Size control and ligand exchange of gold and palladium nanoparticles prepared by single phase method.

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SIZE CONTROL AND LIGAND EXCHANGE OF GOLD AND PALLADIUM NANOPARTICLES PREPARED BY SINGLE PHASE METHOD

by

Weijuan Jia

A Thesis
Submitted to the Faculty of Graduate Studies and Research
Through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada

2004

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Abstract

Metal nanoparticles have become important building blocks for nano-structured materials and nano-sized markers in biochemistry. This thesis focuses on the synthesis and purification of small gold and palladium nanoparticles with average diameters below 5 nm. All particles are prepared by the single-phase method without the presence of a surfactant, an important advantage over the commonly used two-phase method.

Gold and Pd nanoparticles contained inorganic impurities, mostly lithium salts, which are generated when the reaction mixture is quenched with ethanol. An acid wash procedure has been developed that successfully removes the impurities when particles are protected by stable thiol ligands. The removal of inorganic and organic impurities could be easily monitored by TGA and XPS and is discussed in Chapter 2.

Chapter 3 describes the preparation of gold nanoparticles in the presence of bulky thiol ligands. These particles have significantly smaller diameters than nanoparticles prepared in the presence of straight chain alkylthiols at otherwise identical reaction conditions. Highly stable and soluble nanoparticles are obtained with thiols based on dendrimer wedges. Their structure, size, and size distribution was investigated by XRD, HR-TEM, and UV-VIS.

Finally, first attempts to convert Pd nanoparticles into amphiphilic structures by ligand exchange reactions are described in Chapter 4. Hydrophilic and hydrophobic ligands are based on thiocic acid and its ester, respectively, and exchange ratios are estimated from quantitative analysis of FT-IR spectra. Their amphiphilic character is demonstrated in biphasic ether water mixtures.
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<tr>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>Ultra-Violet visible Spectroscopy</td>
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<td>Dichloromethane</td>
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<td>Nuclear Magnetic Resonance</td>
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<td>Surface plasmon band</td>
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<td>MNPs</td>
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<td>Face centered cubic</td>
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<tr>
<td>Thermo Gravimetric Analysis</td>
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Chapter 1. Introduction

1.1 General background

1.1.1 Nanoparticles - a general introduction

A nanoscale material is any material that has nanometer size in either three dimensions (particles), two dimensions (thin films), or one dimension (thin wires). Thus, a nanoparticle (NP) is a solid particle with a diameter between 1-1000nm. Its structure might be a single crystal, a non-crystalline material, or an aggregate of smaller crystallites. A colloid is a stable distribution of NPs in another material, usually a liquid or a glass phase.\(^1\) Particles that only consist of few to about hundred atoms are often called clusters.

NPs have attracted intense attention over the past decade because of their unique chemical and physical properties. At the beginning of the 20\(^{th}\) century, Wilhelm Oswald was the first person to put forward the concept that the surface atoms determine the properties of a NP and he also pointed out that NPs should exhibit novel properties in comparison to bulk materials.\(^1\)

One obvious reason that the reduction of size might cause a major change in properties is the increased ratio of surface atoms to bulk atoms. A particle of 300 atoms has more than 50 % of its atoms sitting at surface sites. Surface atoms are not fully integrated into the lattice of the material but interact with other atoms of the surrounding. These atoms have different energy levels and, therefore, different reactivity. It was also predicted that a description of the physical properties of NP requires quantum mechanical approaches and should differ from bulk properties because of quantum size effects.
The full development of a metallic band structure, for example, requires a minimum number of electronic levels (energy gaps between levels become very small) and electrons can move inside the material by only thermal activation. All properties that we know for a bulk metal derive from the existence of such a band: the electrical conductivity as well as the specific heat, the metallic luster, or the ductility, to cite just a few typical characteristics.

The typical band structure of a bulk material is shown in Figure 1-1 (c) and originates from a non-differentiated infinite number of s and d electrons. Most of the transition metals have unfilled d-orbitals and noble metals such as palladium, platinum, or gold have nearby s-band that can be used for electron transport. In bulk gold, the d shell is completely filled with 10 electrons, which are hidden below the Fermi level, whereas the valence shell contains a single s electron.

A particle of very few atoms has well-separated energy levels as shown in (a). Here, the highest occupied molecular orbital (HOMO) corresponds to the \( E_F \) (Fermi energy). In between these two extremes a situation as shown...
in (b) will occur, which is the typical band structure of a semi-conductor. It is the situation shown in (b), with a small gap between the occupied and un-occupied bands, for which new materials properties are predicted.

Metal particles of less than 2 nm lose the band structure to such an extent that the effects of the situation (b) can be observed. The unstructured s- and d-bands in (c) are split but without forming truly discrete levels as in (a). At this nm size range, quantum mechanical rules have to replace those of classical physics. Size dependent properties arise from a size and structure dependent delocalization of valence electrons and might be extensive. Different chemical and physical properties, such as optical and magnetic properties, melting points, surface reactivity, surface energies, as well as surface morphologies arise from these changes of the electronic structure.[2] Due to these new properties, nanomaterials have potential applications as advanced catalysts,[3] chemical sensors,[4] photochemical patterns,[5] and lithographic materials.[6] Applications of emitting NPs, quantum dots,[7] and as inert tags in biochemistry[8] are already well developed and commercial products are about to hit the market.

1.1.2 Gold NPs

Gold has been appreciated since the early beginning of mankind due to its beauty and resistivity against corrosion. Its high value and noble character, on the other hand, delayed the exploration of the chemistry of gold. Colloidal gold, however, has already been used to color glass and ceramics for more than two thousand years. A famous example is the Lycurgus Cup manufactured in the 5th to 4th century B.C. shown in Figure 1-2. Its red color originates from gold NPs (<20nm) that are doped into the glass.[9]
Modern gold chemistry might date back to 1857, when Michael Faraday reported his famous experiment in which he reduced tetrachloroaurate with white phosphorus to yield a deep-red gold colloid. Modern gold chemistry might date back to 1857, when Michael Faraday reported his famous experiment in which he reduced tetrachloroaurate with white phosphorus to yield a deep-red gold colloid.\textsuperscript{[10]} The first well-defined ligand-stabilized gold NPs, \([\text{Au}_{55}(\text{PPh})_3\text{Cl}_6]\), were prepared by Guenter Schmid in 1981.\textsuperscript{[11]} He used diborate (\(\text{B}_2\text{H}_6\)) as reducing agent that was passed through a benzene solution of \(\text{PPh}_3\text{AuCl}\) at 60 °C to give \(\text{PPh}_3\) protected gold NPs. Thirteen years later, Brust et al. reported a two-phase method for the straightforward synthesis of gold NPs.\textsuperscript{[12]} His paper had a considerable impact on the NP community as gold and other metal NPs could now be synthesized by non-specialized groups. Thus, the number of scientific studies on metal NPs increased exponentially. The advantages and shortcomings of this method are the subject of the following section 1.2, which will discuss different synthetic approaches to gold NPs. This section is followed by sections on commonly used surface passivating ligands and characterization methods for gold NPs.
1.2 Synthesis of gold NPs

A number of different ways to generate gold NPs have been developed, which can be classified into two main groups, physical and chemical methods. The chemical method uses gold (I) or gold (III) salts as starting materials that are reduced to gold (0) by a reducing agent. This reaction has been performed in two-phase and single-phase systems. Physical methods generate gold NPs via the distribution of bulk gold into small gold aggregates by techniques such as laser ablation and radiolysis.

1.2.1 Physical methods

The simplest way is to generate metal atoms in the gas phase followed by their controlled condensation to NPs, which is often regarded as metal vapor synthesis. Numerous modifications of this technique have been successfully employed in the past.

Laser ablation is the most advanced technique and has been used in the gas and liquid phase. It is based on the well expressed plasmon resonance of gold nanoparticles around 520 nm and was used to follow the size and geometry of the particles. Size distributions, however, are rather wide.

Other methods for the preparation of NPs include in seed growth, photochemical methods (UV, Near-IR), sonochemistry, radiolysis, and thermolysis. Most physical methods give wide size distributions while wet-chemistry methods allow for a better size control and are more versatile. However, it is the required properties and desired applications that often dictate what method is best suited.
1.2.2 Chemical methods

1.2.2.1 Two phase synthesis of gold NPs (the Brust-Schiffrin method)

The two-phase synthesis is one of the most common methods for the preparation of gold NPs. Typically, a gold salt (AuCl₄⁻) is first transferred from aqueous solution into the toluene phase by a phase transfer agent such as tetraoctylammonium bromide. It is then reduced by NaBH₄ in the presence of thiols (see Scheme 1-1).

Scheme 1-1 Formation of gold NPs by the two-phase method

\[ \text{AuCl}_4^- (aq) + \text{N(C}_8\text{H}_{17})_4^+ (\text{toluene}) \rightarrow \text{N(C}_8\text{H}_{17})_4^+ \text{AuCl}_4 (\text{toluene}) \]

\[ m\text{AuCl}_4 (\text{toluene}) + n\text{C}_{12}\text{H}_{25}\text{SH(toluene)} + 3\text{me}^- \rightarrow 4m\text{Cl}^- (aq) + [\text{Au}_m(\text{C}_{12}\text{H}_{25}\text{SH})_n] (\text{toluene}) \]

The generated gold NPs are usually air- and thermal-stable and can be repeatedly precipitated from and dissolved in common organic solvents. Their particle size and size distribution might be tuned by changing the reaction conditions such as thiol/gold ratio, the reductant addition rate, and the reaction temperature.²¹

An important drawback of this method is the presence of an ammonium surfactant (phase-transfer reagent) as it can not be completely removed from the nanoparticles surface after the reaction was completed. A content of 1 w% phase-transfer reagent remained in the samples even after repeated precipitations of the NPs from solution.²² This situation was even worse when dendrimeric thiols were used as ligands. Gopidas et al. reported that 5 w% phase-transfer reagent was still trapped inside gold NPs stabilized by dendritic ligands after being purified for one week by selective precipitation.²³ The phase-transfer reagent is difficult to remove as both, the quaternary ammonium cation and the bromide anion, are incorporated in the ligand shell. Br⁻ is known to have a strong specific adsorption on gold²⁴ and also provides additional electrostatic
interactions with the quaternary ammonium cations. The alkyl chains of capping ligands (thiols) and the phase-transfer reagent also interact with each other.

Cecilia A. Waters and coworkers employed Soxhlet extraction for the removal of the phase-transfer reagent.\(^{22}\) In this paper, the NPs were precipitated twice from solution, transferred into a Soxhlet thimble, and then extracted with acetone. After 12 hours of extraction only 0.011\(\text{ w}\%\) phase-transfer reagent was left behind. Therefore, this technique removes most of the phase-transfer reagent but not all. However, a fair amount of the NPs is lost as they can not be easily recovered from the thimble.

