core = dark green, silver shell = light green, nickel = blue, sulfur = yellow.

Dopant: Ni		Charge: -4	
Danad Atom #	Desition	Absolute Energy	Relative Energy
Doped Atom #	Position	(Hartree)	(eV)
P1	Center	-37.2841	0.00
P2	Core	-37.2407	1.18
P3	Core	-37.2401	1.20
P4	Core	-37.2410	1.17
P5	Core	-37.2392	1.22
P8	Core	-37.2445	1.08
P10	Core	-37.2421	1.14
P14	Staple - tri	-37.2518	0.88
P15	Staple - tri	-37.2542	0.81
P16	Staple - tri	-37.2522	0.87
P18	Staple - tetra	-37.2690	0.41
Dopant: Ni		Charge: -3	
Donad Atom #	Desition	Absolute Energy	Relative Energy
Doped Atom #	Position	(Hartree)	(eV)
P8	Core	-37.3107	0.78
P10	Core	-37.3082	0.85
P14	Staple - tri	-37.3393	0.00

Table E-1. Absolute and relative energies at the BP86-D3/DZP level of theory with the dopant optimized at different geometric positions. The most stable dopant position is outlined in bold.

Table E-2. Average bond distances of [Ag₂₉BDT₁₂]³⁻ and [Ag₂₈NiBDT₁₂]⁴⁻ at the optimized ground state geometry at the BP86-D3/DZP level of theory. Atom labels are shown in Figure E-2.

X = Ag, Ni	[Ag ₂₉ BDT ₁₂] ³⁻ S ₀	[Ag ₂₈ NiBDT ₁₂] ⁴⁻ S ₀ P1
X center - Ag core	2.811 ± 0.101	2.709 ± 0.044
Ag core - Ag core	2.948 ± 0.180	2.848 ± 0.065
Ag shell - Ag core tri	2.971 ± 0.092	3.011 ± 0.081
Ag shell - Ag core tetra	2.941 ± 0.048	2.929 ± 0.035
Ag shell - Ag shell	2.983 ± 0.045	2.957 ± 0.036
Ag shell - S crown	2.503 ± 0.030	2.505 ± 0.021
Ag core - S motif	2.525 ± 0.016	2.569 ± 0.018
S crown - S crown	4.225 ± 0.080	4.226 ± 0.066
S crown - S motif	5.561 ± 0.017	5.555 ± 0.018


Figure E-3. The molecular orbital diagram of $[Ag_{29}BDT_{12}]^{3-}$ and $[Ag_{28}NiBDT_{12}]^{4-}$ at the optimized ground state (S₀) geometry at the BP86-D3/DZP level of theory. The molecular orbitals that form superatomic P, D and S orbitals are shown on the left with a contour value 0.0135. There is a yellow dashed circle around the dumbbell shaped P orbitals for clarity, and the axial node is outlined in bright pink.



Figure E-4. Optical absorption spectrum. (A) Experiment (B) Theoretical spectrum of $Ni_6(SPET)_{12}$, $[Ag_{29}BDT_{12}]^{3-}$ and $[Ag_{28}NiBDT_{12}]^{4-}$ at the optimized ground state geometry at the BP86-D3/DZP level of theory



Figure E-5. Theoretical absorption spectrum of [Ag₂₈NiBDT₁₂]⁴⁻ at the (A) BP86-D3/DZP//BP86-D3/DZP level of theory (B) LRCF-D3/DZP//BP86-D3/DZP level of theory

Peak		[Ag ₂₉ (BDT) ₁₂] ³⁻	[Ag ₂₈ Ni(BDT) ₁₂] ⁴⁻	Ni ₆ (SPET) ₁₂	Experiment
(a)	Energy (eV)	2.49	2.57	2.60	2.38-2.45
	Osc. Strength	2.815x10 ⁻²	2.853x10 ⁻²	3.255x10 ⁻²	
	State	158	173	111	
(b)	Energy (eV)	2.85	2.92	2.94	2.90
	Osc. Strength	8.223x10 ⁻²	3.845x10 ⁻²	1.553x10 ⁻²	
	State	243	269	170	
(c)	Energy (eV)	3.40	3.29	3.12	3.14
	Osc. Strength	1.282x10 ⁻²	1.849x10 ⁻²	3.844x10 ⁻²	
	State	484	487	222	
(d)	Energy (eV)	3.95	3.97	3.99	3.99
	Osc. Strength	1.626x10 ⁻²	1.794x10 ⁻²	1.797x10 ⁻²	
	State	1047	1253	731	

Table E-3. Dominant vertical excitations from each peak calculated from the S $_0$ state at BP86-D3/DZP level of theory

Table E-4. Molecular orbital transitions behind the vertical excitation energies listed in table E-2.

	$[Ag_{29}(BDT)_{12}]^{3-1}$	[Ag ₂₈ Ni(BDT) ₁₂] ⁴⁻	Ni ₆ (SPET) ₁₂
(a)	H-29 → L+2	H-32 → L+1	H-21 → L+1
(u)		H-33 → L	H-1 \rightarrow L+6
(b)	H-33 → L+5	H-36 → L+4	H-25 → L
(0)	H-34 → L+5	H-42 → L+2	H-3 → L+14
(a)	H-7 → L+22	H-48 → L+1	H-42 → L+1
(C)	H-9 → L+13	H-11 → L+14	H-30 → L+3
(d)	H-35 → L+8	H-42 → L+6	H-2 → L+32

Table E-5. Average bond distances of S₀ and S₁ in [Ag₂₉BDT₁₂]³⁻ and [Ag₂₈NiBDT₁₂]⁴⁻ at the BP86-D3/DZP level of theory

X = Ag, Ni	[Ag ₂₈ NiBDT ₁₂] ⁴⁻ S ₀ P1	[Ag ₂₈ NiBDT ₁₂] ⁴⁻ S ₁ P1	[Ag ₂₉ BDT ₁₂] ³⁻ S ₀	[Ag ₂₉ BDT ₁₂] ³⁻ S ₁
X center - Ag core	2.709 ± 0.044	2.709 ± 0.062	2.811 ± 0.101	2.809 ± 0.102
Ag core - Ag core	2.848 ± 0.065	2.847 ± 0.067	2.948 ± 0.180	2.945 ± 0.176
Ag shell - Ag core tri	3.011 ± 0.081	2.951 ± 0.085	2.971 ± 0.092	2.926 ± 0.075
Ag shell - Ag core tetra	2.929 ± 0.035	2.911 ± 0.039	2.941 ± 0.048	2.919 ± 0.045
Ag shell - Ag shell	2.957 ± 0.036	2.923 ± 0.074	2.983 ± 0.045	2.956 ± 0.079
Ag shell - S crown	2.505 ± 0.021	2.513 ± 0.034	2.503 ± 0.030	2.509 ± 0.033
Ag core - S motif	2.569 ± 0.018	2.616 ± 0.045	2.525 ± 0.016	2.562 ± 0.041
S crown - S crown	4.226 ± 0.066	4.210 ± 0.097	4.225 ± 0.080	4.213 ± 0.105
S crown - S motif	5.555 ± 0.018	5.553 ± 0.021	5.561 ± 0.017	5.558 ± 0.023



