DISSERTATION

FUNDAMENTAL INSIGHTS INTO THE ALLOY MISCIBILITY AND SURFACE CHEMISTRY OF METAL NANOCLUSTERS

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ABSTRACT

FUNDAMENTAL INSIGHTS INTO THE ALLOY MISCIBILITY AND SURFACE CHEMISTRY OF METAL NANOCLUSTERS

The fascinating and varied properties of metals have captured people's imaginations long before the advent of modern chemistry. Basic metallurgy, dating as far back as the fourth millennium BC, remains one of the most consequential processes in human history. Today we enjoy an effective mastery over metals in their continuous bulk state, complete with alloy phase diagrams which describe properties as a function of temperature and percent composition. The coordination chemistry of single-metal complexes is similarly well-studied, initiated by the pioneering work of Alfred Werner in 1893. Size-dependent properties found at these two extremes (continuous bulk versus discrete molecular) have facilitated a myriad of applications in nearly every aspect of society through the development of unique materials.

Between bulk metals and coordination complexes exists a new and rapidly growing area of chemistry concerned with clusters containing several to hundreds of metal atoms. Although there are commonalities shared with both molecular and bulk systems, these clusters also exhibit notable behavioral differences which can often not be explained through simple classical interpretations. The challenge of working with these species has been considerably eased within the past fifteen years from advancements in synthesis and characterization, in particular for monolayer-protected clusters (MPCs) of gold. These MPCs can be synthesized to precise monodispersity and are therefore defined by a molecular formula instead of the more general average size and dispersity used to define larger (typically > 3 nm) colloidal nanoparticles. Minor adjustments to the nuclearity, metal atom identity, or surface chemistry of gold MPCs have been shown to induce extensive changes in their observed properties and overall stability. Complete regiochemical control over both the metal core composition and surface ligand environment is therefore of immediate interest. This goal is especially important for potential applications in catalysis, electronics, biolabeling, energy conversion/storage, and theranostics.

The work described herein covers two overarching themes: i) examining the alloying ability of gold MPCs with various late transition metals, and ii) an investigation of MPC surface chemistry through the introduction of multidentate ligands. Synthesis and analysis of the classically-immiscible rhodium-gold system using Au₂₅(SR)₁₈ as a template offers a fresh perspective of alloy gold MPCs containing metals with an open d-shell, alongside an updated framework for understanding MPC stability. Acetylide-for-thiolate, thiolate-for-acetylide, and intercluster exchange between acetylide- and thiolate-protected gold MPCs reveal lability which cannot be adequately rationalized through traditional MPC ligand exchange arguments. The first example of a thiolated gold MPC co-protected by several oxygen-containing diglyme ligands is described, which exhibits enhanced thermal stability as a result of the robust gold-diglyme, thiolate-diglyme, and diglyme-diglyme interactions. A straightforward synthetic pathway to fully dithiolate-protected gold MPCs is also described, as well as a post-synthetic ligand exchange study showcasing their resistance against incoming monodentate thiol exchange. Lastly we provide a series of vignettes detailing our efforts towards the synthesis of various MPCs using metals such as osmium, iridium, and bismuth. Overall these studies afford fundamental advancements in the understanding of soluble, air-stable metal nanoclusters and open up new opportunities for their applications.

ACKNOWLEDGEMENTS

Having a penchant for self-reflection is both a blessing and a curse when it comes to writing an acknowledgements section. There are so many people who have shaped my experience and led me to be who I am today. To accurately describe my gratitude to each of them would take its own separate novel. In any case, here are the most notable examples.

First and foremost, I want to express overwhelming appreciation to my mother and grandmother who taught me to be inquisitive and compassionate. Through their constant support I was able to identify my general love of science from a very early age. I was practically raised by two mothers, and I wouldn't have it any other way. Of course, I wouldn't be nearly as interesting a person if it weren't for my best friend of all time, my sister Alexis. We can talk for hours about nothing and anything in what feels like minutes. Her profound wit and ability to make fun out of almost any situation has been a wonderful mental salve throughout the years. These three mean the world to me – I simply cannot imagine how my life would have been without them.

Throughout the whole of my K-12 education, two teachers stand out amongst the rest. My English teacher Mr. Marcus Eure threw a huge wrench in the canonical "in this essay I will" writing style and forced me to think outside of the box. I attribute much of my writing skill to the time spent at his Sisyphean High. While I already knew that my passions fell squarely within the realm of science, Mr. Ed Schmidt was the one who first inspired my career in chemistry. The in-class reaction demonstrations and hands-on approach to active learning produced a unique and exciting experience that I still think back fondly to. Schmidt also nourished my early professional development through shadowing his teaching, as well as providing me the tools to arrange an incredibly valuable summer internship in Dr. David Schuster's fullerene lab at NYU. It was from this that I knew I wanted to conduct research, which is what led me to SUNY Binghamton. So thank you, Schmidt – and sorry again about synthesizing and using nitrogen triiodide when you weren't present.

At SUNY Binghamton I found myself in the organic chemistry classroom of Dr. Eriks Rozners, who welcomed me into his research lab under the HHMI program. Rozners had a special flair for synthesis, encouraging his students to literally dream of their products. I had a great time working in his lab under Dziyana Hnedzko, who taught me a series of convenient synthetic and purification methods. I also learned much from Samwel Cheruiyot, Daniel Mutisya, and Paul Tanui in various capacities. A special thanks to my fellow undergraduate researchers Yannis Karamitas, Brian Cuzzo, and Andrea Wolf; you all made the tougher aspects of lab work much softer through your presence.

It would be rather crude to distill Manar Albrecht and Henryk Haniewicz down to the title of "study buddies", although we did all frantically engage in study sessions throughout our time together at Binghamton. Whether discussing hardcore science, our mutual hobbies, or really just anything at all, Manar and Henryk have been great fellow scientists and friends. It has been an absolute joy to see their lives take off, and I look forward to the day we finally get around to our earth-shattering collaboration paper.

In 2016, I made the decision to move more than 1800 miles away from my comfort zone. Travelling cross-country in a moving truck with all my belongings was simultaneously exhilarating and nerve-wracking. I had never lived outside of the northeastern U.S. but had a good feeling about CSU from visitation weekend. Initially, Chris Ackerson was not on my radar of professors. Based on my time as an undergraduate researcher, I knew I enjoyed synthesis but wasn't so keen on doing pure organic chemistry. Shifting focus to the inorganic realm, I became fascinated with Rick Finke's body of work on nanoparticle nucleation and growth. After being accepted into his group, Rick developed second thoughts and ultimately concluded that he had no current projects that would fit my existing skillset. Needless to say, this was a huge blow to my confidence.

I reached out to Chris on doing a fourth rotation with his group in early 2017, and what followed was equal parts relieving and exciting. I very quickly began to ask myself how I had never looked further into Chris' research, because so much of what they did clicked with my interests. As it turns out, the Ack lab has a history of taking on students well past their first year from other groups. One of those students, a self-described "arrow pusher" Tim Dreier, acted as my first mentor in the lab. He was on his way out, and in the midst of running various synthetic screens in an attempt to obtain new alloy gold clusters.

Tim is exceptionally clever, and despite his departure in March of that year managed to teach me the basics of exploratory cluster synthesis. Later down the road, both Ryan Riskowski and Chris Hosier would play the role of mentor for me. Ryan, a biophysicist by trade, was always there to talk and had a shockingly wide knowledge pool. He was phenomenal at breaking down fundamental concepts and discussing thought experiments, even when he had a horde of other projects of his own to tend to. Ryan impressed upon me the idea of being a "cautious gardener" in the lab – to explore, but not so much that you get lost down rabbit holes. He also had this magic quality of churning excitement out of all his presentations, which I am still trying to emulate to this day.

Hosier was extremely helpful in similar capacities, but more specifically in the realm of crystallography. Most of what I know about practical crystal structure solution originally comes from him. He's also one of the best I've encountered at connecting the fundamental science to

applications. Like Tim, Hosier was a former arrow pusher and so had a good deal of knowledge in the form of practical organic chemistry. Both of their methodologies in the lab had a profound positive impact on my own.

I'd also like to give honorable mention to my two office mates Phillip Window and James Armstrong. We've shared countless vent sessions on U.S. politics over the years (in addition to the occasional video/board game discussion). Phil was very efficient in the lab and would often come up with new time-saving methods. Since both of our projects have dealt considerably with superatom theory, we've shared plenty of mutually beneficial and intriguing discussions on that front. In my first year James very rapidly shifted focus from clusters to Scott Compel's new metallogel materials, but this didn't stop us from engaging in productive shop talk. James was a very proficient scientist despite his semi-regular statements to the contrary. It was always fun sharing bad graphical abstracts with each other as well as some exceedingly obscure jokes about our general field.

I don't think there will ever be a single synthetic chemist to pass through the Ack lab who cannot in some way acknowledge Marcus Tofanelli. An extremely prolific chemist who can't write, yet managed to publish 10 papers during his graduate career. Decrypting his old notebooks should be its own separate degree program. That said, Marcus has offered some good insight over the years which has helped to strengthen my own grasp on theory and cluster chemistry.

During my time as a TA at CSU, Joseph DiVerdi was core to my experience. His lab management style helped keep the job interesting, and it brought with it the feeling of true impact outside the confines of a single semester or syllabus. I've since confirmed these suspicions through discussions with former students. Thanks to the guidance and autonomy provided by Joseph, I was able to hone my personal teaching skills well beyond what you can generally expect from a basic TA assignment.

It's obvious that none of the work in this dissertation would be remotely possible without Chris Ackerson. The Ackerboss has been a fantastic professor to work with by letting me explore my own strengths while still being accessible and helpful when needed. My scientific writing ability has tangibly improved thanks to his mentorship. Ack was also exceedingly understanding when it came to the passing of my grandmother, and went so far as to personally cover the flight costs so that I could attend her funeral. When it comes to my own development into an independent researcher, I cannot think of a better or more creative environment than the Ack lab.

I had a set of expectations when I first moved out to Colorado but none of them included meeting someone as wonderful and supportive as my fiancée Dr. Cynthia McCord. We've been through so much, gone on the most amazing adventures, and have enriched each other's lives to the fullest. I can't wait to see what else lies in store for us. And lastly, a special shout-out to my weekly guys' night mates who have stuck with me this whole time: Eric Haberli, Josiah Bailey, Shawn Bailey, and Brandon Ashley. Our lives are now in very different directions from undergraduate but we manage to still (mostly) keep it together. It will be great to live nearer to you all soon, and hopefully one day we can pitch in to get Eric that new hand.

"There's never enough time to do all the nothing you want." - Calvin & Hobbes

Ian D. Anderson, Ph.D.

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CHAPTER 1: HISTORY OF METAL CLUSTER SYNTHESIS & MODERN BRUST-TYPE APPROACHES

1.1 Synopsis

The subsequent chapters will describe a series of synthetic and post-synthetic studies aimed at probing the surface and core metal chemistry of atomically-precise gold MPCs. For the sake of context, this first chapter serves as an introduction to metal cluster chemistry. This will include: i) a brief history of metal clusters as observable species with early explanations for stability; ii) the highly consequential Brust-Schiffrin gold nanoparticle/cluster synthesis and subsequent gold MPC identification; iii) adaptations to the original Brust-Schiffrin method arising from the first crystal structure analyses (referred to as "Brust-type" methods); iv) an overview of modern gold MPC stability arguments and their relation to ongoing research. Each chapter is then summarized within the context of the overarching research goals of the field.

1.2 Early Metal Cluster Chemistry

The rather late blooming of clusters within scientific research can be directly attributed to their sheer initial scarcity and, to a lesser extent, the absence of unambiguous structural assignment prior to von Laue's conception of X-ray diffraction in 1912. Over 100 years spanned from the first report of chromium (II) acetate to the uncovering of its metal-metal bonding character.¹ The earliest examples of isolated clusters, originally described as polynuclear transition metal complexes, were coincidentally formed in syntheses designed for mononuclear products.² In this period lasting roughly from 1940 to 1960, a crisis developed as a greater number of these species were identified. Werner's classic single-metal center theory could not account for higher nuclearity complexes containing metal-metal bonds such as Rh₆(CO)₁₆.³

In the early 1960s F. A. Cotton introduced a formalized concept of metal clusters as "those containing a finite group of metal atoms which are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the cluster".⁴ Twice the distance of metallic radii (as determined in the solid state) is the general benchmark for deeming a pair/group of metal atoms substantially close enough to be considered bonded. This basic definition enables differentiation of metal clusters from both classic mononuclear complexes as well as larger colloidal particles with a reasonable degree of success.

Despite Cotton's new terminology there remained no sufficient explanation for the stability of metal clusters. This was due in part to the dearth of cluster products given a complete lack of synthetic methodology. Over the next decade, efforts led primarily within the lab of P. Chini pioneered the first direct synthetic routes to metal carbonyl clusters.⁵ The three general methods of oxidative coupling, redox condensation, and thermal condensation were revolutionary at the time and continue to be applied in modern research settings.^{6–8} Solid state X-ray characterization by both L. F. Dahl and V. G. Albano as well as solution phase NMR studies by B. T. Heaton provided an in-depth view of structure and dynamics.^{9–15} This suite of cluster species effectively set the stage for the first theoretical explanations of stability.

Concurrent to this work was a series of structural characterizations for borane clusters led by W.N. Lipscomb, which contained similarly intriguing boron-boron bonds.^{16–18} Noting this connection, in 1971 K. Wade introduced a set of electron counting rules for certain metal and borane cluster compounds which ultimately came to be known as the polyhedral skeletal electron pair theory (PSEPT).¹⁹ D. M. P. Mingos extended the rules to include all main group and transition metal clusters, leading PSEPT to be colloquially referred to as the Wade-Mingos rules.^{20–22} It therefore became possible to compare clusters containing different elements and in entirely different environments (e.g. solid state vs. solution) through relatively simple closed-shell electronic and symmetry arguments. This ruleset was the first of its kind and can generally account for both electron-rich (e.g. transition metal) and electron-deficient (e.g. borane) clusters.

Both Wade and Mingos recognized that clusters have a tendency to adopt closed polyhedral geometries (e.g. icosahedral, cuboctahedral, dodecahedral, etc.) or similar open arrangements with up to 3 missing vertices.^{23–25} As such, PSEPT can be used to predict the structure of certain clusters simply by applying electron counts based on the formula. This serves as a logical extension to the valence shell electron pair repulsion (VSEPR) theory for simple main group molecules, although it should be noted that borane research also directly contributed to the development of VSEPR.²⁶ Eventually PSEPT would grow to explicitly consider wavefunctions, in effect becoming a hybrid between VSEPR and molecular orbital theory.

In the interest of brevity, the specific electron counting rules will not be discussed in detail here as they do not apply to metal clusters larger than roughly a dozen metal atoms. Of greatest relevance to this dissertation is the fact that PSEPT accounts for all of the electrons within the outermost d-shell of a metal atom when calculating the total number of cluster valence electrons. This stands in contrast to modern superatom theory (*vide infra*) which until very recently has emphasized only valence s- or p-shell electrons.

Over time a mathematically rigorous backbone was added to the empirical PSEPT rules in the form of tensor surface harmonic theory (TSHT). Introduced by A. J. Stone in 1980, TSHT treats the cluster valence electrons as if residing upon a perturbed sphere or series of concentric spherical shells.²⁷ The angular portion of each atomic wavefunction is then solved as a vector (i.e. a first rank tensor) of position, whose magnitude is used as the coefficient in a linear combination of atomic orbitals (LCAO) consisting of σ , π , and δ orbitals. Symmetry of these LCAO molecular orbitals is derived from the combination of directions of the individual atomic orbital position vectors, which all obey the same quantum mechanical and spherical harmonics rules. This produces a logical ordering of cluster molecular orbital energies based upon their angular momentum quantum number *l*. Analysis is considerably simplified, as orbitals with a given *l* are deemed degenerate and interactions between orbitals differing in quantum number are assumed to be negligible.

Particularly noteworthy is the effectiveness to which the spherical approximation in TSHT can accurately model molecular orbitals for both diatomic clusters and larger nuclearities (e.g. $[Au_9(PPh_3)_8]^{1+}$).^{28–30} However, this VSEPR analogue rapidly loses its predictive power as cluster nuclearity increases; the cutoff is generally stated to be at a dozen metal atoms but some tenuous analysis can still be done with certain clusters up to around 40 metal atoms. The reason for this lies in the fact that energy differences between alternative packing arrangements become smaller as size increases, causing larger clusters to behave less like small molecules and more like bulk metals or crystallites.³¹ This combination of molecular and bulk behavior produces a hybrid system which cannot be described entirely adequately through standard interpretations.

Although PSEPT and TSHT were radical improvements in appreciating and predicting cluster structure and bonding, the stability of particularly larger metal clusters remained mysterious. A common method for observing an array of cluster sizes in the gas phase is through the use of a molecular beam, which produces bare clusters that are then sent through an inhomogeneous magnetic field to a mass detector.³² Beginning in the 1960s, such experiments consistently produced certain nuclearities in much greater abundance than others.^{33,34} The underlying cause behind this pattern was unclear until a 1984 study on sodium clusters led by W. D. Knight noticed

that the prominent nuclearities (e.g. 8, 20, 40, 58, etc.) correspond to an electronic shell closure, analogous to noble gas configurations.³⁵ This was readily illustrated through numerical solutions to the Schrödinger equation for delocalized sodium 3s electrons bound in a spherically symmetric potential well. Changing the shape of the potential well changes the so-called "magic numbers", granting the ability to apply this method to other quasi-spherical cluster systems.

There is some clear crossover between the Wade-Mingos rules (with TSHT) and the magic number approach, specifically with regards to the spherical treatment of clusters. This demonstrates a general tendency for both ligated and bare clusters to adopt polyhedral arrangements that can be treated as spheres. The key differences between the two approaches are: i) the electron counting applied to individual metal atoms, and ii) the emphasis of clusters as either a single molecule or a single atom. TSHT applies the LCAO molecular orbital method which considers in detail each individual metal atom, complete with the outermost s-, p-, and d-shell electrons. This in turn produces a discrete molecular view of the cluster overall. The magic number approach, however, adopts a more continuous (i.e. bulk metallic) view by assuming a jellium model.³⁶ Each metal valence is considered to be delocalized across the cluster surface, thereby removing the necessity found in TSHT to identify each individual atomic wavefunction. Instead, a cluster wavefunction is obtained by solving the aforementioned Schrödinger equation for valence electrons bound in a spherically symmetric potential well.

This newer jellium-based approach to conceptualizing cluster stability is now commonly referred to as superatom theory, and has been successfully used to describe a variety of different cluster systems extending across the periodic table.^{37–39} Nuclearities corresponding to one of the magic numbers are very common, as they tend to be more stable and therefore isolable. There is a rich chemistry associated with utilizing these superatoms to perform unique reactions through the

removal of a single electron from the cluster to make them "superatom isoelectronic" with elements such as fluorine or chlorine.⁴⁰ This grants such clusters the same basic reactivity as these elements but with the added benefit afforded by their large surface area to volume ratio. Furthermore, assembly into larger nanoscale structures has created the exciting prospect of producing new "supermolecules" from superatomic building blocks, effectively adding a third dimension to the periodic table.^{41,42} Section 1.5 will provide further details on superatom theory as it applies to gold MPCs in modern research.

1.3 The Brust-Schiffrin Synthesis

Thus far our focus has been on collections of metal atoms just above the size regime of classical Werner-type complexes. By 1990, a considerable library of ligated cluster species of this kind had been isolated. Some of the largest at the time included Pt₃₈(CO)₄₄ and Ni₃₈Pt₆(CO)₄₈, although the most common nuclearities sat near one dozen metal atoms.^{6,43–47} While molecular beams could produce larger nuclearities, these bare metal clusters could not be further manipulated outside of the experimental chamber. Issues still persisted for their ligated analogues, however. With some minor exceptions,⁴⁸ inert conditions were required in order to synthesize soluble (i.e. ligated) metal clusters. This naturally stymied larger-scale reactions and general ease of synthetic handling.

Compared to clusters, colloidal metals (i.e. nanoparticles) have a much longer history. Despite this and advancements in preparative conditions over the course of the 20th century, most colloidal metals tend towards agglomeration and eventual decomposition.^{49–51} One remarkable exception to this is Faraday's colloidal gold, which has remained optically active for over 150 years. Faraday synthesized these particles through a two phase approach, using phosphorous in carbon disulfide as the organic phase and an aqueous gold salt.⁵²

To address the issue of colloidal instability, in 1994 M. Brust and coworkers applied a two phase approach with the more recent advancements of ion extraction and gold-thiolate assembly.⁵³ This in turn produced highly stable solutions of thiolate-protected gold particles roughly 1-3 nm in core diameter as determined by transmission electron microscopy (TEM). These products could be precipitated, re-dissolved and chromatographed without any clear signs of decomposition or significant chemical change. X-ray photoelectron spectroscopic (XPS) analysis revealed that the majority of the gold atoms existed in the metallic (Au⁰) state, a somewhat surprising result given the large proportion of thiolate-bound surface gold (based on elemental analysis).

In addition to their ease of post-synthetic handling, these new metallic particles were also prepared through an exceptionally straightforward process under ambient conditions. To summarize, an aqueous solution of gold (III) chloride was mixed with a toluene solution of tetraoctylammonium bromide in order to transfer the gold salt into the organic phase. Dodecanethiol was then added to form gold thiolates, which were subsequently reduced through the addition of an aqueous solution of sodium borohydride. The final products were obtained by concentrating the organic toluene phase and precipitating with ethanol.

This simple preparative method ultimately produced a new area of nanochemistry research, with the original report now having over seven thousand citations approximately 28 years later. This is owed in part to the high degree of tunability possible with the synthetic conditions. M. J. Hostetler and coworkers found that the product distribution could be altered through variation of such parameters as reaction temperature, ligand feed ratio, and the addition rate of the reducing agent.⁵⁴ These studies would serve as the basis for future Brust-type methods, which we distinguish as those syntheses which yield near or completely monodisperse products.

While the original goal of the Brust-Schiffrin method was to provide a robust means of producing stable colloidal gold, subsequent analysis of the polydisperse product mixtures found evidence of both molecular cluster species (i.e. MPCs) and larger traditional nanoparticles.^{55–57} This afforded the opportunity to determine the onset of bulk electronic behavior, one of the central questions of nanochemistry and physics. In order to clarify this and other previously inaccessible aspects of metal cluster chemistry, structural analysis of monodisperse products was required. Some earlier studies were successful in post-synthetic purification, but the characterization techniques of the time often led to erroneous formula assignments.⁵⁸

1.4 Structural Clarification and Brust-Type Methods

The first crystal structure of a thiolate-protected gold MPC was that of $Au_{102}(SR)_{44}$, reported in 2007 by P. D. Jadzinsky and coworkers.⁵⁹ This cluster was isolated as a monodisperse species through systematic variation of the original Brust-Schiffrin synthesis using the water-soluble ligand *para*-mercaptobenzoic acid (*p*-MBA) followed by crystallization based on the 96-well plate conditions commonly applied for large biomolecules.⁶⁰ High quality single crystals enabled the collection of diffraction data at atomic resolution (1.1 Å), thereby producing an extensively detailed and accurate view of the solid state structure of $Au_{102}(p-MBA)_{44}$.

Measuring roughly 2.5 nm in diameter, this MPC is significantly larger than the majority of clusters identified at the time. Despite this the core gold atoms adopt a polyhedral arrangement reminiscent of the common geometries first noted by Wade and Mingos.⁶¹ The most striking aspect of this crystal structure, however, is the ordering of the cluster surface. First, each *p*-MBA ligand belongs to a staple motif comprised of alternating gold(I) and sulfur atoms. These staples are arranged in pairs which extend across the entire structure, which in the case of $Au_{102}(p-MBA)_{44}$ results in a total of 22 symmetry-unique ligand environments. This type of gold-sulfur bonding

has since been confirmed as a ubiquitous protecting mode for thiolates on gold cluster surfaces (Figure 1.1). $^{62-64}$ Second, there is extensive intermolecular attraction between both: i) phenyl rings as well as ii) sulfur atoms and phenyl rings of adjacent *p*-MBA ligands. Chains of these interactions extend over the cluster surface, synchronously producing inter- and intra-cluster ordering.



Figure 1.1. Examples of the two most common staple arrangements, single (left) and double (right). Most bonds to the cluster core are removed for clarity. S = orange, Au = gold, C = gray.

Interestingly, these staple motifs closely resemble the gold (I) thiolate oligomers which act as intermediates in the process of both gold MPC and colloid formation.⁶⁵ Shorter staples (Figure 1.1 left) involve a single gold (I) atom bonded to two neighboring sulfur atoms. Each of these staple atoms are then bonded to metallic gold (Au⁰) within the cluster core. Longer staple arrangements (Figure 1.1 right) can be considered as two fused short staples in a V-shape. This second configuration is typically observed for smaller gold MPCs, which have a more dramatic degree of surface curvature than their larger counterparts.⁶⁶

In 2008, soon after the report on $Au_{102}(p-MBA)_{44}$, two crystal structures of $Au_{25}(PET)_{18}$ (PET = 2-phenylethanethiol) were reported by the groups of R. W. Murray and R. Jin.^{67,68} Amongst the dozens of different nuclearities isolated since, $Au_{25}(PET)_{18}$ remains predominant as a subject of study owing to its particularly high electronic and geometric stability (*vide infra*).⁶⁹ This can be most practically understood through its preponderance as a synthetic product relative to other gold MPCs. The two groups applied different variations of the Brust-Schiffrin two phase synthesis, yet in both cases $Au_{25}(PET)_{18}$ remained as the major product. To isolate this MPC from the crude mixture, both groups grew needle-shaped crystals from saturated solutions that had been layered with a small excess of short chain alcohols (e.g. methanol, ethanol) over a period of several days. Figure 1.2 provides a structural breakdown of $Au_{25}(PET)_{18}$.



Figure 1.2. Crystal structure of $Au_{25}(PET)_{18}$. The depictions are as follows: full cluster with ligand shell (left), inorganic core (middle), and metallic core (right). S = orange, Au = gold, C = gray.

Some noteworthy connections exist between $Au_{25}(PET)_{18}$ and $Au_{102}(p-MBA)_{44}$. Both MPCs are protected by staple motifs that benefit significantly from the presence of aromatic rings. In the case of the former, each PET ligand is paired with another on the opposite side of the cluster, creating a total of 9 symmetry-unique ligand environments. The metal cores of each MPC are also highly symmetric, with $Au_{25}(PET)_{18}$ featuring a nearly ideal icosahedron.⁷⁰ This MPC natively forms with a negative (-1) overall charge, and is therefore accompanied by a large positive counterion in the form of tetraoctylammonium (TOA).

Following these foundational crystal structures, research on gold-thiolate MPCs began to address the issue of product polydispersity, leading to the first Brust-type synthetic approaches. Introducing a methodology referred to as "size-focusing" in 2009, Z. Wu and coworkers reported the synthesis of Au₂₅(PET)₁₈ to precise monodispersity through kinetic control (lowered temperature and controlled stirring rate) of a single phase tetrahydrofuran (THF) reaction.⁷¹ Building off of this work, the group of A. Dass found that the same level of monodispersity can

be achieved in THF at room temperature without any special kinetic control simply by allowing the reaction to proceed over the course of 3 days.⁷²

Larger MPCs (e.g. Au₁₀₂ and Au₆₈) were observed as the predominant products by mass spectrometry within five minutes of reduction, alongside minor products such as Au₄₄, Au₃₈, and Au₂₅. As time progressed, these smaller MPCs grew in relative population until only Au₂₅(PET)₁₈ remained. This type of phenomenon wherein larger clusters are apparently etched down to smaller nuclearities by excess thiol was observed post-synthetically by T. G. Schaaff and R. G. Whetten nearly a decade prior, although in their case elevated temperatures were required.⁷³ A. Dass and coworkers were the first to identify etching as a possible synthetic size-focusing mechanism, one which could operate under ambient conditions.