### 1.2.2.2 Single-phase method

The first single phase synthesis of gold NPs was reported in 1951.\(^{10}\) \([\text{AuCl}_4]^-\) was reduced by sodium citrate in hot aqueous solution to generate gold colloids of 15 nm to 20 nm diameter. In 1973, Frens reported the preparation of gold NPs with a wider size range by tuning the ratio of citrate to gold salt.\(^{25}\)

Citrate acts not only as reducing agent but also as protecting ligands. It is a much weaker ligand than phosphanes and thiols, which is why these particles are only stable in solution. This method is still extensively used for the preparation of gold NP when a rather loose shell of ligands is required for easy ligand exchange reactions. An important shortcoming of this method is the low gold NPs concentration (<0.01M) solution that can be achieved and the limitation to water as solvent.

M.P. Rowe et al.\(^{26}\) recently reported a single-phase synthesis for stable gold NPs protected by 1-octanethiol ligands (Au-C\(_8\)). They investigated different combinations of reducing agents (i.e., NaBH\(_4\) and LiBH\(_4\)) and solvents (i.e., ether, THF, and acetonitrile), as well as a variety of reaction conditions (i.e., reducing agent addition rate, reaction
time, equivalents of reducing agent, and concentration of reaction solution). They found that treatment of HAuCl₄ and the thiol with an excess of LiBH₄ in THF under ambient conditions produces gold nanoparticles in high yields. The advantage of this method is that the reducing agents are mild and do not react with ligands that contain ester and amide groups. The disadvantage is that the reducing agents have low solubilities in THF and ethers, which leads to NPs of wide size distributions.

Xiaogang Peng’s group[27] reported a one-phase method with surfactant. AuCl₃, Ag(CH₃COO)₂, anhydrous Cu(CH₃COO)₂, and PtCl₄ were dissolved in toluene and reduced with either tetrabutylammonium borohydride (TBAB) or its mixture with hydrazine in toluene. Fatty acids or aliphatic amines were added as ligands, not thiols. These conditions are claimed to maintain a tunable activity of both the metal precursors and the reducing reagents. The weak ligands on the surface of the as-synthesized nanocrystals also allow for ligand exchange reactions with a variety of different functional groups.

Yee et al.[28] reported a surfactant-free single-phase method that used Superhydride (lithium triethylborohydride) in THF as reducing agent. Thiol-functionalized gold and palladium NPs were prepared in only 2 h and the purification was much easier than for the two-phase method. Despite its obvious advantages, this method has been used by only few groups and will be studied in detail in this thesis.

1.3 Protecting Ligands for Gold NPs

Ligands that protect the high energy surface of a nanoparticle play a crucial role not only in the synthesis of NPs but also determine properties such as solubility. Most gold nanoparticles and some other metal NPs have been prepared in the presence of thiols that
then attach to the NP’s surface as protecting monolayer. Ligands with other functional
groups, however, also protect the gold NP sufficiently and might provide a wider range of
properties. This section will exclusively discuss gold NPs and is subdivided into 3 parts,
thiols and other sulfur ligands, non-sulfur ligands, and ligand exchange reactions,
respectively.

1.3.1 Thiols and other sulfur ligands

Mulvaney and Giersig first reported the stabilization of gold NPs with alkenethiols in
1993.\textsuperscript{[29]} In their study, gold NPs were prepared from hydrosol and then capped by
alkanethiols. From then on, thiols became the most widely used ligands. The gold-
sulfur bond is partially covalent and partially ionic and relatively strong for a self-
assembling structure.

Most gold NPs stabilized by thiols are stable solid materials with reasonable solubility
in common solvents. Gold nanoparticles stabilized by dodecanethiol can be separated
and kept as solid to do characterization.\textsuperscript{[30]} Gold NPs prepared with weak ligands such
as citrate do not form stable solids.

The stability of the Au-S bond is one of the reasons why gold NPs have become the
pioneer in the research of NPs. Another outstanding feature of gold NPs stabilized by
thiols is that they spontaneously form highly ordered super lattices if they have a narrow
size distribution.\textsuperscript{[31]}

Except that the strong Au-S bond, a number of thiols are important markers for
diagnosing inherited and acquired metabolic disturbances and diseases.\textsuperscript{[32]} (For example:

\begin{center}
\text{Cysteine}
\end{center}

\text{Cysteine} (\text{\rightharpoonup}) deficiency is involved in many syndromes, such as slower growth,
edema, liver damage, and skin lesions\textsuperscript{[33]} Total plasma homocysteine levels have been
found to be an independent risk factor for premature occlusive disease in the coronary, cerebral, and peripheral arteries, and for venous thrombosis.\textsuperscript{[34]} Gold NPs stabilized by this kind of ligands could be a good detector for thiois.

Except from simple alkyl thiols, a variety of structurally diverse organosulfur compounds have been employed for stabilizing gold NPs (e.g. $\sigma$-functionalized alkanethiolates, arenethiolates, and dialkylsulfides). Porter's group described the preparation, isolation, and characterization of 3D SAMs generated by n-octadecyl disulfide, $(C_{18}S)_2$, on the surface of gold nanoparticle. These disulfides formed monolayers on the gold NPs that were higher ordered and more crystalline than those obtained with n-octadecanethiol\textsuperscript{[35]} P.D. Beer group, reported disulfide-functionalized zinc metalloporphyrins self-assembled onto gold NPs exhibit remarkable enhanced anion binding affinities if compared to the free metalloporphyrin. The surface preorganization of optical and electrochemical group functionalized host systems offers the opportunity to prepare highly sensitive sensor materials.\textsuperscript{[36]}

Attachment of water soluble ligands might render the entire gold NP into a water soluble structure. The attachment of thiolated cyclodextrin, for example, was reported by Jian Liu group.\textsuperscript{[37]} These modified gold NPs were soluble in water and behaved as hosts towards conventional cyclodextrin guests. So, the NPs might be useful as multisided hosts in aqueous media.

Carboxylate modified gold NPs have been synthesized by the Sihai Chen group and presents another water soluble example of a NP. These mercaptosuccinic acid stabilized gold NPs are easily dispersible in water and might have potential applications in cell biology as electron microscopy marker.\textsuperscript{[38]}
Thiol ligands based on arborols, starburst polymers, and dendrimers have attracted attention recently.\cite{39} Gold NPs are either prepared as guests in a dendrimer host or dendrimer wedges with thiols at the focal point are used as large ligands. Gold NPs stabilized by dendrimer wedges show high stability and narrow size distributions.\cite{40} Polyphenylene dendrimers with 16 thiomethyl groups at the outside, on the other hand, gave bimodal size distributions.\cite{41} The small particles were mostly single crystals and the large particles consisted of multiple crystal domains. Dendritic polyaryl ether wedges with disulfide groups generated NPs that enclose large void spaces near the metal cluster. These might be used as cavities for guest molecules and could lead to NPs of high catalytic activity.\cite{42}

1.3.2 Non-sulfur ligands

**Phosphine, Phosphine oxide**

Phosphines bind to gold nearly as strongly as thiolates and were the ligand of choice for the early NP work conducted by Schmid et al. in the 1980th.\cite{10} Triphenyl phosphine in particular generated small gold NPs (<1 nm diameter) of very narrow size distributions. Phosphine stabilized NPs are also excellent precursors to functionalized NPs possessing well-defined metallic cores as they can be easily exchanged by thiols.\cite{43} The disadvantages for phosphines as ligands are the required strictly anaerobic conditions and the lower stability of solid NPs derived from them. This is why they lost their favor since the more stable and convenient thiol ligands were available as an alternative.

**Ligands with bioactivity**

Gold NPs have commercial applications such as selective bio-marker. That is why the synthesis and investigation of gold NPs for biological and medicinal applications is a
very active field of research. Gold NPs of narrow size distribution and with high
dispersion stability, particularly in a physiological milieu, have been prepared with
heterobifunctional poly (ethylene glycol) derivatives containing both mercapto and acetal
groups (α-acetal-ω mercapto-PEG).[44] Denisov's[45] group reported the preparation of
soluble monodisperse discoidal lipid/protein particles of controlled size and composition.
They obtained nanodiscs of average sizes form 9.5 to 12.8 nm and with narrow size
distributions (±3%) by varying the type of proteine. These kinds of gold NPs provided a
versatile system to study lipid-protein interactions and a promising tool for solubilization
and molecular studies of membrane components.

Nitrogen containing ligands and other ligands

Amines are rather weak ligands but are sufficient if incorporated in polymers or self-
organized as surfactants. The reduction of a gold salt by NaBH₄ in a mixture of tri-n-
octylphosphine oxide and octadecylamine at 190 °C resulted in the controlled growth of
spherical gold nanoparticles that are stable for months in toluene and formed 2D arrays.[46]
Microemulsions, copolymer micelles, reversed micelles, and membranes are other
systems based on amine containing amphiphiles that have been used to stabilize gold
NPs.[47]

Surfactants are good shape controller even though they are rather weak ligands and
facile to aggregation. Leontidis[48] prepared threadlike gold NPs by reducing a gold salt
in a solution of alkyltrimethylammonium chloride. Gold particles were generated by
photochemical reduction in a clear micellar solution. The study suggests that the
formation of threadlike gold particles occurs primarily through a combination of crystal
aggregation and specific crystal face stabilization and not through templating mechanisms.

In all the previously described cases the NPs were prepared in the presence of the ligand. The next section will describe ligand exchange reactions, an alternative approach to the attachment of ligands with different functionality.

1.3.3 Ligand exchange reactions on NPs

Monolayer protected NPs can also be prepared from monolayer protected NP precursors by ligand exchange reactions. Exchanging ligands at the NP’s surface is a straightforward and widely employed approach for the introduction of novel functionalities. The most important advantage of this approach is that conventional reaction conditions could be used for the preparation of the parent NP and ligands that would otherwise interfere with the reaction conditions (e.g. are reduced by the reducing agent) are introduced afterwards. Weaker ligands might be easily replaced by stronger ligands but equally strong ligands also cause an exchange reaction as has been shown for different thiols. The final ratio between different ligands depends on the relative stabilities and concentrations of the different ligands. A (S_N2) type associate mechanism has been suggested for thiol by thiol exchange reactions.\textsuperscript{[50]}

The ligand exchange between triphenylphosphine stabilized gold NPs and 1-pentadecamine has also been studied under a variety of conditions. The obtained NPs showed a highly ordered packing assisted by a relatively narrow size distribution.\textsuperscript{[49]}
1.4 Characterization Techniques:

Many techniques have been employed for the characterization of NPs but no single method provides a comprehensive analysis of NPs. The following parts give a brief introduction to the characterization methods that have been applied in this thesis.