Figure E-6. Molecular orbital diagram for the S₀ and S₁ states in [Ag₂₉BDT₁₂]³⁻ and [Ag₂₈NiBDT₁₂]⁴⁻ at the BP86-D3/DZP level of theory. The red line is illustrating the decrease in energy in the LUMO after excitation, and the blue line is illustrating the increase in energy in the HOMO after excitation. The green numbers represent the HOMO-LUMO gap in each state.

Dopant: Au		Charge: -3	
Doped Atom #	Position	Absolute Energy (Hartree)	Relative Energy (eV)
P1	Center	-37.2842	0.00
P2	Core	-37.2735	0.29
P3	Core	-37.2736	0.29
P4	Core	-37.2739	0.28
P5	Core	-37.2696	0.28
P8	Core	-37.2787	0.15
P10	Core	-37.2788	0.15
P14	Staple - Tri	-37.2518	0.88
P16	Staple - Tri	-37.2522	0.87
P18	Staple - Tetra	-37.2690	0.41
Dopant: Cu		Charge: -3	
Doped Atom #	Position	Absolute Energy (Hartree)	Relative Energy (eV)
P2	Core	-37.2781	0.55
P3	Core	-37.2783	0.54
P8	Core	-37.2847	0.37
P15	Staple - Tri	-37.2976	0.02
P18	Staple - Tetra	-37.2982	0.00
Dopant: Pt		Charge: -4	
Doped Atom #	Position	Absolute Energy (Hartree)	Relative Energy (eV)
P1	Center	-37.3400	0.00

Table E-6. Absolute and relative energies at the BP86-D3/DZP level of theory with the dopant optimized at different positions. The most stable dopant position is outlined in bold

Table E-7. Average bond distances of S₀ state in [Ag₂₉BDT₁₂]³⁻, [Ag₂₈AuBDT₁₂]³⁻, and [Ag₂₈CuBDT₁₂]³⁻ at the BP86-D3/DZP level of theory

X = Ag, Au	[Ag29BDT12] ³⁻ S0	[Ag28AuBDT12] ³⁻ S ₀ P1	[Ag ₂₈ CuBDT ₁₂] ³⁻ S ₀ P18
X center - Ag core	2.811 ± 0.101	2.792 ± 0.072	2.784 ± 0.090
Ag core - Ag core	2.948 ± 0.180	2.932 ± 0.131	2.919 ± 0.147
Ag shell - Ag core tri	2.971 ± 0.092	2.992 ± 0.106	2.957 ± 0.060
Ag shell - Ag core tetra	2.941 ± 0.048	2.942 ± 0.050	2.907 ± 0.075
Ag shell - Ag shell	2.983 ± 0.045	2.975 ± 0.041	2.979 ± 0.048
Ag shell - S crown	2.503 ± 0.030	2.504 ± 0.029	2.493 ± 0.074
Ag core - S motif	2.525 ± 0.016	2.519 ± 0.015	2.530 ± 0.021
S crown - S crown	4.225 ± 0.080	4.214 ± 0.085	4.226 ± 0.081
S crown - S motif	5.561 ± 0.017	5.560 ± 0.019	5.552 ± 0.022

Table E-8. Average bond distances of S₀ state in [Ag₂₉BDT₁₂]³⁻, [Ag₂₈NiBDT₁₂]⁴⁻, and [Ag₂₈PtBDT₁₂]⁴⁻ at the BP86-D3/DZP level of theory

X = Ag, Ni, Pt	[Ag29BDT12] ³⁻ S0	[Ag28NiBDT12] ⁴⁻ S0 P1	[Ag28PtBDT12] ⁴⁻ S0 P1
X center - Ag core	2.811 ± 0.101	2.709 ± 0.044	2.765 ± 0.080
Ag core - Ag core	2.948 ± 0.180	2.848 ± 0.065	2.902 ± 0.105
Ag shell - Ag core tri	2.971 ± 0.092	3.011 ± 0.081	2.984 ± 0.093
Ag shell - Ag core tetra	2.941 ± 0.048	2.929 ± 0.035	2.927 ± 0.029
Ag shell - Ag shell	2.983 ± 0.045	2.957 ± 0.036	2.964 ± 0.040
Ag shell - S crown	2.503 ± 0.030	2.505 ± 0.021	2.508 ± 0.023
Ag core - S motif	2.525 ± 0.016	2.569 ± 0.018	2.550 ± 0.019
S crown - S crown	4.225 ± 0.080	4.226 ± 0.066	4.233 ± 0.070
S crown - S motif	5.561 ± 0.017	5.555 ± 0.018	5.558 ± 0.019

 $\blacksquare Ag(sp) \blacksquare Ag(d) \blacksquare S(p) \blacksquare X(d) \blacksquare C(p)$



Figure E-7. Atomic orbital contributions in the first few frontier orbitals demonstrating the atomic differences contributing to the 'P' and 'D' superatomic orbitals in each dopant. The molecular orbital diagram is shown below each dopant.



Figure E-8. Theoretical optical absorption spectrum at the respective S_0 state for each dopant at the BP86-D3/DZP level of theory.