Another key component to modern Brust-type methods was reported in 2010 by J. F. Parker and coworkers from the Murray group, who demonstrated an improved yield of $Au_{25}(PET)_{18}$ through the new single phase THF procedure by inclusion of TOA bromide.⁷⁴ In addition to its role as an ion extractor (i.e. phase transfer) reagent in the original two phase procedure, TOA served as a stabilizer for the anionic form of $Au_{25}(PET)_{18}$. In the absence of an appropriate counterion, Au_{25} oxidizes to its neutral charge state when exposed to air.⁷⁵ This improved single phase approach, therefore, also succeeded in maintaining the native overall negative charge of $Au_{25}(PET)_{18}$ through the use of TOA as a counterion.

Furthermore, Parker and coworkers noted that the MPC synthesis only proceeds in the presence of air. When performed under an argon atmosphere, reduction of the gold (I) thiolate oligomers resulted in large insoluble species with no observable etching over time. This led the group to hypothesize that oxygen serves a critical role in the size-focusing process. The

mechanistic details would not be elucidated until 2015 when T. A. Dreier identified that etching is a radical-mediated process and therefore requires oxygen or some other radical initiator.⁷⁶

However, by 2010 etching and the more general concept of size-focusing was understood on a sufficiently basic level to facilitate the development of specialized Brust-type procedures capable of isolating gold-thiolate MPCs other than $Au_{25}(SR)_{18}$. In a majority of cases THF is the solvent of choice, with differences in product outcome induced by the ligand identity.⁷⁷ Sometimes, such as in the synthesis of $Au_{144}(PET)_{60}$, methanol is used to precipitate this larger MPC from solution in order to prematurely arrest the etching process – which would otherwise result in loss of this product.⁷⁸

The inclusion of heterometals with the gold source (i.e. coreduction or alloying) in Brusttype syntheses can also promote a size-focusing effect, based on the difference in metallic radii. Gold and silver are nearly identical in this regard (both approximately 1.44 Å), and so produce a similar dispersity as in the non-alloy case.⁷⁹ In contrast, palladium (1.37 Å) can only be accommodated by certain gold cluster geometries (e.g. Au₂₅, Au₃₈, Au₁₄₄), which aids in restricting the number of potential products.⁸⁰ As will be detailed in chapter 2, rhodium (1.34 Å) favors a comparable degree of size-focusing that can be further tightened through the selection of certain counterions. Overall, the stage of incorporation can determine the alloying ability of heterometals with gold MPCs. Palladium-gold MPCs only form synthetically, but silver- and copper-gold MPCs can be obtained through coreduction or post-synthetic exchange.⁸¹

Whereas alloy MPC product dispersity is generally controlled by the geometric consequences of bonding, ligands dictate surface chemistry through both repulsive steric and attractive dispersion interactions. Post-synthetic ligand exchange is thus far the most commonly applied route.⁸² The series of gold MPCs protected by 4-*tert*-butylbenzenethiol, for example, are

exclusively accessible through a size/shape transformation of pre-synthesized clusters.⁸³ This requires that the steric environment of the incoming excess ligand is significantly different from the outgoing. If the two ligands do not meet this condition, then the original cluster nuclearity and geometry is retained in its new heteroleptic form.^{84–87} A portion of subsequent chapters within this dissertation will explore new cluster surface interactions, as well as an expanded scope for a nascent area of synthetic size-focusing which applies coordinating cosolvents as ligands.

1.5 A Modern Understanding of Gold Cluster Stability

While great strides have been made from the development of Brust-type methods in the past decade, there are areas of general MPC chemistry which remain unclear or relatively unexplored. This is not due to a lack of study, but rather the formidable array of possible synthetic and post-synthetic outcomes combined with the high complexity of species comprised of hundreds to thousands of individual atoms. Older theoretical descriptions for this many-body problem were outlined in a preceding section, alongside the establishment of superatoms as a concept. Although this contemporary model shares certain similarities with the Wade-Mingos rules and TSHT, superatom theory mainly differs in its treatment of clusters as analogous to individual atoms versus molecules. It remains the most successful and accurate framework for understanding the special stability of coinage metal clusters spanning a large range of sizes.

Gold MPCs were first described as superatom complexes in a 2008 collaborative article between experimentalists and theoreticians.⁸⁸ Facilitated by the crystal structure solution of Au₁₀₂(SR)₄₄, M. Walter and coworkers utilized density-functional calculations to demonstrate the ubiquity of the superatom concept for gold clusters protected by thiolates or a combination of phosphines/halides. The delocalized superatomic orbitals, which upon filling satisfy stable electron shell closures (i.e. magic numbers), were derived by treating the gold MPCs as approximately spherical and residing energetically within an anharmonic mean-field potential. This potential well shape produces a non-traditional aufbau rule: $1S^2$, $1P^6$, $1D^{10}$, $2S^21F^{14}$, $2P^61G^{18}$, and so on.

A simple equation is used to determine the total electron count for a given gold MPC formula (see Appendix A for a detailed example). This treatment considers the superatomic orbitals to be of primarily gold 6s character, with surrounding ligands either acting as electron withdrawing/localizing species (e.g. thiolates, halides) or as weak Lewis base species which do not add or subtract electrons (e.g. phosphines). The overall cluster charge is also included. It is with such a system that M. Walter and coworkers demonstrated that the three different cluster formulas $Au_{11}(PR_3)_7Cl_3$, $Au_{11}(PR_3)_7(SMe)_3$, and $Au_{13}(PR_3)_{10}Cl_2^{3+}$ are "superatom isoelectronic"; that is, all three correspond to a total electron count of eight.

Density-functional analysis of Au₁₀₂(SR)₄₄ confirmed the dominant superatomic G orbital character near the HOMO-LUMO gap, as expected based on the shell-closing magic number of 58 which places the highest energy electrons within the 2P⁶1G¹⁸ shell. This, combined with the general applicability independent of chemical differences in the ligand shell, made superatom theory a robust standard for assessing and comparing the electronic stability of gold MPCs. Since this initial report the theory has been successfully expanded to include other ligands such as acetylides and N-heterocyclic carbenes.^{89,90}

As mentioned briefly in the preceding section, an extensive collection of chemical transformations have been reported for gold MPCs. This includes both ligand and metal exchange. Given the focus on the metal-containing portion of the cluster, superatom theory is applied more frequently to the latter over the former.^{91–93} Changes in ligand identity may produce no net effect

from this framework, such as between $Au_{25}(PET)_{18}$ and $Au_{25}(C_6H_{14}S)_{18}$. Likewise, replacement of gold atoms with copper or silver does not change the superatom electron configuration.

Some size/shape transformations can be rationalized as the tendency to remain superatom isoelectronic. For example, a total electron count of eight is retained in the transformation from $Au_{11}(PPh_3)_8Cl_3$ to $Au_{25}(SG)_{18}$ (SG = glutathione).⁹⁴ This same principle can be applied for the comparison of $Au_{25}(PET)_{18}^{1-}$ with HgAu₂₄(PET)₁₈⁰, in which the extra s-shell electron in mercury (relative to gold) effectively adjusts the overall cluster charge to zero while retaining the same configuration of $1S^21P^{6.95}$

Although superatom theory is effective at describing certain phenomena, it is not always sensible to view gold MPCs strictly through this lens. Comparison to molecular/bulk systems and the application of concepts from both have also helped to advance the field. MPC ligand exchange, for example, is traditionally viewed as essentially analogous to the associative- and dissociative-type reactions observed for small molecular complexes.⁹⁶ Recent crystallographic evidence, however, has also demonstrated the propensity for ligands to migrate across the surface en route to a thermodynamically favorable exchange product.⁸⁷ It is clear that the goal of complete regiochemical control over the cluster surface and core can only be achieved through a combination of various practical approaches and frameworks.

Accordingly, there are three main branches of contemporary gold MPC research: i) the development of additional size-focusing methods; ii) establishing greater control over dynamic surface chemistry; and iii) the production of alloy materials with electronic properties otherwise inaccessible in the bulk state. Depending on the nature of the study, there is significant potential for the simultaneous progression of more than one of these areas. Chapter 2 presents a size-focusing method for a rhodium-gold MPC which exhibits unexpected stabilizing interactions. We

determine that the concept of isoelectronic substitution is insufficient for describing gold MPCs doped with open d-shell metals. The explanation we provide has since been verified for other similar systems.⁹⁷

Chapter 3 focuses on the post-synthetic surface chemistry of both thiolate- and acetylideprotected gold MPCs. Previous to our study, thiolate-for-acetylide exchange was considered unfavorable based on bond dissociation energy arguments as well as previous observations of the enhanced stability of acetylides versus thiolates on cluster surfaces. In contrast to this assertion we observe that exchange is facile in both directions, which can be explained through net enthalpy arguments. This essentially opens up a new basis for MPC ligand exchange that builds upon the traditional associative/dissociative viewpoint.

Chapters 4 and 5 report new synthetic procedures for the production of highly monodisperse gold MPCs through the use of multidentate ligands. In the first case, diglyme is used as both co-solvent and ligand in the formation of a diglyme-thiolate gold MPC. The chelation and apparent stacking of multiple diglyme on the surface significantly enhances the overall cluster stability. In the second case, a series of alkyl- and aryl-dithiolates are screened for their size-focusing ability. It is found that successful reactions have a tendency towards highly monodisperse products, although the degree of mono- versus bi-dentate attachment appears to vary. These dithiolate MPCs are also resistant to displacement by monothiolates, a promising feature that may help reduce undesired intercluster exchange.

Chapter 6 outlines preliminary work done in the fledgling research area of applying Brusttype methods to non-coinage metals. Compared to other active areas of cluster research, the critical success of coinage metal MPCs generates an enticing and solid foundation with which to expand to other chemical systems. This penultimate chapter therefore serves as a record of current successes and failures towards the development of simple, air-stable particle/cluster syntheses for a selection of late- and post-transition metals. Lastly, chapter 7 offers both retrospective and prospective remarks concerning the state of metal cluster chemistry.

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CHAPTER 2: OBSERVABLE BUT NOT ISOLABLE — THE $RhAu_{24}(PET)_{18}^{1+}$ NANOCLUSTER^{*}

2.1 Synopsis

The synthesis and characterization of RhAu₂₄(PET)₁₈ (PET = 2-phenylethanethiol) is described. The cluster is co-synthesized with Au₂₅(PET)₁₈ and rhodium thiolates in a co-reduction of RhCl₃, HAuCl₄, and PET. Rapid decomposition of RhAu₂₄(PET)₁₈ occurs when purified from the other reaction products, precluding the study of isolated cluster. Mixtures containing RhAu₂₄(PET)₁₈, Au₂₅(PET)₁₈, and rhodium thiolates were therefore characterized. Mass spectrometry, X-ray Photoelectron Spectroscopy, and chromatography methods suggest a combination of charge-charge and metallophilic interactions among Au₂₅(PET)₁₈¹⁻, rhodium thiolates and RhAu₂₄(PET)₁₈ resulting in stabilization of RhAu₂₄(PET)₁₈. The charge of RhAu₂₄(PET)₁₈ is assigned as 1+ on the basis of its stoichiometric 1:1 presence with anionic Au₂₅(PET)₁₈, and its stability is contextualized within the superatom electron counting rules. This analysis concludes that the Rh atom absorbs one superatomic electron to close its d-shell, giving RhAu₂₄(PET)₁₈¹⁺ a superatomic electron configuration of $1S^21P^4$. Overall, an updated framework for rationalizing open d-shell heterometal dopant electronics in thiolated gold nanoclusters emerges.

2.2 Introduction

Atomically precise thiolate-protected gold nanoclusters (NCs) have stimulated extensive research interest due to their unique optical, magnetic, catalytic, and electrochemical properties.¹⁻ ⁴ With a now vast library of thiolated gold NCs to draw from, the incorporation of heterometals

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into well-established clusters represents a new frontier. The reduced size of gold NCs significantly alters their miscibility with heterometals compared to the bulk case, opening the path for novel alloy materials.⁵⁻¹²

Heterometal doping of gold NCs is achieved through 3 general routes: i) addition of the corresponding heterometal salt during the NC synthesis, known as co-reduction;¹³ ii) exchange between a previously-synthesized NC and a complex or thiolate oligomer of the heterometal through a redox-mediated process, known as anti-galvanic reaction (AGR);¹⁴ iii) exchange between separately-synthesized NCs of gold and the heterometal, known as intercluster reaction (ICR).¹⁵ The accessibility of alloy gold NCs through these routes varies considerably as a function of metal identity and can be rationalized by viewing these NCs as superatom complexes (*vide infra*).^{16-18,29} In brief, these NCs are considered to behave as a single unit analogous to an atom whereby the valence electrons are delocalized throughout the metal core.

With the exception of iridium, all published reports of heterometallic thiolated gold NCs involve late transition metals with closed d-shells.¹⁹ The effect of the interaction between partially-filled heterometal d-orbitals and the gold s-orbitals on the stability of the resulting alloy NC is largely unexplored experimentally. Theoretical calculations predict the manifestation of interesting magnetic properties from these alloy clusters.²⁰⁻²¹ Previous efforts in our group have demonstrated the difficulty associated with successful doping of gold NCs using open d-shell heterometals.²²

In this work, we describe the synthesis and attempted isolation of a rhodium-doped gold NC. We chose $Au_{25}(PET)_{18}$ as the starting cluster, given its particularly facile synthesis, high stability, and ease of functionalization.²³ To explore the role of ligand type, the recently-reported acetylide-protected analogue of Au_{25} was also tested.²⁴ Through an exhaustive screening of

conditions, a novel cluster assigned as RhAu₂₄(PET)₁₈ was observed by mass spectrometry and Xray Photoelectron Spectroscopy. Our results establish the first empirical study on rhodium as a dopant for thiolated gold NCs and highlight the intricacies associated with alloy clusters containing a combination of closed/open d-shell metals.

2.3 Results and Discussion

RhAu₂₄(PET)₁₈ was synthesized through an adaptation of the previously reported coreduction conditions for PdAu₂₄(PET)₁₈.²⁵ The crude synthetic product was assessed by Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry. **Figure 2.1a** shows that the synthesis creates two dominant cluster products. The peak at 7396 m/z is assigned as Au₂₅(PET)₁₈ (expected mass= 7394 Da). The peak at 7302 m/z is separated from the Au₂₅(PET)₁₈ parent peak by 94 m/z, in excellent agreement with the mass difference between gold and rhodium (94 Da). This peak is therefore assigned as RhAu₂₄(PET)₁₈ (expected mass= 7300 Da). Under all explored conditions, RhAu₂₄(PET)₁₈ forms concurrently with Au₂₅(PET)₁₈ as well as a rhodium thiolate species, herein Rh-PET.



Figure 2.1. Representative positive-ion MALDI mass spectra of (i) $RhAu_{24}(PET)_{18}$ and (ii) $Au_{25}(PET)_{18}$. (a) Synthesized using the [TOA][Br] co-reduction procedure. (b) Fraction from silica column chromatography showing an enrichment in $RhAu_{24}(PET)_{18}$ content. (c) Synthetic enrichment obtained from the [TBA][PF₆] co-reduction procedure. * refers to a fragment/adduct peak related to $RhAu_{24}(PET)_{18}$.

We observed a lack of appreciable signal for RhAu₂₄(PET)₁₈ and its related fragments/adducts under negative ionization mode, and so report only the positive-ion MALDI mass spectra. To validate the peak assigned as RhAu₂₄(PET)₁₈, mass spectra were taken as varying laser intensities (Appendix A, **Figure A1**). The product distribution does not change at different intensities, suggesting that the peak assigned as RhAu₂₄(PET)₁₈ is not the result of a MALDI-induced fragmentation/recombination process between Rh-PET and Au₂₅(PET)₁₈. Additional peaks in the full mass spectrum are observed and are assigned as fragments and/or adducts of the primary products (Appendix A, **Figure A2**). All fragment/adduct peaks were assigned as such on the basis of exhibiting a laser power dependence on peak intensity relative to the parents. The minor peak between the two parents at 7344 m/z is assigned as the Rh₁(PET)₁ adduct of the fragment RhAu₂₃(PET)₁₈.

Silica gel column chromatography can enrich $RhAu_{24}(PET)_{18}$ relative to other reaction products (**Figure 2.1b**). The $RhAu_{24}(PET)_{18}$ fraction from the silica gel column, however, coelutes from the column as a mixture with $Au_{25}(PET)_{18}$ and Rh-PET. Iterative column runs suggest that the limit of $RhAu_{24}(PET)_{18}$ purity from this purification method is a 1:2 ratio of $RhAu_{24}(PET)_{18}:Au_{25}(PET)_{18}$, with Rh-PET also present (Appendix A, **Figure A3**).

Solvent extraction to purify RhAu₂₄(PET)₁₈ was attempted. It is known, for instance, that $Au_{25}(PET)_{18}^{0}$ is insoluble in acetonitrile, whereas the cationic and anionic species are soluble. Sufficiently dry ethanol is also capable of charge-based extraction selectivity.²⁵ The complete solubility of RhAu₂₄(PET)₁₈ and Au₂₅(PET)₁₈ in acetonitrile implies that both NCs exist as charged species. In addition to acetonitrile, the crude product mixture showed solubility in common organic solvents (toluene, dichloromethane, and tetrahydrofuran) as well as sufficiently dry ethanol. The passage of Au₂₅(PET)₁₈ through a silica column is known to oxidize Au₂₅(PET)₁₈¹⁻ to Au₂₅(PET)₁₈^{0.26} Thus, the combination of silica gel oxidation of Au₂₅(PET)₁₈ followed by solvent extraction should allow separation of RhAu₂₄(PET)₁₈ from Au₂₅(PET)₁₈. However, we observed that leading fractions from a silica column contained neutral Au₂₅(PET)₁₈ as indicated by MALDI-MS and UV/Vis absorption measurements (Appendix A, **Figure A4**), followed by a mixture of RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET, wherein the RhAu₂₄(PET)₁₈ was relatively enriched up to the 1:2 ratio of RhAu₂₄(PET)₁₈:Au₂₅(PET)₁₈. The failure of silica gel chromatography to completely separate RhAu₂₄(PET)₁₈ from Au₂₅(PET)₁₈ is noteworthy, as such chromatographic methods are established for separating NCs of the same nuclearity.²⁷⁻²⁸

Combined, these observations suggest an ion-pairing between oppositely charged $Au_{25}(PET)_{18}^{1-}$ and $RhAu_{24}(PET)_{18}^{n+}$. Here, the ion-pairing of the 2 clusters appears to protect $Au_{25}(PET)_{18}^{1-}$ from the usual oxidation in silica gel. The peak ratios suggest a net 2+ charge for $RhAu_{24}(PET)_{18}$ following silica gel column purification, assuming similar ionization potentials between $RhAu_{24}(PET)_{18}$ and $Au_{25}(PET)_{18}$. We propose, however, that $RhAu_{24}(PET)_{18}$ forms synthetically in the 1+ charge state, which is presumably more stable on the basis of superatom analysis (*vide infra*).^{18,29} The solvent extraction behavior of the enriched fraction remained unchanged from the original mixture of $RhAu_{24}(PET)_{18}$, $Au_{25}(PET)_{18}$, and Rh-PET.

The finding that $RhAu_{24}(PET)_{18}$ appears to require large ('soft') counteranions such as $Au_{25}(PET)_{18}^{1-}$ for its stability suggests the possibility of synthetic enrichment through the introduction of an additional soft anion. This type of enrichment strategy is well-known for thiolated gold clusters; $[TOA]^{1+}$ (TOA = tetraoctylammonium), for example, acts as a soft stabilizing cation which enriches formation of $Au_{25}(PET)_{18}^{1-.30}$ We find that the replacement of [TOA][Br] with $[TBA][PF_6]$ (TBA = tetrabutylammonium) in the co-reduction procedure results

in significant enrichment/stabilization of RhAu₂₄(PET)₁₈ within the product mixture (**Figure 2.1c**). The RhAu₂₄(PET)₁₈:Au₂₅(PET)₁₈ peak ratio is 2:1, indicative of an increase in the preferential formation of RhAu₂₄(PET)₁₈. The presence of [TBA][PF₆] notably enhances the longevity of RhAu₂₄(PET)₁₈ within the reaction mixture. This enables a greater degree of size-focusing, to the extent that exclusively RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET remain as products (Appendix A, **Figure A5**).

Both $[PF_6]^{1-}$ and $[BF_4]^{1-}$ are well-documented as bulky, weakly-coordinating anions for cationic transition metal complexes and clusters.³¹⁻³² We hypothesized that their inclusion would aid in the stabilization of cationic RhAu₂₄(PET)₁₈. **Figure A6** shows that a reaction performed with $[TBA][BF_4]$ yields a similar enrichment in RhAu₂₄(PET)₁₈ content as in the case of $[TBA][PF_6]$. On the other hand, synthesis in the presence of fluoride anions, which are small ('hard') and highly-coordinating, fails to produce RhAu₂₄(PET)₁₈ in observable quantities. Use of a larger soft anion, such as dodecaborate, results in a drastic change in precursor speciation which fails to produce NC products (see Appendix A, section 2). **Figures A7-A8** offer further detail on the effect that changes in precursor speciation has on the amount of RhAu₂₄(PET)₁₈ produced. Combined, these observations of soft anions stabilizing RhAu₂₄(PET)₁₈ support its assignment as a cationic species, in agreement with the observed enrichment from silica gel column chromatography. This charge-state assignment has important implications regarding its superatomic stability.

Ion exchange resins are effective at separation of charged metal species, as well as larger charged biomolecules.³³⁻³⁷ Assuming that $RhAu_{24}(PET)_{18}/Au_{25}(PET)_{18}$ only interact as an ion pair, resins with cationic templates should be able to selectively remove $Au_{25}(PET)_{18}^{1-}$, leaving behind $RhAu_{24}(PET)_{18}^{1+}$ and Rh-PET. We observe no change in the $RhAu_{24}(PET)_{18}/Au_{25}(PET)_{18}/Rh-PET$ product mixture when exposed to cationically-templated resin in acetonitrile, for up to 24 hours of

exposure (see Appendix A, section 1). The failure of ion exchange suggests an additional, stronger interaction between $RhAu_{24}(PET)_{18}^{1+}$ and $Au_{25}(PET)_{18}^{1-}$ beyond that of an ion pair. We hypothesize that metallophilic interactions further stabilize the ion pair.

Metallophilic interactions are among the foundational aspects of metal cluster chemistry.³⁸⁻⁴² Reports cite metal-metal as well as metal-sulfur attraction between thiolated NC surfaces as an explanation for the spontaneity of the ICR process.^{31-32,43} This behavior has also been observed in monometallic gold/silver cluster dimers in the gas phase.⁴⁴⁻⁴⁵ Various supramolecular NC assemblies have been described which also result from metallophilic interactions.⁴⁶ Therefore, we propose that the inclusion of $[PF_6]^{1-}$ or $[BF_4]^{1-}$ in the synthesis of RhAu₂₄(PET)₁₈ does not result in its exclusive formation due to additional stabilization afforded by metallophilic interactions between RhAu₂₄(PET)₁₈, Au₂₅(PET)₁₈, and Rh-PET.

The purification of Rh-PET from RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈ is achievable *via* selective fractional precipitation from dichloromethane with acetonitrile. Addition of [TMA][Cl] to an acetonitrile solution of Rh-PET results in its precipitation following centrifugation (see Appendix A, section 3). Sample degradation of the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET mixture is observed when excess [Cl]¹⁻ is present, so [TMA][BH₄] was introduced in the co-reduction synthesis instead of NaBH₄,⁴⁷ as detailed in Appendix A, section 1. It should be noted that the replacement of [Na]¹⁺ with [TMA]¹⁺ does not significantly alter the solubility of RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈ *while Rh-PET is still present*. Complete removal of Rh-PET from the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈ mixture was confirmed by the disappearance of its UV/Vis signature, a peak centered at 360 nm (**Figure 2.2b**).



Figure 2.2. Stack plots showing the (a) change in MALDI mass spectral peak intensity of $RhAu_{24}(PET)_{18}$ and $Au_{25}(PET)_{18}$ as Rh-PET is removed and (b) disappearance of signal attributable to Rh-PET by UV/Visible absorption spectroscopy. Matching color spectra correspond to the same sample. The final absorption spectrum (10:1, blue trace) shows features attributable exclusively to $Au_{25}(PET)_{18}$, in agreement with the mass spectrum.

The removal of Rh-PET complexes reveals that their presence stabilizes $RhAu_{24}(PET)_{18}$ against decomposition. **Figure 2.2a** shows that as iteratively more Rh-PET is removed by the precipitation method described above, $RhAu_{24}(PET)_{18}$ disappears through a route that we assign as decomposition. $RhAu_{24}(PET)_{18}$ is not found within the precipitate, which appears to contain exclusively Rh-PET, as determined by mass spectrometry.

Re-addition of Rh-PET to the mixture containing RhAu₂₄(PET)₁₈ and Au₂₅(PET)₁₈ fails to regenerate RhAu₂₄(PET)₁₈, making this apparent degradation/conversion irreversible. Combined, these observations indicate that some stabilizing interaction exists between RhAu₂₄(PET)₁₈, Rh-PET, and Au₂₅(PET)₁₈ which if perturbed results in the degradation of RhAu₂₄(PET)₁₈. To the best of our knowledge this is the first example of this type of net interaction involving thiolate protected metal clusters. We therefore propose that the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET product mixture may be described as a supramolecular alloy system, stabilized primarily through a combination of coulombic and metallophilic attraction. Interactions between PET ligands in solution (π - π stacking) also likely play a stabilizing role.

For greater insight into this system, we performed a series of X-ray Photoelectron Spectroscopy (XPS) experiments (Appendix A, **Figures A10-A14**). A high-resolution spectrum within the rhodium 3d region reveals a pair of peaks for a sample containing RhAu₂₄(PET)₁₈, Rh-PET, and Au₂₅(PET)₁₈ (**Figure 2.3**). Curve fitting determines the two $3d_{5/2}$ peaks to be centered at 308.6 eV and 306.7 eV. The former binding energy (308.6 eV) matches exactly with the $3d_{5/2}$ binding energy assigned as belonging to Rh-PET, by comparison to XPS taken of Rh-PET alone (Appendix A, **Figure A12**). The 306.7 eV binding energy is indicative of rhodium in a low (metallic) oxidation state, as supported by previous XPS studies.⁴⁸⁻⁴⁹ The pair of peaks associated with this lower binding energy are only observed when RhAu₂₄(PET)₁₈ is present.



Figure 2.3. High-resolution XPS spectrum (solid black trace) of the Rh 3d region for a sample containing $RhAu_{24}(PET)_{18}$ from the co-reduction [TBA][PF₆] synthesis. Fits for the 2 pairs of peaks are assigned as belonging to $RhAu_{24}(PET)_{18}$ (dotted red trace) and Rh-PET (dotted blue trace).

Previous XPS experiments on alloy gold NCs have demonstrated that heterometals (e.g. Pd, Pt) generally exhibit metallic binding energies when located within the core of the Au₂₅(PET)₁₈ framework.^{13,50-52} It was recently shown by Fei and coworkers that the mercury within HgAu₂₄(PET)₁₈ can exhibit metallic binding energies despite the dopant being located on the icosahedral shell instead of the core.⁹ This is a remarkable result which may also apply to the case of RhAu₂₄(PET)₁₈. The core-doped assignment, however, is consistent with Density Functional Theory based computational studies of RhAu₂₄(SR)₁₈.⁵³ Other simulated structural isomers (i.e. shell- and staple-doped) exhibited a significant destabilization of the Rh d-shell, making them less energetically favorable. Differences in the electronics between mercury and rhodium (closed vs open d-shell) as well as size may change the preferred (lowest-energy) dopant position.^{18,54} A crystal structure, which we were unable to obtain due to the inability to grow crystals from the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET mixture, could unequivocally determine the position of rhodium within RhAu₂₄(PET)₁₈.

Superatom theory provides a framework for rationalizing the electronic stability of thiolated Au NCs.²⁹ Details regarding the theory and its formulation can be found within section 5 of Appendix A. Very briefly, each Au atom is assumed to contribute one superatomic electron, and each thiolate ligand is assumed to subtract one superatomic electron. Electronic shells close at 2, 8, 18, 34, etc. electrons, with $Au_{25}(SR)_{18}^{1-}$ corresponding to an 8-electron superatom. The contributions of Rh and other open d-shell transition metals to the superatom electron count are not yet established.