1.4.1 UV-VIS Spectroscopy

Some metal NPs (colloids), such as gold, exhibit unusual optical properties that are conveniently elucidated by conventional optical spectroscopy. The use of colloidal gold as a colorant for glass dates back to the Roman's and still exhibits aesthetic, technological, and intellectual value. The color of gold NPs is generated by a phenomenon that is called surface plasmon (SP) band. It is a collective oscillation of the electron gas at the surface of a NP that is correlated with the electromagnetic field of the incoming light, i.e., the excitation of the coherent oscillation of the conduction band. The nature of the SP band was first explained by Mie in 1908. According to the Mie theory, the total cross section composed of the SP absorption and scattering is the summation of electric and magnetic oscillations. The Mie theory ascribed the plasmon band to the dipole oscillations of the free electrons in the conduction band.\[51\]

Several parameters, such as particle size and shape, the dielectric constant of the medium, and the temperature, affect the UV-vis absorption of gold colloids.

1.4.1.1 Size effect

Plasmon resonance of gold NPs is a size-dependent phenomenon. A dramatic increase in width is accompanied with the decrease of the particle size when the mean diameter is smaller than 25nm.\[52\]
Figure 1-3\textsuperscript{[52]} Absorption spectra of the gold NPs of different size: 8 nm (dash-dot line), 3.2 nm (dash line), 2.6 nm (solid line), and 1.9 nm (lowest dash line).

Step-like spectral structures are indicative of transitions to the discrete lowest unoccupied levels of the conduction band and have been observed in spectra of solutions of monodisperse Au NPs with core diameters from 1.1 to 1.9 nm.\textsuperscript{[53]}

Figure 1-4\textsuperscript{[54]} Upper frame contains spectra (normalized at 4ev) from 2.5nm diameter gold NPs. In the lower frame, several spectra of differently obtained 1.7nm gold NPs are offset from each other: (top to bottom) passivated by SC\textsubscript{6}, SC\textsubscript{12}, SC\textsubscript{18}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1-3.png}
\caption{Absorption spectra of the gold NPs of different size: 8 nm (dash-dot line), 3.2 nm (dash line), 2.6 nm (solid line), and 1.9 nm (lowest dash line).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1-4.png}
\caption{Upper frame contains spectra (normalized at 4ev) from 2.5nm diameter gold NPs. In the lower frame, several spectra of differently obtained 1.7nm gold NPs are offset from each other: (top to bottom) passivated by SC\textsubscript{6}, SC\textsubscript{12}, SC\textsubscript{18}.}
\end{figure}
1.4.1.2 The effect of the solvent refractive index

A change of the refractive index of a solvent induces a shift of the SP band. For instance, solutions of dodecanethiolate gold NPs (5.2 nm mean diameter) reveal a 8 nm shift of SP band maximum as the solvent index is varied from $n_d^{20}$ 1.33 to 1.55. This can be predicted by the Mie theory if the monolayer of alkanethiolate is included in the calculations.\textsuperscript{[53]} Thiolate ligands generate a strong ligand field interaction with the surface electron cloud.

1.4.1.3 Core charge

When electrons are transfered from a reducing agent to a metal particle, the electrons are given to the conduction band. This can cause a rise of the free electron density and, consequently, the metal plasma frequency also rises and generates a change in absorption. Shifts to higher energy are expected if there is excess electronic charge on the core, whereas electron deficiency causes shifts to lower energy.

The unique optical properties of metal NPs have found many applications, especially in biology and for sensors. Their use in optical filters, as labels for bio-macromolecules, in reversible photosensitive monochromatic glasses, for intensity enhancement in Raman spectroscopy (SER effect), for optical switching based on their large, ultrafast nonlinear optical response, and for optical trapping (or “tweezers”) based on their high polarizability has been reported.\textsuperscript{[55]} For their beauty and resilience, colloidal gold suspensions have also found numerous decorative applications.

1.4.2 X-ray diffraction (XRD)

X-ray diffraction is scattered by the electrons of a material and, therefore, diffraction patterns derived from constructive and destructive interference map electron density
profiles. The distance between scattering contrasts (regions of higher e-density) is inversely proportional to the observed scattering angle.

This behaviour is quantified by Bragg's Law. Theta \( \theta \) is the diffraction angle, \( d \) is the distance between atomic layers in a crystal, \( \lambda \) is the wavelength of the incident X-ray beam, and \( n \) is an integer.

**Scheme 1-2 Deriving Bragg's Law**

\[
AB = d \sin \theta \quad (1).
\]

Because \( AB = BC \) (2)

\[
n\lambda = 2AB = d \sin \theta \quad (3);
\]

(In order to produce a maximum, the path difference \( 2d \sin \theta \) must be equal to an integral multiple of the wavelength.)

Substituting eq. (2) in eq. (3) we have,

\[
n\lambda = 2 d \sin \theta, \quad (4) \text{(Bragg's Law.)}
\]
Diffraction methods received particular attention for the examination of gold and other metal NPs because the sample preparation is simple and no artificial impurities are introduced. Besides, the sample volume is comparatively large, so that averaged properties of the material can be evaluated. X-ray diffraction can be used to estimate the average particle size and size distribution. It also can be employed to study the microstructural characteristics, phase composition as well as other features like texture and residual stresses.

It is possible to compare the XRD results with results obtained with other methods, in particular HR-TEM (see part 1.4.3). HR-TEM visualizes individual particles and can identify internal atomic arrangements, which might be helpful for the interpretation and analysis of the diffraction patterns. Although HR-TEM permits direct imaging of atomic positions, the image-contrast is strongly dependent on the NP orientation, which makes a reliable statistical characterization of a complex NP system a difficult task. Determination of statistical bulk properties is the domain of XRD.

Two diffraction methods are widely used for a statistical analysis of NPs, the line broadening analysis (wide angle, scattering by crystalline individual particles) and the small angle scattering (periodic scattering of NP arrays). The line broadening analysis studies the shape of a diffraction peak to extract the information on crystallite size distributions, dislocation densities, point defect concentrations, and probabilities of planar defects. Small angle techniques such as grazing incidence small angle X-ray scattering and small angle neutron scattering elucidate to sizes and ordered distributions of NPs in a matrix.
The first application of the line broadening techniques was performed by Scherrer. He put forward an equation for the calculation of the particle size:\textsuperscript{[56]}

\[ L = \frac{0.94\lambda}{\beta \cos(\theta)} \]

\( L \): crystallite dimension, \( \beta \): the full width in radians subtended by the half maximum intensity width of the powder pattern peak. This method neglects the presence of crystal lattice defects, so that the entire broadening is attributed to a finite size of the crystalline domains.

As the average size and size distribution of NPs are important parameters, several other methods have been developed for and applied to the characterization of gold NPs. The Debye function analysis (DFA) is based on the calculation of individual diffraction patterns for a set of model particles, covering the range of sizes and structures that may occur in the sample. The experimental data are simulated by finding the appropriate relative weightings for these different profiles.\textsuperscript{[57]}

Gold NPs of sizes between 2-5 nm cause an evident line-broadening and possible crystal structures for these NPs are decahedra (dec), icosahedra (ico), and face centered cubic (fcc).\textsuperscript{[58]} Daniel V. Leff \textit{et al.}\textsuperscript{[59]} normalized X-ray diffraction powder patterns for samples of thiol-capped gold nanoparticles of four different sizes (shown in Figure 1-5). Particle sizes decreases from top to bottom (a-d), with the sizes and Au/SR reactant initial molar ratios being 201.6 ± 38.38, (6.0:1), 68.3 ± 3.88, (3.5:1), 29.5 ± 2.08, (3.0:1), and 15.5 ± 3.08,(2.0:1), respectively. In Figure 1-5 a,b, the (111), (200), (220), and (311) reflections are all resolved. Figure 1-5 c shows that as particle size approaches ~ 30 Å, the (200) and (111) reflections become convoluted. In fact, in Figure 1-5 d the
(200) reflection is seen as merely a shoulder of the (111) peak. From this figure, we can see that the peak broaden with smaller particle sizes.

The reliability of crystal structure analysis of NPs depends strongly on the structural models that are used for the simulation either of the reverse Fourier transform (radial electron density distribution function) or, more directly, of the measured intensity function. These structural models are adopted from theoretical predictions and probable cluster morphologies observed by HR-TEM. As an example, Figure 1-6\textsuperscript{[60]} shows three of those model clusters of similar size (1.6 nm), namely a three-shell cuboctahedron, a three-shell icosahedron, and a Marks type decahedron. It is clear that even at these small sizes, X-ray diffraction can distinguish between these ideal alternative structures.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1-5.png}
\caption{X-ray diffraction powder patterns for four different sizes of gold nanocrystals. The sizes are (a) 201.6 ± 38.3 Å, (b) 68.3 ± 3.8 Å, (c) 29.5 ± 2.0 Å, and (d) 15.5 ± 3.0 Å. Note that the resolving power of the syntheses to yield different size nanoparticles (as measured by XRD) is well within 15 Å.}
\end{figure}
Interpretations must become complex when several different crystal structures are present in sample. Wide-angle XRD measurements are dominated by larger coherent regions of structure in a sample and, therefore, an analysis of XRD data actually yields information about the distribution of domain sizes. Domain sizes, however, are only indirectly related to the size distribution of the NPs.

1.4.3 High Resolution Transmission Electron Microscopy (HR-TEM)

A TEM works much like a slide projector. A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide. These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide. TEMs work the same way except that a beam of electrons (like the light) shine through a specimen (like the slide). Whatever part is transmitted is projected onto a phosphor screen for the user to see.
TEM is definitely the most used and effective technique for the study of morphological features such as particle size, size distribution, and structure of NPs. TEM is rather suited to evaluate particle size because their determinations are not affected by the presence of structural defects. Histograms provide the size distribution of nanoparticle cores, which can give crucial information on the size dispersion of the sample.

Sample preparations are particularly important and might be difficult when nanomaterials are involved. In general, the preparation involves the distribution of very dilute particle suspensions onto carbon-coated copper grids. Another useful technique is the imbedding of NPs in a solid organic polymer, which is then sliced into very thin sections.

Typical problems are nanostructural rearrangement, aggregation, or decomposition that might be caused by the electron beam (especially at high eVs used for HR-TEM) and the preparation procedure of the samples. An inherent problem is the interpretation of three-dimensional samples from two dimensional images and the small sample sizes. Only a finite number of nanoclusters may be examined and counted, which may not be representative of the sample as a whole.
Figure 1-7. Typical HRTEM micrographs of NPs stabilized by dodecanethiol 4.1 nm sample. (a) fcc clusters, (b and c) decahedra, (d-f) multidomain particles.