Table E-9. Dominant vertical	excitations from e	each peak calculat	ted from the S ₀ state at
BP86-D3/DZP level of theory			

Peak		Ag	Ni	Pt	Au	Cu
(a)	Energy (eV)	2.49	2.57	2.36	2.50	2.47
	Osc. Strength	2.815x10 ⁻²	2.853x10 ⁻²	1.075x10 ⁻²	1.723x10 ⁻²	2.452x10 ⁻²
	State	158	173	88	147	162
(b)	Energy (eV)	2.85	2.92	2.81	2.86	2.82
	Osc. Strength	8.223x10 ⁻²	3.845x10 ⁻²	1.721x10 ⁻²	2.193x10 ⁻²	3.057x10 ⁻²
	State	243	269	183	234	238
(c)	Energy (eV)	3.40	3.29	3.30	3.66	3.58
	Osc. Strength	1.282×10^{-2}	1.849x10 ⁻²	1.704x10 ⁻²	1.029×10^{-2}	1.072×10^{-2}
	State	484	487	447	714	666
(d)	Energy (eV)	3.95	3.97	3.97	3.92	3.99
	Osc. Strength	1.626x10 ⁻²	1.794x10 ⁻²	1.071x10 ⁻²	1.458x10 ⁻²	1.013x10 ⁻²
	State	1047	1253	1105	991	1133

	Ag	Ni	Pt	Au	Cu
(a)	H-29 → L+2	$H-32 \rightarrow L+1$	H-10 \rightarrow L+4	$H-20 \rightarrow L+4$	$H-29 \rightarrow L+1$
	H-33 → L+5	$H-33 \rightarrow L$ $H-36 \rightarrow L+4$	H-11 \rightarrow L+5 H-34 \rightarrow L+2	$H-29 \rightarrow L+2$ $H-6 \rightarrow L+7$	$H-30 \rightarrow L+1$ $H-5 \rightarrow L+7$
(b)	H-34 \rightarrow L+5	H-42 \rightarrow L+2	H-20 \rightarrow L+4	H-31 \rightarrow L+4	H-36 \rightarrow L+3
(c)	H-7 \rightarrow L+22	H-48 → L+1	$H-4 \rightarrow L+23$	$H-28 \rightarrow L+8$	H-53 \rightarrow L+3
	$H-9 \rightarrow L+13$ $H-35 \rightarrow L+8$	H-11 \rightarrow L+14 H-42 \rightarrow L+6	$H-38 \rightarrow L+5$ $H-26 \rightarrow L+18$	$H-13 \rightarrow L+20$ $H-12 \rightarrow L+31$	$H-55 \rightarrow L+2$ $H \rightarrow L+40$
(d)	H-9 \rightarrow L+43	H-29 \rightarrow L+10	$H-21 \rightarrow L+21$	H-37 → L+6	H-14 \rightarrow L+32

 Table E-10. Molecular orbital transitions responsible for the vertical excitation energies

 listed in table E-7.

Table E-11. Emission energy and radiative lifetime value from the optimized S₁ state for each doped cluster at the BP86-D3/DZP level of theory.

Cluster	S ₁ Emission Energy (eV)	Radiative Lifetime (µs)
Ni	1.18	12.65
Pt	1.23	7.85
Ag	1.08	12.34
Au	1.11	21.48
Cu	1.06	10.18

Table E-12. Average bond distances of S_0 and S_1 states in $[Ag_{28}NiBDT_{12}]^{4-}$ and $[Ag_{28}PtBDT_{12}]^{4-}$ at the BP86-D3/DZP level of theory

X = Ag, Ni, Pt	[Ag28NiBDT12] ⁴⁻ S0 P1	[Ag28NiBDT12] ⁴⁻ S1 P1	[Ag28PtBDT12] ⁴⁻ S0 P1	[Ag ₂₈ PtBDT ₁₂] ⁴⁻ S ₁ P1
X center - Ag core	2.709 ± 0.044	2.709 ± 0.062	2.765 ± 0.080	2.766 ± 0.083
Ag core - Ag core	2.848 ± 0.065	2.847 ± 0.067	2.902 ± 0.105	2.903 ± 0.113
Ag shell - Ag core tri	3.011 ± 0.081	2.951 ± 0.085	2.984 ± 0.093	2.922 ± 0.079
Ag shell - Ag core tetra	2.929 ± 0.035	2.911 ± 0.039	2.927 ± 0.029	2.909 ± 0.035
Ag shell - Ag shell	2.957 ± 0.036	2.923 ± 0.074	2.964 ± 0.040	2.925 ± 0.079
Ag shell - S crown	2.505 ± 0.021	2.513 ± 0.034	2.508 ± 0.023	2.517 ± 0.035
Ag core - S motif	2.569 ± 0.018	2.616 ± 0.045	2.550 ± 0.019	2.589 ± 0.043
S crown - S crown	4.226 ± 0.066	4.210 ± 0.097	4.233 ± 0.070	4.223 ± 0.098
S crown - S motif	5.555 ± 0.018	5.553 ± 0.021	5.558 ± 0.019	5.557 ± 0.022

X = Ag, Au	[Ag ₂₈ AuBDT ₁₂] ³⁻ S ₀ P1	$[Ag_{28}AuBDT_{12}]^{3-} \\ S_1 P1$	[Ag ₂₈ CuBDT ₁₂] ³⁻ S ₀ P18	$[Ag_{28}CuBDT_{12}]^{3-} \\ S_1$
X Center - Ag core	2.792 ± 0.072	2.794 ± 0.066	2.784 ± 0.090	2.789 ± 0.123
Ag core - Ag core	2.932 ± 0.131	2.935 ± 0.147	2.919 ± 0.147	2.925 ± 0.152
Ag shell - Ag core tri	2.992 ± 0.106	2.944 ± 0.109	2.957 ± 0.060	2.912 ± 0.058
Ag shell - Ag core tetra	2.942 ± 0.050	2.924 ± 0.043	2.907 ± 0.075	2.880 ± 0.066
Ag shell - Ag shell	2.975 ± 0.041	2.948 ± 0.078	2.979 ± 0.048	2.954 ± 0.069
Ag shell - S crown	2.504 ± 0.029	2.509 ± 0.035	2.493 ± 0.074	2.500 ± 0.078
Ag core - S motif	2.519 ± 0.015	2.555 ± 0.037	2.530 ± 0.021	2.563 ± 0.032
S crown - S crown	4.214 ± 0.085	4.199 ± 0.114	4.226 ± 0.081	4.215 ± 0.105
S crown - S motif	5.560 ± 0.019	5.558 ± 0.023	5.552 ± 0.022	5.552 ± 0.024

Table E-13. Average bond distances of S₀ and S₁ states in [Ag₂₈AuBDT₁₂]³⁻ and [Ag₂₈CuBDT₁₂]³⁻ at the BP86-D3/DZP level of theory



Figure E-9. HOMO - LUMO gaps at the S₁ optimized geometry for each dopant at the BP86-D3/DZP level of theory. Pictures of the electronic density in the HOMO and LUMO MOs are shown above and below the corresponding dopant.

Appendix F - Supporting Information for "Deciphering the Dual Emission in the Photoluminescence of Au₁₄Cd(SR)₁₂: A Theoretical Study using TDDFT and TDDFT+TB"



Figure F-1. Theoretical absorption spectrum of Au₁₄Cd(S-Adm)₁₂ comparing the TDDFT (blue) methodology to TDDFT+TB (green dashed) at the X α /DZ level of theory. The convolved spectrum shows a similar shape between methods although the oscillator strength is slightly higher for TDDFT+TB in the high energy region.