For $PtM_{24}(SR)_{18}$ (M = Au, Ag) NCs it was shown previously that Pt prefers to completely fill its d-shell, changing from its typical ground-state configuration of [Xe]4f¹⁴5d⁹6s¹ to [Xe]4f¹⁴5d¹⁰6s⁰.^{50,55} Rhodium has a ground-state electron configuration of [Kr]4d⁸5s¹. One possibility, therefore, is that Rh may subtract one electron from the superatomic electron cloud, in order to close its d-shell (from $[Kr]4d^{9}5s^{0}$ to $[Kr]4d^{10}5s^{0}$). This would give Rh a formal charge of -1, which is a previously described oxidation state.⁴⁸⁻⁴⁹

If the RhAu₂₄(PET)₁₈ superatom is synthetically produced as an 'initial' superatomic configuration of $1S^21P^5$ (superatom isoelectronic with neutral Au₂₅(PET)₁₈) then the donation of a superatomic electron to the Rh center would result in an overall $1S^21P^4$ configuration. From these considerations a full formula of RhAu₂₄(PET)₁₈¹⁺ is assigned, consistent with our other observations. This filling of the Rh d-shell by a superatomic electron is shown schematically in **Figure 2.4**. Notably, the $1S^21P^4$ configuration makes RhAu₂₄(SR)₁₈¹⁺ superatom isoelectronic with Au₂₅(SR)₁₈¹⁺, PdAu₂₄(SR)₁₈⁰, and PtAu₂₄(SR)₁₈^{0.50,54,56}



Figure 2.4. Electron energy diagram of $RhAu_{24}(SR)_{18}^{1+}$ depicting the interaction between the atomic rhodium d-shell and the superatomic 1P electrons; the 1S orbital has been left out for clarity (d orbital degeneracy assumed).

This model of superatomic electron donation to the d-shell of Rh is consistent with our observations, as well as a very recent report by Hirai and coworkers on non-thiolate $M@Au_{12}$ superatoms (M = Au, Pt, Ir, Rh).⁵⁷ Through electrochemical analysis their report concludes that group 9 dopants (e.g. Ir, Rh) possess a formal charge of -1, concomitant with subtraction of a single electron from the superatomic electron count.

The most stable theoretical isomer (i.e. the largest calculated HOMO-LUMO gap) for RhAu₂₄(SR)₁₈ assumes superatomic shells as completely filled, maintaining a $1S^{2}1P^{6}$ configuration (superatom isoelectronic with anionic Au₂₅(PET)₁₈) and giving an overall charge of 3-.⁵³ This would give Rh an electron configuration of [Kr]4d¹⁰5s¹ and therefore a formal charge of -2. At this time we find no empirical evidence to support the experimental stability of RhAu₂₄(PET)₁₈¹⁻, as this anionic species should be easily separable from anionic Au₂₅(PET)₁₈.

The excess of BH_4^- present in the synthesis represents excess electrons and should enable complete filling of all stable superatomic electron shells. If the title cluster initially forms with an overall negative charge, it could be rapidly oxidized by ambient atmosphere similar to $PdAu_{24}(PET)_{18}$.²⁵ Future mechanistic studies should shed light on these potential transformation pathways. Given the robust stability of $Au_{25}(PET)_{18}^{1-}$ (and comparative instability of $Au_{25}(PET)_{18}^{1+}$), we postulate that a combination of coulombic (charge-charge) and metallophilic interactions with $Au_{25}(PET)_{18}^{1-}$ stabilizes the 1+ form of $RhAu_{24}(PET)_{18}$, therefore making it the most favorable charge state.⁵⁶

The finding that RhAu₂₄(PET)₁₈ degrades as Rh-PET is removed implies a similar (albeit seemingly weaker) mode of metallophilic stabilization. We propose that the Rh^{II} of Rh-PET is interacting with the Au^I surface of RhAu₂₄(PET)₁₈. The propensity for Rh-PET to form adducts with RhAu₂₄(PET)₁₈ fragments within the MALDI-MS flight chamber is in support of this claim. This surface interaction appears key to the overall stability of RhAu₂₄(PET)₁₈, although details such as the precise location and extent of surface coverage are currently unknown.⁵⁸⁻⁶⁰

The enhancing effect of $[PF_6]^{1-}$ can be rationalized by comparing the size of $[PF_6]^{1-}$ with Au₂₅(PET)₁₈; the smaller hexafluorophosphate anion should be able to more easily approach the surface of RhAu₂₄(PET)₁₈ in the presence of substantial Rh-PET. However, complete removal of

 $Au_{25}(PET)_{18}$ from the system is not achievable, suggesting the persistence of these two NCs pairs, enforced by metallophilic interactions.⁶¹ Over the course of our study, we did not observe a species by mass spectrometry that would match with a combined adduct of RhAu₂₄(PET)₁₈, Rh-PET, and $Au_{25}(PET)_{18}$. The persistence of Rh-PET in the system, however, may have stymied our efforts to grow single-crystals.

The existing binary phase data for the bulk Au-Rh system strongly suggests that the two metals have large positive enthalpies of mixing, rendering them highly immiscible.⁶² This is similar to the case of Au and Pt; two metals immiscible in the bulk which have been proven miscible on the nanoscale (e.g. PtAu₂₄(SR)₁₈). Several reports exist of large Au-Rh nanoparticles (NPs), wherein the degree of mixing appears to vary as a function of Au:Rh ratio, preparation method, and whether the NP is surface-immobilized or unbound in solution.⁶³⁻⁶⁸ However, these large NPs lack the precise monodispersity and known surface structure of smaller NCs.

Femoni and coworkers recently reported a carbonyl-protected Au/Rh NC of formula $Rh_{16}Au_6(CO)_{36}^{6-}$, obtained through a mixture of $Rh_7(CO)_{16}^{3-}$ and Au(III) halides.⁶⁹ Its crystal structure provides evidence of direct and substantial Au-Rh bonding at a nuclearity near that of $Au_{25}(PET)_{18}$. In terms of stability, the difference between carbonyl and thiolate ligands (electron-donating vs electron-withdrawing) renders further comparison tenuous. Smaller nuclearity alloy clusters (less than a dozen metal atoms) containing multiple Au-Rh bonds have been known for some time, but these also involve non-thiolate ligands.⁷⁰⁻⁷¹

Bhat and coworkers recently reported $Ir_3Au_{22}(SR)_{18}$ as the sole product resulting from the ICR between $Au_{25}(SR)_{18}$ and $Ir_9(SR)_6$.^{19,72} While the crystal structure remains to be solved, a combination of experimental data and theoretical calculations determined that the most stable isomer of $Ir_3Au_{22}(SR)_{18}$ places Ir_3 in a triangular arrangement. No singly doped $IrAu_{24}(SR)_{18}$

species were observed, suggesting that the Ir-Ir bonds within Ir₃ may play a significant role in stabilizing this open-d alloy Au NC. It is not obvious how the electron configuration of Ir $([Xe]4f^{14}5d^76s^2)$ may change upon incorporation as a dopant, although the recent work by Hirai and coworkers suggests it behaves similarly to Rh.⁵⁷ Current theoretical work gives the most stable isomer of IrAu₂₄(SR)₁₈ as a negatively charged (3-) species.⁵³ Empirically, however, Ir₃Au₂₂(SR)₁₈ is of neutral charge. Based on the available data from Bhat's study and ours, it appears that isoelectronic substitution of the Au₂₅(PET)₁₈¹⁻ superatom is insufficient for describing the stability of thiolated open-d dopants to Au NCs.

If possible, post-synthetic doping of Au₂₅(PET)₁₈ with rhodium *via* ICR or AGR would be ideal. Both doping methods have been well reported within the literature to be facile processes that can yield monodisperse alloy products.⁷³⁻⁸¹ In the case of ICR, there are no reported cases of an atomically precise thiolated rhodium NC to our knowledge. Previous reports on AGR with Au₂₅(PET)₁₈ have not involved rhodium thiolates within the study scope. Through our study, we have determined that general rhodium thiolates (in addition to Rh-PET) can be synthesized under a variety of conditions (Appendix A, section 3). Rhodium thiolates are highly inert and resistant to further reduction, inhibiting transformation into a metallic thiolated NC.

This non-reactivity is reminiscent of the recently characterized crown-like $[Pd(PET)_2]_n$ species (n = 4-20), which are known to form as significant side products in the co-reduction synthesis of PdAu₂₄(PET)₁₈.^{54,82-83} For Rh-PET, efforts in our lab to crystallize or otherwise purify into individual Rh_x(PET)_m species have proved fruitless. These rhodium thiolates were used as a rhodium doping source for both thiolate- and acetylide-protected Au₂₅L₁₈ (Appendix A, **Figures A15-A16**). We observed a complete lack of post-synthetic exchangeability of Rh-PET with

 $Au_{25}L_{18}$, in agreement with its robust chemical inertness as well as previous AGR studies on similar Pt and Pd thiolates.¹⁶

2.4 Conclusion

In summary, we present a detailed study of rhodium as a dopant for $Au_{25}(SR)_{18}$ through all known methods. This is the first report of a rhodium-doped thiolated gold NC, RhAu₂₄(PET)₁₈¹⁺. The overall positive (1+) charge on this new NC can be rationalized by viewing the rhodium as subtracting one superatomic electron to fill its d-shell, giving an overall $1S^21P^4$ configuration. The existence of a stabilizing interaction between RhAu₂₄(PET)₁₈, Rh-PET, and Au₂₅(PET)₁₈ is unprecedented and suggests additional factors dictating alloy miscibility. We expect that our study will provide insight into alloy-forming reactions on the nanoscale, and will serve as a valuable resource for all future work on thiolated alloy gold NCs involving open d-shell heterometals.

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CHAPTER 3: ACETYLIDE-FOR-THIOLATE AND THIOLATE-FOR-ACETYLIDE EXCHANGE ON GOLD NANOCLUSTERS[†]

3.1 Synopsis

Acetylide-protected gold nanoclusters represent a recently described class of nanocluster compounds that are computationally predicted to be more stable than well-studied thiolate-protected clusters. Ligand exchange of thiolates-for-acetylides on these clusters as well as the reverse reaction are so-far unknown. Such reactions can inform a practical understanding of stability and other differences between thiolate- and acetylide-protected gold clusters. Here it is shown that acetylide-for-thiolate ligand exchange is facile when using either a lithium phenylacetylide or a gold(I)-phenylacetylide complex as incoming ligand to thiolate-protected gold clusters, whereas the reaction fails when using phenylacetylene. Both partial and full exchange are possible, as is the reverse reaction. While the overall reaction resembles ligand exchange, it may be better described as a metathesis reaction. Notably, while the simple thiolate-for-acetylide exchange reaction is enthalpically unfavorable, metathesis reactions between these ligands are enthalpically favorable. Intercluster exchange is also observed between thiolate-protected clusters.

3.2 Introduction

Soluble inorganic nanoclusters and nanoparticles are typically stabilized or protected by a passivating ligand shell. Ligand exchange is a fundamental reaction of such systems, and the interaction strength of ligand with metal can underlie and/or define kinetics, thermodynamics, and regiochemistry of ligand exchange. Because the ligand shell

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determines nanocluster or nanoparticle solubility, stability and reactivity, ligand exchange reactions can enable functionalization of metal clusters/nanoparticles for their use in bioimaging, catalysis, theranostics, and sensing applications.¹⁻⁴ Thiolate-protected gold nanoclusters have received substantial interest over the past two decades due to their ease of synthesis and overall stability.⁵⁻⁷ Recent work has highlighted the propensity for rapid exchange of metal atoms and/or ligands between dissolved thiolate-protected coinage metal clusters.⁸ Furthermore, thiolate-protected clusters are unstable to oxidative conditions.⁹

Whereas thiolate-protected gold clusters represent a now very well-defined class of atomically precise inorganic nanoparticles, gold nanoclusters ligated with organometallic ligands such as acetylides and N-heterocyclic carbenes have emerged only recently as alternatives that may present improved stability and/or catalytic properties.¹⁰⁻¹² Acetylides in particular attract interest as robust ligands for protecting gold nanoclusters. Such clusters are suggested as more stable than the widely studied thiolate-protected clusters, with calculations suggesting that acetylide-gold bonds are stronger by 6 to 52 kcal/mol than thiolate-gold bonds.¹³⁻¹⁵ Acetylide-coated gold surfaces show more consistent conductance measurements, are less susceptible to oxidation, and maintain similar packing densities compared to thiolate-coated surfaces.¹⁶ Furthermore, higher catalytic conversion efficiencies have been reported when using acetylide ligands on a gold nanocluster, and the ability for acetylides to adopt different binding motifs on cluster surfaces can potentially produce new properties in previously studied clusters.^{10,17}

Synthesis of acetylide-protected clusters proceeds most often by reduction of Au(I)acetylide complexes.¹⁸⁻²⁰ Only two examples of post-synthetic acetylide exchange on gold nanoparticles are so-far reported: Tsukuda and co-workers demonstrated that N-

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vinylpyrrolidone-protected clusters undergo exchange with free phenylacetylene to afford a series of homoleptic phenylacetylide-protected clusters, and Konishi later showed acetylide-for-chloride exchange by using free phenylacetylene in the presence of a base.^{21,22} Examples of acetylide-for-thiolate exchange reactions and/or the reverse reaction are sofar unreported.

Herein, we reveal acetylide-for-thiolate and thiolate-for-acetylide exchange on gold nanoclusters for the first time. We provide insight into the nature of exchange by observing success or failure of exchange with different acetylide derivatives and/or reaction conditions (**Figure 3.1**). Overall, we find that forward exchange, reverse exchange, and interparticle ligand exchange are all facile reactions provided incoming ligands are suitable.



Figure 3.1. Current reaction scheme.

3.3 Results and Discussion

The most straightforward reaction attempted – exchange between thiolate-protected clusters (e.g. $Au_{25}(SR)_{18}$ in our studies) and soluble phenylacetylene – resulted in no reaction. The reaction failed in all tested incoming ligand concentrations (up to a 100-fold molar excess of phenylacetylene), temperatures (up to 60 °C attempted), and in the presence of an exogenous base (Appendix B, **Figures B2-B5**). However, when phenylacetylene is introduced as a gold(I) or lithium phenylacetylide complex, exchange is successful in mild conditions. **Figure 3.2** shows MALDI-MS spectra of phenylacetylide (PA) for phenylethanethiolate (PET) exchange after 30 minutes when gold(I)-phenylacetylide is added in 1 or 10 equivalents to solutions containing

 $Au_{25}(PET)_{18}$. The distribution of exchange products increases with time and eventually results in a Gaussian-like distribution commonly observed in partial exchange reactions (Appendix B, **Figure B6**).⁸ To determine the extent of exchange that can be obtained, we reacted 100 equivalents of gold(I)-acetylide with $Au_{25}(PET)_{18}$ for 18 hours. While MALDI-MS shows a large distribution of products, we observe a peak at m/z 6744.34, corresponding closely to the calculated mass of 6744.47 for $Au_{25}(PA)_{18}$ (Appendix B, **Figure B7**).



Figure 3.2. Positive ion MALDI mass spectra of the resulting $Au_{25}(PET)_{18-x}(PA)_x$ from reacting $Au_{25}(PET)_{18}$ with 1 and 10 equivalents of gold(I)-phenylacetylide.

This suggests an exchange-based synthetic route to a recently reported homoleptic acetylide-protected gold cluster, Au₂₅(CCAr)₁₈, which was synthesized by reduction of gold(I)-acetylide precursors.¹⁷ We have not attempted isolation of this specific compound at this time due to the apparent large number of competing exchange products.

Our results differ somewhat from a recent report by Wang where addition of a gold(I)phenylacetylide derivative to bis-phosphine-protected Au₉(BINAP)₄ resulted not in exchange but in addition of the gold(I)-phenylacetylide complex to the cluster.²³ Differences in the nature of the initial ligand layer (i.e.-monodentate ligands v. bidentate ligands, phosphines v. thiolates) between the clusters in the current reaction and the cluster in the reported reaction may account for this difference in reactivity. We observe that lithium phenylacetylide, like gold(I)phenylacetylide, can ligand-exchange onto $Au_{25}(PET)_{18}$. Exchange of lithium phenylacetylide onto $Au_{25}(PET)_{18}$ in mild conditions is shown in **Figure B8** of Appendix B.

Notably, only the acetylide and thiolate ligands exchange in this case as no masses corresponding to lithium-for-gold exchange were observed. Since gold(I)-acetylide and lithium(I)-acetylide bond strengths are expected to be similar (and small), the success of lithium(I)-acetylide exchange suggests that both Li⁺ and Au⁺ may be spectators in the exchange reaction and not active participants. Overall, this implies an important mechanistic insight – that the overall exchange is a metathesis reaction – which we describe below.

We also examined the reverse reaction, specifically the exchange of thiolates onto $Au_{25}(CCAr)_{18}$, where CCAr = 3,5-bis(trifluoromethyl)phenylacetylide (**Figure 3.3**).



Figure 3.3. Negative ion MALDI mass spectra of the reaction between $Au_{25}(CCAr)_{18}$ and 1 equivalent of PET. The peak labelled 0 corresponds to the parent peak of $Au_{25}(CCAr)_{18}$, while those labelled 1-3 correspond to the value x in the formula $Au_{25}(CCAr)_{18-x}(PET)_x$. The average distance between said peaks is m/z 100.03 (calc. CCAr-PET = 99.9). Smaller peaks correspond to fluorine adducts of the adjacent peak.

The crystal structure of $Au_{25}(CCAr)_{18}$ has been recently reported as the acetylide-protected analogue to $Au_{25}(SR)_{18}$.²⁷ Synthetic details can be found in Appendix B.

MALDI-MS reveals exchange after simple mixing of thiols at room temperature with the Au₂₅(CCAr)₁₈ cluster, even at a short time scale. This result contrasts a previous report by Zheng and co-workers where addition of free thiol to the Au₂₄Ag₂₀(2-SPy)₄(PA)₂₀Cl₂ cluster results only in thiolate-for-halide exchange and not in thiolate-for-acetylide exchange.²⁴ The difference between these results and the results reported herein may be attributed to differences in metal doping (single metal versus mixed), ligand identities (homoleptic versus mixed ligand layers, aliphatic thiolate versus aromatic thiolate), or acetylide binding motifs (μ_2 versus μ_3).

Recent works by Pradeep and Bürgi have demonstrated that thiolate-protected gold clusters readily undergo intercluster exchange of ligands.^{8,25} As such, we attempted to determine if intercluster exchange occurs between thiolate- and acetylide-protected clusters. Multiple intercluster ligand exchange products derived from Au₂₅(PET)₁₈ and Au₄₄(PA)₂₈ are observed within five minutes of mixing, indicating that thiolate-for-acetylide intercluster exchange is a similarly facile process like thiolate-for-thiolate intercluster exchange (**Figure 3.4**).



Figure 3.4. Positive ion MALDI mass spectra of the product clusters A) $Au_{25}(PET)_{18-x}(PA)_x$ and B) $Au_{44}(PA)_{28-x}(PET)_x$ after mixing $Au_{25}(PET)_{18}$ with $Au_{44}(PA)_{28}$ for 5 minutes, where x is equal to the number of ligands exchanged.

Combined, the failure of phenylacetylene-for-thiolate exchange with the success of thiolate-for-acetylide, lithium phenylacetylide-for-thiolate and gold(I)-phenylacetylide-for-thiolate exchanges suggest that the net exchange reaction may be described as a metathesis reaction involving cluster, thiolate, acetylide, and hydrogen when present. Three versions of this metathesis reaction are shown in **Figure 3.5**.



Figure 3.5. Balanced reactions and net change in bond energies for exchange reactions with terminal alkynes, terminal acetylides, and thiols.

Net bond enthalpies for each metathesis reaction can help rationalize observed reaction successes and failures. Given that reported bond energies suggest that the carbon-hydrogen bond in an alkyne is 46 kcal/mol stronger than the sulfur-hydrogen bond and that previous computational results suggest the gold cluster-alkynyl bond is 6–20 kcal/mol stronger than the gold-thiolate bond, the enthalpic favorability of the overall metathesis reaction accounting for thiol-for-acetylide exchange is between -26 and -40 kcal/mol.^{15,16,26} The reverse reaction of phenylacetylene exchanging onto thiolate-protected clusters would be enthalpically unfavorable by the same value
(i.e. between +26 and +40 kcal/mol) and thus should not occur). The predicted favorability for these reactions matches with our experimental results.

The bond enthalpies of lithium-acetylide and gold(I)-acetylide are presently unknown. As such, we are unable to estimate the enthalpies of the overall metathesis reactions involving gold(I)-phenylacetylide and lithium phenylacetylide. However, the success of the metathesis reaction with thiolate-protected clusters when these are used as incoming ligands suggests that the differences between lithium-acetylide/lithium-sulfur and gold(I)-acetylide/gold(I)-sulfur bonds are much smaller than the enthalpy difference between hydrogen-alkyne/hydrogen-sulfur bonds.

3.4 Conclusion

We report herein the apparent criteria for successful incorporation of acetylides into thiolate-protected clusters. The present work suggests that acetylide-protected clusters are more susceptible to exchange with thiolates than previously assumed and/or computationally predicted, and that intercluster exchange of thiolate-for-acetylide ligands is also spontaneous at room temperature. These results may be rationalized by considering reactions as metathesis reactions rather than traditional cluster ligand exchange reactions.

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CHAPTER 4: ENHANCED SURFACE STABILIZATION OF Au₂₀(SR)₁₅ THROUGH DIGLYME COORDINATION[‡]

4.1 Synopsis

We report the synthesis of Au₂₀ cluster monomers protected by a combination of thiolates and diglyme (yield: 40%). A combination of NMR spectroscopy, mass spectrometry, IR spectroscopy, optical absorption spectroscopy and thermal analysis shows the empirical molecular formula of the compound as $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ (PET = phenylethanethiol, DG = diglyme). This cluster exhibits enhanced thermal stability compared to an all-thiolate analogue, $Au_{20}(PET)_{16}$. We also observe evidence for a stacking motif between surface-bound and excess diglyme surrounding the cluster. Notably, this cluster is resistant to dimerization/polymerization unlike previously reported metal-thiolate-glyme assemblies.

4.2 Introduction

Atomically-precise thiolate passivated gold nanoclusters represent a sub-set of metal cluster chemistry subject to intense contemporary research.¹ The ease of handling these species relative to other metal clusters enables downstream applications that depend on their robustness. Most work on thiolate protected gold nanoclusters follows the facile Brust-Schiffrin synthesis and related derivatives.² The strength of the gold-sulfur bond (~40 kcal/mol) combined with the flexibility of gold³ has successfully enabled a wide array of cluster nuclearities ranging from a few dozen to hundreds of gold atoms.^{4–11}

In addition to thiolates, a wide range of ligands such as phosphines, N-heterocyclic carbenes (NHCs), acetylides, and halides are also used to ligate gold clusters.^{12–15} Since the ligand

[‡] The work presented herein is a collaboration between the C. J. Ackerson and C. M. Aikens labs which has been submitted to *Nanoscale* and is pending further peer review. Ian D. Anderson's contributions include experimental design, data gathering & interpretation, and preparation of the manuscript. Computations were done by Y. Wang.

shell imparts solubility, stability and reactivity, the introduction of non-thiolate ligands in traditional syntheses can unlock products with properties inaccessible with thiolate ligands alone.^{16–18} Regiochemical control within the ligand shell is also of interest for catalysis, optics, magnetic data storage, bioimaging, theranostics, and sensing applications.^{19–21} In particular, studies employing bidentate ligands (e.g. NHCs, diphosphines, dithiolates) have demonstrated a number of advantageous properties such as enhanced optical response, surface rigidity, and self-assembly into larger nanoscale materials.^{22–27}

Coordinating solvents are well known for their ability to direct syntheses and transformations, sometimes to surprising effect.^{28–33} Glycol ethers, more commonly referred to as glymes, are a class of coordinating solvents comprised of saturated non-cyclic polyethers.^{34–36} Glymes typically share a myriad of properties[§] which make them attractive for both research and commercial settings. There remains significant untapped potential in the use of coordinating solvents towards development of simpler formation pathways for mono-functional clusters, which are commonly used in biolabeling.³⁷ Recent works by Wilson and Owen have demonstrated the size-focusing ability of glymes when applied in the synthesis of lead chalcogenide nanocrystals.^{38,39} Incorporation of glymes into the final products were not reported in these cases, however.

Our group has investigated the role of glymes in the synthesis, assembly, and optical properties of gold nanoclusters. We previously found that when diglyme is used as a synthetic co-solvent, it both acts as a size-focusing facilitator and is incorporated as a ligand in the resulting products. In the case of $Au_{20}(PET)_{15}(DG)_1$, we previously reported a dynamic equilibrium between

[§] Glymes have miscibility with both water and various organic solvents; a wide liquid range (> 200 °C); low viscosity; high chemical/thermal stability; relatively low vapor pressure and low toxicity (versus common organic solvents). Cleaning products, inks, adhesives, coatings, batteries, and pharmaceutical formulations are among some of the many products for which glymes have already seen use in.

this cluster monomer and its dimer Au₂₀(PET)₁₅-DG-Au₂₀(PET)₁₅.⁴⁰ A modified Brust-Schiffrin synthesis in a mixture of diglyme/tetrahydrofuran produced this unique cluster, whose dimerization was mediated by the weak gold-oxygen (~2 kcal/mol) interactions between the cluster surfaces and DG. The dimer dissociation constant was determined to be 20.4 μ M. Subsequent femtosecond transient absorption spectroscopic measurements of this dimer revealed distancedependent intercluster electronic coupling.⁴¹ Increasing the n-glyme length (n = di, tri, tetra) resulted in smaller time constants for electronic relaxation, indicative of stabilization of the dimerspecific excited states.

Our group also synthesized a water-soluble cluster $Au_{25}(p-MBA)_{17}(DG)_1$ (*p*-MBA = *para*mercaptobenzoic acid), which exhibited diglyme-gold interactions strong enough to resist ligand exchange by incoming thiolates.⁴² Unlike $Au_{20}(PET)_{15}(DG)_1$, there was no evidence for cluster dimers or larger diglyme-connected structures. This was attributed to the enhanced pi-pi stacking ability of PET versus *p*-MBA, as well as steric hindrance and charge repulsion from the carboxylic acid groups on the latter.

The surprisingly robust interaction of DG to gold in $Au_{25}(p-MBA)_{17}(DG)_1$ evokes other recent findings within citrate-capped gold colloid chemistry. Detailed surface characterization of large (~40 nm) gold colloids by Park and Shumaker-Parry revealed that instead of a monolayer, citrates stack as chains which result in a ligand network strong enough to resist displacement by thiolates. Shumaker-Parry concludes that a ligand exchange reaction previously considered spontaneous due to the large difference in gold-sulfur and gold-oxygen bond energies is, in fact, substantially incomplete on citrate passivated gold nanoparticles.^{43,44}

Here we report on a new heteroleptic diglyme-thiolate Au₂₀ cluster monomer, discovered through testing the synthetic conditions of the Au₂₀ dimer-monomer system. Characterization

reveals diglyme-gold and diglyme-thiolate interactions to be more robust than expected based on simple bond dissociation energy arguments. Interestingly, this cluster exhibits a similar degree of resistance to dimerization/polymerization as Au₂₅(*p*-MBA)₁₇(DG)₁, despite use of the PET ligand. A comparative analysis to previous synthetic studies as well as Park and Shumaker-Parry's findings provides insight into the formation requirements and stability origin of this new class of atomically-precise gold nanoclusters.