Considerable studies focused on the structure of gold NPs. TEM analysis combined with matrix-assisted laser desorption ionization (MALDI) MS and theoretical calculations, suggested that a more likely structure of the Au core is a truncated octahedron. TEM can also provide a mean diameter, $d$, of the cores, which allows for the determination of the mean number of gold atoms, $N_{Au}$, in the cores: $N_{Au} = 59\,\text{nm}^{-3}(\pi/6)\,(D_{MS})^3$. These data combined with elemental analysis data that provide a Au/S ratio, allow for a calculation of the average number of S ligands. This number might also be deduced from thermogravimetric analysis (details see 1.4.4).

1.4.4 Thermo Gravimetric Analysis (TGA)

TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principal uses include measurements of a material's thermal stability and composition.
TGA is the preferred technique for estimating the total organic content of NPs and their thermal stability. Generally, the TGA curve of a NP sample reveals several weight losses during a heating range from 30 °C to 1000 °C. In the temperature range from 30-105°C, the mass might decrease due to the evaporation of remaining organic solvent and moisture that is trapped in the NPs and might account for up to 3 w%. A substantial mass loss is observed between 100 °C and 500 °C, which is attributed to the decomposition and desorption of all organic ligands. TGA measurements that have previously published, to our best knowledge, have been limited to a maximum temperature of 550 °C. We found that the temperature range between 500 °C and 1000 °C often shows a third weight loss that is caused by the evaporation of inorganic impurities (e.g. lithium salts). What remains at last is assumed to be relatively pure gold.

![Figure 1-8](image_url)  
**Figure 1-8** TGA of a crude gold NPs stabilized by dodecanethiol, Step 1 is assumed to be caused by the evaporation of organic solvents and moisture trapped in the gold NPs, Step 2 is the loss of the thiol ligands, in this case dodecanethiol, Step 3 is mostly attributed to the loss of lithium salts which were trapped in the gold NPs as concluded from the increased CO₂ and H₂O signals in MS and the reduction of the Li and oxygen signals in XPS.
TGA results combined with HR-TEM results allow for the estimation of several average properties of the NP sample. TEM contributes numbers for the average size and shape of the NP polyhedra that allow for an estimation of the average surface area and the number of gold atoms at surface sites. The ratio of organic ligands to total gold atoms is obtained from the TGA measurement. A combination of all sets of data then provides the average number of organic ligands per gold particle as well as the number of ligands per surface gold atoms.\textsuperscript{[65]}

1.4.5 Other characteristic technique

**Fourier-Transform Infrared Spectroscopy (FT-IR)**

FT-IR is a powerful technique for studying the conformations and crystallinity of alkyl chains adsorbed to NPs surfaces.\textsuperscript{[66]} In particular, the frequencies of the symmetric and antisymmetric stretching vibrations of methylene groups are known to be related to the population of trans and gauche conformers.\textsuperscript{[67]}

Long chain alkyl thiols attached to gold nanoparticles have been shown to be essentially in an all-trans (zigzag) conformation at room temperature in the solid phase, with 5-25\% of gauche defects at both inner and terminal locations. A combination of IR, NMR, and DSC studies revealed the order-disorder transitions of the alkyl chains in gold NPs depending on the temperature and the length of the alkyl chains.\textsuperscript{[68]} Shorter alkyl chains ($<\text{C}_8$) tend to be more disordered with large amounts of gauche defects present (similar to alkanes in their liquid state), while longer alkane chains ($>\text{C}_{10}$) are predominantly in the all trans zigzag conformation and have a high degree of crystallinity. The degree of crystallinity increases towards the surface of the NP as the packing density increases.

**X-ray photoelectron (XPS):**
XPS is a surface limited elemental analysis method with a penetration depth of 2-3 nm. Thus, entire particles must be of 1.5 nm core diameter or smaller to be fully measured. Larger particles do not give reliable ratios of Au to organic ligands. XPS is also sensitive to the chemical environment of the elements and has been used to study the oxidation of NPs (e.g. thiolates oxidize to sulfonates at the NP surface) and the presence of impurities.

XPS studies on small NPs to established that the Au-S bonding is comparable in 2D (Au(111) surface) and 3D (gold NP) self-assembled monolayers, even though the bonding ratios are different as discussed before. The high surface area of NP makes it easy to probe surface properties by both bulk and surface sensitive spectroscopic techniques.

Brust et al. used the binding energies of the Au 4f\(\frac{7}{2}\) (83.8 eV) and Au 4f\(\frac{5}{2}\) (87.5 eV) peaks to determine a ratio between Au\(^0\) and Au\(^1\) species. Au\(^1\) (84.9eV), however, was not found at all although about 1/3 of the gold atoms were located at the surface and bonded to thiols in these NPs. The study verifies that the gold-thiol(ate) bond does not have the character of a gold sulfide bond.

1.5 Palladium NPs

In comparison to gold NPs, very few studies are concerned with palladium NPs. Wei Lu et al. synthesized thiol-stabilized palladium NPs of different sizes and with narrow size distributions by the two-phase method and also by ligand-exchange reaction. They found that NaBH\(_4\) quickly reduces Pd (II) ions to Pd atoms, which results in the formation of amorphous Pd NPs, while ethanol reduces Pd (II) ions slowly and gives
crystalline Pd NPs. The HR-TEM images and electron diffraction patterns clearly reveal the different structures of the crystalline and amorphous Pd particles.

Quiros et al. synthesized palladium NPs in a range of 1.3-3.9 nm by using two-phase method. They claim that smaller particles are obtained when longer chain thiols are used.

1.6 Applications:

There are a lot of practical and potential applications on gold NPs. Only the hot areas are introduced below.

Biology:

Gold NPs have already found commercial applications as markers for biochemical investigations. Current areas of investigation include conjugates of gold NPs with oligonucleotides because they have the potential use of the programmability of DNA base-pairing to organize nanocrystals in space and multiple ways of providing a signature for the detection of precise DNA sequence. The group of Mirkin reported extremely sensitive colorimetric methods for the DNA analysis capable of detecting trace amounts of a particular oligonucleotide sequence. It also allowed them to distinguish between perfectly complementary DNA sequences and those that exhibit different degrees of base pair mismatches.

The recognition of proteins has been for some time the subject of research on bio-devices for diagnostics based on the interaction between gold NPs and antibody conjugates.

Catalyst:
Gold like most transition metals functions as a catalyst in different chemical reactions. It otherwise is chemically rather inert (e.g. resistant to oxidation), which is important for the long time stability of catalysts in commercial processes.

The first description the catalytic activity of bulk gold occurred at the beginning of the past century when Bone and Wheeler showed in 1906 that gold foils catalyze the combustion of dihydrogen and dioxygen to give water. The catalytic activity of Au (0) was rediscovered in 1989 when Haruta et al. reported that the oxidation of CO to CO₂, a technologically relevant reaction, could be effectively catalyzed by supported-Au (0). Moreover, it was later observed that the reaction occurs even at 200 K. It soon became apparent that the key to this success was twofold: a) the presence of gold nanoparticles in the gold catalysts and b) a strong co-catalytic role played by the support that had to be an inorganic oxide such as Fe₂O₃, TiO₂, or Co₃O₄. It also became apparent that the optimal nanocluster diameter was about 3 nm, the size at which metal nanoclusters start to exhibit quantum-size behavior.

Thin films of gold NPs have been shown to change their electrical conductivity rapidly and reproducibly in the presence of organic vapors. This effect is based on the reversible swelling of the material upon gas absorption, which leads to an increase in the spacing between the metal cores. Since the typical electron hopping conductivity in these materials depends very sensitively on this distance, the absorption of organic vapor leads to a strong decrease in electrical conductivity. This phenomenon has been exploited for the development of novel gas sensors.[75]
1.7 Goal of this thesis

The objective of this thesis was the development of a reliable preparation and characterization of gold and palladium NPs based on a single-phase method free of any surfactants. We expected the single-phase method to be superior to the two-phase method as it should produce cleaner NPs and might also allow for a better size control. We aim for NPs of average core diameters below 4 nm and of small size distribution.

Based on the optimized reaction conditions developed by a former PDF Dr. Xu for Au-C_{12} NPs, this thesis will focus on the investigation of different thiol ligands. Obtained NPs are planned to be investigated by a range of characterization methods, such as HR-TEM, XRD, TGA-MS, UV-VIS, FT-IR, NMR, and XPS. An assessment of the reliability and information content of each of the methods is expected to eventually provide a shorter list of essential characterization methods.

As long term objective, we aim for the preparation of NP surfactants by ligand exchange reactions and the investigation of their self-organizing (mesomorphism) and self-assembling properties.

Reference:


2.1 Introduction

Au NPs stabilized by straight chain alkylthiols have been widely studied but the majority of the compounds were prepared by the two-phase method as described in chapter 1.2.1.1. Only few papers have described the synthesis of Au NPs by the single-phase method[1] (chapter 1.2.3) but no systematic study has been conducted on the purity of these NPs.

We are interested in smaller than 5nm NPs for subsequent ligand exchange reactions and expected the single-phase method to be the better and cleaner approach. The avoidance of phase-transfer conditions, necessary for the two-phase method, should allow for a faster and more accurate control of the NP growth and also avoids the tedious removal of remaining phase-transfer agent from the NP’s surface.[2]

It was known that the size of the NPs can be tuned by changing the reaction temperature, the relative amounts of reagents, as well as the addition rates of thiol and reducing agent to the gold salt solution in THF.[3] Optimized conditions for the preparation of small Au NPs by the single-phase method were developed in our group by Dr. Xu for dodecanethiol ligands.

NPs in this section were prepared according to the following optimized general procedure: Thiol (2.53 mmol) was added to a THF solution of hydrogen tetrachloroauration (III) hydrate (1 mmol) and stirred for half an hour. A THF solution of Superhydride® (1 M, 15mL, 15mmol) was added to the reaction mixture via a syring
pump at a rate of 30 mL/h and the mixture was stirred for another 2 hours after the addition was completed. The reaction mixture was quenched with ethanol (dry 30 mL) and the precipitated NPs were filtered off and dried in house vacuum.

In this Chapter, we extended Dr. Xu's work and used alkylthiols of different chain length (octanethiol, dodecanethiol, and octadecanethiol) for the preparation of Au NPs and studied the properties of these particles in more detail.

**2.2 Results and discussion**

Au-C8 (Octanethiol), Au-C12 (dodecanethiol) and Au-C18 (octadecanethiol), respectively, were prepared following exactly the same procedure described above. Other work-up procedures than precipitation with ethanol were tested on two different batches of NPs but occurred to be inferior to the ethanol method because they are more time consuming and yield similar particles.