From the spectra in Figure F-1, it is apparent that the vertical excitation energies obtained from TDDFT and TDDFT+TB are quite similar, resulting in a similar absorption shape. This excited state methodology is of interest as the TDDFT+TB method is extremely effective at reproducing TDDFT calculations for large nanoparticles at a fraction of the computational cost.¹ TDDFT+TB targets the computationally expensive coupling matrix in TDDFT by applying a first order monopole approximation to the transition density in the linear response formulation.² Unlike time-dependent density functional tight binding (TDDFTB), a semi-empirical method that uses the same monopole approximation to calculate the coupling matrix, TDDFT+TB uses a

DFT ground state reference and Löwdin partial charge analysis inside the coupling matrix. These two differences make TDDFT+TB more applicable for modeling a wide variety of systems as the partial charge analysis is more suitable with larger basis set size, and DFTB may only be applied to molecules in which the DFTB parameters exist for the particular combination of atoms; in comparison, TDDFT+TB can be implemented for any chemical species of interest.²

References

1. Asadi-Aghbolaghi, N.; Rüger, R.; Jamshidi, Z.; Visscher, L. TD-DFT+TB: An Efficient and Fast Approach for Quantum Plasmonic Excitations. *J. Phys. Chem. C* **2020**, 124, 14, 7946-7955.

2. Rüger, R.; van Lenthe, E.; Heine, T.; Visscher, L. Tight-binding approximations to time-dependent density functional theory — A fast approach for the calculation of electronically excited states. *J. Chem. Phys.* **2016**, 144, 184103.



Figure F-2. A. HOMO and LUMO molecular orbitals on the X α /DZ level of theory of the second enantiomer. The HOMO forms a superatomic P shape in the core and the LUMO forms a superatomic D_z² shape in the core. B. Theoretical absorption spectrum obtained from TDDFT+TB using X α /DZ level of theory. The theoretical peak occurs at 1.65 eV. This value is calculated to be slightly higher than enantiomer 1 due to variations in the numerical results of the computations; these values can be considered as the same to the expected numerical accuracy for the calculations. C. Experimental absorption spectrum with a peak at 2.25 eV and shoulder at 2.95 eV (data adapted with permission from Nat. Commun. 11 2897 (2020).



Figure F-3. Graphical image of the excitation/relaxation process in the second enantiomer of Au₁₄Cd(S-Adm)₁₂. The first emissive point occurs at 1.08 eV with a lifetime of 3.11 μ s and the second emissive point occurs at 0.89 eV with a lifetime of 2.49 μ s. These values are the same as those for enantiomer 1 to the expected numerical accuracy for the calculations.



Figure F-4. Pictorial image of how the bonds move during excitation or relaxation in enantiomer 2. The blue/pink solid lines represent the specific bond enlarging, while the red/orange dotted lines represent the specific bond shortening. Slight variations are observed relative to the calculations for enantiomer 1; these are attributed to numerical variations in the calculations.

Table F-1. Average bond lengths of the ground state and both emissive states in Au₁₄Cd(S-Adm)₁₂ enantiomer 2 on the X α /DZ level of theory. These values are the same as those for enantiomer 1 to the expected numerical accuracy for the calculations.

Average Bond Length (Å)			
Bond	So	S ₁	S ₁ '
Au core - Au core	2.796 ± 0.126	2.789 ± 0.132	2.830 ± 0.160
Au shell - Au shell	2.947 ± 0.106	2.895 ± 0.071	2.855 ± 0.111
Au core - Cd core	2.805 ± 0.046	2.893 ± 0.188	2.902 ± 0.154
Au shell - S terminal	2.463 ± 0.024	2.473 ± 0.024	2.497 ± 0.045
Cd core - S terminal	2.537 ± 0.000	2.627 ± 0.000	2.655 ± 0.000
Au shell - S staple	2.404 ± 0.040	2.424 ± 0.055	2.432 ± 0.057



Figure F-5. Molecular orbital diagram of the ground and two emissive minima compared to the ground state in enantiomer 1. The left image shows the HOMO (bottom) and LUMO (top) orbitals of each state, and the HOMO-LUMO gap is presented on the right where the emissive points are represented by a cartoon with a single electron in one of the D orbitals.



Figure F-6. Different viewpoints of the HOMO and LUMO molecular orbitals in Au₁₄Cd(S-Adm)₁₂ enantiomer 1. (A) HOMO molecular orbital where the two lobes are outlined by the peach circles, and the xy nodal plane is marked by the green line (contour value = 0.019). (B) LUMO molecular orbital where the three lobes are outlined by the peach circles, and the z axis is marked by the green line (contour value = 0.019). (C) HOMO and LUMO molecular orbitals along the corresponding x,y and z axis (contour value = 0.0135).

Coordinates for Optimized Structures

Enantiomer 1 S₀:

Au	18.826345	11.272164	9.567460
Au	18.469915	8.650764	8.944262
Au	17.140821	12.378987	6.093773
Au	16.794273	9.871098	5.348319
Au	17.651789	7.215748	6.466013
Au	14.369307	11.462205	6.005779
Au	16.126333	11.758879	3.321629
Au	19.420858	12.232007	4.365086
Au	20.184269	13.375444	7.791636
Au	21.176804	9.610722	9.399049
Au	18.916336	8.286575	11.727984
Au	16.651943	9.928868	10.838837
Au	16.523851	13.143375	9.414584
S	15.548258	12.098143	11.332938
S	16.636312	7.574785	11.683198
S	21.176605	9.030694	11.732130
S	21.570730	10.333101	7.145338
S	19.090502	6.355518	8.170394
S	16.077164	7.605872	4.705819
S	13.885732	12.375561	3.827033
S	18.292740	11.227481	2.501222
S	17.179813	14.393845	7.479259
S	19.726419	13.494112	10.126856
S	21.105061	13.381914	5.609379
S	14.153061	10.887336	8.300911
С	12.461898	8.677827	1.294819
Н	11.843113	7.862346	0.861631
Н	13.460014	8.634235	0.805762
С	23.237036	14.262275	13.097463
Н	22.516743	14.804696	13.748757
Н	24.230324	14.304024	13.594947
С	19.283518	5.701394	1.837207
Н	19.834938	5.386483	0.924447
Н	19.823627	5.278194	2.712634
С	16.336151	6.359889	14.184708
Н	17.443485	6.272870	14.231618
Н	15.952109	5.483279	13.619395
С	17.091026	7.257508	0.652745
Н	16.560516	7.672299	-0.230997
С	24.427683	6.386346	11.527991
Н	25.504467	6.611297	11.376948
С	15.482041	12.629740	14.069567
Н	15.403023	11.534685	14.232032