4.3 Results and Discussion

Figure 4.1 shows the MALDI-MS spectrum of the obtained synthetic product. Full details regarding the synthesis can be found within Appendix C. In comparison to our previous dimermonomer synthesis involving $Au_{20}(PET)_{15}(DG)_1$, the major difference is that in this current work reduction with NaBH₄ is initiated before dilution with a gross excess of diglyme. The parent peak at 6266 m/z is in excellent agreement with the formula $Au_{20}(PET)_{15}(DG)_2$ (calculated mass: 6266.2 Da). The inset of Figure 4.1 shows possible alternative assignments, as well as expected fragments. None of the observed fragments can be associated with the loss of units containing diglyme. This is in notable contrast to the $Au_{20}(PET)_{15}(DG)_1$ monomer-dimer system, wherein the single diglyme is bound too weakly to remain bound to the intact cluster under MALDI conditions.⁴⁰



Figure 4.1. Positive ion MALDI mass spectrum of the Au_{20} synthetic product, with its parent peak indicated by the green dashed line. Inset table i) lists alternative formulae close in mass to the best match (highlighted in green). Inset table ii) lists potential fragments of primary interest. The label * refers to a combination fragment/adduct peak related to $Au_{20}(PET)_{15}(DG)_2$.

NMR spectroscopy is a powerful analytical tool for clusters in providing evidence of purity, structure, dynamic surface interactions, and magnetism at high spectral resolution.^{45–50} **Figure 4.2** shows the ¹H NMR spectrum of the cluster sample versus that of unbound PET and DG. The broadening of peaks is characteristic of ligands closely associated with a gold cluster surface. This suggests a ligation-type interaction for both PET and DG.⁴⁵



Figure 4.2. ¹H NMR spectra of a) free PET, b) free DG, and c) the Au_{20} synthetic product in CD_2Cl_2 with peak assignments for clarity. Peaks labelled with * appear to correspond with diglyme but cannot be unambiguously assigned.

The cluster preparation was washed extensively with excess methanol, which is expected to remove diglyme acting as solvent (e.g., not directly interacting with the cluster). Despite this, peak magnitudes for DG are similar to those for the ethylene linker of PET. Furthermore, the ethylene linker protons are shifted downfield by approximately 0.3 ppm from the chemical shift observed for a comparable fully-thiolated gold cluster, $Au_{25}(PET)_{18}$ (Appendix C, **Figure C1**). We attribute this de-shielding effect to the surface-bound DG causing a lowering of the overall electron density on the ethylene linker through the shared gold surface. Intriguingly, the PET phenyl ring protons remain in the same relative position as those on the surface of $Au_{25}(PET)_{18}$. Combined, these data suggest that the ligated DG is interacting more closely with the ethylene linker than the phenyl ring.

Because the cluster product fails to crystallize (facilitating total structure determination), we computationally modelled several possible structures of a $Au_{20}(SCH_3)_{15}DG$ model system. Multiple isomers of the cationic $Au_{20}(SCH_3)_{15}DG$ system were optimized and the lowest energy structure is shown in **Figure 4.3**. Overall, the diglyme displays a crown-like structure bound to the surface of the gold cluster.



Figure 4.3. The fully optimized BP86/TZP structure for $Au_{20}(SCH_3)_{15}DG^+$. Atoms 117 and 118 are the two hydrogen atoms with the most upfield and most downfield chemical shifts, respectively. Hydrogen atom 111 is the hydrogen atom which is connected to the same carbon atom as atom 118. Gold = gold, carbon = gray, sulfur = yellow, oxygen = red and hydrogen = white. Coordinates provided in Appendix C.

Table 4.1 displays the ¹H NMR shielding calculations performed for all hydrogen atoms within the diglyme molecule. Interaction with the $Au_{20}(SCH_3)_{15}$ cluster increases the chemical shifts of several hydrogen atoms in the diglyme molecule. We observe that hydrogen atom 117 has the most upfield chemical shift at 3.79 ppm; this atom is oriented away from the gold nanocluster. Hydrogen atom 118 has the highest chemical shift, which is very downfield (6.81 ppm); this hydrogen atom is oriented towards the Au atoms. Hydrogen atom 111 is connected to the same

carbon atom as hydrogen atom 118, but this atom is not oriented towards the gold core. Atom 111 has a calculated chemical shift of 4.43 ppm. Therefore, unlike pure diglyme (Appendix C, **Table C1**), the chemical shift is not dominated by the proximity to neighbouring oxygen and carbon atoms; these atoms do not dominate the chemical shifts nearly as much as the proximity to the Au atoms.

Table 4.1. Calculated ¹H NMR chemical shifts for the hydrogen atoms of diglyme in $Au_{20}(SCH_3)_{15}DG^+$.

hydrogen atom	chemical shifts (ppm)
105	5.06
106	3.93
107	4.95
108	4.11
109	4.97
110	3.92
111	4.43
112	4.02
113	3.88
114	5.55
115	4.43
116	4.10
117	3.79
118	6.81

Figure 4.4 shows the ¹H-¹H COSY NMR spectrum of the cluster. We observe no interaction between the phenyl ring protons of PET and the DG protons. However, we observe strong correlation between the PET ethylene linker and DG protons. This suggests that the DG ligands are in a closer vicinity to the ethylene linker than the phenyl ring.



Figure 4.4. ¹H-¹H COSY spectrum of the Au₂₀ synthetic product in CD₂Cl₂. Off-diagonal signal is indicative of spin-spin coupling between different ligand environments.

Due to the dynamic behaviour of cluster ligand layers in solution,^{51–53} we would expect some observable degree of spin-spin coupling between DG and the phenyl ring if DG were ligated in a monodentate fashion. A multidentate arrangement would enhance the overall strength of the gold-diglyme interaction, and the chelating ability of DG and other glymes is well documented.^{28,34}

Based on the high signal strength of the DG protons relative to the PET protons from NMR analysis, we hypothesized that more than two diglyme molecules were present per formula unit. In order to test this hypothesis, we performed Thermal Gravimetric Analysis (TGA) on the cluster monomer in dry powdered form. **Figure 4.5** shows the TGA curve of the powdered cluster. Differential thermal analysis revealed the precise onset of the two weight loss events (Appendix C, **Figure C2**). The final weight % is representative of the proportion of the cluster consisting of gold. Conversely, the total weight % loss should match closely with the proportion consisting of the ligands. Assuming a cluster of formula $Au_{20}(PET)_{15}(DG)_2$ the ligand loss is equivalent to 37.1%, which is significantly different from the observed total loss of 45.8%. Furthermore, this formula does not account for the initial weight loss event of 8%.



Figure 4.5. TGA curve of powdered $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$. Inset provides a clearer view of the onset temperatures for the two weight loss events.

A significantly better match to the TGA data is obtained by considering the full formula: $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ (calculated mass: 6803 Da). We propose that this 'excess' diglyme is not directly bound to the gold surface and is therefore easier to remove. The loss of 4 DG molecules is equivalent to a 7.8% loss and the subsequent loss of $(PET)_{15}(DG)_2$ is equivalent to 34.2% (total = 42%). It is possible that this 'excess' diglyme is unevenly distributed within the powdered sample, which could help explain the discrepancy between observed and calculated weight loss values.

The onset of decomposition for the all-thiolate $Au_{20}(PET)_{16}$ cluster under comparable thermal conditions is at approximately 125 °C.⁵⁴ This is considerably lower than $[Au_{20}(PET)_{15}(DG)_2]\cdot4[DG]$, whose inner ligand shell does not desorb until approximately 156 °C. Similarly, $Au_{20}(PET)_{15}$ -DG- $Au_{20}(PET)_{15}$ does not begin to shed its ligand shell until approximately 150 °C.⁴⁰ It is therefore evident from both our previous and current work that the coordination of diglyme to thiolate-protected gold nanoclusters results in a significant enhancement of surface stability. The calculated binding energies between $Au_{20}(SCH_3)_{15}^+$ and the first diglyme is around 147 kJ/mol (Appendix C, **Table C2**), which is consistent with the experimental observation for the strong diglyme-gold interaction.

The linear absorption spectrum of $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ is comprised of a single broad peak centered at 512 nm (Appendix C, **Figure C3**). This is less complex than the absorption spectra of $Au_{20}(PET)_{16}$ and $Au_{20}(PET)_{15}$ -DG- $Au_{20}(PET)_{15}$, but is similar to $Au_{20}(PET)_{15}(DG)_1$.^{40,54} Based on the presence of multiple diglyme per formula unit and their novel arrangement, we expect electron relaxation dynamics unique from that of the single-diglyme monomer.

Solution-phase FT-IR analysis of the cluster shows a lack of vibrations in the region of 2000-1750 cm⁻¹ (Appendix C, **Figure C4**). This set of vibrations is observable within the dimer $Au_{20}(PET)_{15}$ -DG- $Au_{20}(PET)_{15}$, arising from strong ligand-layer vibrational coupling between the

two Au₂₀ monomer units.⁴⁰ We find no compelling evidence for such interactions within this new cluster, therefore establishing it as a purely monomeric species.

 $[Au_{20}(PET)_{15}(DG)_2]\cdot 4[DG]$ can be repeatedly dried and re-suspended up to three times without any indication of decomposition. The low vapor pressure and wide liquid range of diglyme appears to help facilitate this degradative resistance. Furthermore, the solution-phase shelf life is remarkable, with no significant decomposition following storage in chloroform at 0 °C for up to 18 months. To test whether $[Au_{20}(PET)_{15}(DG)_2]\cdot 4[DG]$ is capable of hierarchical assembly, we performed a series of heating experiments. Highly-concentrated chloroform solutions of the cluster monomer were set in water baths ranging from 30-60 °C and allowed to equilibrate at each temperature for up to one hour; additional experiments involving a gross excess of diglyme were also conducted (Appendix C, **Figure C5**). Overall, we observed no change in the absorption profile of $[Au_{20}(PET)_{15}(DG)_2]\cdot 4[DG]$ over the course of these experiments, demonstrating that it is highly resistant to dimerization/polymerization.

Modification of the reducing agent addition step is known to greatly influence the product distribution in Brust-type gold nanocluster syntheses.^{55,56} It is also well-known that clusters only begin to form once a significant electron reservoir (i.e. the reducing agent) is introduced. The synthetic conditions to obtain $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ are nearly identical to that for the dimermonomer system, with the exception of this step.

As mentioned previously, the dimer-monomer synthesis introduces the reducing agent after diluting the reaction solution with a gross excess of diglyme (523.7 eq relative to HAuCl₄· $3H_2O$).⁴⁰ Our modified synthesis reverses the order, instead adding the reducing agent prior to the dilution step. Cluster formation therefore begins with a significantly lower diglyme content: 87.3 eq for $[Au_{20}(PET)_{15}(DG)_2]$ ·4[DG] versus 611 eq in the case of the dimer-monomer system. Notably,

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 $Au_{25}(p-MBA)_{17}(DG)_1$ also formed using a lower diglyme content (74.2 eq).⁴² Combined, our results indicate that modification of the diglyme content directly influences the final cluster product identity.

It is interesting that gold-thiolate nanocluster syntheses have a propensity for incorporation of glymes within the final products, unlike in the case of lead chalcogenide nanocrystals where they appear to only control the size.^{37,38} We posit that the different predominant formation pathways for lead chalcogenide nanocrystals (nucleation and growth) and gold-thiolate nanoclusters (etching) play a significant role in this difference of outcome. Further mechanistic studies in both of these areas need to be performed in order to fully appreciate the directing role of glymes in synthesis.

Even at the minimum laser intensity, the high energy conditions of MALDI-MS are more than sufficient to ablate weakly-interacting ligands from the surfaces of gold nanoclusters.^{49,57} It is remarkable that two molecules of diglyme are strongly bound enough to remain on the intact cluster. The only other example of such a phenomenon to date is from our own report on Au₂₅(*p*-MBA)₁₇(DG)₁.⁴² In addition, the diglyme-diglyme interactions of $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ are notably stronger than the gold-sulfur interactions of the all-thiolate analogue within a thermal decomposition context (desorption at 138 °C versus 125 °C).⁵⁴

As Park and Shumaker-Parry's studies initially revealed, oxygen-containing coordinating ligands can exhibit remarkably strong surface chemistry due to inter-ligand stacking networks.^{43,44} In the case of citrates, one of the prominent intermolecular forces was identified as van der Waal attractions between neighbouring chains *via* proximal CH₂ moieties. Our work extends this unique surface chemistry to atomically-precise clusters with glymes.

The strong hydrogen-bond acceptor ability of diglyme is well-documented.⁵⁸ Attraction between CH₂ moieties within PET and diglyme is evident from our ¹H-¹H NMR spectral data. Furthermore, the difference in formulation between mass spectrometry and TGA suggests that at least two configurations of diglyme with significantly different binding strengths are at play. Our current working hypothesis is that the 'excess' 4[DG] is stacked in a similar fashion to what is observed in Park and Shumaker-Parry's citrate-capped colloids. Based on the observed lack of correlation with the PET phenyl ring, the specific diglyme stacking arrangement must be 'buried' alongside the ethylene linkers of PET. To our knowledge, this is the first example of such a protecting motif in gold nanoclusters. Assuming an even distribution between the two directly surface-bound diglyme, [Au₂₀(PET)₁₅(DG)₂]·4[DG] should therefore have two groups of threediglyme long stacks.

Thus far, [Au₂₀(PET)₁₅(DG)₂]·4[DG] has proven resistant to hierarchical assembly. This may be due to suboptimal positioning of the outermost diglyme, although the presence of a gross excess of diglyme in our thermal activation study should be able to serve as 'bridges' between adjacent clusters.⁴⁰ We posit that the strength of the diglyme-diglyme interaction decreases the further it gets from the cluster surface, eventually reaching a point of diminishing returns which make longer diglyme stacks energetically unfavourable.

One open question which remains is the precise orientation of both the inner DG ligands and the outer excess DG. We have some insight from theory as well as the ¹H and ¹H-¹H spectra with regard to the former, but this has yet to be unambiguously confirmed through crystallography. Simulated structures of gas-phase bare Au_{20} as well as empirical data on phosphine-protected Au_{20} arrange all gold atoms within a highly stable tetrahedral structure (i.e. all gold is exposed to the surface).^{59,60} If true, this would create a scenario wherein up to five gold atoms are not directly coordinated to one of the 15 thiolate ligands, freeing them up for potential chelation with glymes.

4.4 Conclusion

The use of coordinating cosolvents such as glymes in Brust-type syntheses is relatively unexplored, and represents a handle for modification of cluster surface chemistry. It is likely that through careful tuning of reaction conditions, a series of diglyme-ligated gold nanoclusters can be produced. Whether all nuclearities would have enhanced surface stability remains a point of conjecture, as the curvature of the cluster surface necessarily plays a significant role in the orientation of diglyme. For [Au₂₀(PET)₁₅(DG)₂]·4[DG], post-synthetic modification studies on traditional ligand exchange and intercluster metal/ligand exchange are of immediate interest. If the ligated DG exhibit resistance to exchange by incoming thiolates, a 100% diglyme-protected gold nanocluster may be completely shielded from intercluster exchange (typically a facile process).

We anticipate that excited state absorption measurements of this cluster monomer will provide a detailed view of its electronic energy landscape, which may help to explain its resistance to hierarchical assembly. X-ray absorption experiments could offer more insight into the various coordination environments unique to this cluster, if a crystal structure is not forthcoming. The strong stabilizing effect of diglyme, in addition to the myriad existing research and commercial applications of glymes, makes heteroleptic clusters such as $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ exceptional models with which to probe glyme-cluster interactions with atomic precision.

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CHAPTER 5: SYNTHETIC BASIS FOR ATOMICALLY PRECISE DITHIOLATE PROTECTED GOLD NANOCLUSTERS WITH SOME STRUCTURAL INSIGHTS

5.1 Synopsis

The fundamental chemistry of soluble metal particles is deeply influenced by the ligand shell. A majority of atomic-level knowledge in this area is owed to monothiolate protected gold nanoclusters (NCs). Access to additional coordination modes beyond monodentate is essential to the further development of nanoscience but has proved elusive. We herein present a practical approach for the synthesis of homoleptic dithiolate protected gold NCs. In a screen of 14 commercially available ligands, seven were found to produce stable NCs as observed by mass spectrometry and linear absorbance spectroscopy. Reaction successes and failures are attributed to differences in overall ligand rigidity and the relative proximity of sulfur headgroups. Some NCs exhibit spontaneous assembly into hierarchical structures. Lastly, we demonstrate a resistance of dithiolate NCs against exchange with 2-Phenylethanethiol (PET) under both free ligand and intercluster exchange conditions. Rapid metal exchange between clusters is still found to occur, however.

5.2 Introduction

Monolayer protected transition metal nanoclusters (NCs) are a fascinating class of materials consisting of discrete collections of metal atoms stabilized by a ligand shell.^{1–3} Their unique size between small molecular complexes and larger colloidal particles grants them a combination of properties reminiscent of both regimes.^{4,5} The task of studying metal NC chemistry was substantially eased by the advent of the Brust-Schiffrin synthesis for thiolate protected gold clusters and colloids.⁶ These species of comparatively high stability (relative to other NCs) are formed under ambient conditions and can be handled in a manner similar to small molecules.^{7,8}

Gold-thiolate NCs, therefore, have attracted considerable interest for a wide variety of contemporary research objectives. Among these is included the structure and dynamics of the ligand-metal interface, which plays a central role in determining solubility and assembly properties.^{9–13}

While much progress has been made with respect to this research aim, the overall stability of monolayer protected gold NCs could be improved in some contexts. Intercluster metal/ligand exchange was recently identified as a spontaneous process, even between clusters of the same metal as evidenced through isotopic labelling.^{14–18} Different thiolate ligand conformations exhibit low barriers to stereoisomerization,¹⁹ and there is compelling crystallographic evidence for the migration of ligands over time.^{20–22} Several downstream applications, in particular those related to biological systems,^{23–27} rely on clusters operating as truly distinct species. The identification of a ligand set capable of hindering or entirely resisting such processes is of immediate concern.

Previous work by several groups have recognized the potential of dithiolate ligands to suppress displacement. The chelate effect provides enhanced surface stabilization, resulting in more controlled packing density on self-assembled monolayers (SAMs) and a resistance against ligand exchange on colloidal particles.^{28–33} Post-synthetic partial ligand exchange studies on gold NCs demonstrate a similar degree of enhancement, as well as stabilization against stereoisomerization in the case of chiral dithiolates.^{34–44} Depending on the mode of attachment, certain ligands can induce hierarchical assembly through covalent linkages between individual clusters or colloids.^{45–54}

The majority of post-synthetic and synthetic studies thus far, however, have been limited to incomplete heteroleptic protecting modes involving a combination of dithiolates with

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monothiolates or phosphines.^{55,56} Existing synthetic pathways produce large/polydisperse colloids or involve custom-made ligands that offer minimal insight into the general formation process.^{57–74}

Herein we report our findings on the establishment of a straightforward methodology for the production of fully dithiolate protected gold NCs. All of the candidate ligands are commercially available and share certain structural similarities in order to obtain a more nuanced understanding of which features appear to encourage NC formation. Furthermore, we observe new surface chemical behavior in alignment with both resistance against exchange and a tendency towards hierarchical assembly.

5.3 Results and Discussion

NCs were synthesized using a modification of the conditions for the single phase Brust-Schiffrin procedure.⁷⁵ Complete details can be found in Appendix D. Briefly, gold (III) chloride trihydrate was co-dissolved in tetrahydrofuran with tetraoctylammonium (TOA) bromide. The candidate dithiolate was subsequently added and allowed to mix overnight in order to form highly monodisperse gold-dithiolate oligomers.⁷⁶ Following this, a freshly prepared aqueous solution of sodium borohydride was added to induce reduction to metallic NC species which were allowed to react for a full 24 hours.

Figure 5.1 outlines which of the candidate ligands were successful in producing stable NCs. To our knowledge, eight of these 14 candidate ligands have been applied in previous studies. These include the five basic alkane dithiols as well as **4**, **6**, and **11**.^{38,39,56,66} With the exception of **6** and **11**, prior to this work these were strictly examined within the context of post-synthetic treatments. It is therefore particularly interesting that only half of these previously used ligands are found to produce stable fully dithiolate protected NCs (**1**, **2**, **4**, and **6**) under the explored conditions. The subtraction or addition of a single methylene group between **1** and **12** (or **2** and **14**) yielded

significantly different results. Too long or short of a linker length between sulfhydryl groups produces irreversibly cross-linked agglomerates of clusters/particles. For the alkane dithiols we attribute this to the variable binding modes possible for such conformationally flexible ligands.³⁹



Figure 5.1. Reaction outcome versus ligand type (success = blue, failure = red).

Both **9** and **13** produced insoluble agglomerates, despite only differing from **2** by substitution of the central methylene group with either an oxygen or sulfur atom. These atom types can interact more strongly with gold surfaces (relative to methylene), which may result in a preference for low-curvature colloids.^{77,78} Alternatively, the reduced dispersive force may inhibit interactions with solvent or other ligands, rendering cluster formation entropically unfavorable. The majority of cluster-forming ligands contain aromatic rings (**3-7**), which are well-documented in gold NC chemistry for their stabilizing ability.^{79–81} Ligands **3-5** share the same number of carbon centers between sulfhydryl groups as **8**. We attribute two main contributing factors to the observed difference in outcome: the presence of favorable π - π interactions and the steric hindrance provided by the phenyl group.

A comparison between **6** and **10** offers further insight on the influence of steric hindrance. Additional methyl groups on **6** result in a wider cluster cone angle, thereby restricting the possible number of inter-ligand configurations.⁸² The ineffectiveness of **10** is likely due to cross-linking interactions made possible through the absence of methyl groups. Both **1** and **6** contain four carbon centers between sulfhydryl groups, although the latter conformationally restrains each group to be considerably closer. Ligands **7** and **2** exhibit a similar spacing relationship but with a greater overall sulfhydryl separation than the previous comparison, given the meta positioning of the methanethiol groups.

The identity and distribution of successful reactions were assessed by matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. **Figure 5.2** shows that ligand **1** produces three general cluster nuclearities. Despite a high degree of fragmentation, each bracketed region matches well with the calculated masses for $Au_{25}(C_4H_8S_2)_9$ (6006 Da), $Au_{44}(C_4H_8S_2)_{14}$ (10.35 kDa), and $Au_{130}(C_4H_8S_2)_{25}$ (28.61 kDa). The Gaussian-like peak distribution is a common feature amongst all dithiolate NC products in this study, which persists even at minimal laser fluence. Based on relative peak intensities and the measured absorption profile (*vide infra*), we find the nuclearity Au_{25} to be the major product for **1**. Further in-depth fragment analysis, including that of **2-7**, can be found in Appendix D (**Figures D1-D7**).



Figure 5.2. Negative-ion MALDI mass spectrum of 1. Inset: three possible binding modes on the Au_{25} structure.

The conformational flexibility of alkane dithiols such as **1** and **2** presents a number of potential binding modes. This ranges from simple monodentate (**Figure 5.2a**), intra-staple bidentate (**Figure 5.2b**), to inter-staple bidentate (**Figure 5.2c**). The latter binding mode may involve one or two alkane dithiol molecules, depending on the number of methylene linkers. The theoretical basis of inter- versus intra-staple binding was established in a previous study by Jupally and coworkers involving post-synthetic alkane dithiolate-for-monothiolate exchange.³⁹ Optimized computational models of $Au_{25}(C_4H_8S_2)_9^-$ found that bidentate inter-staple binding is more energetically favorable by 18 kcal/mol versus intra-staple.

Having observed up to six exchanges experimentally (i.e. 12 of the 18 possible sites), Jupally and coworkers proposed that binding occurred between the middle site of one RS-Au-SR-Au-SR unit and one terminal site of a neighboring staple (i.e. middle-terminal coupling). In terms of the complete alkane dithiolate coverage observed in our study, the three specific modes of middle-terminal, middle-middle, and terminal-terminal coupling cannot be unambiguously discounted without a crystal structure. The reversible assembly of samples of **1** and **2** into amorphous superclusters (Appendix D, **Figure D8**) is suggestive of dangling or otherwise labile sulfhydryl groups which can act as covalent cross-linkers between individual NCs. We therefore posit that a combination of different binding modes exist for these two alkane dithiolate ligands.

Table 5.1 describes the product distribution for ligands 1-7. In light of these synthetic outcomes, it is clear that this set of conditions favors certain cluster nuclearities over others (e.g. Au_{25} , Au_{38} , and Au_{44}). The relationship between ligand identity and cluster surface is similar to that of a lock and key.⁸³ We therefore propose that ligands 8-14 may prove effective in the future, given the appropriate conditions. The presence of TOA bromide produces a size-focusing effect in gold NC syntheses, which generally favors $Au_{25}L_{18}$ as a major product for monothiolates.⁸⁴⁻⁸⁶ This

can help explain the preponderance of this nuclearity across the successful set of ligands. Other parameters such as duration of the gold-ligand precursor formation step also serve important roles in product identity and dispersity.⁷⁶

Ligand	Observed Peak Range	Matching General	Formula Mass Range
Entry	(m/z)	Formula	(Da)
1	4,044-6,760	$Au_{25}(1)_x (x = 9-15)$	6,006-6,728
	8,325-12,050	$Au_{44}(1)_x (x = 14-28)$	10,350-12,033
	28,500-31,620	$Au_{130}(1)_x (x = 25-50)$	28,612-31,618
2	3,397-6,960	$Au_{25}(2)_x (x = 9-15)$	6,132-6,938
3	10,030-14,900	$Au_{52}(3)_x (x = 16-32)$	12,486-14,730
4	5,000-9,900	$Au_{25}(4)_x (x = 9-18)$	6,312-7,701
		$Au_{38}(4)_x (x = 12-16)$	9,336-9,953
5	29,875-29,960	$Au_{124}S_x(5)_{26} (x = 0-3)$	29,861-29,957
6	4,470-8,460	$Au_{25}(6)_x (x = 9-18)$	6,691-8,458
	8,660-10,720	$Au_{38}(6)_x (x = 12-16)$	9,841-10,626
	10,930-12,170	$Au_{44}(6)_x (x = 14-18)$	11,415-12,200
7	4,690-7,450	$Au_{25}(7)_x (x = 9-15)$	6,439-7,448
	7,600-10,120	$Au_{38}(7)_x (x = 12-15)$	9,504-10,009
	10,300-14,000	$Au_{44}(7)_x (x = 14-28)$	11,022-13,379

Table 5.1. NC products for successful ligands, as observed by mass spectrometry.

To better understand the reaction pathway, we performed a series of variations of the synthesis with **1** (see Appendix D). We find that stable NC products fail to form when TOA bromide is not included. Moreover, shortening the gold-ligand precursor step from 15 hours to 30 minutes leads to a similar result. We note that a majority of previous synthetic studies included TOA bromide or some other size-focusing agent.⁵⁷⁻⁷⁴ The major difference from these studies and our own is the duration of the gold-ligand precursor step, which were typically on the order of several minutes to half an hour. Our findings indicate that dithiols are especially sensitive to this step in gold NC synthesis.

Figure 5.3 shows a comparison between the linear absorption profiles of **1**, **2**, and **6**. The preponderance of Au₂₅ within these samples is readily apparent based on their high similarity to the absorption profile of crystal-pure Au₂₅(PET)₁₈ (PET = 2-phenylethanethiol) as seen in Appendix D, **Figure D9**. The greater relative amount of other nuclearities present in **6** results in

overall diminished peak intensities due to broad overlap of features from different molecular NC species. **1** and **2** are nearly indistinguishable, aside from slight differences in peak center for the feature attributable to the HOMO-LUMO transition (near 650-750 nm). From this analysis it appears that the electronic structure of Au_{25} remains relatively unchanged when conformationally flexible alkane dithiols are used, in agreement with previous observations from partial exchange.³⁹



Figure 5.3. UV/Visible absorption spectra for 1 (black trace), 2 (blue trace), and 6 (red trace) in dichloromethane.

Absorption profiles of the remaining ligand entries can be found in Appendix D (**Figures D10-D13**). Most noteworthy is that of **3**, which both produces a highly monodisperse NC product and apparently significantly alters its electronic structure. Previously the monothiolate $Au_{52}(SR)_{32}$ was exclusively accessible through post-synthetic etching of a polydisperse mixture of $Au_x(TBBT)_y$ (TBBT = 4-*tert*-butylbenzenethiol).⁸⁷ The feature attributable to the HOMO-LUMO transition is considerably blueshifted, from 800-850 nm to 600-650 nm.⁸⁸ This may indicate a complete reordering of the cluster shape to accommodate restrictive S-Au-S angles imposed by the proximity of the sulfhydryl groups.