Particles were precipitated by ultracentrifugation and occurred to be purer according to TGA results, but the obtained NPs were larger than for the ethanol method. We assume the high RCF (gravitational acceleration 'g') necessary for their sedimentation caused coagulation, which might also account for the lower yields. Further tests, however, were not possible as the ultracentrifuge was no longer available. RCF can be calculated from the formula: speed (rpm) =946(RCF/R)^{1/2} (R is the diameter of centrifuge tube).

In another test, NPs were precipitated at low temperatures (4 °C), which resulted in particles of similar size as for the ethanol method. This precipitation, however, needed several days for completion and larger amounts of impurities were entrapped in NPs. Consequently, the precipitation of NPs by the addition of ethanol and subsequent separation by filtration or centrifugation appeared to be the fastest and most reliable
method. The obtained size distributions represent all NPs of each batch as no fractional precipitation was conducted. Isolated yields of dried Au NPs were typically around 60% based on the initial amount of gold salt.

TGA and XPS measurements of these particles indicated a contamination with basic inorganic impurities (see part 2.2.1) and an acid wash procedure was developed. Typically, 50 mg of NPs were partially dissolved in 20 mL THF, 0.5 M HCl\textsubscript{aq} were added until a pH = 6 was reached, and add 30mL 50% ethanol to precipitate and then filter; dissolve the filtration in 5-10ml THF and then add 30mL 50% ethanol to precipitate and then filter to get powders. Repeat the process for three times. Acetic acid was tested as a milder replacement for 0.1 M HCl\textsubscript{aq} but it did not always wash away all inorganic impurities.

Most of these impurities were removed by the acid wash, as verified by TGA and XPS measurements, and from then on the acid wash was integrated in the quenching and work-up process. Typically, the reaction solution was first quenched with 0.5 M HCl\textsubscript{aq} until the pH = 6 and then fully precipitated by the addition of ethanol.

2.2.1 TGA-MS and XPS investigations

All 3 samples showed 3 distinct weight losses (Figure 2-1) before they were washed with dilute acid. Step 1 was attributed to the evaporation of remaining organic solvents and moisture and usually accounted for 1 w\% or less. Step 2 covers the temperature range at which the thiol ligands desorb\cite{4} and the third step above 600 °C is attributed to the loss of lithium salts. The presence of Li and carbon oxides was elucidated by XPS and MS showed an increase in the CO\textsubscript{2} and OC\textsubscript{2}H\textsubscript{5} signals in the temperature range of step 3. All TGA data are summarized in Table 2-1. It is assumed that these inorganic
impurities were generated by the reaction of excess LiBE$_3$H with water and ethanol during the work-up.

![Graph showing TGA of Au-C12 before and after acid wash.](image)

**Figure 2-1** TGA of Au-C12 before and after acid wash

All TGA measurements on Au NPs described in literature have been limited to a temperature range of 30 °C to 600 °C and, consequently, the presence of inorganic impurities has never been reported. Our results show that TGA is a powerful method for determining the presence and amount of inorganic impurities when run to a temperature of 1000 °C.
Scheme 2-1 Lithium salts that might be generated in single-phase method and contaminate Au NPs

\[
\begin{align*}
H^+ + H_2O & \rightarrow OH^- + H_2 \\
Li^+ + OH^- & \rightarrow LiOH \\
LiOH + CO_2 & \rightarrow LiHCO_3 \\
H^+ + CH_3CH_2OH & \rightarrow CH_3CH_2O^- + H_2 \\
Li^+ + CH_3CH_2O^- & \rightarrow LiOCH_2CH_3
\end{align*}
\]

TGA measurements on Au-C8, -C12, and -C18 after acid wash treatment revealed only one major weight loss between 150 °C and 500 °C, which is attributed to the desorption of thiols. Very little weight losses above 600 °C were detected and indicate the absence of most of the inorganic impurities (Figure 2-1 and Table 2-1).

XPS investigations were carried out to verify our hypothesis with regard to Li based inorganic impurities in the NPs. Measurements were conducted on original samples of Au-C12 and Au-C8 as well as samples that were washed with 0.1 M HCl\text{aq} or heated to 500 °C in a stream of N\textsubscript{2} for 30 min prior to the measurement. XPS measurements were performed by Seyed Tadayyon in Peter Norton’s group at UWO. These measurements confirmed the presence of Li as well as CHO, CH (OH), and CO\textsubscript{2} species as well as the absence of any Cl and B species in the original samples. XPS signals for CH (OH) and CO\textsubscript{2} almost vanished after the particles were washed with dilute acid but the Li content remained almost unchanged. Treatment of original samples at 500 °C removes all CH and S signals but the signals for Li, CH (OH), and CO\textsubscript{2} remained unchanged. Thus, the XPS results agree with our interpretation of the TGA results.
Figure 2-2 Deconvoluted Au-signals of the XPS of the original Au-C12 sample (before acid wash)

Figure 2-3 Deconvoluted C-signals of the XPS of the original Au-C8 sample (before acid wash)
Table 2-1 TGA of Three Gold NPs Stabilized by C₈, C₁₂-, and C₁₈- Alkylthiols

<table>
<thead>
<tr>
<th>Au-C₈-b</th>
<th>AuC₁₂-b</th>
<th>Au-C₁₈-b</th>
<th>Au-C₈-a</th>
<th>AuC₁₂-a</th>
<th>Au-C₁₈-a</th>
</tr>
</thead>
<tbody>
<tr>
<td>w% loss of step 1 (integration limits in °C)</td>
<td>1.3% (30-120)</td>
<td>1.5% (30-150)</td>
<td>0% (30-200)</td>
<td>0% (30-120)</td>
<td>1.2% (30-150)</td>
</tr>
<tr>
<td>w% loss of step 2 (integration limits in °C)</td>
<td>5.7% (120-500)</td>
<td>10.5% (150-500)</td>
<td>22.1% (200-500)</td>
<td>7.0% (120-500)</td>
<td>13.8% (150-500)</td>
</tr>
<tr>
<td>w% loss of step 3 (integration limits in °C)</td>
<td>19.8% (500-1000)</td>
<td>8.6% (500-1000)</td>
<td>4.7% (500-1000)</td>
<td>0.04% (500-1000)</td>
<td>0.21% (500-1000)</td>
</tr>
<tr>
<td>Au/thiol ratio in (mol%)</td>
<td>9.80</td>
<td>6.68</td>
<td>2.50</td>
<td>9.78</td>
<td>6.65</td>
</tr>
<tr>
<td>Onset temperatures for steps 1-3 (°C)</td>
<td>80</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Core diameter (nm)</td>
<td>4.0</td>
<td>4.2</td>
<td>3.9</td>
<td>4.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Atoms in ave NPs</td>
<td>1976</td>
<td>2287</td>
<td>1831</td>
<td>1976</td>
<td>2287</td>
</tr>
<tr>
<td>No. of thiol on per NPs</td>
<td>203</td>
<td>346</td>
<td>341</td>
<td>200</td>
<td>342</td>
</tr>
<tr>
<td>No. of thiol on per nm²</td>
<td>1.01</td>
<td>1.55</td>
<td>1.78</td>
<td>1.00</td>
<td>1.55</td>
</tr>
</tbody>
</table>

b = original particles before acid wash, a = original particles after acid wash, these values are corrected for the losses of steps 1 and 2, the NP weight was set to total weight minus losses of steps 1 and 3.

Core diameter data came from the TEM images.
Atoms in ave. NPs: \(N_{Au} = 59 \text{ nm}^{-3} (\pi/6) (D_{Mg})^3\)

No. of thiol on per NPs calculated from TGA and atoms in ave.\(^3\) \((\text{TGA\% of thiol}/M_{thiol})/(\text{TGA\% of gold}/M_{gold})*\text{Atoms in ave. NPs.}\)

No. of thiol on per nm\(^2\) calculated from TGA and diameters of NPs.\(^3\) \((\text{No. of thiols on per NPs})/A_{perc}\).

Thiol to gold ratios might be calculated from the TGA data (Table 2-1) and these ratios could be used to estimate the number of thiols that are attached to each Au-NP. This estimation, however, requires information on the average size, the crystal structure, and the shape of the NPs. From the HR-TEM and XRD data, we know that the prevalent structure of the NPs is truncated octahedron. Such a NP might be constructed by adding layer by layer to a first central gold atom assuming that incomplete shells are energetically disfavored. These numbers are known as Chini’s Magic Numbers\(^5\) and obey the equation:

\[
\text{Number of atoms per shell} = 10n^2 + 2, \text{ with } n = \text{number of shell}
\]

Table 2-2 Calculated Size Related Values for Ideal Gold Clusters

<table>
<thead>
<tr>
<th>Number of shells</th>
<th>Total number of atoms</th>
<th>Number of surface atoms (last added shell)</th>
<th>% of surface atoms</th>
<th>MW (g/mol)</th>
<th>estimated diameter of gold core in nm(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1 gold atom)</td>
<td>1</td>
<td>0</td>
<td>100</td>
<td>197</td>
<td>0.24</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>12</td>
<td>92</td>
<td>256122</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>42</td>
<td>76</td>
<td>10,835</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Estimations are based on perfect fcc structure and a nearest neighbor distance of 0.278 nm (0.288 nm in bulk gold). The given diameter was averaged over the D_{111} and D_{100} cross sections.\[^5\]

Accordingly, our 4 nm NPs should consist of roughly 2000 gold atoms of which about 600 are surface atoms. The surface gold to thiol ratio on flat Au (111) surface has been shown to be exactly 3 for straight chain thiols while surface gold to thiol ratios for gold NPs varied between 1.6-2.5.\[^6\] This difference can be reasoned with gold surface atoms sitting at edges and corners of a truncated octahedron of a NP and are bond to thiolate in 2:1 and 1:1 ratios, respectively. Calculated thiol weight % values for Au-C8, -C12, and -C18 assuming surface gold to thiolate ratios of 2:1 and 3:1 are given in Table 2-3.

Comparison of these calculated data with our TGA results shows that the values found roughly agree with the predicted values for Au-C8, Au-C12, and Au-C18. The values for Au-C18 are slightly too high probably because of free thiol that is still attached to the NPs. Au-C18 has been shown to have partially crystalline areas in the aliphatic
hydrocarbon layer\textsuperscript{[7]} in contrast to the shorter chain thiolate layers, and might entrap guest ions and molecules more strongly. Also, Au-C\textsubscript{18} has the lowest solubility in ethanol of the three thiol and the particles had to be extensively washed with acetone/ethanol mixtures to remove most of the non-bond thiols.

**Table 2-3** Thiol Weight % Values for Au-C\textsubscript{8}, -C\textsubscript{12}, and -C\textsubscript{18} Assuming Surface Gold to Thiolate Ratios of 2:1 and 3:1

<table>
<thead>
<tr>
<th></th>
<th>Au-C\textsubscript{8}</th>
<th>Au-C\textsubscript{12}</th>
<th>Au-C\textsubscript{18}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight % of</td>
<td>10</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>thiol for 2:1 ratio of surface gold to thiolate\textsuperscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight % of</td>
<td>7</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>thiol for 3:1 ratio of surface gold to thiolate</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1}This number is based on the assumption that all gold surface atoms are equally bond to thiolate.