Η	14.456851	13.014674	13.879959
С	23.314323	14.937808	11.723110
Н	23.624683	15.997783	11.840941
С	16.378546	12.918501	12.866332
С	21.948217	6.703874	13.075042
Н	22.287273	7.368479	13.898096
Н	20.861567	6.512158	13.221210
С	18.040306	4.893253	8.857543
С	14.391409	8.994865	15.539240
Н	14.107304	9.937152	15.021961
Н	13.949440	9.030134	16.558525
С	23.634583	7.705302	11.515133
Η	23.763319	8.229346	10.541793
Н	24.001398	8.382890	12.315718
С	21.654133	6.490405	10.607823
Н	21.765734	7.019500	9.633697
Н	20.565264	6.316360	10.742857
С	12.371929	7.585881	10.087224
Η	12.200005	7.412890	11.171573
С	22.160852	7.380964	11.726687
С	22.495798	12.702656	10.014802
Н	22.522474	13.162130	9.000452
Н	22.167633	11.643475	9.876977
С	13.481129	9.604789	3.377825
Н	14.497550	9.590401	2.929123
Н	13.625081	9.479209	4.475733
С	17.073627	7.106460	3.139269
С	16.554197	5.210129	8.829572
Н	16.348721	6.105963	9.451582
Н	16.259151	5.451288	7.781586
С	17.777121	12.367493	13.103792
Н	18.406643	12.563958	12.212234
Η	17.740532	11.264494	13.236318
С	16.289032	7.588803	16.371239
Н	15.870063	7.603831	17.400511
Н	17.393744	7.506791	16.463259
С	24.326746	14.194136	10.843544
Н	25.335056	14.233632	11.310239
Н	24.400066	14.685728	9.849174
С	24.422096	7.558875	5.874734
Н	25.470465	7.444628	6.223113
С	10.574474	9.880519	3.200270
Η	9.577721	9.921572	3.687010
С	23.756620	8.700511	6.659501
Н	23.753498	8.474106	7.749085
Н	24.314634	9.649764	6.515471

С	13.487202	6.716899	8.019222
Н	14.127227	5.915117	7.595390
С	16.216393	3.701356	10.792477
Н	16.011797	4.585067	11.435467
Н	15.640571	2.842031	11.201271
С	12.684855	11.158762	1.595781
Н	13.691873	11.143022	1.125207
Н	12.228125	12.150264	1.388708
С	20.027725	17.199587	3.095717
Н	19.424637	16.573580	2.402099
Н	19.980433	18.245100	2.720434
С	24.407095	7.900298	4.379053
Н	24.900789	7.089360	3.800721
Н	24.981405	8.834481	4.197238
С	22.739561	5.385640	13.090261
Н	22.593126	4.886959	14.071316
С	18.505863	4.590272	10.277619
Н	18.345673	5.475969	10.928446
Н	19.592468	4.352141	10.274092
С	14.208868	6.496263	15.500711
Н	13.761330	6.492740	16.517982
Н	13.797485	5.619136	14.955255
С	11.028470	7.620002	9.348318
Н	10.383033	8.422418	9.767157
Н	10.493780	6.655593	9.489139
С	20.265888	18.009487	5.454554
Н	20.225075	19.066750	5.113477
Н	19.837412	17.972080	6.479300
С	22.189428	6.766845	4.144178
Н	22.652878	5.940502	3.561775
Н	21.142284	6.872398	3.793039
С	21.541435	7.582330	6.413793
Н	20.483814	7.704712	6.085956
Н	21.515415	7.356249	7.500480
С	12.820601	10.942343	3.098054
С	11.455464	11.004028	3.773431
Н	11.579877	10.883101	4.871928
Н	10.980183	11.992980	3.598112
С	14.335161	14.669207	7.380732
Н	14.333769	14.427647	8.468086
Н	14.294058	13.692930	6.838028
С	17.099634	5.582973	3.068907
Н	16.064260	5.179779	3.058708
Н	17.607862	5.183400	3.973906
С	13.154369	15.808395	5.490888
Η	13.095436	14.852277	4.928491

Η	12.275113	16.423986	5.200010
С	16.346457	7.683887	1.928227
Н	16.322079	8.793182	2.002548
Н	15.297735	7.314608	1.902443
С	16.443275	14.423501	12.623103
Н	15.424685	14.818297	12.417540
Н	17.066557	14.623960	11.722660
С	19.444851	17.120628	4.511843
Н	18.386654	17.461306	4.502223
С	14.438939	7.773352	13.357096
Н	14.182041	8.707648	12.812237
Н	14.032706	6.917919	12.774031
С	15.918398	8.882248	15.634738
Н	16.326546	9.757938	16.184307
С	22.435209	5.173298	10.612959
Н	22.059992	4.527170	9.790483
С	12.143757	6.747558	7.281195
Н	11.625673	5.769781	7.390960
Н	12.316179	6.910412	6.193979
С	22.958479	8.071628	3.903783
Н	22.945532	8.324844	2.822317
С	11.269541	7.869157	7.853077
Н	10.296868	7.901450	7.317174
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Η	17.542050	8.712325	14.227054
С	14.050188	8.149680	7.913636
Н	15.012878	8.113547	8.473939
Н	14.286256	8.411261	6.856965
С	13.141964	9.212511	8.519723
С	15.786322	7.725989	13.435707
С	21.458595	12.834388	12.001830

Η	20.734239	13.397059	12.625868
Η	21.088141	11.790977	11.906818
С	15.475899	6.465369	15.559052
Н	15.679781	5.506125	16.079757
С	22.843191	12.852753	12.670551
Н	22.764415	12.382046	13.673503
С	17.978838	13.717679	-1.589899
Н	17.940529	14.519657	-2.358923
Н	18.155103	12.757796	-2.122348
С	13.059405	6.443681	9.455141
Н	12.567961	5.447829	9.525726
Η	14.009886	6.394521	10.031845
С	11.836712	9.285314	7.732719
Η	11.188401	10.085139	8.149288
Η	12.061263	9.558668	6.678147
С	24.067161	5.605382	13.125114
Η	24.445661	6.266835	13.934120
Η	24.644101	4.657046	13.176506
С	18.236056	3.802831	7.715070
Η	19.314858	3.540762	7.762536
Η	18.007079	4.109397	6.671036
С	22.610736	8.719398	6.430701
С	12.858643	8.876669	9.983541
Η	12.230457	9.672604	10.437653
Η	13.819674	8.847550	10.540336
С	12.721507	8.213723	3.035129
Η	13.249386	7.285874	3.343785
С	22.023453	14.926804	10.751232
Η	21.292346	15.506961	11.354948
Η	22.073068	15.392866	9.743783
С	12.059409	9.659964	1.098827
Η	12.095415	9.776121	-0.005034
С	23.930978	12.718831	10.420530
Η	24.636386	12.147521	9.780715
С	14.675876	16.459594	4.966204
Η	14.783014	16.630925	3.873517
С	22.069600	4.386393	12.228491
Η	20.989484	4.167653	12.379239
Н	22.614079	3.418498	12.271881
С	22.659925	9.088158	4.950141
Н	23.186048	10.056839	4.811757
Н	21.623818	9.218595	4.565746
С	17.413966	3.357509	10.502563
Н	17.658320	3.071569	11.547857
С	17.764430	5.794063	0.558528
Η	18.339152	5.525216	-0.354268