Furthermore, **3** is found to spontaneously form dendritic crystalline material in large patterned networks (Appendix D, **Figures D14-D15**). Work is ongoing within our lab to obtain high-quality single crystals for X-ray diffraction studies. Although **5** also forms a similar material

(Appendix D, **Figure D16**), **4** thus far does not exhibit this ability. We posit that whatever aromatic interactions responsible for such ordering are disrupted by the presence of the methyl group on **4**. It is interesting that the two chlorides on **5** do not interfere in this manner, possibly due to the much larger cluster formed by **5** (versus **4**) possessing a less curved surface which can better accommodate the functional groups.^{89–91} The relatively greater degree of monodispersity found in **3** and **5** may also help explain their comparative ease of crystallization.

We performed a series of preliminary exchange reactions involving mixing both free PET and $Au_{25}(PET)_{18}$ with the dithiolate protected NCs (see Appendix D). Figure 5.4 shows that no incorporation of dithiolates into $Au_{25}(PET)_{18}$ is observed over a period of 24 hours when mixed with NC samples of 1-7.



Figure 5.4. Positive-ion MALDI mass spectra resulting from $Au_{25}(PET)_{18}$ samples being mixed with NCs of 1-7 for 24 hours at room temperature in dichloromethane.

Further analysis of these samples after storage at 4 °C for one week produces the same result (Appendix D, **Figure D17**). This is in contrast to previous reports of free dithiols rapidly exchanging with monothiolate protected gold NCs,³⁴⁻⁴⁴ suggesting that bound dithiolates are

considerably less reactive in this regard. We observe a similar lack of exchange between free PET and NCs of **1-7** (Appendix D, **Figures D18-D24**).

We also tested the reactivity of **1-7** towards metal exchange, through mixture of each dithiolate NC sample with $Ag_{44}(DFTP)_{30}$ (DFTP = 3,4-difluorothiophenol). Unlike in the above cases for monothiolate ligands, we observe a rapid and extensive exchange of gold atoms into $Ag_{44}(DFTP)_{30}$ as evidenced by the shift of its corresponding peak envelope to higher m/z ratios (Appendix D, **Figures D25-D31**). Recent kinetics studies on intercluster metal exchange have proposed that the process occurs through a transient dimer which briefly connects the cores of the two NCs.¹⁸ This introduces the possibility that two incompatible ligand shells (e.g. mono- and dithiolate) may still exchange metal atoms if portions of the NC core are solvent-exposed. It is also possible that the greater electron-withdrawing nature of the DFTP ligands (versus PET) renders exchange more likely.

To this end, there is a considerable body of evidence regarding the interplay between structural rigidity, sterics, and the propensity for exchange between clusters.^{14–18,92–94} The observed resistance towards ligand exchange and proclivity towards metal exchange in our study underpins the complex nature of structure-reactivity relationships found in atomically precise NCs. We propose that further investigation of multidentate ligands, including those with three or more potential coordination sites, may provide the means necessary to completely shut down all intercluster exchange processes.

5.4 Conclusion

In summary, we identify a general synthetic route to fully dithiolate protected gold NCs and establish a rationale for reaction successes and failures. We determine the importance of both TOA bromide and the gold-ligand precursor step in forming cluster products. There is a clear
preference for certain linker lengths and sulfhydryl group proximities, which we envision can be altered based on the exact reaction environment. These new NCs exhibit a strong resistance to monothiolate ligand exchange, yet remain susceptible to metal exchange. Furthermore, amorphous or dendritic crystalline assemblies are observed for some of the cluster samples. Overall, we offer a new experimental basis for studying the surface chemistry of gold NCs.

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CHAPTER 6: ADAPTING BRUST-TYPE METHODS TO NON-COINAGE METALS

6.1 Synopsis

Variations on the original Brust-Schiffrin synthesis for gold have successfully produced atomically precise NCs of both silver and copper. Extension of similar methods to elements beyond group 11 is particularly enticing given the high degree of ease and tunability Brust-type methods offer relative to other cluster synthetic protocols. However, this has proven a difficult task with a current dearth of successful reports. Herein we summarize our efforts in this area for three noncoinage metals and offer guidelines for future exploratory work.

6.2 Introduction

As detailed in chapter 1, the original study of metal clusters was stymied by a lack of synthetic methods. This was first addressed through breakthroughs involving carbonyl protected clusters, although the strict requirement of inert conditions rendered these pathways generally unaccommodating beyond a limited window of products.¹ The foundation laid by Brust and Schiffrin has subsequently proven to be the most robust means of producing stable metal NCs thus far.²

Contemporary research has succeeded in broadening the scope of Brust-type syntheses to include new ligand groups such as acetylides,³ N-heterocyclic carbenes (NHCs),⁴ hydrides,⁵ glymes,⁶ and very recently dithiolates. An array of alloy NCs comprised of gold, silver, and/or copper have also been identified, among other mixtures including late transition metals from groups 9, 10, and 12.⁷ It naturally follows, therefore, to assert the possibility of accessing new metal NCs through the further extension of Brust-type methods. Favorable redox chemistry is the

most important aspect of a candidate metal, given the prerequisite for more mild reducing agents capable of being used outside of a glovebox.

This area remains considerably unexplored, with several major fundamental questions left open. These include: which of the non-coinage metals are capable of forming NCs under ambient conditions? What are the structural patterns (i.e. geometric stabilization)? Can their electronic stabilization be easily understood through superatom theory, or is some other framework more appropriate? To what extent can these syntheses be tuned relative to the gold-based method?

In 2016 S. Bhat and coworkers reported the first successful synthesis of thiolate protected iridium NCs through a solid phase adaptation of the typical Brust conditions.⁸ Around the same time, we were beginning to explore a similar reaction space in the solution phase. Our attempts to follow their procedure initially produced insoluble aggregates. Following extensive correspondence with S. Bhat and various modifications we discovered that the solid phase synthesis is highly sensitive to the local climate. A rough imitation of the tropical environment of southern India through the use of a steam bath is able to produce an observable amount of the iridium NCs.

Overall we establish that the comparatively dry, cold environmental setting of northern Colorado is much better suited to reactions performed in the solution phase, as far as iridium is concerned. Our most recent attempts have addressed the issue of reproducibility, although we have yet to identify a matrix that offers sufficiently low fragmentation for observation by matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. Electrospray ionization (ESI) has also proven ineffective but successful conditions for either or both may be found in the future. Characterization efforts include linear absorption spectroscopy, nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM). Results from other late transition metals have generally proven less agreeable. We have documented in great detail the case of rhodium (see appendix A), which forms a series of chemically inert crown complexes upon interaction with thiols. Other ligands such as acetylides appear capable of producing large rhodium colloids, but so far have not been shown to form smaller sizes within the cluster regime. Palladium behaves analogous to rhodium with respect to thiols, as previous studies have outlined.⁹ In the case of platinum, cadmium, mercury, ruthenium, rhenium, and tungsten we have unfortunately only managed to compile a set of failed strategies.

Osmium has exhibited a small degree of potential, in that it does not produce aggregates and its thiolated form appears indefinitely stable. One primary concern of continued work is the possible formation of highly poisonous OsO₄ from the reaction of osmium metal with atmospheric oxygen. If appropriate caution is taken, this should be avoidable. Very recently we have also identified the post transition metal bismuth as a viable NC-forming candidate through the use of water-soluble thiolates. Bismuth is comparatively much safer and possesses some interesting possible applications in biological contrast imaging.¹⁰ Furthermore, the valence p-shell orbitals should impart an electronic structure unique from the primarily s- and d-shell interactions present in late transition metals.

This chapter is intended to serve as a guide for future members of the Ackerson lab seeking to continue the pursuit of Brust-type methods for non-coinage metal NCs, although it should also prove useful as a template for general exploratory nanochemistry. In the interest of brevity only the three most promising metals (iridium, osmium, and bismuth) are outlined herein. Each procedure is associated with a particular notebook page, with any corresponding rough data immediately following said entry. This should aid in streamlining any reference to the source material.

6.3 General Experimental Procedures

All reactions were performed with commercially available reagents without any further purification. UV/Visible spectra were collected on a Thermo Fisher NanoDrop spectrophotometer and analyzed in Microsoft Excel. NMR data was collected on a Bruker Neo400 using 5-10 mg of sample dissolved in minimal deuterated solvent. MNova was used for subsequent analysis of the NMR spectra. TEM data was collected on a JEOL JEM-2100F with samples dropcast on carbon-coated copper grids. Micrograph analysis was done using ImageJ.

6.4 Iridium

IA-001-005

IrCl₃·1.5H₂O (50 mg, 0.154 mmol, 1.00 eq) was dissolved in a 3.5 mL acetonitrile solution of tetraoctylammonium bromide (104 mg, 0.189 mmol, 1.23 eq). The solution became completely homogeneous after stirring for five minutes, upon which 2-phenylethanethiol (111 μ L, 0.833 mmol, 5.41 eq) was added and stirring continued for 1.5 hours. A freshly prepared solution of sodium borohydride (59 mg, 1.55 mmol, 10.08 eq) in 1.25 mL of cooled 0 °C water was then added in one portion. The reaction was allowed to stir overnight (approx. 17 hours), after which the solution appeared clear with brown agglomerates. Excess methanol was added and the mixture was transferred to a conical tube for centrifugation. The solid precipitate was washed with additional methanol to completely remove excess thiol. Re-suspension in dichloromethane yielded a solution of large colloidal particles, based on the observed plasmon band near 350 nm in the linear absorbance spectrum.

IA-001-006 (based on R. Vankayala et al. J. Mater. Sci. Mater. Med. 1993, 24, 1993-2000)

IrCl₃·1.5H₂O (50 mg, 0.154 mmol, 1.00 eq) was dissolved in a 6 mL toluene solution of tetraoctylammonium bromide (104 mg, 0.189 mmol, 1.23 eq). The solution became completely

homogeneous after stirring for ten minutes, upon which 2-phenylethanethiol (111 μ L, 0.833 mmol, 5.41 eq) was added and stirring continued for 30 minutes. A freshly prepared solution of sodium borohydride (59 mg, 1.55 mmol, 10.08 eq) in 1.5 mL of cooled 0 °C water was then added in one portion. Following a 2 hour stirring period at room temperature, the reaction vessel was heated to 100 °C using an oil bath and refluxed for 30 minutes. This produced a dark brown solution, which was washed repeatedly with methanol *via* centrifugation in conical tubes until excess thiol was completely removed from the precipitate. Most of the isolated solid remained soluble in toluene. The re-suspended washed sample was passed through a toluene SEC column and subsequently analyzed by TEM (see IA-001-012, digital copy unavailable). Result: large particles which fragmented easily under the electron beam.

IA-001-052 (1st attempt of S. Bhat et al. *RSC Adv.* **2016**, 6, 26679-26688)

IrCl₃·1.5H₂O (20 mg, 0.061 mmol, 1.00 eq) and 2-phenylethanethiol (33 μ L, 0.25 mmol, 4.00 eq) were mixed together by grinding in a small agate mortar and pestle. Following roughly ten minutes the paste mixture had turned yellow from the initial black, indicating the formation of iridium thiolates. To this was added solid sodium borohydride (55.4 mg, 1.46 mmol, 24.0 eq), which upon grinding changed the color to a light brown. Once the mixture was mixed to homogeneity (roughly five minutes), extraction with toluene was performed which was then washed with water using a separation funnel. Increased reactivity was observed upon toluene addition. The toluene solution was concentrated *via* rotary evaporation and washed repeatedly with methanol *via* centrifugation until excess thiol was completely removed from the precipitate. Result: very low yield of presumably larger particles, although not confirmed due to lack of signal from both MALDI-MS and UV/Vis spectroscopy.

IA-001-089 (variation #1 of S. Bhat et al. procedure)

Same general procedure as IA-001-052, except for the extraction being performed with dichloromethane instead of toluene. A noticeable further increase in reactivity was observed during the extraction step with this solvent variation. Result: greater amount of final products, which appear to be a mixture of small clusters based on the lack of a plasmon band or other distinguishing peaks by UV/Vis spectroscopy. Absorption profile has a similar slope to that of S. Bhat and coworkers. MALDI-MS failed to provide any observable peaks despite same conditions as report.



Figure 6.1. Linear absorbance spectrum of IA-001-089 in dichloromethane.

IA-001-139 (variation #2 of S. Bhat et al. procedure)

IrCl₃· 1.5H₂O (50 mg, 0.154 mmol, 1.00 eq) and 2-phenylethanethiol (82 μ L, 0.614 mmol, 4.00 eq) were mixed together by grinding in a small agate mortar and pestle. Following roughly ten minutes the paste mixture had turned yellow from the initial black, indicating the formation of iridium thiolates. To this was added solid sodium borohydride (139.6 mg, 3.69 mmol, 24.0 eq), which upon grinding changed the color to a light brown. Once the mixture was mixed to homogeneity (roughly five minutes), extraction with toluene was performed which was then washed with water using a separation funnel. Increased reactivity was observed upon toluene addition. The toluene solution was concentrated *via* rotary evaporation and washed repeatedly with

methanol *via* centrifugation until excess thiol was completely removed from the precipitate. Result: scaling the original reaction by 2.5 times yields an observable amount of products by UV/Vis spectroscopy, which appears similar to IA-001-089. Both dichloromethane and toluene as initial extraction solvents seem to aid in the formation of a similar set of products, although the former offers a noticeably higher yield.



Figure 6.2. Linear absorbance spectrum of IA-001-139 in dichloromethane.

IA-001-141 (variation #3 of S. Bhat et al. procedure)

Changed formula for iridium salt to anhydrous as per S. Bhat's suggestion. IrCl₃ (20 mg, 0.067 mmol, 1.00 eq) and 2-phenylethanethiol (36 μ L, 0.268mmol, 4.00 eq) were mixed together by grinding in a small agate mortar and pestle. To simulate the average room temperature in southern India, the reaction vessel was placed atop a heat plate set to 34 °C and allowed to equilibrate for 30 minutes, half of which was spent grinding into the typical yellow paste. To this was added solid sodium borohydride (60.9 mg, 1.61 mmol, 24.0 eq), which upon grinding changed the color to a light brown. Once the mixture was mixed to homogeneity (roughly five minutes), extraction with toluene was performed which was then washed with water using a separation funnel. Increased reactivity was observed upon toluene addition. The toluene solution was concentrated *via* rotary evaporation and washed repeatedly with methanol *via* centrifugation until

excess thiol was completely removed from the precipitate. Result: increased temperature aids in the formation of a greater amount of products, which appear similar by UV/Vis spectroscopy to previous successful variations.



Figure 6.3. Linear absorbance spectrum of IA-001-141 in dichloromethane.

IA-002-067 (variation #4 of S. Bhat et al. procedure)

Same general conditions as IA-001-141, with the exception of the heat plate. Instead, the mortar and pestle were exposed to steam evolving from a heated water bath. This served as a means to approximate both the heat and humidity of southern India. Given the paste-like nature of the iridium thiolate mixture, the reaction vessel (i.e. mortar) could be inverted over the steam bath for complete exposure without any loss. Alternating intervals of inversion and grinding were on the order of roughly one minute for the full extent of the reaction. The initial addition of the solid sodium borohydride was performed with the mortar in an upright position and the pestle imbued with moisture from the steam bath. Result: the inclusion of hot steam throughout the reaction also appears to aid in formation of the desirable products, as judged by solution optical density and matching UV/Vis spectrum.



Figure 6.4. Linear absorbance spectrum of IA-001-067 in dichloromethane.

IA-002-078 (variation #5 of S. Bhat et al. procedure)

Followed the same basic procedure of the initial report with S. Bhat's recommended formula for the iridium salt and without any special heating conditions. Instead, the equivalents of 2-phenylethanethiol was increased from 4 to 10. Result: unlike previous observations for gold thiolate NCs, a change in ligand feed ratio does not noticeably affect the outcome for this solid phase reaction. Extremely low yield as was observed with IA-001-052.

IA-003-038 (variation #6 of S. Bhat et al. procedure)

Similar method as previous entry, except with equivalents unchanged from initial report (i.e. 1.00 eq IrCl₃, 4.00 eq PET, 24.0 eq NaBH₄). Sodium borohydride was introduced to the reaction vessel as a solution in 1 mL of water as opposed to a solid. This caused a significantly greater degree of reactivity. Subsequent extraction with dichloromethane did not exhibit increased reactivity as had been previously observed, presumably due to the prior addition of solvent. Result: incorporation of water without any heat also yields the desired products as judged by UV/Vis spectroscopic measurements. Based on this and previous results from heat and/or steam inclusion, the mass diffusion limitations of the solid phase relative to solution phase clearly introduces further complications to NC synthesis.



Figure 6.5. Linear absorbance spectrum of IA-003-038 in dichloromethane.

IA-003-047 (single phase solution version #1)

IrCl₃ (60 mg, 0.201 mmol, 1.00 eq) was added to 6 mL of tetrahydrofuran in a 25-mL roundbottom flask and sonicated until fully dissolved. 2-phenylethanethiol (108 μ L, 0.804 mmol, 4.00 eq) was then added and the mixture stirred for 1 hour. Over this time the initial dark brown solution gradually turned a light green followed by a faint yellow. A freshly prepared room temperature solution of sodium borohydride (182.4 mg, 4.82 mmol, 24.0 eq) in 3 mL of water was then added carefully in one portion, which turned the reaction mixture a deep brown/black. After an additional hour of stirring, dichloromethane and water were added to separate the organosoluble and water-soluble species respectively. This water wash was performed using a separation funnel and repeated once before concentrating the dichloromethane solution *via* rotary evaporation. Precipitation of the solid products and further washing was performed through the addition of excess methanol to this concentrated solution and subsequent centrifugation in conical tubes. Once no excess thiol was apparent within the isolated solid, it was dried and re-suspended in dichloromethane. Result: significantly larger quantity of products formed which more closely

match the absorption profile of S. Bhat's initial report. Issues persist with mass spectrometric characterization due to fragmentation. Proton NMR analysis shows a broadening of peaks attributable to 2-phenylethanethiol, which is generally indicative of ligands bound on a cluster/particle surface.



Figure 6.6. Linear absorbance spectrum of IA-003-047 in dichloromethane.



Figure 6.7. ¹H NMR spectrum of IA-003-047 in DCM-d₂.

IA-003-054 (single phase solution version #2)

Same general procedure as IA-003-047, but allowed the reaction to stir for 20 hours following the addition of sodium borohydride (increased from 1 hour). Results: exhibits similar characteristics to previous entry from linear absorption and NMR spectroscopy. TEM shows a

tight dispersion in the cluster size range of 1-2 nm. D-spacing measurements of the lattice planes yielded an average value of 0.65 nm.



Figure 6.8. Linear absorbance spectrum of IA-003-054 in dichloromethane.



Figure 6.9. ¹H NMR spectrum of IA-003-054 in DCM-d₂.



Figure 6.10. Representative TEM image of IA-003-054.

IA-003-074 (single phase solution version #3)

Same general procedure as IA-003-047, but allowed the reaction to stir for 48 hours following the addition of sodium borohydride. Results: UV/Vis and TEM data are comparable to IA-003-054 despite doubling the reduction time. Appears that etching either does not occur for this system or is much faster than in the case of gold thiolate NCs.



Figure 6.11. Linear absorbance spectrum of IA-003-074 in dichloromethane.



Figure 6.12. Representative TEM image of IA-003-074.

6.5 Osmium

IA-001-094 and IA-001-096 (3 conditions)

The equivalents of 2-phenylethanethiol were varied across 3 reactions: 2.00 equivalents (17 μ L, 0.124 mmol), 4.00 equivalents (33 μ L, 0.248 mmol), and 6 equivalents (50 μ L, 0.372 mmol). OsCl₃·1.5H₂O (20 mg, 0.062 mmol, 1.00 eq) and 2-phenylethanethiol were mixed together by grinding in a small agate mortar and pestle for approximately ten minutes until a yellow paste formed. To this was added solid sodium borohydride (56 mg, 1.48 mmol, 24.0 eq), which upon grinding changed the color to a dark black. Once the mixture was mixed to homogeneity (roughly five minutes), extraction with dichloromethane was performed which was then washed with water using a separation funnel. Increased reactivity was observed upon dichloromethane addition. The solution was concentrated *via* rotary evaporation and washed repeatedly with methanol *via* centrifugation until excess thiol was completely removed from the precipitate. Results: similar absorption profile as that observed in S. Bhat's initial report for iridium NCs. Lack of a prominent plasmon band is suggestive of smaller clusters/particles. UV/Vis spectrum does not appreciably differ between different ligand feed ratios, unlike typical gold thiolate NC syntheses.



Figure 6.13. Stacked linear absorbance spectra of IA-001-094 2.00 eq, IA-001-094 4.00 eq, and IA-001-096 6.00 eq PET in dichloromethane.

IA-001-148 (decreased NaBH₄ equivalents)

The same general procedure as previous entries was followed, except for the equivalents of NaBH₄ being reduced to 5.00 from the typical 24.0 eq. Result: initial extraction with dichloromethane did not yield a considerable product, however subsequent extraction of the remaining crude paste with methanol afforded increased reactivity. This methanol extract was dried, washed with water several times, and then re-suspended in dichloromethane whereupon unique absorption features became observable by UV/Vis spectroscopy. These features may be attributable to clusters, small complexes or a combination thereof.



Figure 6.14. Linear absorbance spectrum of IA-001-148 in dichloromethane.

6.6 Bismuth

IA-004-063

Bi(NO₃)·5H₂O (100 mg, 0.206 mmol, 1.00 eq) and *para*-mercaptobenzoic acid (127.2 mg, 0.825 mmol, 4.00 eq) were combined with 6.5 mL of a 0.3 M NaOH solution in a 20-mL scintillation vial. This was vortexed to form a cloudy, bright orange mixture which was subsequently set in an ice bath and stirred for 15 minutes. A freshly prepared solution of sodium borohydride (1.56 mg, 0.041 mmol, 0.20 eq) in 2 mL of cooled 0 °C water was then added in two 1-mL doses *via* glass pipette. This turns the reaction mixture a deep black. After 1 hour of stirring,

excess ethanol was added and the solution was transferred to a conical tube and centrifuged. The precipitate was washed once more with ethanol and re-suspended in water. The UV/Vis profile lacks the characteristic plasmon band of bismuth colloids near 460 nm,¹¹ suggesting the sample is comprised of smaller clusters and/or complexes.



Figure 6.15. Linear absorbance spectrum of IA-004-063 in water.

6.7 Conclusion

The composite works outlined above illustrate both some promising pathways to noncoinage metal NCs as well as the primary associated difficulties. Throughout our studies we have observed a lack of the synthetic tunability common to gold thiolate NCs in particular. Although there does appear to be some degree of size focusing, these reactions remain largely unaffected by changes in ligand feed ratio. Combined with the retention of size/dispersity irrespective of reduction time observed in the case of the solution phase iridium syntheses, this suggests that etching is not the main formation mechanism. As expected based on the various redox chemistries, the equivalents of reducing agent were noticeably more impactful. Lower NaBH₄ feed ratios appear favorable for both bismuth and osmium, whereas iridium thus far benefits most from higher ratios. For almost all of the explored conditions, we intentionally limited the ligand scope to 2phenylethanethiol (PET), whose substantial representation in Brust-type coinage metal NC products speaks to its general applicability. The presence of an aromatic ring also produces a greater degree of order within the ligand shell, which can lead to single crystal formation. Extension to other ligands, particularly those with similar crystal-forming potential, is of immediate interest for future exploratory reactions in this area. The ligand *para*-mercaptobenzoic acid (*p*-MBA) is one of the best candidates for this purpose in water-soluble syntheses.

Our general screen of various MALDI matrices failed to produce any data of reasonable quality. These included DCTB (the traditional coinage metal NC matrix), sinapinic acid, 2,5dihydroxybenzoic acid, and α -cyano-4-hydroxycinnamic acid. We encountered marginally worse outcomes with ESI mass spectrometry using cesium acetate. Despite this, we managed to obtain good insight into reaction products through a combination of linear absorption spectroscopy, NMR spectroscopy, and TEM imaging. The latter is expensive and so does not serve as a good method for high-throughput characterization.

NMR spectroscopy is comparatively cheap and has seen revived use in NC research in recent years. Both UV/Vis and NMR spectroscopy can serve as reliable handles for assessing general product identity and purity. Other techniques such as photoelectron spectroscopy can also provide information on local chemical environment. Once sufficiently pure as deemed through these techniques, the sample may yield single crystals which effectively negate the necessity for mass spectrometric identification.

Overall, we find that the synthesis of certain non-coinage metal NC products under ambient conditions is possible with appropriate conditions. This proof-of-concept is currently limited to only a few metals but should technically be achievable with other late and post transition metals.

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The tendency of early transition metals to form oxides renders them generally unfavorable for these studies. Future research should focus on the screening of additional ligand types, air-stable reducing agents, and solvents. Other methods for achieving size focusing, particularly those from the Ackerson lab involving coordinating solvents, may ultimately yield the desired atomically monodisperse products.

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CHAPTER 7: SUMMARY AND CONCLUDING REMARKS

The research reported in this dissertation describes a series of advancements in both synthetic and post-synthetic methods for atomically precise metal NCs with an emphasis on gold. Herein we will readdress the major findings from each chapter alongside the cutting edge of general metal cluster chemistry. In Chapter 2, careful selection of the appropriate counterion enabled a rare view of a new rhodium-gold cluster alloy which exhibited unexpectedly robust intermolecular attraction with co-synthesized species. Compelling evidence was observed for the electron-withdrawing nature of open d-shell dopants, in contrast with the previously assumed isoelectronic substitution model. We anticipate that further study of related cluster alloys will lead to the development of new pathways in nanoscale material design. Other open d-shell dopants such as iridium, ruthenium, and osmium should prove more accessible through our synthetic approach.

Chapter 2 also highlights the adaptability of the superatom concept, which will most likely remain the dominant qualitative model for describing electronic stability. Considerable progress has been made within computational cluster chemistry such that non-spherical geometries can now be treated as superatom complexes, albeit with different magic numbers.¹ Very recently this theory has also been expanded to include group 10 (e.g. platinum, palladium, and nickel) carbonyl protected clusters,² through a view intriguingly analogous to our own for rhodium. The metal core is considered to gain s-shell bonding character through the withdrawal of electrons from the carbonyl ligand shell.

This naturally has some exciting implications for future work in the area of air-stable noncoinage metal clusters. Based on this and our findings from Chapter 6, a set of conditions which discourage metal oxide formation while simultaneously introducing electron-donating ligands

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should have a particularly heightened chance of enabling cluster formation. Coincidentally, carbon monoxide has recently demonstrated its cluster-forming ability for gold.³ Although the less favourable redox chemistry of non-coinage metals may preclude complete reduction to metallic clusters by carbon monoxide, it may offer the intermediate protection necessary to inhibit oxides outside of a glove box setting. Other currently underutilized coordination methods, such as the heavier phosphine analogue stibine,⁴ may also provide the requisite stabilization.

Use of heavier metals in the periodic table are now at the early stages of development, similar to the state of transition metal cluster chemistry in the first half of the 20th century. The first isolable ligand protected thorium cluster containing extremely rare actinide-actinide bonds was reported in the summer of 2021.⁵ Contrary to theoretical simulations which predict a localized scheme, this cluster features a three-center two-electron σ -aromatic bond resulting in a closed-shell diamagnetic ground state. The same authors have also established how the reactivity of the precursor thorium source determines whether cluster formation occurs or not.⁶ Although this synthesis is currently restricted to the glove box, it remains an important first step in better understanding the actinide chemistry central to the safe and efficient operation of nuclear power plants.⁷

Chapters 3-5 presented greater emphasis on the ligand monolayer than the metal core. In certain aspects, gold NC ligand chemistry is both more approachable than alloy chemistry as well as more aligned with immediate applications.⁸ One of the most pressing issues which this area may address, as best outlined in Chapter 5, is through the control of atom migration. Acting as somewhat of a barrier to the outside world, judicious choice of an appropriate ligand type should be capable of entirely preventing undesired intercluster exchange.