\textsuperscript{2}Example calculation: 300 x 146.3/((300 x 146.3) + (2000 x 197)) = 10

XPS results suggest a distinct loss of thiolate after acid wash but no evidence for this was found in the TGA data of Au-C\textsubscript{8} and Au-C\textsubscript{12}. We have no explanation for this disagreement and hope that additional XPS and TGA measurements will shine more light on this puzzle.
2.2.2 HR-TEM

HR-TEM measurements on all 3 original and acid washed samples were conducted by Fred Pearson at McMaster. From the images (see below) can be concluded that the majority of the particles represent single crystals of fcc structure. Some images have high enough resolution so that the shape of a truncated octahedron and the crystal lattices are visible (Figure 2-7).

TEM also revealed the presence of small numbers (< 1 %) of larger NPs that clearly show the grain boundary of twinned single crystals (Figure 2-8). Twinning or coalescence occurs during sonication of NP solutions in THF but can be reversed or suppressed if a small amount of thiol is added to the NP solution during the sonication. Coalescence is also observed during TEM measurements if electron beams of higher energy are used.\textsuperscript{[5]} These particles and also overlapping particles were not included in the average size measurements and calculations as they are believed not to be present in the sample before preparation for TEM.

Figure 2-4 HR-TEM of Au-C8 before (left) and after acid wash (middle and right)
Figure 2-5 HR-TEM of Au-C12 before (left) and after acid wash (middle and right)

Figure 2-6 HR-TEM of Au-C18 before (left) and after acid wash (middle and right was treated by plasma)
The average size of Au-C8, Au-C12, and Au-C18 is $4 \pm 1$ nm and remains the same after the acid wash treatment. The size distributions based on TEM differ slightly. Au-C12 has the narrowest distribution followed by Au-C8 and Au-C18. Larger particles that were clearly generated by coalescence of smaller particles where not counted for reasons discussed before. Images of overlapping but independent particles, as clearly seen in Figure 2-7 right, were deconvoluted and counted as individual particles. The observed size distribution of $4 \pm 1$ nm (Figure 2-9) is significant narrower then what has been reported for Au-NPs prepared by the two-phase method and, thus, occurs to be another advantage of the single-phase method.
2.2.3 UV-VIS spectroscopy in solution

The colors of NPs are due to the surface plasmon (SP) band and it is described in Chapter 1.4.1. For gold NPs, the SP band arises from interband transitions between the highly polarizable Au $5d^{10}$ band and the unoccupied states of the conduction band. The decrease in NPs size leads to a broadening of the SP band absorption as well as a decrease in intensity of the peak maximum.

In this thesis, the dependence of the NP absorption on the NP size and shape was only used as a qualitative measure for the presence of NPs and their size range. Au NPs larger than 2 nm typically have a plasmon band in the range of 500-550 nm in addition to a featureless absorption that increases monotonically towards higher energies. Au-NPs of particle sizes smaller than 2 nm do not exhibit a SP band.
All three samples showed the typical surface plasmon (SP) band at around 515-517 nm and no significant difference between the original and the acid washed NPs was observed. **Au-C12** displays a more intense and narrower SP peak than the other two NPs, which suggests the presence of larger NPs. This difference in size was not confirmed by TEM. This surprising difference in SP absorption was not studied in detail but it is known that the SP band is also affected factors such as type of surface species and solvent. However, the widths and maxima of the SP absorption bands agrees with what has been reported for Au-NPs in a size range between 3 nm and 5nm.\(^8\)
2.2.4 XRD

XRD patterns were analyzed qualitatively by comparing them to patterns available from literature. The positions of the observed broad peaks roughly agree with the diffraction pattern of bulk gold with fcc structure. Careful deconvolution of the individual peaks, however, might reveal the presence of small amounts of other gold crystal structures.

The crystallite size of these particles might be deduced from the line broadening by applying the Scherrer equation: \( D = \frac{0.9\lambda}{B\cos\theta} \). \( D \) is the diameter of the particles, \( \lambda \) is the wavelength of the X-ray beam, \( \theta \) is the diffraction angle, \( B \) is the broadening of the diffraction line measured at half its maximum intensity (radian). \( D \) values obtained from the breadth of the 111 peaks are given in Table 2-3 and were calculated with this equation. They were in agreement with TEM results for samples for Au-C18 and Au-C12 but were too small for Au-C18. A deviation from the real values is not surprising, however, as this simple equation does not distinguishes between the different factors that could cause line broadening (see Chapter 1.4.2).
Table 2-4 XRD diffraction peaks for Au-C8, -C12, -C18 NPs before (B) and after acid wash (A)

<table>
<thead>
<tr>
<th></th>
<th>111</th>
<th></th>
<th>200</th>
<th></th>
<th>220</th>
<th></th>
<th>311</th>
<th></th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b 20 dÅ</td>
<td>b 20 dÅ</td>
<td>b 20 dÅ</td>
<td>b 20 dÅ</td>
<td>b 20 dÅ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-C12 (B)</td>
<td>2.04</td>
<td>38.1</td>
<td>2.36</td>
<td>2.37</td>
<td>44.4</td>
<td>2.04</td>
<td>2.40</td>
<td>64.55</td>
<td>1.44</td>
</tr>
<tr>
<td>Au-C12(A)</td>
<td>2.02</td>
<td>38.5</td>
<td>2.33</td>
<td>2.48</td>
<td>44.4</td>
<td>2.04</td>
<td>2.32</td>
<td>64.81</td>
<td>1.44</td>
</tr>
<tr>
<td>Au-C8(B)</td>
<td>1.81</td>
<td>38.21</td>
<td>2.35</td>
<td>2.15</td>
<td>44.3</td>
<td>2.04</td>
<td>2.11</td>
<td>64.79</td>
<td>1.44</td>
</tr>
<tr>
<td>Au-C8(A)</td>
<td>1.46</td>
<td>38.4</td>
<td>2.34</td>
<td>2.56</td>
<td>44.5</td>
<td>2.02</td>
<td>2.26</td>
<td>64.5</td>
<td>1.44</td>
</tr>
<tr>
<td>Au-C18(B)</td>
<td>2.89</td>
<td>38.4</td>
<td>2.34</td>
<td>2.64</td>
<td>44.7</td>
<td>2.02</td>
<td>2.65</td>
<td>54.72</td>
<td>1.44</td>
</tr>
<tr>
<td>Au-C18(A)</td>
<td>2.80</td>
<td>38.2</td>
<td>2.35</td>
<td>2.79</td>
<td>44.4</td>
<td>2.04</td>
<td>3.12</td>
<td>65.15</td>
<td>1.43</td>
</tr>
</tbody>
</table>

**Figure 2-11** XRD diffraction patterns of Au-C8, -C12, -C18 a, before acid wash and b, after acid wash

A comparison of diffraction patterns of NPs before and after acid wash suggests that the average sizes of Au-C12 and -C18 remain constant while the average particle size of...
Au-C8 increased. This, again, disagrees with the TEM results and might have to do with, for example, more crystal defects in the Au-C8 NP that also cause a peak broadening.

2.3 Conclusions

The single-phase method, in contrast to the two-phase method, gives Au-NPs of smaller size distribution that are free of surfactant impurities. These NPs, however, contain lithium salts as impurities that originate from the quenching of excess reducing agent with ethanol. Most of these inorganic impurities could be washed away with dilute aqueous hydrochloric acid. NPs for electrochemical applications that contain only small amounts of ionic impurities should be available by this method.

HR-TEM is still the most reliable method for determining the shape, size, and size distribution of these NPs. Average size distributions obtained from TGA and XRD measurements were not always reliable, mainly because too many other factors than size influence the obtained results. TGA measurements, however, allow for a fast and quantitative determination of the amount of inorganic impurities in Au-NPs prepared by the single-phase method.

Reference:


Chapter 3. Effect of Bulkiness of Thiols on Size and Size Distribution of Au Nanoparticles

3.1. Introduction

The shape-anisotropy and packing density of thiols at the gold surface do not seem to significantly influence the size of the formed nanoparticles when the two-phase method is used. Size dependence was suggested for straight chain thiols of different length. Bulky thiols based on dendrimer wedges give nanoparticles of similar size as straight chain alkylthiols via two-phase method.[1]

Differences in shape-anisotropy and packing density of thiol ligands might affect the size and size distribution of NPs prepared by the single-phase method more significantly because of the absence of surfactant molecules and the much shorter reaction times. This chapter discusses the synthesis and characterization of gold NPs protected by branched alkylthiols, alkylthiols containing phenyl groups, and a thiol based on a 1st-generation Freche dendron (Table3-1). Also discussed is the preparation of Au NPs in THF/polyethylene glycol solutions as a solvent of higher viscosity. At the end of the chapter, we discuss the ligands exchange between bulky ligands and longchain alkylthiol ligands.

**Table 3-1. Structures of Used Thiol Ligands and Their Acronym Used Throughout This Thesis**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ligands</th>
<th>Ligand structure</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>J3</td>
<td>2-methyl-2-</td>
<td></td>
<td>Dry THF</td>
</tr>
<tr>
<td></td>
<td>propanethiol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

54
| J4   | 2-methyl-1-propanethiol | \[
\begin{align*}
\text{H}_3\text{C}-\text{C}^\text{H} \text{CH}_2\text{SH} \\
\text{CH}_3
\end{align*}
\] | Dry THF |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>J7</td>
<td>Cyclohexanethiol</td>
<td><img src="image" alt="Cyclohexanethiol" /></td>
<td>Dry THF</td>
</tr>
<tr>
<td>J9</td>
<td>Phenylmethanethiol</td>
<td><img src="image" alt="Phenylmethanethiol" /></td>
<td>Dry THF</td>
</tr>
<tr>
<td>J10</td>
<td>2-phenylethanethiol</td>
<td><img src="image" alt="2-phenylethanethiol" /></td>
<td>Dry THF</td>
</tr>
<tr>
<td>J11</td>
<td>1-dodecanethiol</td>
<td>C\text{\textsubscript{12}}\text{H}_{25}\text{SH}</td>
<td>THF and poly (ethylene glycol) dimethyl ether.</td>
</tr>
<tr>
<td>J12</td>
<td>dendrimer-like ligand</td>
<td><img src="image" alt="Dendrimer-like ligand" /></td>
<td>Dry THF</td>
</tr>
<tr>
<td>J13</td>
<td>2-methyl-2-propanethiol</td>
<td><img src="image" alt="2-methyl-2-propanethiol" /></td>
<td>THF and poly (ethylene glycol) dimethyl ether.</td>
</tr>
<tr>
<td>J14</td>
<td>2-methyl-2-propanethiol, 1-Octadecanethiol.</td>
<td>C\text{\textsubscript{18}}\text{H}_{37}\text{SH} and <img src="image" alt="2-methyl-2-propanethiol, 1-Octadecanethiol." /></td>
<td>Dry THF</td>
</tr>
</tbody>
</table>
3.2 Syntheses

The following reaction conditions were referred to all NPs preparations except as stated otherwise: thiols (2.53 mmol) were added to the solution of hydrogen tetrachloroaurate(III) hydrate (1mmol) dissolved in distilled THF. After stirred for half an hour at room temperature under the protection of argon, superhynride was added to the solution dropwise by the rate of 30ml/hour. After 2 more hours stirring, the precipitate of the NPs was filtrated and dried in vacuum.