Η	16.753396	5.342172	0.459291
С	10.599978	9.620172	1.568774
Н	10.070590	8.768169	1.089430
С	15.607172	4.150144	8.960077
Η	14.536742	4.427711	8.888060
С	19.046717	7.937612	0.799656
Η	19.644276	7.710385	-0.110029
Η	18.963505	9.042370	0.886498
С	14.686739	17.801665	5.707888
Η	13.852330	18.440218	5.345579
Η	15.634488	18.346751	5.502459
С	18.469904	5.235086	1.800035
Н	18.549748	4.130380	1.720739
С	15.895762	2.977122	8.017560
Н	15.259229	2.107161	8.289604
Η	15.643846	3.258815	6.971439
С	22.197549	17.178410	5.245178
Н	22.984915	17.712055	5.818374
С	17.375408	2.592872	8.115926
Η	17.595863	1.750073	7.427237
С	15.850879	15.597300	5.454547
Η	15.863809	14.614777	4.928243
Н	16.816991	16.107109	5.243186
С	16.410194	14.874480	15.075373
Η	16.884409	15.382479	15.943208
Η	15.384370	15.289714	14.969209
С	16.648142	13.659581	-0.828832
Η	15.817929	13.454720	-1.537004
С	17.549758	15.269514	0.867447
Η	17.372062	16.232523	1.392437
С	21.396793	16.556140	2.950780
Н	21.603667	16.641117	1.861945
С	18.879166	15.327801	0.103815
Η	18.851807	16.153334	-0.640779
Η	19.717090	15.544091	0.801800
Cd	16.543909	10.456206	8.092673
Au	19.367270	10.373994	6.658952
Н	10.074845	10.550648	1.261198

Appendix G - Supporting Information for "Understanding the

Ligand-Dependent Photoluminescent Mechanism in Small Alkynyl

Protected Gold Nanoclusters"

Table G-1: Comparison of the computational details between TDDFT and TDDFT+TB calculations at the BP86/DZ level of theory on Au₂₂(ETP)₁₈.



Figure G-1: Comparison of the absorption shape and excitation energies between TDDFT and TDDFT+TB at the BP86/DZ level of theory on Au₂₂(ETP)₁₈.

Properties of Au₂₂(ETP)₁₈



Figure G-2: Theoretical circular dichroism spectrum of $Au_{22}(ETP)_{18}$ and Au_7 core from the S₀ geometry at the BP86/DZ level of theory. As the cluster has four superatomic valence electrons, the core has a +3 charge.



Figure G-3: Molecular orbitals responsible for the main electronic transitions at the 2.40 eV shoulder peak at the BP86/DZ level of theory with a contour value of 0.0135.



Figure G-4: Molecular orbitals responsible for the main electronic transitions at the 2.63 eV peak at the BP86/DZ level of theory with a contour value of 0.0135.



Figure G-5: Molecular orbitals responsible for the transition from H-3 (red/blue) \rightarrow L+9 (teal/orange) in the 2.63 eV peak at the BP86/DZ level of theory with a contour value of 0.0135. There is little to no overlap in electronic density, showing that this excitation has charge transfer character. A similar comparison can be seen with the other transitions in this cluster.



Figure G-6: Spin density from the T1 state in Au22(ETP)18 at the BP86/DZ level of theory



Figure G-7: Geometric changes in the core between the ground state and different excited states in Au₂₂(ETP)₁₈ at the BP86/DZ level of theory.



Figure G-8: Proposed theoretical PL mechanism for Au₂₂(ETP)₁₈ showing LMMCT.

Loval of Theory		Average Bond	Distances (Å)	
Level of Theory	\mathbf{S}_0	S_1	T_1	S ₁₅
Au Center – Au Core	2.771 ± 0.025	2.768 ± 0.018	2.790 ± 0.037	2.788 ± 0.034
Au Core – Au Core	2.800 ± 0.039	2.827 ± 0.062	2.824 ± 0.068	2.821 ± 0.063
Au Core – Au Ring	2.981 ± 0.040	2.991 ± 0.067	2.977 ± 0.065	2.996 ± 0.047
Au Sigma – Au Ring	3.094 ± 0.171	3.054 ± 0.140	3.055 ± 0.155	3.102 ± 0.187
Au Ring – Au Ring	3.150 ± 0.143	3.156 ± 0.118	3.113 ± 0.144	3.150 ± 0.199
Au Sigma – Au Pi	3.139 ± 0.278	3.143 ± 0.269	3.166 ± 0.249	3.158 ± 0.283
Au Pi – Au Ring	2.940 ± 0.011	2.922 ± 0.019	2.897 ± 0.043	2.944 ± 0.013
Au Pi – C Cusp	2.537 ± 0.472	2.541 ± 0.479	2.537 ± 0.475	2.538 ± 0.457

Table G-2: Average bond lengths in angstrom of different electronic states at the BP86/DZ level of theory in Au₂₂(ETP)₁₈.

	Crystal	So	S 1	T_1	S15
A-B-C	126.2	125.4	127.0	128.5	125.9
A-B-D	96.2	95.6	96.6	97.6	95.9
A-B-E	84.8	94.1	95.4	96.3	94.4
A-B-F	63.1	65.2	65.4	66.4	65.0
A-B-G	44.3	38.9	39.5	41.9	44.1
A-B-H	32.0	32.6	33.1	34.4	34.2
E- F -G	145.2	128.1	133.7	136.9	141.7
D-F-H	160.7	161.3	164.7	165.8	167.4
D-E-I	163.7	178.4	178.3	177.0	175.0
H-G-J	160.2	170.3	170.4	170.2	170.6

Table G-3: Average bond angles in degrees of the optimized geometry for each excited state listed in Au₂₂(ETP)₁₈ at the BP86/DZ level of theory.