In our own work we have found that metals can still exchange rapidly between NCs even when the ligands do not. Furthermore, as highlighted in Chapter 3, the unexpected non-innocence of certain ligand types such as acetylides remains an open problem. The extension of detailed exchange studies to other new ligand types (e.g. glymes, N-heterocyclic carbenes [NHCs]) is therefore of immediate interest, to reveal the true extent to which gold NCs can be treated as distinct species. We also expect that further investigation into dithiolates will prove useful for this purpose.

There are also some major questions to be addressed with both newer and more traditional ligands. First, the mechanism behind size/shape cluster transformations induced by certain thiolate-for-thiolate exchanges remains poorly understood at a molecular level.⁹ Similarly, there is a lack of precise mechanistic information for the traditional Brust-Schiffrin synthesis and related Brust-type methods.¹⁰ While the general process of radical-mediated etching has been revealed,¹¹ more detailed speciation studies are necessary in order to gain a level of synthetic insight concomitant to that found within organic chemistry.¹² We expect that utilization of the modern tools found in high-resolution separation,¹³ mass spectrometry,¹⁴ ion-mobility experiments,¹⁵ X-ray absorption,¹⁶ and nuclear magnetic resonance¹⁷ will help in clarifying these processes.

In the case of NHCs, which have only very recently been used in gold NC synthesis,¹⁸ the above questions apply all the more strongly. Whether formation still occurs through etching as it does for thiolates remains a point of active debate. The organic radical nature of NHCs may alter or altogether remove the role of radical oxygen,¹⁹ but this has yet to be experimentally verified. There is also a dearth of knowledge with regard to cluster transformations possible with NHCs, with the only existing examples being NHC-for-phosphine.²⁰ The comparatively substantial steric bulk of NHCs versus thiolates should result in dramatic changes to the NC structure.
Glymes are substantially underexplored, with published research currently limited to within the Ackerson group.^{21–23} Although their size-focusing ability has been clearly demonstrated, a fully glyme protected gold NC has not yet been identified. The gross molar excess of glyme present within the currently-explored set of conditions should enable formation of such a species. Fundamental experiments, such as post-synthetic ligand exchange and systematic reduction of the thiolate (or other co-ligand) feed ratio, remain open to exploration.

Dithiolates are comparatively much more widely studied, although prior to our investigation their cluster-forming ability was obscure. The sound foundation we have provided enables more comprehensive research for both this and other future multi-dentate ligands. Overall, the original research outlined in this dissertation spans a considerable range of modern gold cluster chemistry and will serve as a good resource for future work.

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APPENDIX A: SUPPLEMENTAL TO CHAPTER 2

Section 1: Experimental Methods

All starting materials were purchased from Sigma Aldrich or Thermo Fisher Scientific and, unless otherwise stated, were \geq 98% pure. Rhodium(III) chloride hydrate (Sigma, CAS #20765-98-4) was used as received, but in calculations was treated as anhydrous RhCl₃. Water was nanopure (from an in-house filtration system, 18 M Ω ·cm), ethanol was 200-proof (i.e. absolute); all other solvents were reagent grade. Conical tubes used for centrifugation were purchased from Falcon, and the centrifuge speed was 4000 rpm, or 2845 G (radius of rotation = 158.8 mm).

I. RhAu₂₄(PET)₁₈ synthesis with [TOA][Br]:

In a 20-mL scintillation vial, HAuCl₄· $3H_2O$ (100 mg, 0.254 mmol, 1 eq) was dissolved in a solution of [TOA][Br] (219.3 mg, 0.401 mmol, 1.58 eq) in 7.5 mL of THF and stirred for 30 minutes. During this time, a THF solution of RhCl₃ (15.5 mg in 2.5 mL, 0.074 mmol, 0.29 eq) and an aqueous chilled (0 °C) solution of NaBH₄ (123.9 mg in 2.5 mL, 3.27 mmol, 12.9 eq) were prepared. Once 30 minutes had passed, PET (261 µL, 1.95 mmol, 7.67 eq) was added and the resulting mixture was stirred for 15 minutes. Then, the RhCl₃ solution was added in one portion followed immediately by the NaBH₄ solution, which was added via pipet over a period of 1 minute.

In order to maintain comparable preparation/addition times for NaBH₄ across multiple runs, a conventional digital timer was used during these steps. The preparation time for the NaBH₄ solution was kept to 30 minutes, i.e. the solid NaBH₄ was added to the chilled H₂O precisely 30 minutes prior to its addition. This is critical for maintaining comparable reducing power across different syntheses. 2-µL aliquots were taken at various times and mixed with a 10 mg/mL solution of DCTB for analysis by MALDI-MS. The reaction was typically quenched with an excess (40 mL) of methanol and re-suspended in THF (10 mL) following at least 2 additional methanol washes.

II. RhAu₂₄(PET)₁₈ synthesis with [TBA][PF₆]:

In a 20-mL scintillation vial, HAuCl₄·3H₂O (100 mg, 0.254 mmol, 1 eq) was dissolved in a solution of [TBA][PF₆] (155.4 mg, 0.401 mmol, 1.58 eq) in 7.5 mL of THF and stirred for 30 minutes. During this time, a THF solution of RhCl₃ (15.5 mg in 2.5 mL, 0.074 mmol, 0.29 eq) and an aqueous chilled (0 °C) solution of NaBH₄ (123.9 mg in 2.5 mL, 3.27 mmol, 12.9 eq) were prepared. Once 30 minutes had passed, PET (125 μ L, 0.93 mmol, 3.67 eq) was added and the resulting mixture was stirred for 15 minutes. Then, the RhCl₃ solution was added in one portion followed immediately by the NaBH₄ solution, which was added via pipet over a period of 1 minute.

In order to maintain comparable preparation/addition times for NaBH₄ across multiple runs, a conventional digital timer was used during these steps. The preparation time for the NaBH₄ solution was kept to 30 minutes, i.e. the solid NaBH₄ was added to the chilled H₂O precisely 30 minutes prior to its addition. This is critical for maintaining comparable reducing power across different syntheses. 2-µL aliquots were taken at various times and mixed with a 10 mg/mL solution of DCTB for analysis by MALDI-MS. The reaction was typically quenched with an excess (40 mL) of methanol and re-suspended in THF (10 mL) following at least 2 additional methanol washes.

III. Separate reduction of precursor salts:

The same general procedure was used here as in those described immediately above, with the exception that exclusively one of the two metal precursor salts (HAuCl₄ or RhCl₃) were involved for a given reaction. This was done to assess what products form when only HAuCl₄ or RhCl₃ are individually exposed to PET and NaBH₄. In both reactions the metal precursor salt was added at the very beginning to ensure an equal amount of exposure time to PET.

IV. [TOA][Au₂₅(PET)₁₈] synthesis:

In a 300 mL roundbottom flask, HAuCl₄·3H₂O (1 g, 2.54 mmol, 1.00 eq) was dissolved in a solution of [TOA][Br] (1.56 g, 2.85 mmol, 1.56 eq) in 70 mL of THF. After 30 minutes of stirring, PET (1.8 mL, 13.4 mmol, 5.27 eq) was added and the solution was stirred until colorless (approximately 2-3 hours). A freshly-prepared and chilled (0 °C) aqueous solution of NaBH₄ (0.97 g in 24 mL, 25.5 mmol, 10.03 eq) was then added in one portion under vigorous stirring. The reaction was then covered and stirred for 2 days. Following this, any remaining water was removed and the remaining solution was concentrated by rotary evaporation, forming an oily mixture. The precipitate was washed 4 times with 100 mL of methanol and isolated by centrifugation. Crystals of [TOA][Au₂₅(PET)₁₈] were obtained by slowly adding ethanol to a toluene solution of the product until the precipitate contains Au₂₅ (as judged by UV/Vis spectroscopy) followed by slow cooling (-20 °C) over an average period of 2 weeks.

V. [Na][Au₂₅(CCAr)₁₈] synthesis:

In a foil-wrapped 20 mL scintillation vial, 200 mg chloro(dimethylsulfide)gold(I) was added to 10 mL acetone under vigorous stirring. 126 μ L 3,5-bis(trifluoromethyl)phenylacetylene (CCAr) and 99 μ L triethylamine were then added sequentially, and this mixture was stirred for 2 hours. The resulting precursor Au(I)-CCAr was isolated by drying the solution under rotary evaporation and washing twice with water. 208 mg Au(I)-CCAr was subsequently added to 30 mL of a chloroform:methanol mixture (5:1) in a 100 mL foil-wrapped roundbottom flask under vigorous stirring. A freshly-prepared aqueous solution of sodium borohydride (5.4 mg in 4.7 mL water) was added dropwise followed by 94 μ L triethylamine. The mixture was allowed to stir for

20 hours, where-upon a dark solid was obtained following rotary evaporation. This solid was extracted in methanol, which after brief centrifugation gave crude $Au_{25}(CCAr)_{18}$ in the supernatant. For crystallization, this crude was dried and re-suspended in 1:1 dichloromethane:toluene and layered with hexanes in 20 mL scintillation vials. Crystals of [Na][Au₂₅(CCAr)₁₈] were observed in a few days at room temperature.

VI. Rhodium Phenylethanethiolate (Rh-PET), solid phase synthesis:

In an agate mortar (6.4 cm basin diameter), RhCl₃ (20 mg, 0.10 mmol, 1 eq) was added and crushed into a fine powder using a pestle. Then, PET (54 μ L, 0.40 mmol, 4 eq) was added and the mixture was mixed by grinding for 10 minutes. After this, NaBH₄* (90.8 mg, 2.40 mmol, 24 eq) was added and mixed by grinding for an additional 10 minutes. A dichloromethane (DCM) extraction was performed and washed 4 times with water. The final product(s) could be precipitated from solution by addition of excess (typically 5:1 or greater) methanol and resuspended in common organic solvents.

*The addition of NaBH₄ does not affect the final product identity.

VII. Rh-PET, solution phase synthesis:

A 20-mL scintillation vial was charged with an ethanolic solution of RhCl₃ (20 mg in 5 mL, .02 mM, 1 eq). Then, PET (54 μ L, 0.40 mmol, 4 eq) was added and the cloudy orange mixture was allowed to stir for 30 minutes. Rh-PET was precipitated and washed several times with excess (typically 5:1 or greater) methanol to remove excess PET. The dark orange powder obtained in this way exhibits the same UV/Vis, IR, and XPS signatures as the Rh-PET obtained through the solid-phase procedure.

VIII. Exchange reaction between [TOA][Au₂₅(PET)₁₈] and Rh-PET:

To a 20-mL scintillation vial containing crystals of $[TOA][Au_{25}(PET)_{18}]$ (typically 1-3 mg), a volume of THF or toluene was added to set the resulting solution concentration at 1 mg/mL. Then, an equivalent mg amount of solid Rh-PET was added and the resulting mixture was covered and allowed to stir for up to 48 hours. For some iterations of the exchange reaction, a slight excess of PET (50 µL) or NaBH₄ (20 mg) was added. 2-µL aliquots were taken at various times and mixed with a 10 mg/mL DCM solution of DCTB for analysis by MALDI-MS.

IX. [TBA][PF₆] co-reduction synthesis of RhAu₂₄(PET)₁₈ with [TMA][BH₄]:

A similar procedure was followed for this synthesis as is described above under subsection II. The only difference is the use of [TMA][BH₄] (336.4 mg in 2.5 mL H₂O, 3.78 mmol, 14.9 eq) over NaBH₄.

X. General purification methods:

The following purification methods are based on previous work found in the NC literature.¹ Extractions of the crude product were conducted using the following solvents: THF, DCM, toluene, hexanes, acetonitrile, and ethanol (200-proof). Size exclusion chromatography (SEC) was performed using S-X1 styrene divinylbenzene beads (exclusion range: 600-14000 Da) with a mobile phase of THF or toluene; fractions were collected in 2-3 mL amounts. Selective decomposition was explored through exposure of the crude product to the following conditions: excess PET, excess NaBH₄, heightened temperature, 30 wt% H₂O₂ (aqueous), as well as combinations of heightened temperature and the other conditions. For silica column chromatography purification, the initial mobile phase was a 1:1 mixture of tetrahydrofuran (THF) and hexanes. The ratio of THF:hexanes was incrementally increased until the mobile phase consisted of 100% THF; this gave the best resolution.

XI. Exposure of RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET to Ion Exchange Resins:

Both AmberLite[®] IRA900 chloride form and Amberlyst[®] A26 hydroxide form resins (both from Sigma) were tested for their ability to remove Au₂₅(PET)₁₈¹⁻ from the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET product mixture. In a typical experiment, a 20-mL scintillation vial containing said mixture (in acetonitrile) was charged with the resin beads at various load amounts ranging from 10 mg (a few beads) to 200 mg. The vial was then sealed and secured upon a vortexer within a refrigerator, wherein it was left to mix at 4 °C for a period of up to 24 hours. Each sample was checked periodically by both UV/Vis absorption and MALDI-MS measurements. Control experiments confirmed that neither IRA900 nor A26 resin beads degraded within acetonitrile under the stated conditions. We observed no change in the product mixture by these measurements over the course of these experiments, which was performed using samples from both the [TOA][Br] and [TBA][PF₆] methods. Additional experiments involving an increase in solution temperature failed to produce positive results.

XII. Instrumentation:

Ultraviolet/Visible (UV/Vis) absorption spectroscopy measurements were performed on a NanoDrop 2000c instrument in the range of 190-840 nm. The absorption data were normalized by finding the maximum value in the range of 300-840 nm. Centrifugation was performed on an Eppendorf 5810 R. Fourier Transform Infrared (FT-IR) spectroscopy measurements were conducted on a Nicolet iS-50 in the range of 500-3500 cm⁻¹. IR samples were analyzed as solutions.

Matrix-Assisted Laser Desorption/Ionization mass spectrometry (MALDI-MS) measurements were collected on a Microflex LRF from Bruker with a TOF detector. Matrix concentrations were kept constant at 10 mg/mL, and the sample to matrix ratio was 1:100. The matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (aka DCTB) was

used unless otherwise stated. The sample/matrix mixture was applied to a steel plate and air-dried. Mass spectra were typically collected in both linear positive and negative mode, and all compared spectra (unless otherwise stated) were obtained at the same laser power. Negative mode spectra were of consistently lower quality than that of the positive mode, and failed to capture the full content of the sample (i.e. no observable RhAu₂₄(PET)₁₈).

X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a PE-5800 using a monochromatic Al K α source (hv = 1486.6 eV). Samples were drop cast onto HF-etched silica wafers prior to analysis, and binding energies were calibrated to the C 1s peak at 284.8 eV. Curve fitting was performed on the in-house software CasaXPS by applying symmetric Gaussians to each peak following background subtraction.

Section 2: MALDI-MS Control Experiments

Various experiments were performed to further assess the conditions under which $RhAu_{24}(PET)_{18}$ might form. First, mixtures of separately-reduced Au/Rh species (as described in subsection III of section 1 above) were analyzed by MALDI-MS (**Figure A1**). This was done to determine whether $RhAu_{24}(PET)_{18}$ forms within the instrument as a result of some fragmentation/recombination process between Rh-PET and $Au_{25}(PET)_{18}$. Rh-PET does not give appreciable signal above baseline noise in the region of interest. No additional peaks attributable to $RhAu_{24}(PET)_{18}$ or other $Rh_xAu_{25-x}(PET)_{18}$ species were observed over a range of laser intensities. We therefore conclude that $RhAu_{24}(PET)_{18}$ exclusively forms through the co-reduction method and not within the MALDI-MS instrument.



Figure A1. MALDI mass spectra of a mixture of Rh-PET and $Au_{25}(PET)_{18}$ taken at varying laser intensities (increasing in order from black, red, orange traces). Inset shows the region where the parent peak of $Au_{25}(PET)_{18}$ is located, with clear indication of the absence of RhAu₂₄(PET)₁₈.

Next, we assign some fragmentation/recombination peaks local to the $RhAu_{24}(PET)_{18}$ and $Au_{25}(PET)_{18}$ parents (**Figure A2**). We show a representative MALDI mass spectrum of a sample obtained from the [TOA][Br] co-reduction method, as it gives the greatest clarity at threshold laser intensity.



Figure A2. MALDI mass spectrum of a sample containing the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET product mixture. Peaks labeled B/ β correspond to the Au₂₅(PET)₁₈ parent and related fragments, respectively. Those peaks labeled A/ α correspond to the RhAu₂₄(PET)₁₈ parent and related fragments/adducts, respectively. The peak labeled α^* (7104 m/z) refers to the loss of one gold atom from RhAu₂₄(PET)₁₈.

 $RhAu_{24}(PET)_{18}$ is more prone to fragmentation than $Au_{25}(PET)_{18}$ within the MALDI instrument, as evidenced by the number of peaks attributable to $RhAu_{24}(PET)_{18}$ fragments/adducts. The association of Rh-PET on the surface of $RhAu_{24}(PET)_{18}$ may encourage this greater degree of fragmentation.

There are a series of peaks attributable to adducts containing a single $Rh_1(PET)_1$ unit. The peak centered at 7344 m/z is assigned as the $Rh_1(PET)_1$ adduct of the fragment peak located at 7104 m/z (obs. = 240 m/z, calc. = 240.1 Da; labelled as α^* in Figure S11). This fragment peak corresponds to the loss of one gold atom from $RhAu_{24}(PET)_{18}$, whose peak is observed at 7302 m/z (obs. = 198 m/z, calc. = 196.9 Da). The peak centered at 7062 m/z corresponds to the loss of $Au_1(PET)_1$ from $Au_{25}(PET)_{18}$, which is a commonly observed fragment for this NC (obs. = 334.1 Da).

The peak at 6968 m/z is precisely 94 m/z away from the aforementioned fragment peak; the same degree of separation as between the parent peaks for RhAu₂₄(PET)₁₈ and Au₂₅(PET)₁₈. We therefore assign this peak to the loss of Au₁(PET)₁ from RhAu₂₄(PET)₁₈ (obs. = 334 m/z, calc. = 334.1 Da). The peak centered at 6907 m/z is assigned as corresponding to the loss of two gold atoms from RhAu₂₄(PET)₁₈ (obs. = 395 m/z, calc. = 393.8). Lastly, the wider peak centered near 7160 m/z is thought to be two peaks overlapping one another; the loss of PET from RhAu₂₄(PET)₁₈ and the Rh₁(PET)₁ adduct of the 6907 m/z fragment peak. This would explain the strange shape of the peak. The observation of these Rh₁(PET)₁ adduct peaks suggests a significant degree of attraction between Rh-PET and RhAu₂₄(PET)₁₈ within the MALDI instrument flight path, and agrees with our working hypothesis of a stabilizing surface interaction.

Previous reports on thiolated alloy gold NCs have employed a variety of post-synthetic treatments to isolate the desired novel product.¹ These include processes such as solvent extraction, chromatography, and selective decomposition. When applied column to the RhAu24(PET)18/Au25(PET)18/Rh-PET system, none of these treatments yielded complete purification. Instead, successful treatments resulted in an enrichment of the relative content of RhAu₂₄(PET)₁₈ versus Au₂₅(PET)₁₈, as determined by mass spectrometry. Selective decomposition with excess ligand, NaBH₄, H₂O₂, elevated temperatures or relevant combinations thereof resulted in degradation of RhAu₂₄(PET)₁₈ over Au₂₅(PET)₁₈. Herein we will present only those purification treatments in detail which yielded neutral (no change) or positive (enrichment) results.

Throughout the extraction screening process we found no single solvent or mixture that showed selectivity for removal of $Au_{25}(PET)_{18}^{1-}$ (which should be the native charge state). By passing the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET mixture through a silica gel column, we expected the complete oxidation of $Au_{25}(PET)_{18}^{1-}$. $Au_{25}(PET)_{18}^{0}$ should therefore be separable from a charged RhAu₂₄(PET)₁₈ species following solvent extraction. As discussed within chapter 2, subsequent fractions beyond the leading fraction gave the enriched RhAu₂₄(PET)₁₈. The enriched fraction could not be enriched beyond a peak ratio of 1:2 following iterative silica gel columns (**Figure A3**).



Figure A3. Stack plot of MALDI mass spectra obtained from iterative silica gel column runs of the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET mixture (blue trace: run 1; green trace: run 2; red trace: run 3).

Leading fractions contained exclusively Au₂₅(PET)₁₈⁰, as indicated by MALDI-MS and UV/Vis absorption (Figure A4). Significantly smaller amounts of $Au_{25}(PET)_{18}^{0}$ were obtained as leading fractions from these iterative columns, until the 3^{rd} where no separated Au₂₅(PET)₁₈⁰ was observed.



Figure A4. MALDI mass spectrum (main figure) and UV/Vis absorption spectrum (inset) of the leading fraction obtained from silica gel column chromatography of the product mixture RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET, indicative of molecularly pure Au₂₅(PET)₁₈⁰.

In the [TOA][Br] co-reduction route, which requires short reduction times to prevent loss of RhAu₂₄(PET)₁₈, size exclusion chromatography (SEC) was successful in removing larger-sized NCs from the crude product. RhAu₂₄(PET)₁₈ and Au₂₅(PET)₁₈ are inseparable by SEC given their identical hydrodynamic radius, and thus elute as a mixture with Rh-PET. The [TBA][PF₆] co-reduction route is capable of much longer reduction times without significant loss of RhAu₂₄(PET)₁₈. This allows for size-focusing of the crude product, giving a final mixture of predominantly RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET similar to that obtained by SEC through the [TOA][Br] route (**Figure A5**). It is worth noting that through the [TOAB][Br] route, multiple SEC runs are necessary to achieve the same degree of purity as that obtained synthetically through the [TBA][PF₆] route.



Figure A5. MALDI mass spectrum showing the predominance of RhAu₂₄(PET)₁₈ and Au₂₅(PET)₋₁₈ cluster products (main figure) as obtained through the [TBA][PF₆] co-reduction method. Inset shows the area of interest for the two clusters, as depicted in Figure 2.1c within chapter 2.

To confirm the role of the $[PF_6]^{1-}$ anion, we performed control reactions using [TBA][X], where $[X] = [BF_4]^{1-}$ and $[F]^{1-}$. **Figure A6** shows that the bulky, weakly-coordinating $[BF_4]^{1-}$ anion yields a similar enrichment in RhAu₂₄(PET)₁₈ content as in the case of $[PF_6]^{1-}$. On the other hand, the fluoride anion (which is small and highly-coordinating) fails to produce $RhAu_{24}(PET)_{18}$ in observable quantities. If this anion had no role in the formation of $RhAu_{24}(PET)_{18}$ we would not expect such a drastic difference.



Figure A6. MALDI mass spectra of RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET detailing the difference in RhAu₂₄(PET)₁₈ content (relative to Au₂₅(PET)₁₈) when [TBA][BF₄] (green trace) or [TBA][F] (red trace) is used in the co-reduction synthesis.

We attempted to synthesize $RhAu_{24}(PET)_{18}$ using a tetrabutylammonium salt of the dodecaborate dianion, $[B_{12}H_{12}]^{2-}$. The dodecaborate dianion is far bulkier and more weakly-coordinating than $[PF_6]^{1-}$ or $[BF_4]^{1-}$, and has been used to stabilize reactive cationic species. $[TBA]_2[B_{12}H_{12}]$ was formed through the facile exchange between [TBA][I] and $K_2[B_{12}H_{12}]$ in water. $[TBA]_2[B_{12}H_{12}]$ precipitates as a white powder; the water filtrate was confirmed to contain KI through the addition of AgNO₃ and resulting precipitation of AgI. Unfortunately, this reaction variation failed to produce any gold NCs, as the presence of $[TBA]_2[B_{12}H_{12}]$ appears to drastically alter intermediate formation.

Alternative syntheses which replaced the rhodium salt precursor RhCl₃ with other salts failed to produce positive results. Syntheses performed using Rh(PPh₃)₃Cl and Rh(PPh₃)₂(CO)Cl yielded no gold NC product, likely due to a similar reason as that of the dodecaborate dianion (i.e., change in precursor speciation). Use of rhodium (II) acetate dimer, Rh₂(OAc)₄, appears to inhibit

the production of gold NCs as evidenced by the low-intensity signal seen for $Au_{25}(PET)_{18}$ (**Figure A7**). No RhAu₂₄(PET)₁₈ is observed through this synthetic route. This is especially noteworthy as palladium (II) acetate, Pd(OAc)₂, was the precursor salt used in the recent synthesis of PdAu₂₄(PET)₁₈ reported by our lab.² We hypothesize that this is due to their differing structures; Rh₂(OAc)₄ is an octahedral dimer whereas both molecular and polymeric Pd(OAc)₂ exist in a square planar coordination environment. This enables greater accessibility to the metal center in the case of Pd(OAc)₂.



Figure A7. MALDI mass spectrum taken in the area of interest of a sample taken following the $[TBA][PF_6]$ co-reduction procedure with $Rh_2(OAc)_4$ instead of the typical RhCl₃. No RhAu₂₄(PET)₁₈ is observed.

We assessed the dependence of the RhCl₃ equivalents on the formation of RhAu₂₄(PET)₁₈. **Figure A8** shows the stark contrast in RhAu₂₄(PET)₁₈ content when 0.09 equivalents of RhCl₃ are used instead of the typical 0.29 equivalents. This difference is more noticeable when [TBA][PF₆] is used instead of [TOA][Br], given the increased preferential formation of the desired product through ion-pairing.



Figure A8. MALDI mass spectra detailing the effect of changing RhCl₃ equivalents on the relative amount of observed RhAu₂₄(PET)₁₈ for both the [TOA][Br] (left) and [TBA][PF₆] (right) coreduction procedures. For both procedures, the red trace refers to 0.29 equivalents of RhCl₃, while the blue trace refers to 0.09 equivalents.

Section 3: Synthesis of Rhodium Thiolates (Rh-PET)

In an effort to synthesize a rhodium NC, we adapted the mortar-and-pestle grinding method from the synthesis of $Ir_9(PET)_6$.³ 2-Phenylethanethiol (PET) was used for a majority of syntheses, although the ubiquity of the process has been confirmed with various other thiols (e.g. butanethiol, hexanethiol, dodecanethiol). The descriptor Rh-PET refers to the rhodium-phenylethanethiolate species both before and after exposure to NaBH₄ (see subsections VI and VII of section 1 above).

The absorbance spectrum of Rh-PET shows a single broad, sloping peak centered at 360 nm (**Figure A9, left**). The insolubility of RhCl₃ in solvents such as dichloromethane (DCM) or toluene is good evidence for the replacement of chloride with PET. It is worth noting that a similar broad, sloping absorption feature was reported for Ir₉(PET)₆. Absence of the S-H stretch peak (at ca. 2566 cm⁻¹) on the FT-IR spectrum, in addition to the presence of peaks associated with C-H stretching (2800-3100 cm⁻¹), is further indication that PET is bound to rhodium (**Figure A9, right**).



Figure A9. (Left) UV-Visible absorbance spectrum of Rh-PET. (Right) Absorbance FT-IR spectrum of Rh-PET (black trace) vs that of free PET (red trace). The blue star indicates the peak related to the S-H stretching frequency. In both instances, the sample was suspended in DCM.

When dissolved in acetonitrile, the orange solution of Rh-PET becomes cloudy upon addition of [TMA][Cl] or [TMA][BH₄]. Centrifugation results in the precipitation of an orange powder with a completely clear, colorless supernatant. Re-suspension of this orange powder in DCM and analysis by UV/Vis absorption confirms its identity as Rh-PET. As discussed within the main text this quality of Rh-PET enabled its separation from the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET product mixture when [TMA][BH₄] was employed in the co-reduction procedure. The following section details further experimental characterization of Rh-PET.

Section 4: XPS Characterization of Rh-PET and RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET

An XPS survey of Rh-PET detected rhodium, carbon, sulfur, and oxygen (**Figure A10**). The presence of oxygen peaks are due to the fresh oxide layer produced by the HF treatment of the silica wafer. No peaks attributable to chlorine were observed. High-resolution scans were taken in the rhodium 3d and sulfur 2p regions to further assess the chemical state of these elements.



Figure A10. XPS survey spectrum of a drop-cast sample of Rh-PET.

The sulfur 2p pair of peaks (**Figure A11**) have closely-spaced spin-orbit splitting (1.16 eV) but could not be fit to the expected area ratio of 1:2 (for $2p_{1/2}$: $2p_{3/2}$). This is attributed to the presence of an intermediate shoulder peak, which could be a result of two chemically-similar bonding environments. The binding energy of the S $2p_{3/2}$ peak at 162.8 eV is indicative of metal-sulfur bonding, in agreement with FT-IR measurements.