J11, J13: The solvent is prepared by mixing 4.5 g THF and 12.5 g polyether, stirred while heated until all polyether melt to form solution. 15mL Superhydride were added to an opaque brown suspension of 1mmol HAuCl₄ in THF/polyether. The mixture turned to brown black and 0.5 molar HClₐq was added until pH = 6 was reached. The mixture was then precipitated in 30mL of ethanol, filtered off, and re-precipitated from THF solution 3 more times.

J14, 50 mg of as-prepared nanoparticles and the appropriate amount of incoming ligands were co-dissolved in 25 mL of distilled THF and stirred for 72 h. The ligand-exchanged nanoparticles were purified by centrifugation and precipitation.

Some different phenomena were observed. The colors of the dilute fresh reaction solution of gold NPs stabilized by bulky ligands are pink or yellow, whereas the solution colors of those gold NPs stabilized by long chain alkyl-ligands are red. J3 and J7 produce more insoluble particles in THF after working up. Besides, the yields of gold NPs stabilized by bulky ligands are lower than those prepared by long alkylthiol ligands.
3.3. Characterization

3.3.1. TGA measurements

TGA measurements and calculations were conducted as described in Chapter 2.2.2.1. The main results are summarized in Table 3-2. The on-set temperatures for the desorption of the thiol ligands were at around 100 °C for J3,4,7,9,10, which is significant lower than for the NPs protected by longer straight-chain thiols discussed in Chapter 2. This trend seems to follow the changes in volatility of the thiols and has also been found in NPs protected by straight-chain thiols (Chapter 2.2.1.1). More volatile thiols are easier to remove thermally.

However, it has also been reported that the binding of thiols to the gold surface changes with size. Au NPs with diameters of 4 nm or larger bind most thiols in a 3:1 ratio (3 gold atoms are bond to one thiolate), similar to what was found for thiol layers on Au(111) surfaces, while smaller NPs have ratios of 2:1 or lower. This can be explained with an increasing number of surface gold atoms that sit at edges and corners where the maximal bonding ratios are expected to be 2:1 and 1:1, respectively, because of sterical considerations. The strength of the Au-S bond is assumed to be independent of the attached organic group. In contrast, the strength of the S-C bond is expected to change with the type of organic group. Benzylic ligands are expected to break off most easily while straight-chain alkyl groups should show highest stability. This distinction is important when thermal and photochemical stabilities are compared. Thermal desorption exclusively breaks the Au-S bond while radiation breaks the S-C bond.
Table 3-2. TGA Data of Gold NPs Stabilized by Bulky Thiols

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lost step</th>
<th>T1 °C</th>
<th>J3</th>
<th>J4</th>
<th>J7</th>
<th>J9</th>
<th>J10</th>
<th>J12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before washing</td>
<td>First step</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>First step</td>
<td>90.1</td>
<td>91.1</td>
<td>95.6</td>
<td>97.3</td>
<td>114</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss 1%</td>
<td>6.24</td>
<td>4.17</td>
<td>5.80</td>
<td>5.64</td>
<td>4.51</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second step</td>
<td>T2 °C</td>
<td>639</td>
<td>709.5</td>
<td>740</td>
<td>691</td>
<td>724</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Loss 2%</td>
<td>3.26</td>
<td>6.80</td>
<td>12.40</td>
<td>4.70</td>
<td>41.53</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>After washing</td>
<td>First step</td>
<td>T1 °C</td>
<td>92.5</td>
<td>98.2</td>
<td>116</td>
<td>189</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss 1%</td>
<td>8.30</td>
<td>-</td>
<td>9.86</td>
<td>8.96</td>
<td>30.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au:S ratio</td>
<td>Molar ratio</td>
<td></td>
<td>6.5</td>
<td>9.7</td>
<td>8.0</td>
<td>9.9</td>
<td>11.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Core radius (nm)</td>
<td></td>
<td>3.5</td>
<td>3.5</td>
<td>5.8</td>
<td>3.0</td>
<td>2.6</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Atoms in ave NPs</td>
<td></td>
<td>1323</td>
<td>1323</td>
<td>6024</td>
<td>833</td>
<td>543</td>
<td>608</td>
<td></td>
</tr>
<tr>
<td>No. of thiol on per NPs</td>
<td></td>
<td>199</td>
<td>136</td>
<td>159</td>
<td>83</td>
<td>58</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>No. of thols on per nm² surface</td>
<td></td>
<td>1.29</td>
<td>0.88</td>
<td>0.38</td>
<td>0.73</td>
<td>0.68</td>
<td>1.69</td>
<td></td>
</tr>
</tbody>
</table>

NPs coagulated to bulk material during acid treatment; Acidic work-up conditions were chosen; all temperatures are on-set temperatures.

Before being washed by acid, the particles were precipitated in ethanol for three times. The ethanol washing can get rid of partial impurities. However, for different thiols, the only ethanol washing process gave different results. The amounts of entrapped inorganic impurities were low with 4-6% for all particles except for J10 that contained an unexplained record amount of 41%. At the same time, the values for gold NPs stabilized by long-chain alkylthiols were varying from 4.47-19.82%. It seems as if the gold NPs stabilized by bulky ligands contain less inorganic impurities or these impurities are more easily by the washing steps with ethanol.
The acid wash procedure could again successfully remove these inorganic impurities but compounds J3 and J7 were not stable to the acidic conditions and coagulated to macroscopic gold particles. A possible explanation for this finding might be that \( t \)-butylthiol and phenylthiol are less densely packed at the NP surface and, thus, protons can more easily protonate the thiolate ligands. Protonated ligands will more easily be desorbed and generate large holes in the protecting layer. Two or more NPs that collide where the protecting layers have partially removed are likely to coagulate to larger particles. Acetic acid was tested as a less acidic reagent but it could not remove all the impurities.

3.3.2. High resolution of transmission electron micrograph (HR-TEM) characterization

The high resolution of transmission electron micrograph and size distribution of gold nanoparticles stabilized by bulky ligands are shown in Figure 3-1. Almost half of particles of J3 are around 2nm; the bigger ones are about 5nm. For J4, the image shows that most particles diameters are about 3-4 nm; only a few particle are about 5nm size. Therefore, the size distribution of this sample (J4, 2-methyl-1-propanethiol) is narrower than that of sample J3 (2-methyl-2-propanethiol). The images were taken from the J4 samples which had been washed in diluted HCl acid show most of particles are still around 3nm, but some particles are about 5nm big, or even as big as 7nm. There are two size-distributions in the images of J9. One is about 2nm, and the other is about 4.5nm. The images of J10 shows more nanoparticles are 2-3 nm big, and the bigger nanoparticles are as large as 4-5nm.
Figure 3-1. HR-TEM images and size distribution of gold nanoparticles a, J3 before washing; b, J4 before washing; c, J4 after washing; d, J9; e, J10. The samples of J4 after washing, J9 and J10 were taken after plasma treatment.

Some samples were apparently contaminated with an organic compound of unknown structure and origin. This contamination caused a carbon deposition during the measurements and drastically decreased the contrast. Plasma treatment of the prepared copper grids eventually gave satisfactory results. This treatment, however, might also cause a coagulation of the NPs on the grid.

Another step at which coagulation might have occurred is the sonication in dilute THF solution prior to their application to the grid. This is particular for particles that have less strongly bond with thiol ligands. Recent experiments showed that insoluble particles can be partially dissolved if they are sonicated in THF that contains free thiol ligand. This result clearly demonstrates that NPs are not inert to sonication.

In conclusion, we are still not sure whether the observed size distributions reflect the original size distributions or were changed by the described treatments. Additional TEM measurements of purified and non-sonicated samples are presently conducted and will hopefully clarify some of the issues discussed above.

Despite the uncertainty of the origin of the broad size distribution, we can conclude from the TEM results that more bulky thiol ligands generate smaller NPs than aliphatic
straight-chain thiols at otherwise identical reaction conditions. The origin of this effect might lie in the steric bulk that is better accommodated by smaller particles with larger curvature and more gold surface atoms at edge and corner positions. The weaker attachment of these ligands, as suggested by TGA results, should result in a better growth control and smaller size distributions but also a larger average size, which is in contrast to what has been observed.

3.3.3. Ultraviolet-visible measurement

All new particles showed plasmon absorption bands that were much broader than for the straight alkyl thiols discussed in Chapter 2. This agrees with smaller average particle sizes and J3 and J12 should have the smallest diameters as their band is almost disappeared. J7 exhibited a plasmon band maximum at much lower energy, about 620 nm, but we have no explanation for this unusual behavior. The UV-VIS spectra of samples J3 and J7 disappeared (flat baseline) after being washed with dilute acid. This indicates coagulation to bulk gold during the washing process and gold pieces have actually been visibly observed.
Figure 3-2. Ultraviolet-visible spectra of gold NPs a) UV-vis of J3-J12; b) J3 before and after wash (saturated solution in THF)
3.3.4. X-ray powder diffraction (XRD)

The XRD patterns and data of gold NPs stabilized by bulky ligands are shown in Figure 3-3 and Table 3-2. The XRD patterns of all investigated gold NPs are similar to the pattern of an fcc structure, except for J12 that seems to be amorphous. Peaks are broadened in comparison to the straight chain alkyl thiol NPs, which again agrees with the presence of smaller NPs. Broadening, however, could also be due to the presence of crystals with different structures and an increase in the number of crystal defects. We did not attempt an accurate qualitative or quantitative estimation of how many different crystal packings (e.g. fcc, ico, and dec) are present in our samples. Normally, the fcc structure is predominant for particles of 4 nm and larger.

![Graph showing XRD patterns and intensity vs. B(nm⁻¹)]
Figure 3-3. XRD patterns of gold NPs J3, J4, J7, J9, J10, J12 (top) and patterns for J3 before and after acid wash (bottom), B=2sin(θ)/λ.