Comparison between ligands

Table G-4: Average bond angles in degrees of the optimized geometry for BP86/DZ and CC-AllGold BP86-D3-COSMO/DZ levels of theory.

			A	VERAC	θE	CC-AllGold	AVERAGE		θE
Crystal	ETP	P BP86/DZ	ETP	PA	ET	BP86-D3- COSMO/DZ	ETP	PA	ET
A-B-C	126.2	A-B-C	125.4	138.4	139.8	A-B-C	126.2	126.2	126.2
A-B-D	96.2	A-B-D	95.6	106.5	108.1	A-B-D	95.8	95.9	96
A-B-E	84.8	A-B-E	94.1	96.8	95.1	A-B-E	82.6	82.5	82.9
A-B-F	63.1	A-B-F	65.2	71.1	70.1	A-B-F	63.1	63.1	63.1
A-B-G	44.3	A-B-G	38.9	47.7	47.4	A-B-G	52.1	52.5	50.7
A-B-H	32	A-B-H	32.6	33.6	33.5	A-B-H	34.6	34.6	33.7
E-F-G	145.2	E-F-G	128.1	131.4	131.4	E-F-G	169.3	169.4	175.2
D-F-H	160.7	D-F-H	161.3	170.7	173.1	D-F-H	148.0	148.6	151.6
D-E-I	163.7	D-E-I	178.4	158.3	162.0	D-E-I	162.1	159.4	155.1
H-G-J	160.2	H-G-J	170.3	165.6	161.4	H-G-J	161.7	157.5	160.2



Figure G-9: Molecular orbitals responsible for the main electronic transitions at the ~3.50 eV shoulder peak for Au₂₂(ETP)₁₈, Au₂₂(PA)₁₈ and Au₂₂(ET)₁₈ at the LRCF-D3-COSMO/DZ level of theory from the optimized CC-AllGold BP86-D3-COSMO/DZ geometry.



Figure G-10: Molecular orbitals responsible for the main electronic transitions at the ~3.75 eV peak for Au₂₂(ETP)₁₈, Au₂₂(PA)₁₈ and Au₂₂(ET)₁₈ at the LRCF-D3-COSMO/DZ level of theory from the optimized CC-AllGold BP86-D3-COSMO/DZ geometry.



Figure G-11: Theoretical circular dichroism spectrum with 800 points and 10 nm spacing. Au₂₂(R)₁₈ was calculated at the LRCF-D3-COSMO/DZ level of theory on the CC-Allgold-BP86-D3-COSMO/DZ S₀ geometry. The core, $[Au_7]^{3+}$, was calculated at the LRCF-D3-COSMO/DZ level of theory on the BP86-D3-COSMO/DZ S₀ geometry. (A) Au₂₂(R)₁₈ for R = ETP, PA, and ET which are denoted by the solid blue, green dashed and red doubled lines respectively. (B) R = ET, where the core is denoted by the orange dashed line (C) R = PA, where the core is denoted by the green solid line (D) R = ETP, where the core is denoted by the light blue doubled line.

Benchmark/trends between ligands

		BP86/D2	Ζ	Xa/DZ			
(Å)	ETP	PA	ET	ETP	PA	ET	
Au Center - Au Core	2.771	2.758	2.748	2.696	2.698	2.695	
Au Core - Au Core	2.800	2.790	2.797	2.755	2.736	2.743	
Au Core - Au Ring	2.981	3.024	3.037	2.892	2.961	2.983	
Au Sigma - Au Ring	3.094	3.195	3.215	3.068	3.124	3.159	
Au Ring - Au Ring	3.150	3.181	3.228	3.082	3.112	3.141	
Au Sigma - Au Pi	3.139	3.488	3.547	3.051	3.392	3.437	
Au Pi - Au Ring	2.940	2.940	2.942	2.833	2.844	2.858	
Au Pi - C Cusp	2.537	2.358	2.291	2.453	2.319	2.241	

Table G-5: Average bond lengths in angstrom of the S₀ state with BP86/DZ and X α /DZ levels of theory.

BP86-D3-	BP86-D3- AVERAGE		E	BP86-D3-		AVERAGE			
COSMO/DZ	ETP	PA	ET	COSMO/TZP	ETP	PA	ET		
A-B-C	127.8	136.4	134.1	A-B-C	133.4	134.2	132.4		
A-B-D	94.4	103.8	103.1	A-B-D	103.6	102.9	100.5		
A-B-E	99.3	94.5	89.4	A-B-E	96.4	90.1	86.7		
A-B-F	61.8	69.5	66	A-B-F	69	68.1	67.3		
A-B-G	44.1	48.6	45.5	A-B-G	44.9	31.8	49.9		
A-B-H	33	33.6	32.8	A-B-H	32.5	33.9	34.1		
E-F-G	137.9	138.0	120.7	E-F-G	126.1	146.6	147.9		
D-F-H	164.8	168.5	160.8	D-F-H	174.1	161.9	163.3		
D-E-I	173.8	162.2	168.6	D-E-I	171.0	160.1	163.1		
H-G-J	163 5	165 3	164.6	H-G-J	161.5	160.2	160.2		

Table G-6: Average angles in degrees between different atoms inside the three oligomers of Au₂₂(ETP)₁₈, Au₂₂(PA)₁₈ and Au₂₂(ET)₁₈ at the BP86-D3-COSMO/DZ and BP86-D3-COSMO/TZP levels of theory.



Figure G-12: Theoretical absorption spectrum at different levels of theory. The ETP, PA, and ET ligands are in solid blue, dashed green, and red doubled lines respectively. (A) BP86-D1/DZ level of theory from the BP86-D1/DZ S₀ state (B) BP86-D3/DZ level of theory from the BP86-D3/DZ S₀ state

Table G-7: Average bond distances between the three R groups with different dispersion parameters. The bond closest to the crystal structure between the two dispersion methods is bolded.