Figure A11. High-resolution photoelectron spectrum of Rh-PET in the S 2p region (solid black trace), alongside fits for the $2p_{1/2}$ (dotted green trace) and $2p_{3/2}$ (dotted blue trace) peaks.

The Rh 3d pair of peaks (**Figure A12**) have well-separated spin-orbit splitting (4.7 eV), with a 3d_{5/2} binding energy of 308.6 eV. Based on the binding energy reported by NIST for RhCl₃ (310 eV), the rhodium present in Rh-PET is of a lower oxidation state than the starting material.

If a thiolated rhodium NC had formed, the presence of substantial metal-metal bonding should result in a $3d_{5/2}$ binding energy close to that of metallic rhodium. In the case of $Ir_9(PET)_6$, the Ir $4f_{7/2}$ peak is within 0.1 eV of Ir^0 (60.9 eV).³ NIST reports a binding energy of 307 eV for metallic rhodium, making it unlikely for Rh-PET to contain any Rh⁰.



Figure A12. High-resolution photoelectron spectrum of Rh-PET in the Rh 3d region.

These data suggest that Rh-PET is not a canonical thiolated NC species, but instead some form of Rh^{II} thiolates. It is worth noting that these measurements do not appreciably change when Rh-PET is synthesized in solution-phase or without NaBH₄ present. This has led us to conclude that: i) the formation of Rh-PET occurs without further assistance upon combination of RhCl₃ and PET; ii) the resulting presumptive $Rh_x(PET)_m$ species are robust enough to resist further reduction by a relatively strong reducing agent.

We also performed a series of XPS experiments on the RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET system as discussed in chapter 2. **Figure A13** below shows the full survey spectrum of that shown in Figure 2.3, and indicates the presence of the expected elements Au, Rh, S, C, N, P, O, and F. The O peaks are attributed to the cleaning method applied to the silica wafers prior to sample deposition, which produces a fresh oxide layer on the wafer surface.



Figure A13. XPS survey spectrum of a drop-cast sample of RhAu₂₄(PET)₁₈, Au₂₅(PET)₁₈, and Rh-PET.

Figure A14 shows the high-resolution spectrum of the Au 4f region, with corresponding fit traces. The $4f_{7/2}$ peak centered at 84.0 eV matches with previous XPS studies on Au₂₅(PET)₁₈ and related gold clusters, and corresponds with metallic gold.⁴⁻⁶ The $4f_{5/2}$ peak centered at 87.7 eV has well-separated spin-orbit splitting from the $4f_{7/2}$ peak (3.7 eV).



Figure A14. High-resolution XPS spectrum of the Au 4f region for the sample containing RhAu₂₄(PET)₁₈/Au₂₅(PET)₁₈/Rh-PET.

Section 5: Treatment of Gold Nanoclusters as Superatom Complexes

Superatom theory treats metal clusters as a single spherical complex containing the delocalized valence electrons of the metal atoms.⁷ Previously, Knight and coworkers determined *via* mass spectrometry experiments that gas-phase, bare metal clusters with specific electron counts of $n^* = 2, 8, 18, 34, 58$, and so on were especially abundant.⁸ These counts were proposed to be

associated with electronically closed shells, which are considered analogous to atomic noble gas electron configurations. The following equation was previously developed by Walter and coworkers (reference 9) for determining the shell-closing electron count n^* of $Au_x(SR)_m^z$ NCs:

$$n^* = Nv_A - M - z$$

where N is the # of metal atoms, v_A is the metal atom valence, M is the # of electron-withdrawing (or electron-localizing) ligands, and z is the overall charge of the NC. Thiolate ligands are considered to withdraw one electron each from the metal core. Applying equation 1 to $Au_{25}(PET)_{18}^{1-}$, we find that the complex satisfies an electronically closed shell of $n^* = 8$. These electrons fill into superatomic orbitals (e.g. 1S, 1P, 1D, etc.) which obey the same rules as their atomic analogues, giving a configuration of $1S^2 1P^6$.

In the case of heterometal doping, the predictive value of equation 1 has been demonstrated for a number of group 10-12 closed d-shell metals. Jiang and Dai predicted a series of $MAu_{24}(SR)_{18}^{z}$ NCs prior to their experimental synthesis and characterization.⁹ Their analysis applied the concept of isoelectronic substitution to $Au_{25}(SR)_{18}^{1-}$, i.e. the value for n* remained fixed at 8 in their calculations. In order to keep this value fixed, the overall NC charge z was adjusted as the heterometal valence removed (e.g. Pd, Pt) or added (e.g. Cd, Hg) electrons.

Empirically, no group has proven that isoelectronic substitution is operative in the case of open d-shell heterometals. Both $RhAu_{24}(SR)_{18}$ and $IrAu_{24}(SR)_{18}$ are predicted by isoelectronic substitution to have a large net negative charge (-3). The observation that $Ir_3Au_{22}(SR)_{18}$ and $RhAu_{24}(SR)_{18}$ appear to be of net neutral and positive charge, respectively, strongly suggests that the same principles applied to closed d-shell heterometals cannot be applied to those with an open d-shell. As covered in the main text, our observations combined with the recent findings of Hirai and coworkers appear to agree that group 9 metals (e.g. Ir, Rh) subtract a single electron from the

overall superatomic electron count in order to fill their d-shells.¹⁰ Additional studies involving these and other open d-shell heterometals are necessary to further confirm the ubiquity of this process.

Section 6: Post-Synthetic Exchangeability of Rhodium with Au₂₅L₁₈ (L = Thiolate, Acetylide)

A series of exchange reactions were performed using Rh-PET as the rhodium source. Given the non-metallic nature of Rh-PET, this type of post-synthetic exchange cannot truly be classified as an ICR process. Rather, AGR is a more apt description since this route typically involves interaction between the Au NC and the heterometal in a nonmetallic oxidation state. Other groups have previously found success with doping of $Au_{25}(PET)_{18}$ using oligomeric heterometal thiolates *via* AGR.¹¹

[TOA][Au₂₅(PET)₁₈] (TOA = tetraoctylammonium) was synthesized according to the Brust-Schiffrin one-phase procedure.¹² Crystals were obtained through slow cooling of a mixed toluene/ethanol solution. In a typical exchange reaction, these crystals were then mixed with an equal amount of Rh-PET dissolved in DCM. Aliquots of the reaction mixture were taken subsequently over a period of 48 hours and analyzed by MALDI-MS. A number of variations of this general reaction were explored, including dissolution in THF or toluene, increased/decreased amounts of Rh-PET, and the addition of PET or NaBH₄ in slight excess.

Over the course of these post-synthetic exchange studies, no products attributable to $Rh_xAu_{25-x}(PET)_{18}$ species were observed under any conditions. A representative MALDI-MS spectrum of an aliquot taken at 48 hours is shown in (**Figure A15**). The calculated mass difference between gold and rhodium is 94.06 Da, which is well outside the range of prominent $Au_{25}(PET)_{18}$ fragment peaks. No peaks with a similar m/z difference from the parent peak were observed over a period of 48 hours. Similar to the cases of palladium and platinum, it appears that no exchange

occurs between rhodium and $Au_{25}(PET)_{18}$ post-synthetically. Unless in a mass ratio higher than 1:1, no noticeable degradation of $Au_{25}(PET)_{18}$ is observed.



Figure A15. Representative MALDI mass spectrum resulting from the mixture of Rh-PET and crystalline $Au_{25}(PET)_{18}$ in a 1:1 mass ratio. Dotted lines indicate expected peak positions of the exchange products $Rh_xAu_{25-x}(PET)_{18}$, with the labels 1-4 representing the value x.

Acetylide-protected Au NCs such as $[Na][Au_{25}(CCAr)_{18}]$ (CCAr = 3,5bis(trifluoromethyl)phenylacetylene) have been isolated in recent years and described as more stable analogues of thiolated Au NCs.¹³ These stability arguments are primarily based on a greater resistance to oxidation or degradation under oxidative conditions. Our lab recently revealed a surprising metathesis-like exchange between lithium- or gold-acetylides and thiolated Au NCs.¹⁴ In addition to this acetylide-for-thiolate exchange, thiolate-for-acetylide exchange was observed by mixing free thiol with $[Na][Au_{25}(CCAr)_{18}]$. Both directions of exchange were observed simultaneously in a novel ICR between $Au_{25}(PET)_{18}$ and $Au_{44}(PA)_{28}$ (PA = phenylacetylene). The facile nature and short timescales of these exchange reactions prompted us to assess the exchangeability of Rh-PET with $Au_{25}(CCAr)_{18}^{1-}$. Given the solubility of $Au_{25}(CCAr)_{18}^{1-}$ in methanol, we were also able to perform exchange reactions with the RhCl₃ starting material.

 $Au_{25}(CCAr)_{18}^{1-}$ was prepared and crystallized based on the report by Li and coworkers.¹³ The exchange conditions applied here are the same as those described for $Au_{25}(PET)_{18}$. Over the course of 48 hours, no exchange products were observed for Rh-PET or RhCl₃ (**Figure A16**). Since no AGR methods have thus far been applied to $Au_{25}(CCAr)_{18}^{1-}$, we cannot with complete certainty attribute the failure to exchange solely on the rhodium sources. It is possible that the greater resistance to oxidation significantly hinders any exchange *via* AGR, as it is considered a redoxmediated process. Based on the existing data, however, we hypothesize that for the case of Rh-PET its demonstrated inertness is the primary factor contributing to its failure to exchange. Even in the presence of excess PET, the mixture of $Au_{25}(CCAr)_{18}^{1-}$ and Rh-PET exclusively yields $Au_{25}(PET)_x(CCAr)_{18-x}^{1-}$ species. At mass ratios greater than 1:10 RhCl₃: $Au_{25}(CCAr)_{18}^{1-}$, significant degradation of $Au_{25}(CCAr)_{18}^{1-}$ was observed.



Figure A16. Representative MALDI mass spectrum resulting from the mixture of Rh-PET and crystalline $Au_{25}(CCAr)_{18}^{1-}$ in a 1:1 mass ratio. Dotted lines indicate expected peak positions of the exchange products $Rh_xAu_{25-x}(CCAr)_{18}^{z}$, with the labels 1-4 representing the value x (z = charge). The smaller peak on the shoulder of the parent $Au_{25}(CCAr)_{18}^{1-}$ peak is a fluoride adduct.

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APPENDIX B: SUPPLEMENTAL TO CHAPTER 3

Section 1: Experimental Methods

Gold (III) chloride trihydrate (Sigma-Aldrich, ACS reagent, $\geq 49.0\%$ Au basis), chloro(dimethylsulfide)gold(I) (TCI America, >97% Purity) tetra-n-octylammonium bromide (Acros Organics, 98% purity), sodium borohydride (Sigma-Aldrich, ≥98.0% purity), 2phenylethanethiol (Sigma-Aldrich, ≥99% Purity), phenylacetylene (Alfa Aesar, 98+% Purity), lithium phenylacetylide (Sigma-Aldrich, 1.0M in THF), 3,5-bis(trifluoromethyl)phenylacetylene (Sigma-Aldrich, 97%), tetrahydrofuran (Fisher Scientific, certified, stabilized with 0.025%) butylated hydroxytoluene), dichloromethane (Sigma-Aldrich, ACS grade, \geq 99.5%, stabilized with 40-150 ppm amylene), toluene (Sigma-Aldrich, ACS reagent, ≥99.5%), methanol (Fisher Scientific, certified ACS, 99.9% assay), acetone (Industrial Chemical Corporation, tech grade), chloroform (EMD Millipore, ≥99.8% assay, stabilized with ethanol), ethanol (Pharmco-Aaper, 200 and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyliden]malononitrile (Sigma proof), Aldrich, ≥99.0% [HPLC]) were all used without further purification. Triethylamine (Fisher, \geq 99.0%), pyridine (Fisher, \geq 99.0%), and diethyl ether (Fisher, \geq 99.0%, BHT stabilized) were purified using a SG Water USA glass contour solvent system prior to use. Water was obtained using a Thermo Scientific Barnstead Nanopure set to 18.2 M Ω ·cm.

I. MALDI-MS data collection:

2 mg *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile was dissolved in 0.2 mL dichloromethane. To this solution was added 2.0 μ L of nanocluster sample dissolved in dichloromethane. 0.2 μ L of the combined solution was spotted on a metal plate for MALDI-MS and allowed dry for one hour. Data was collected using a Bruker Microflex LFR

MALDI-TOF. Positive mode spectra were collected as they provided better signal-to-noise ratios relative to negative mode spectra.

II. Synthesis of Au₂₅(PET)₁₈TOA:

A previously published method was adapted for the synthesis of Au₂₅(PET)₁₈TOA.¹ In brief, 2.0 g HAuCl₄•3H₂O and 3.12 g tetra-*n*-octylammonium bromide were added to 140 mL tetrahydrofuran in a 300 mL roundbottom flask. The solution was stirred for 30 minutes until a dark orange color was observed. 3.6 mL of 2-phenylethanethiol was then added to flask, and the resulting solution was stirred overnight. A separate solution containing 1.94 g sodium borohydride and 48 mL H₂O was produced in a 125 mL Erlenmeyer flask. This solution was cooled to 0 °C prior to adding it to the gold-containing solution. The combined solutions were then stirred for 48 hours, followed by separation and evaporation of the organic layer. The resulting brown oil was re-dissolved in several milliliters of dichloromethane and separated into four 50 mL conical vials. The conical vials were filled with methanol and placed in a centrifuge at 4000 RPM for 30 minutes. The supernatant was decanted and the precipitate was washed twice more by addition of methanol and centrifugation. The final product was extracted from the resulting powder using dichloromethane and evaporated to dryness.

III. Synthesis of gold(I)-phenylacetylide:

Conditions were utilized from a previously published report.² In brief, 100 mg chloro(dimethylsulfide)gold(I) was added to 10.0 mL dichloromethane, 47.8 μ L phenylacetylene, and 60.3 μ L triethylamine in a 20 mL scintillation vial and stirred in the dark for two hours. The solution was then evaporated to approximate dryness and the resulting powder was washed with excess water, ethanol, and diethyl ether.

IV. Gold(*I*)-phenylacetylide exchange reactions on Au₂₅(PET)₁₈:

Ligand exchange was performed on $Au_{25}(PET)_{18}TOA$ by adding 12.0 mg (1.53 µmol) $Au_{25}(PET)_{18}TOA$ to 3.03 mL dichloromethane in a 20 mL scintillation vial at room temperature. 0.450 mg (1.53 µmol) gold(I)-phenylacetylide was added to the solution containing the Au_{25} cluster and stirred for 30 minutes, after which the solvent was evaporated. The crude product was then extracted using dichloromethane to remove any remaining gold(I)-phenylacetylide and evaporated to dryness. A similar procedure was used to generate a higher amount of ligand exchange but using 4.50 mg (15.3 µmol) or 450 mg (153 µmol) of gold(I)-phenylacetylide.

V. Exchange of lithium phenylacetylide with Au₂₅(PET)₁₈:

Ligand exchange was performed by purging a sealed 20 mL scintillation vial containing 20.0 mg (2.54 μ mol) Au₂₅(PET)₁₈TOA and a stir bar with argon for 30 minutes. To this vial was added 25.4 μ L (25.4 μ mol) lithium phenylacetylide. The solution was stirred for 30 minutes under argon at room temperature, after which a 2.0 μ L aliquot of the solution was removed for MALDI-MS analysis.

VI. Synthesis of [Na][Au₂₅(CCAr)₁₈]:

Conditions were adapted from a previously published report.³ In a foil-wrapped 20 mL scintillation vial, 200 mg chloro(dimethylsulfide)gold(I) was added to 10 mL acetone under vigorous stirring. 126 μ L 3,5-bis(trifluoromethyl)phenylacetylene and 99 μ L triethylamine were then added sequentially, and this mixture was stirred for 2 hours. The resulting precursor Au(I)-CCAr was isolated by drying the solution under rotary evaporation and washing twice with water. 208 mg Au(I)-CCAr was subsequently added to 30 mL of a chloroform:methanol mixture (5:1) in a 100 mL foil-wrapped roundbottom flask under vigorous stirring. A freshly-prepared aqueous solution of sodium borohydride (5.4 mg in 4.7 mL water) was added dropwise followed by 94 μ L

triethylamine. The mixture was allowed to stir for 20 hours, whereupon a dark solid was obtained following rotary evaporation. This solid was extracted in methanol, which after brief centrifugation gave crude Au₂₅(CCAR)₁₈ in the supernatant. For crystallization, this crude was dried and resuspended in 1:1 dichloromethane:toluene and layered with hexanes in 20 mL scintillation vials. Crystals were observed in a few days at room temperature. All characterizations and post-synthetic modifications described herein for Au₂₅(CCAr)₁₈ were performed with crystal-pure sample. MALDI-MS and UV/Visible absorbance measurements further confirm the purity of the sample (Figures B9, B10).

VII. Thiolate ligand exchange on [Na][Au₂₅(CCAr)₁₈]:

13 mg (1.41 μ mol) Au₂₅(CCAr)₁₈ was suspended in 1 mL dichloromethane in a 20 mL scintillation vial at room temperature. A solution of 1 μ L 2-phenylethanethiol in 100 μ L dichloromethane was prepared. 19 μ L of this solution, equating to 1 equivalent per cluster, was added to the Au₂₅(CCAr)₁₈ solution under vigorous stirring. An aliquot of this mixture was removed for MALDI-MS analysis following a period of 30 minutes.

VIII. Synthesis of Au₄₄(PA)₂₈:

Conditions were adapted from a previously published report.⁴ In brief, 44.7 mg gold(I)phenylacetylide was added to 4.0 mL chloroform and stirred. A solution of 0.95 mg sodium borohydride in 1.0 mL ethanol was prepared and added to the solution containing gold(I)phenylacetylide. The combined solutions were stirred in the dark for 16 hours. Afterwards, 0.3 mL phenylacetylene and 0.3 mL pyridine were added and stirred for 24 hours in the dark. The solution was subsequently evaporated to near dryness and washed with 15 mL hexanes to afford a dark powder. This powder was purified by size exclusion chromatography to afford the purified product.

IX. Thiolate ligand exchange on Au44(PA)28:

Ligand exchange was performed on $Au_{44}(PA)_{28}$ by adding 2.8 mg (0.24 µmol) $Au_{44}(PA)_{28}$ to 0.48 mL dichloromethane in a 20 mL scintillation vial at room temperature. 0.59 µL (0.61 mg, 4.41 µmol) 2-phenylethanethiol was added to the solution containing the Au₄₄ cluster and stirred for 5 minutes, after which an aliquot of the solution was removed for MALDI-MS analysis.

X. Intercluster exchange between Au₂₅(PET)₁₈ and Au₄₄(PA)₂₈:

1.16 mg (0.148 μ mol) Au₂₅(PET)₁₈TOA and 1.70 mg (0.148 μ mol) Au₄₄(PA)₂₈ were combined in 0.29 mL dichloromethane and stirred for five minutes. The solution was then evaporated to dryness and re-dissolved in a minimal amount of DCM for MALDI-MS analysis.

Section 2: Supporting Figures



Figure B1: Positive ion MALDI-MS of $Au_{25}(PET)_{18}$. The peak corresponding to this compound is labelled. Other peaks correspond to fragmentation products.



Figure B2: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 1 eq. phenylacetylene in DCM for 30 minutes. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$ B) $Au_{25}(PET)_{17}S_1$ C) $Au_{25}(PET)_{17}D$) $Au_{25}(PET)_{16}S_1$ E) $Au_{25}(PET)_{16}$.



Figure B3: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. phenylacetylene in DCM for 30 minutes. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$; B) $Au_{25}(PET)_{17}S_1$; C) $Au_{25}(PET)_{17}$; D) $Au_{25}(PET)_{16}S_1$; and E) $Au_{25}(PET)_{16}$.



Figure B4: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 10 eq. phenylacetylene and 1 eq. triethylamine in DCM for 30 minutes. A sodium adduct of $Au_{25}(PET)_{18}$ is labelled. The calculated mass spectrometry result for $Au_{25}(PET)_{18} \cdot 2Na^+$ is 7437.91 m/z.



Figure B5: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. phenylacetylene in toluene for 30 minutes at 60 °C. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$; B) $Au_{25}(PET)_{17}S_1$; C) $Au_{25}(PET)_{17}$; D) $Au_{25}(PET)_{16}S_1$; and E) $Au_{25}(PET)_{16}$.


Figure B6: Normalized positive ion MALDI-MS spectra after mixing $Au_{25}(PET)_{18}$ with 10 eq. gold(I)-phenylacetylide in THF for 5 minutes (black), 15 minutes (red), and 30 minutes (blue). The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$; B) $Au_{25}(PET)_{17}(PA)_1$; C) $Au_{25}(PET)_{16}(PA)_2$; D) $Au_{25}(PET)_{15}(PA)_3$; E) $Au_{25}(PET)_{14}(PA)_4$; F) $Au_{25}(PET)_{13}(PA)_5$; G) $Au_{25}(PET)_{12}(PA)_6$; H) $Au_{25}(PET)_{11}(PA)_7$; I) $Au_{25}(PET)_{10}(PA)_8$; J) $Au_{25}(PET)_9(PA)_9$; K) and $Au_{25}(PET)_8(PA)_{10}$.



Figure B7: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. gold(I)phenylacetylide in DCM for 18 hours. The peak corresponding to the mass of $Au_{25}(PA)_{18}$ is labelled.



Figure B8: Positive ion MALDI-MS spectrum of $Au_{25}(PET)_{18-x}(PA)_x$ obtained after mixing $Au_{25}(PET)_{18}$ with 10 eq. of lithium phenylacetylide in DCM under argon for 5 minutes. Other peaks correspond to fragmentation products.



Figure B9: Negative ion MALDI-MS spectrum of crystal-pure $Au_{25}(CCAr)_{18}$. The peak corresponding to the compound is labelled. The peak labelled # is a fragment peak corresponding to the loss of gold from the parent cluster. The peak labelled * is an adduct peak corresponding to the parent peak plus a fluorine.



Figure B10: UV/Visible absorbance spectrum of crystal-pure $Au_{25}(CCAr)_{18}$. The position and relative intensity of absorption peaks matches well with that reported by Li et al. (reference 3).

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APPENDIX C: SUPPLEMENTAL TO CHAPTER 4

Section 1: Experimental Methods

Gold(III) chloride trihydrate (Sigma-Aldrich, ACS reagent, \geq 49.0% Au basis), sodium borohydride (Sigma-Aldrich, \geq 98.0% purity), tetra-n-octylammonium bromide (Acros Organics, 98% purity), 2-phenylethanethiol (Sigma-Aldrich, \geq 99% purity), diethylene glycol dimethyl ether (diglyme, anhydrous, Sigma-Aldrich, 99.5%), tetrahydrofuran (Fisher Scientific, certified, stabilized with 0.025% butylated hydroxytoluene), dichloromethane (Sigma-Aldrich, ACS grade, \geq 99.5%, stabilized with 40-150 ppm amylene), dichloromethane-d₂ (Sigma-Aldrich, 99.5 atom % D), methanol (Fisher Scientific, certified ACS, 99.9% assay), chloroform (EMD Millipore, \geq 99.8% assay, stabilized with ethanol), ethanol (Pharmco-Aaper, 200 proof), and DCTB (i.e. trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyliden]malononitrile, Sigma Aldrich, \geq 99.0% [HPLC]) were all used without further purification. Water was obtained using a Thermo Scientific Barnstead Nanopure set to 18.2 MΩ·cm.

I. Synthesis of Au₂₅(PET)₁₈:

A previously published method was adapted for the synthesis of $Au_{25}(PET)_{18}TOA$.¹ In brief, 2.0 g HAuCl₄•3H₂O and 3.12 g tetra-*n*-octylammonium bromide were added to 140 mL tetrahydrofuran in a 300 mL roundbottom flask. The solution was stirred for 30 minutes until a dark orange color was observed. 3.6 mL of 2-phenylethanethiol was then added to the flask, and the resulting solution was stirred overnight. A separate solution containing 1.94 g sodium borohydride and 48 mL H₂O was produced in a 125 mL Erlenmeyer flask. This solution was cooled to 0 °C prior to adding it to the gold-containing solution. The combined solutions were then stirred for 48 hours, followed by separation and evaporation of the organic layer. The resulting brown oil was re-dissolved in several milliliters of dichloromethane and separated into four 50 mL conical vials. The conical vials were filled with methanol and placed in a centrifuge at 4000 RPM for 30 minutes. The supernatant was decanted and the precipitate was washed twice more by addition of methanol and centrifugation. The final product was extracted from the resulting powder using dichloromethane and dried in order to oxidize the cluster from its native -1 charge state to neutral. *II. Synthesis of [Au₂₀(PET)₁₅(DG)₂]·4[DG]:*

Conditions were adapted from a previously published report.² In brief, 48 mL of THF was added to a 250 mL Erlenmeyer flask followed by 643 µL of 2-phenylethanethiol (4.8 mmol, 3 eq). 630 mg HAuCl₄•3H₂O (1.6 mmol, 1 eq) dissolved in 16 mL diglyme was added to the reaction vessel under constant magnetic stirring. Over the course of 3 hours the initial cloudy yellow solution transitioned to a completely opaque milky white. Approximately five minutes prior to the end of this 3 hour period, a suspension of 15.1 mg sodium borohydride (0.4 mmol, 0.25 eq) in 4 mL diglyme was sonicated at room temperature. At the 3 hour mark this suspension was then added dropwise over the course of 1 minute, followed by 120 mL diglyme. During the sodium borohydride addition, the solution turned dark black but quickly transitioned to a deep orange following the addition of the gross excess of diglyme. The reaction was stirred for an additional hour, whereupon the solution was passed through a Büchner funnel with a medium frit to remove insoluble byproducts. Quenching was performed by transferring this filtered solution to a 1-L fleaker and adding methanol to 1 L. The precipitated nanocluster product was isolated as an orange solid by passing this quenched solution through a Büchner funnel with a fine frit and further rinsing with excess methanol. For solution-phase studies, this solid product was dried overnight and resuspended in either dichloromethane or chloroform. Yield was calculated with reference to the precursor gold salt HAuCl₄•3H₂O and the full cluster formula, including the 4 excess diglyme.

III. Hierarchical assembly test:

In a typical experiment, a 20 mg/mL solution of nanocluster sample in 2 mL chloroform was stored in a 5-mL scintillation vial and covered with a thin layer of parafilm to allow for the safe dispersal of any vapor. This vial was submerged halfway in a Büchi B-100 water bath set to the desired temperature (30 °C, 40 °C, 50 °C, or 60 °C) and held in place by a clamp for the duration of one hour. The vial was then removed and placed within an ice water bath in order to rapidly cool the solution prior to analysis by UV/Vis linear absorption spectroscopy. For each temperature, additional experiments were performed with an excess (2 mL) of diglyme added to the 2 mL nanocluster solutions, providing a total of eight experiments.

IV. MALDI mass spectrometry:

2 mg DCTB was dissolved in 200 μ L dichloromethane. To this solution was added 2.0 μ L of a 10 mg/mL nanocluster sample dissolved in dichloromethane. 0.2 μ L of the combined solution was spotted on a stainless steel plate for MALDI-MS and allowed to dry for one hour. Data was collected using a Bruker Microflex LFR MALDI-TOF. Mass spectra were collected in the positive ionization mode, as this consistently gave the best signal-to-noise ratios (versus those collected in negative ionization mode).

V. NMR spectroscopy:

For nanocluster samples, 10 mg was dissolved in 1.0 mL dichloromethane- d_2 . For free ligand samples, 100 μ L was dissolved in 1.0 mL dichloromethane- d_2 . Data was collected using a Bruker Neo400.

VI. Thermal gravimetric analysis:

A TA TGA Q500 was used for data collection. Powdered nanocluster (2.0310 mg) was placed in a platinum pan. Under constant N_2 flow (55 mL/min), the temperature was increased at 10 °C/min to 00 °C.

VII. Infrared spectroscopy:

14.0 mg of nanocluster sample was dissolved in 1.0 mL chloroform, which was measured on a Thermo Nicolet iS-50 FT-IR spectrometer using ATR on a ZnSe crystal.

VIII. UV/Vis spectroscopy:

1.0 mL of a 10 mg/mL nanocluster sample dissolved in chloroform was taken and diluted until the absorbance output was within a reasonable range with good signal-to-noise ratio. Data was collected on a NanoDrop 2000c spectrophotometer.

Section 2: Supporting Experimental Figures



Figure C1. ¹H spectra of $Au_{25}(PET)_{18}$ (top, blue) and $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ (bottom, red) in dichloromethane-d₂. The central position of the peaks corresponding to the ethylene linker protons of PET are indicated for both samples.



Figure C2. Differential thermal analysis (DTA) plot of the TGA data for $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$, obtained by taking the difference of every adjacent pair of weight % values and dividing by the time change. The raw DTA values were smoothed using a Savitzky-Golay filter with a window of 10 °C.



Figure C3. Linear absorption spectrum of $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ in chloroform. Inset shows a 10 mg/mL solution of the nanocluster, showcasing its gold-orange hue.



Figure C4. FT-IR spectrum of $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ in chloroform. Inset shows a zoomedin view of the region (2000-1750 cm⁻¹) which corresponds to intercluster ligand interactions brought about by dimerization. These peaks are notably absent in $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$, further affirming its lack of dimerization/polymerization. See reference 2 for further details.



Figure C5. Stacked linear absorption spectra of $[Au_{20}(PET)_{15}(DG)_2] \cdot 4[DG]$ when exposed to different temperatures without (left) and with (right) excess diglyme.

Section 3: Computatonal Methods and Associated Figures

All calculations were performed at the BP86/TZP^{3,4} level of theory with the Grimme3 dispersion correction⁵ using the Amsterdam Modeling Suite (AMS) 2021.102 software.⁶ After geometry optimization, NMR shielding calculations were performed. ¹H NMR calculations were performed on hydrogen atoms in the diglyme molecule with respect to TMS (tetramethyl silane) to be consistent with the experimental results.

I. NMR calculations:

Because the terminal methyl group of diglyme can rotate freely at room temperature, two structures for linear diglyme, labeled diglyme-GS and diglyme-TS (**Figure C6**), are considered. Diglyme-GS is the global minimum structure and diglyme-TS is a transition state related to rotation of the terminal methyl groups. Diglyme-GS is lower in energy than diglyme-TS by 18.9 kJ/mol.



Figure C6. Fully optimized BP86/TZP structures for diglyme-GS and diglyme-TS. These structures differ in the orientation of the terminal methyl groups. Hydrogen atoms are labeled 12, 13, 14, 15, 16, 17, and 18 respectively. Carbon = gray, oxygen = red, and hydrogen = white.

From **Table C1**, it can be noted that averaging the chemical shifts for diglyme-GS and diglyme-TS leads to chemical shifts that are consistent with the experimental results in Figure 4.2 of chapter 4, as would be expected due to free rotation of the methyl groups. Thus, the calculated results are consistent with a linear diglyme molecule in pure solution indergoing free methyl rotation. Hydrogen atoms in CH_2 groups have chemical shifts at around 3.8 ~ 4.0 ppm, which are only about 0.4 ppm higher than those determined experimentally.

	hydrogen atom	chemical shifts (ppm)		hydrogen atom	chemical shifts (ppm)
	12	3.93		12	3.83
	13	3.93		13	3.83
	14	3.84		14	3.98
diglyme-GS	15	3.84	diglyme-TS	15	3.98
	16	3.56		16	3.97
	17	3.84		17	3.26
	18	3.56		18	3.97

Table C1. Calculated ¹H NMR chemical shifts for hydrogen atoms 12, 13, 14, 15, 16, 17, and 18 in diglyme-GS and diglyme-TS.

II. Binding energy analysis:

To examine the binding strength between $Au_{20}(SCH_3)_{15}^+$ and diglyme, we consider the binding of these fragments to form the full $Au_{20}(SCH_3)_{15}DG^+$ system. The optimized $Au_{20}(SCH_3)_{15}DG^+$ coordinates (below) are split into fragments that are considered without further optimization (i.e. frozen fragments). We also fully optimize the fragments and determine the binding energy to form $Au_{20}(SCH_3)_{15}DG^+$. For diglyme, we consider the crown-like minimum similar to the arrangement on the nanoparticle (crown) and its global energy minimum (linear).

Optimization of diglyme changes the energy by less than 8 kJ/mol, whereas optimization of the $Au_{20}(SCH_3)_{15}^+$ fragment leads to an energy stabilization of 52.5 kJ/mol; indicating that the binding of diglyme has resulted in a significant geometrical rearrangement of the Au_{20} cluster compared to the structure without diglyme (**Table C2**).

		Frozen fragments	Optimize	d fragments
Relative energies	Au ₂₀ (SCH ₃) ₁₅ +	52.5	0	
(kJ/mol)	DG	7.9	2.6 (Crown)	0 (Linear)
Binding energies (kJ/mol)		-204.7	-146.7	-141.8

Table C2. Relative energies of $Au_{20}(SCH_3)_{15}^+$ and diglyme fragments before and after fragment optimization, followed by binding energies of fragments to form $Au_{20}(SCH_3)_{15}DG^+$.

Optimized BP86/TZP coordinates for Au₂₀(SCH₃)₁₅DG⁺:

Au	14.241138	11.425786	-0.092579
Au	14.241138	11.425786	-0.09257

- Au 14.660912 12.251971 3.376269
- Au 16.246342 13.555258 0.224274
- Au 15.895334 14.373573 -2.511098
- Au 14.739907 15.898072 -0.469852
- Au 15.684812 18.447517 2.438385
- Au 13.357622 16.638112 1.762807
- Au 14.164861 18.700721 -0.380090
- Au 13.615731 21.571629 -0.053126
- Au 12.310963 19.366933 2.574677
- Au 14.470293 15.888862 4.558413
- Au 15.939093 15.543087 2.062360
- Au 13.904047 12.796653 -3.800841
- Au 11.244799 14.259763 -0.652962
- Au 13.762272 13.931420 1.325519
- Au 12.692210 18.303376 -3.258133

- Au 15.473678 16.989291 -2.913062
- Au 15.343591 20.093681 -2.990275
- Au 14.013887 16.035165 -5.496651
- Au 13.240172 15.444077 -2.718252
- S 14.836927 18.212715 4.606876
- S 12.967591 21.574103 2.197114
- S 16.460128 18.828150 0.257394
- S 14.003806 13.657116 5.127302
- S 15.421705 10.675476 1.811379
- S 17.574291 12.867902 -1.671712
- S 11.443013 17.236763 3.065730
- Н 12.061195 10.023818 -3.471969
- S 13.423990 18.320889 -5.490587
- S 14.184406 22.003524 -2.280891
- S 11.940617 18.161298 -1.034916
- S 14.506864 13.761899 -5.858877
- S 12.877038 11.727478 -1.975290
- S 11.384824 13.700205 1.607318
- S 16.844719 18.587566 -4.019838
- S 10.976345 14.635804 -2.950240
- C 16.905591 20.608422 0.178889
- C 12.165436 13.646304 5.097635
- Н 13.665115 9.550168 -2.820550

- C 14.551742 21.750383 3.119739
- C 16.288108 18.391074 5.728489
- C 10.032291 17.017252 1.896996
- C 17.065053 11.160699 -2.120637
- C 14.473206 9.152202 2.261237
- C 10.907944 19.635217 -0.683916
- C 16.350309 13.741769 -5.919050
- C 9.864873 16.093659 -3.088176
- C 12.590019 21.883828 -3.194399
- C 11.868748 18.334854 -6.484288
- C 18.353644 18.662357 -2.961307
- C 11.095849 11.883998 1.669764
- C 12.693732 9.989524 -2.578533
- Н 17.848340 20.746363 0.720082
- H 16.114603 21.236689 0.605082
- Н 17.030428 20.859166 -0.883251
- H 11.822147 14.316358 5.893012
- H 11.834541 12.622313 5.301230
- Н 11.797328 13.988813 4.124641
- Н 12.196949 9.410558 -1.792491
- Н 11.643352 11.387576 0.860694
- Н 10.020634 11.696309 1.578223
- H 14.318957 21.661802 4.186365

- Н 14.961960 22.741840 2.900553
- Н 15.257908 20.959839 2.832803
- Н 15.949671 18.157163 6.743717
- Н 16.622164 19.433062 5.674753
- Н 17.080573 17.707985 5.411795
- Н 9.664892 15.995319 2.035944
- Н 10.366704 17.143878 0.862953
- Н 9.254587 17.744277 2.152649
- Н 15.975595 11.058294 -2.048762
- Н 17.554212 10.463863 -1.431420
- Н 17.395015 10.975475 -3.148867
- H 14.858931 8.798646 3.223491
- H 14.657315 8.403636 1.483764
- Н 13.404792 9.367760 2.338463
- Н 10.730543 19.650137 0.400927
- Н 9.963054 19.525015 -1.227671
- Н 11.420929 20.559184 -0.973534
- Н 16.769235 14.227523 -5.030354
- Н 16.650969 14.278155 -6.825171
- Н 16.670929 12.696095 -5.972078
- Н 10.082326 16.816798 -2.298277
- Н 8.833129 15.733954 -3.007158
- Н 10.031916 16.554702 -4.068272

- Н 12.164812 20.875920 -3.094189
- Н 12.811090 22.081876 -4.248762
- Н 11.909339 22.645408 -2.799685
- Н 11.190975 17.540997 -6.161467
- Н 12.149517 18.187700 -7.532724
- Н 11.398779 19.315596 -6.354579
- Н 18.085761 18.584182 -1.903406
- Н 18.867932 19.608311 -3.162983
- Н 18.992357 17.819468 -3.248070
- Н 11.468356 11.530702 2.638978
- O 18.001130 16.277071 3.935011
- C 18.661342 15.217199 4.645754
- C 18.910697 17.160381 3.258313
- C 19.411011 16.592543 1.943657
- C 17.690795 14.061428 4.777501
- O 18.290821 16.433157 1.078172
- O 17.279126 13.544396 3.506028
- C 18.666845 16.062500 -0.253199
- C 18.293845 12.768751 2.851218
- H 18.961022 15.568003 5.649615
- Н 19.572053 14.902429 4.112599
- Н 18.325427 18.070452 3.055280
- Н 19.761440 17.417687 3.910886

- Н 19.932439 15.626008 2.083290
- Н 20.137048 17.300525 1.502137
- Н 18.137703 13.262923 5.394090
- Н 19.110794 15.053924 -0.278686
- Н 19.383981 16.790841 -0.664840
- Н 17.749844 16.072652 -0.853987
- H 18.610938 11.929666 3.490601
- Н 17.836576 12.382620 1.930680
- Н 19.167221 13.379677 2.576638
- Н 16.768288 14.411084 5.262760

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APPENDIX D: SUPPLEMENTAL TO CHAPTER 5

Section 1: Experimental Methods

Gold (III) chloride trihydrate (Sigma-Aldrich, ACS reagent, \geq 49.0% Au basis), silver nitrate (Alfa Aesar, ACS, ≥99.9% Ag basis), sodium borohydride (Sigma-Aldrich, ≥98.0% purity), tetra-n-octylammonium bromide (Acros Organics, 98% purity), tetraphenylphosphonium bromide (Thermo Scientific, 99% purity), triethylamine (Fisher, ≥99.0%), 2-phenylethanethiol (Sigma-Aldrich, ≥99% purity), 3,4-difluorothiophenol (Sigma-Aldrich, 96%), 1,2-ethanedithiol (Alfa Aesar, 298%), 1,3-propanedithiol (Sigma-Aldrich, 99%), 1,4-butanedithiol (Sigma-Aldrich, 97%), 1,5-pentanedithiol (Sigma-Aldrich, 96%), 1,6-hexanedithiol (Sigma-Aldrich, 96%), 2,2'thiodiethanethiol (Sigma-Aldrich, technical grade, 90%), bis(2-mercaptoethyl) ether (Sigma-Aldrich, 95%), 1,2-benzenedithiol (Sigma-Aldrich, 96%), 3,4-toluenedithiol (Sigma-Aldrich, technical 90%), 3,6-dichloro-1,2-benzenedithiol (Sigma-Aldrich, 95%), grade, 4,5bis(mercaptomethyl)-o-xylene aka durene- α_1, α_2 -dithiol (TCI, >96% [GC]), 1.3benzenedimethanethiol (Sigma-Aldrich, 95%), 1,2-benzenedimethanethiol (Sigma-Aldrich, 95%), 1,3-benzenedithiol (Sigma-Aldrich, 99%), tetrahydrofuran (Thermo Scientific, certified, stabilized with 0.025% butylated hydroxytoluene), ethanol (Pharmco-Aaper, 200 proof), methanol (Thermo Scientific, certified ACS, 99.9% assay), hexanes (Thermo Scientific, certified ACS), dichloromethane (Sigma-Aldrich, ACS grade, ≥99.5% stabilized with 40-150 ppm amylene), toluene (Sigma-Aldrich, ACS reagent, ≥99.5%), and DCTB aka trans-2-[3-(4-tert-butylphenyl)-2methyl-2-propenyliden]malonitrile (Sigma-Aldrich, ≥99.0% [HPLC]) were all used without further purification. Water was obtained from an in-house Thermo Scientific Barnstead Nanopure set to 18.2 M Ω ·cm.

I. Characterization methods:

UV/Visible spectroscopic measurements were made using a NanoDrop 2000c spectrophotometer. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometric measurements were made using a Bruker Microflex LFR MALDI-TOF. For sample preparation, 2 mg DCTB was dissolved in 200 μ L dichloromethane. To this was added 2.0 μ L of a highly concentrated (typically 10 mg/mL) solution of NC sample in dichloromethane, in order to achieve an approximate sample:matrix ratio of 1:100. 0.2 μ L of the combined solution was spotted on a stainless steel plate and allowed to dry for one hour. Mass spectra for samples containing Au₂₅(PET)₁₈ were collected in the positive ionization mode, as this tended to provide the best signal-to-noise ratios. For samples containing only dithiolate NCs or those containing Ag₄₄(DFTP)₃₀, mass spectra were collected in the negative ionization mode for similar reasons.

II. Synthesis of dithiolate gold NCs:

In a 300 mL roundbottom flask, HAuCl₄· $3H_2O$ (500 mg, 1.27 mmol, 1.00 eq) was dissolved in a solution of [TOA][Br] (776.4 mg, 1.42 mmol, 1.12 eq) in 35 mL of THF. After 30 minutes of stirring, one of the dithiols **1-7** (2.00 eq) was added and the solution was stirred overnight (approximately 15 hours). A freshly-prepared and chilled (0 °C) aqueous solution of NaBH₄ (481.9 mg in 12 mL, 12.74 mmol, 10.03 eq) was then added in one portion under vigorous stirring. The reaction was then covered and stirred for 24 hours. Following this, any remaining water was removed and the remaining solution was concentrated by rotary evaporation, forming an oily mixture. The precipitate was washed 4 times with 100 mL of ethanol and isolated by centrifugation. Cluster products were extracted in dichloromethane and passed through a 0.22 μ m syringe filter. This solution was subsequently stored at 4 °C.

III. Individual observations from gold-ligand formation step for each candidate ligand:

- 1: Within minutes of ligand addition, the initial red-orange solution turned a pale yellow. This proceeded overnight to the formation of an opaque solution with white precipitates, presumably long-chain oligomeric networks of gold with **1**.
- 2: Within minutes of ligand addition, the initial red-orange solution turned a pale yellow. This proceeded overnight to the formation of an opaque solution with white precipitates, presumably long-chain oligomeric networks of gold with **2**.
- 3: Within minutes of ligand addition, the initial red-orange solution turned a light green. Overnight this progressed to a deep emerald green. Most likely a mixture of small oligomers/complexes of gold with 3.
- 4: No obvious change in the initial red-orange solution was observed upon addition of 4.
 Overnight, this proceeded to a moderate green color, presumably a mixture of small oligomers/complexes of gold with 4.
- 5: Within minutes of ligand addition, the initial red-orange solution turned a light green.Overnight this progressed to a deep emerald green. Most likely a mixture of small oligomers/complexes of gold with 5.
- 6: Within minutes of ligand addition, the initial red-orange solution turned a pale yellow.Overnight, the intensity of color lessened within the solution but retained its yellow hue.Most likely a mixture of smaller oligomers of gold with 6.
- 7: A slower transition from the initial red-orange to a pale yellow solution was observed over the course of roughly 30 minutes. This proceeded overnight to an opaque solution with white precipitates, presumably a mixture of long-chain oligomeric networks of gold with 7.

- 8: Within minutes of ligand addition, the initial red-orange solution turned a cloudy orange.
 Overnight this became more opaque with a retention of the orange color, alongside some white precipitates (smaller relative population than 1 or 2). Subsequent reduction yields large insoluble black precipitates.
- 9: Within minutes of ligand addition, the initial red-orange solution turned a pale yellow. This progressed overnight to a colorless solution comprised of large insoluble white precipitates (larger relative population than 1 or 2). Subsequent reduction yields large insoluble black precipitates.
- 10: Similar solution observations as 9. Produced large insoluble black precipitates.
- 11: Similar solution observations as 9. Produced a highly viscous black gel with no discernable UV/Vis signal or features by MALDI-MS.
- 12: Within minutes, the initial red-orange solution turned a highly cloudy yellow-white suspension. This solution character was generally retained overnight, with a noticeable increase in large yellow-white precipitates. Subsequent reduction yields large insoluble black precipitates.
- 13: Within minutes, the initial red-orange solution turned a highly cloudy yellow. Overnight this progressed to the formation of large white precipitates (larger relative population than 1 or 2). Subsequent reduction yields large insoluble black precipitates.
- 14: Within minutes, the initial red-orange solution turned a light yellow-orange. This proceeded overnight to become a pale white solution with small white precipitates (smaller relative population than 1 or 2). Subsequent reduction yields large insoluble black precipitates.

IV. Alternative dithiolate NC synthesis #1 (no TOA bromide):

Same general procedure as outlined in subsection II above, but without the inclusion of [TOA][Br]. This was performed using the ligand **1**. Result: large, insoluble black precipitates. *V. Alternative dithiolate NC synthesis #2 (increased ligand feed):*

Same general procedure as outlined in subsection II above, but with 5.27 equivalents of ligand instead of 2.00 equivalents. This was performed using the ligand **1**. Result: large, insoluble black precipitates.

VI. Alternative dithiolate NC synthesis #3 (fast gold-ligand step):

Same general procedure as outlined in subsection II above, but with a gold-ligand formation step of only 30 minutes instead of 15 hours. This was performed using the ligand **1**. Result: large, insoluble black precipitates.

VII. Synthesis of [TOA] [Au₂₅(PET)₁₈]:

Based on a previous report.¹ In a 300 mL roundbottom flask, HAuCl₄·3H₂O (1 g, 2.54 mmol, 1.00 eq) was dissolved in a solution of [TOA][Br] (1.56 g, 2.85 mmol, 1.56 eq) in 70 mL of THF. After 30 minutes of stirring, PET (1.8 mL, 13.4 mmol, 5.27 eq) was added and the solution was stirred until colorless (approximately 2-3 hours). A freshly-prepared and chilled (0 °C) aqueous solution of NaBH₄ (0.97 g in 24 mL, 25.5 mmol, 10.03 eq) was then added in one portion under vigorous stirring. The reaction was then covered and stirred for 2 days. Following this, any remaining water was removed and the remaining solution was concentrated by rotary evaporation, forming an oily mixture. The precipitate was washed 4 times with 100 mL of methanol and isolated by centrifugation. Crystals of [TOA][Au₂₅(PET)₁₈] were obtained by slowly adding ethanol to a toluene solution of the product until the precipitate contains Au₂₅ (as judged by UV/Vis spectroscopy) followed by slow cooling (-20 °C) over an average period of 2 weeks.

VIII. Synthesis of [PPh4]4[Ag44(DFTP)30]:

Based on a previous report.² A 50 mL mixture of dichloromethane and methanol (9:1 by volume) in a 150-mL roundbottom flask was set in an ice bath and allowed to cool to 0 °C. To this was added AgNO₃ (100 mg, 0.589 mmol, 1.00 eq), followed by 3,4-DFTP (56 μ L, 0.501 mmol, 0.85 eq) and [PPh₄][Br] (59.3 mg, 0.141 mmol, 0.24 eq). After a stirring period of 20 minutes, a freshly prepared aqueous solution of NaBH₄ (225.1 mg in 5 mL, 5.95 mmol, 10.1 eq) was then added in one portion followed immediately by triethylamine (247 μ L, 1.77 mmol, 3.00 eq). The temperature was maintained overnight (approximately 12 hours) near 0 °C through transfer of the reaction vessel and stir plate to a large refrigerated lab case. Following this, the mixture was washed several times with water and concentrated by rotary evaporation. The concentrated product was precipitated through the addition of 100 mL hexanes and subsequent centrifugation. Crystals were obtained through the slow diffusion of hexanes into concentrated dichloromethane solutions of the crude washed precipitate under low temperature (approximately -20 °C) conditions over a period of 6 to 7 days.

IX. Attempted exchange between Au₂₅(*PET*)₁₈ and dithiolate NCs:

To a 20-mL scintillation vial containing crystals of $[TOA][Au_{25}(PET)_{18}]$ (typically 1-3 mg), a volume of dichloromethane was added to set the resulting solution concentration at 1 mg/mL. Then, an equivalent mg amount of dithiolate NCs were added and the resulting mixture was covered and allowed to stir for up to 24 hours at room temperature. 2-µL aliquots were taken at various times and mixed with a 10 mg/mL DCM solution of DCTB for analysis by MALDI-MS. An aliquot was also taken of the mixture following a storage period of 1 week at 4 °C.

X. Attempted exchange between [PPh4]4[Ag44(DFTP)30] and dithiolate NCs:

To a 20-mL scintillation vial containing crystals of $[PPh_4]_4[Ag_{44}(DFTP)_{30}]$ (typically 1-3 mg), a volume of dichloromethane was added to set the resulting solution concentration at 1 mg/mL. Then, an equivalent mg amount of dithiolate NCs were added and the resulting mixture was covered and allowed to stir for up to 24 hours at room temperature. 2-µL aliquots were taken at various times and mixed with a 10 mg/mL DCM solution of DCTB for analysis by MALDI-MS. *XI. Attempted exchange between free PET and dithiolate NCs:*

To a 20-mL scintillation vial containing a 1 mL dichloromethane solution of dithiolate NCs, 10 equivalents of 2-phenylethanethiol were added. The equivalents were determined on the basis of the formula assigned by MALDI-MS; for samples with multiple predominant cluster nuclearities (e.g. **6** and **7**), equivalence was estimated by taking the average amount from each of the possible formulae. Each mixture was allowed to stir at room temperature for a period of up to 4 hours. $2-\mu$ L aliquots were taken at various times and mixed with a 10 mg/mL DCM solution of DCTB for analysis by MALDI-MS. An aliquot was also taken of the mixture following a storage period of 1 week at 4 °C.

Section 2: Supporting Experimental Figures



Figure D1. Detailed view of the Au25 region of the MALDI mass spectrum for NCs of **1**. Common fragments are labelled with the closest matching elements/formula.



Figure D2. MALDI mass spectrum for NCs of 2. Inset shows fragments labelled with the closest matching elements/formula.



Figure D3. MALDI mass spectrum for NCs of **3**, with an asterisk near the envelope position matching closely the formula of $Au_{52}(1,2-BDT)_{16}$ (calculated: 12,486.3 Da, observed: 12,484.83 m/z). Inset shows fragments labelled with the closest matching elements/formula.



Figure D4. MALDI mass spectrum for NCs of 4. Inset shows fragments labelled with the closest matching elements/formula



Figure D5. MALDI mass spectrum for NCs of **5**. The center of the only observable envelope, labelled in the inset at 29,915.85 m/z, matches closely with the formula for $Au_{124}S_2(DCBT)_{26}$ (calculated mass: 29,925.66 Da).



Figure D6. MALDI mass spectrum for NCs of 6. Inset shows fragments labelled with the closest matching elements/formula.



Figure D7. MALDI mass spectrum for NCs of 7. Inset shows fragments labelled with the closest matching elements/formula.



Figure D8. Diagram depicting the temperature-dependent solution phase assembly behavior of alkane dithiolate NCs.



Figure D9. Linear absorbance spectrum of crystal-pure Au₂₅(PET)₁₈ in dichloromethane.



Figure D10. Linear absorbance spectrum for NCs of 3 in dichloromethane.



Figure D11. Linear absorbance spectrum for NCs of 4 in dichloromethane.



Figure D12. Linear absorbance spectrum for NCs of 5 in dichloromethane.



Figure D13. Linear absorbance spectrum for NCs of 7 in dichloromethane.



Figure D14. Various images of the crystalline solid formed by NCs of **3**. Top: full vial views. Bottom: microscope images of a larger crystalline assembly (bottom left) and smaller microcrystals (bottom right).



Figure D15. Top: examples of the needle-like crystal growth of NCs of **3** from a saturated solution of ethanol and dichloromethane (9:1 by volume). Bottom: microscope image of the thin square-shaped crystals obtained from solvent layering of 1:1 ethanol and dichloromethane.



Figure D16. Microscope image of the microcrystalline solid formed by NCs of 5.



Figure D17. Full MALDI mass spectra resulting from the mixing of Au₂₅(PET)₁₈ with NCs of 1-7 for a total period of 1 week. Following the initial 24 hour mixing period at room temperature, each sample was stored at 4 °C until a full week had passed.



Figure D18. Comparison between the MALDI mass spectra of NCs of **1** before (bottom, black) and after (top, purple) exposure to 10 equivalents of 2-phenylethanethiol. The purple trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D19. Comparison between the MALDI mass spectra of NCs of **2** before (bottom, black) and after (top, blue) exposure to 10 equivalents of 2-phenylethanethiol. The blue trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D20. Comparison between the MALDI mass spectra of NCs of **3** before (bottom, black) and after (top, brown) exposure to 10 equivalents of 2-phenylethanethiol. The brown trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.


Figure D21. Comparison between the MALDI mass spectra of NCs of **4** before (bottom, black) and after (top, red) exposure to 10 equivalents of 2-phenylethanethiol. The red trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D22. Comparison between the MALDI mass spectra of NCs of **5** before (bottom, black) and after (top, purple) exposure to 10 equivalents of 2-phenylethanethiol. The purple trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D23. Comparison between the MALDI mass spectra of NCs of **6** before (bottom, black) and after (top, blue) exposure to 10 equivalents of 2-phenylethanethiol. The blue trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D24. Comparison between the MALDI mass spectra of NCs of **7** before (bottom, black) and after (top, green) exposure to 10 equivalents of 2-phenylethanethiol. The green trace is following an exposure time of 4 hours. Insets show the similarity between the two traces more closely. As no new peaks appear, we consider the NCs to be un-reacted.



Figure D25. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (purple trace) exposure to NCs of **1** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 12.89 Au atoms incorporated per silver NC.



Figure D26. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (brown trace) exposure to NCs of **2** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 13.09 Au atoms incorporated per silver NC.



Figure D27. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (blue trace) exposure to NCs of **3** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 13.86 Au atoms incorporated per silver NC.



Figure D28. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (green trace) exposure to NCs of **4** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 14.98 Au atoms incorporated per silver NC.



Figure D29. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (gold trace) exposure to NCs of **5** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 15.88 Au atoms incorporated per silver NC.



Figure D30. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (orange trace) exposure to NCs of **6** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 15.03 Au atoms incorporated per silver NC.



Figure D31. Comparison between the MALDI mass spectra of $Ag_{44}(DFTP)_{30}$ before (black trace) and after (pink trace) exposure to NCs of **7** after a mixing period of five minutes. Analysis of the peak envelope centers shows an average of 16.71 Au atoms incorporated per silver NC.



Figure D32. Linear absorbance spectrum of crystal-pure [PPh₄]₄[Ag₄₄(DFTP)₃₀] in dichloromethane. Matches exactly with that reported in reference 2.

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