			BP86-D1/DZ		BP86-D3/DZ			
(Å)	Crystal	ETP	PA	ET	ETP	PA	ET	
Au Center - Au Core	2.702	2.892	2.717	2.821	2.692	2.696	2.711	
Au Core - Au Core	2.750	2.697	2.726	2.711	2.813	2.817	2.786	
Au Core - Au Ring	3.095	3.643	3.197	3.697	2.916	2.922	2.994	
Au Sigma - Au Ring	3.109	3.408	3.381	3.418	3.080	3.049	3.087	
Au Ring - Au Ring	3.446	3.327	3.416	3.317	3.277	3.324	3.225	
Au Sigma - Au Pi	3.432	3.722	3.658	3.696	2.990	2.908	3.191	
Au Pi - Au Ring	3.429	2.773	3.111	2.802	2.995	3.065	2.959	
Au Pi - C Cusp	2.184	2.402	2.283	2.312	2.443	2.420	2.383	



Figure G-13: Theoretical absorption spectrum at different levels of theory. The ETP, PA, and ET ligands are in solid blue, dashed green, and red doubled lines respectively. (A) BP86-D3/DZ level of theory from the BP86-D3/DZ S₀ state (B) BP86-D3-COSMO/DZ level of theory from the BP86-D3-COSMO/DZ S₀ state

Appendix H - Appendix for "Analytical Excited State Gradients for

Time-Dependent Density Functional Theory plus Tight Binding

(TDDFT+TB)"

Derivative of Fock Matrix

$$\begin{split} \sum_{\mu} \frac{\partial (F_{ab}\delta_{ij} - F_{ij}\delta_{ab})}{\partial C_{\mu p}} C_{\mu q} &= \sum_{\mu} \sum_{\mu'\nu'} \frac{\partial (C_{\mu'a}F_{\mu'\nu'}C_{\nu'b}\delta_{ij})}{\partial C_{\mu p}} C_{\mu q} \\ &- \sum_{\mu} \sum_{\mu''\nu''} \frac{\partial (C_{\mu''i}F_{\mu''\nu''}C_{\nu''j}\delta_{ab})}{\partial C_{\mu p}} C_{\mu q} \\ &= \sum_{\mu} \sum_{\mu'\nu'} \left[\delta_{\mu\mu'}\delta_{pa}\delta_{ij}F_{\mu'\nu'}C_{\nu'b}C_{\mu q} + C_{\mu'a}F_{\mu'\nu'}\delta_{\mu\nu'}\delta_{pb}\delta_{ij}C_{\mu q} \right] \\ &- \sum_{\mu} \sum_{\mu''\nu''} \left(\delta_{\mu\mu''}\delta_{pi}\delta_{ab}F_{\mu''\nu''}C_{\nu''j}C_{\mu q} + C_{\mu''i}F_{\mu''\nu''}\delta_{\mu\nu''}\delta_{pj}\delta_{ab}C_{\mu q} \right) \\ &+ \delta_{ij}(\delta_{p\in occ}2(ab|pq) + \delta_{p\in occ}2f_{abpq}^{XC}) - \delta_{ab}(\delta_{p\in occ}2(ij|pq) + \delta_{p\in occ}2f_{ijpq}^{XC}) \\ &= \delta_{ij}(\delta_{pa}F_{qb} + \delta_{pb}F_{aq} + \delta_{p\in occ}2(ab|pq) + \delta_{p\in occ}2f_{abpq}^{XC}) \\ &- \delta_{ab}(\delta_{pi}F_{qj} + \delta_{pj}F_{iq} + \delta_{p\in occ}2(ij|pq) + \delta_{p\in occ}2f_{ijpq}^{XC}) \end{split}$$

Derivative of Coupling Matrix
Derivatives Vital to Z-Vector Equation

1)

$$\sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial F_{ia}}{\partial C_{\mu p}} C_{\mu q} = \sum_{ia} Z_{ia} (\delta_{pi} \delta_{qa} \varepsilon_a + \delta_{pa} \delta_{iq} \varepsilon_q)$$

$$+\sum_{pq} \delta_{p \in occ} 2((ab|pq) + f_{abpq}^{XC}) Z_{pq}$$

2)

$$\sum_{\mu} \frac{\partial S_{rs}}{\partial C_{\mu p}} C_{\mu q} = \sum_{\mu} (\delta_{pr} \delta_{qs} + \delta_{ps} \delta_{qr})$$

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Chapter 1 References

Figure 1.1:

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Figure 1.2:

Gold–Thiolate Ring as a Protecting Motif in the Au20(SR)16 Nanocluster and Implications



Author: Chenjie Zeng, Chong Liu, Yuxiang Chen, et al Publication: Journal of the American Chemical Society Publisher: American Chemical Society Date: Aug 1, 2014

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Figure 1.3.1:



Quantum Dots: A Primer

Author: Catherine J. Murphy, Jeffery L. Coffer Publication: Applied Spectroscopy Publisher: SAGE Publications Date: 2002-01-01

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Figure 1.3.2:

Diversification of Metallic Molecules through Derivatization Chemistry of Au25 Nanoclusters



Author: Yitao Cao, Tiankai Chen, Qiaofeng Yao, et al Publication: Accounts of Chemical Research Publisher: American Chemical Society Date: Nov 1, 2021

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Figure 1.3.3:

Nanoscale

Publication type: Journal Article: Au25(SR)18: the captain of the great nanocluster ship.

ISSN: 2040-3364 Publication Year: 2009 - Present Publisher: RSC Pub Language: English

Country: United Kingdom of Great Britain and Northern Ireland Rightsholder: Royal Society of Chemistry Authors: Guo jia na mi ke xue zhong xin (China); Royal Society of Chemistry (Great Britain) View less details

Figure 1.3.4:

Electronic and Geometric Structure, Optical Properties, and Excited State Behavior in Atomically Precise Thiolate-Stabilized Noble Metal Nanoclusters



Author: Christine M. Aikens Publication: Accounts of Chemical Research Publisher: American Chemical Society Date: Dec 1, 2018

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Figure 1.3.5:

Chapter 3 Reference

Zeng, Y.; Havenridge, S.; Gharib, M.; Baksi, A.; Weerawardene, K. L. D. M.; Ziefub, A. R.; Strelow, C.; Rehbock, C.; Mews, A.; Barcikowski, S.; Kappes, M. M.; Parak, W. J.; Aikens, C. M.; Chakraborty, I. Impact of Ligands on Structural and Optical Properties of Ag₂₉ Nanoclusters. *J. Am. Chem. Soc.* **2021**, 143, 25, 9405-9414.

Impact of Ligands on Structural and Optical Properties of Ag29 Nanoclusters



Author: Yuan Zeng, Shana Havenridge, Mustafa Gharib, et al Publication: Journal of the American Chemical Society Publisher: American Chemical Society Date: Jun 1, 2021

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Ghabin, M.; Aikens, C. M. Das, A. Crystal Structure and Optical Properties of a Chiral Mixed

Thiolate/Stibine-Protected Au₁₈ Cluster. J. Am. Chem. Soc. 2022, 144, 1, 478-484.

Crystal Structure and Optical Properties of a Chiral Mixed Thiolate/Stibine-Protected Au18 Cluster



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