Table 3-3. XRD Results of Gold NPs Stabilized by Bulky Ligand

<table>
<thead>
<tr>
<th></th>
<th>110</th>
<th></th>
<th>111</th>
<th></th>
<th>200</th>
<th></th>
<th>220</th>
<th></th>
<th>311</th>
<th></th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WH</td>
<td>2θ</td>
<td>d A</td>
<td>WH</td>
<td>2θ</td>
<td>d A</td>
<td>WH</td>
<td>2θ</td>
<td>d A</td>
<td>WH</td>
<td>2θ</td>
</tr>
<tr>
<td>J3 B</td>
<td>1.03</td>
<td>3.05</td>
<td>29.0</td>
<td>3.36</td>
<td>38.70</td>
<td>2.32</td>
<td>/</td>
<td>2.00</td>
<td>64.45</td>
<td>1.43</td>
<td>3.08</td>
</tr>
<tr>
<td>J3 A</td>
<td>1.74</td>
<td>3.55</td>
<td>25.6</td>
<td>0.65</td>
<td>38.30</td>
<td>2.34</td>
<td>0.92</td>
<td>44.5</td>
<td>2.03</td>
<td>0.89</td>
<td>64.79</td>
</tr>
<tr>
<td>J4 B</td>
<td>0.62</td>
<td>2.78</td>
<td>31.4</td>
<td>1.58</td>
<td>38.31</td>
<td>2.35</td>
<td>2.01</td>
<td>44.2</td>
<td>2.05</td>
<td>1.33</td>
<td>64.75</td>
</tr>
<tr>
<td>J4 A</td>
<td>0.52</td>
<td>2.80</td>
<td>31.4</td>
<td>2.71</td>
<td>38.65</td>
<td>2.33</td>
<td>3.65</td>
<td>45.3</td>
<td>2.00</td>
<td>3.04</td>
<td>65.1</td>
</tr>
<tr>
<td>J7 B</td>
<td>1.19</td>
<td>3.45</td>
<td>26.3</td>
<td>1.43</td>
<td>38.55</td>
<td>2.33</td>
<td>2.85</td>
<td>43.65</td>
<td>2.04</td>
<td>1.94</td>
<td>65.16</td>
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<tr>
<td>J7 A</td>
<td>1.29</td>
<td>3.45</td>
<td>25.2</td>
<td>1.57</td>
<td>38.50</td>
<td>2.34</td>
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<tr>
<td>J9 B</td>
<td>/</td>
<td>2.11</td>
<td>38.25</td>
<td>2.35</td>
<td>2.15</td>
<td>43.4</td>
<td>2.08</td>
<td>2.35</td>
<td>65.54</td>
<td>1.42</td>
<td>/</td>
</tr>
<tr>
<td>J9 A</td>
<td>0.69</td>
<td>2.93</td>
<td>30.1</td>
<td>2.53</td>
<td>38.25</td>
<td>2.35</td>
<td>/</td>
<td>2.46</td>
<td>64.65</td>
<td>1.44</td>
<td>2.85</td>
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<tr>
<td>J10B</td>
<td>0.82</td>
<td>3.86</td>
<td>22.9</td>
<td>2.91</td>
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<td>2.35</td>
<td>2.69</td>
<td>44.40</td>
<td>2.04</td>
<td>2.75</td>
<td>64.70</td>
</tr>
<tr>
<td>J10A</td>
<td>0.43</td>
<td>2.54</td>
<td>35.2</td>
<td>2.33</td>
<td>38.45</td>
<td>2.33</td>
<td>2.63</td>
<td>43.9</td>
<td>2.06</td>
<td>2.63</td>
<td>65.15</td>
</tr>
<tr>
<td>J10A</td>
<td>0.74</td>
<td>3.86</td>
<td>23.1</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>
Note: Sign "\(/") means no peaks were observed in the experiments. D is diameter calculated by the empirical formula as explained in chapter 2.2.4. WH is peak width at half-height. B means the samples before washed by dilute acid. A means the samples were washed by dilute acid.

Sample J3 and J7 (before acid wash), showed weak and broad peaks, which suggests a small particle size. Both samples showed the diffraction pattern of bulk gold (sharp peaks) after the acid wash (Figure 3-3 bottom). Thus, XRD confirms that J3 and J7 are not stable to the acidic conditions.

The XRD patterns of samples J4, J9 were similar before and after acid wash, which confirms that these particles are not much affected by the acid treatment. XRD, in principle, is also sensitive to crystalline organic and inorganic impurities. However, J10 was the only sample that showed additional peaks, which we attributed to organic and/or inorganic impurities, and they disappeared after the acid wash treatment.

J12 is thought to be amorphous as no gold peaks were observed. The sample showed only one peak at small angles, which is not untypical for amorphous substance in the condensed state. The essential feature of the diffraction pattern of amorphous condensed matter is the presence of a ring or maximum of intensity for a certain angle of diffraction.

3.3.5. Gold NPs prepared in the presence of a polyether solvent

We prepared gold NPs stabilized by dodecanethiols in the mixed solvent of poly(ethyleneglycol) dimethyl ether and THF to study how the solvent affect the NPs size and size distribution. All the characterization of HR-TEM, UV-vis, XRD, TGA results showed as below.
Figure 3-4. HR-TEM in the presence of poly (ethyleneglycol) dimethyl ether and THF (weight ratio, 3:1) (dodecanethiol as ligand, the scale in images is 10nm)

Figure 3-5. HR-TEM of gold NPs prepared by dodecanethiol in THF (the scale in images is 10nm)
UV-vis measurements

a,

b,

Figure 3-6. UV-vis of gold nanoparticles prepared in THF and mixed solvent a, dodecanthiol as ligand b, tert-butylthiol as ligand
XRD patterns

**a,**

![Graph showing XRD patterns for gold nanoparticles in THF and mixed solvent with dodecanethiol as ligand.]

**b,**

![Graph showing XRD patterns for gold nanoparticles in mixed solvent with tert-butylthiol as ligand.]

Figure 3-7. XRD patterns of gold nanoparticles prepared in THF and mixed solvent. a, dodecanethiol as ligand. b, tert-butylthiol as ligand.
Table 3-4 Summarized data from TGA measurements for selected samples

<table>
<thead>
<tr>
<th>Ligands</th>
<th>solvent</th>
<th>Decompose T (°C)</th>
<th>Organic fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dodecanethiol</td>
<td>THF</td>
<td>216</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>polyether and THF</td>
<td>240</td>
<td>41.8</td>
</tr>
<tr>
<td>Tert-butylthiol</td>
<td>THF</td>
<td>129</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>polyether and THF</td>
<td>160</td>
<td>26.9</td>
</tr>
</tbody>
</table>

All experimental results (HR-TEM, UV-vis, and XRD) confirm that gold NPs prepared in the mixed solvent of poly(ethyleneglycol)dimethyl ether and THF are much smaller than those prepared in pure THF, but the latter have a narrower size distribution. Peaks in the XRD patterns and UV-vis spectra (plasmon absorption) are broader and HR-TEM shows smaller average particle sizes.

TGA measurements surprisingly suggest an increase in thermal stability of Au-C12-ether and Au-tert-butylthiol-ether when compared to the parent compounds. The organic content is much higher than in Au-tert-butylthiol and Au-C12, which we attribute to the smaller size. We can exclude the presence of larger amounts of polyether as EA data for J11 are consistent with the TGA values (carbon 29.68 %, hydrogen 5.32 %).

Several factors might contribute to the observed decrease in NP size. Firstly, poly(ethyleneglycol) dimethyl ether increases the viscosity of the solvent and should slow down larger gold clusters and prevent them from aggregation and coagulation during their formation. Secondly, polyethers have also been shown to function as reducing agent and an increase in the amount of reducing agent would generate smaller particles. Finally, polyethers will participate as co-ligands and consequently increase the overall concentration of effective ligands, which should also decrease the average size of the particles.
3.3.6. Exchange ligand for gold NPs:

It was demonstrated earlier that t-butylthiol and other branched alkane ligands generate smaller gold NPs than straight chain ligands at otherwise identical conditions. The drawback of the branched ligands is their much low stability and solubility. To combine both properties, an in-situ ligand exchange was attempted. (scheme 4-1) The particles were synthesized in the presence of t-butylthiol under standard conditions but octadodecanethiol was then added and stirred for 72 h before the sample was quenched by the addition of ethanol. The sample was studied by HR-TEM, UV-VIS, XRD, FT-IR, and TGA.

Scheme 3-1 Exchange ligand scheme
Figure 3-8. UV-vis spectra of gold NPs stabilized by tert-butylthiol before and after exchanged with octadecanethiol, and gold NPs stabilized by octadecanethiol.

UV-vis spectroscopy is a convenient method for the in-situ investigation of gold NPs. The gold NP stabilized by tert-butylthiol as synthesized did not have an observable plasmon absorption around 520 nm, which is indicative of particle sizes below 2 nm. Addition of octadecanethiol increased the size of the particles as a typical plasmon band occurs in the UV-vis. UV-vis suggests, however, that the average size is still smaller than for Au-C18 prepared without the aid of tert-butylthiol.

XRD of the isolated particles supports this assumption. XRD patterns of a sample that was removed before the addition of octanethiol suggest that gold NPs are either amorphous or smaller than 2nm as no gold peaks are present. Those peaks occurred after the exchange and the diffraction pattern was similar to the pattern of Au-C18.

TEM results are less conclusive as the images suggest identical bimodal size distributions for both samples (before and after exchange). One of the average sizes is around 1nm and another is around 5nm.
Quantitative IR measurements conducted by Ramon Alvarez, a PFD in Dr. Aroca’s group, revealed a thiol ratio after exchange of 95% octadecanethiol and 5% tert-butylthiol.

**XRD:**

![XRD Patterns](image)

*Figure 3-9: XRD patterns of gold NPs stabilized by tert-butylthiol before and after exchanged with octadecanethiol, and gold NPs stabilized by octadecanethiol*
Figure 3-10 HR-TEM images of gold NPs stabilized by tert-butylthiol before and after addition of octadecanethiol.

Table 3-5 TGA of before and after exchange gold NPs and gold NPs stabilized by octadecanethiol

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Decomposition T (°C)</th>
<th>Organic content</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-butyl (Au-tBu-ether)</td>
<td>175</td>
<td>27.57</td>
</tr>
<tr>
<td>Exchanged (Au-(tBu)-C18)</td>
<td>256</td>
<td>54.49</td>
</tr>
<tr>
<td>Octadodecanethiol (Au-C18)</td>
<td>260</td>
<td>37.02</td>
</tr>
</tbody>
</table>

3.3.7 Conclusions

More bulky thiols generate smaller gold NPs than straight chain alkylthiols at otherwise identical one-phase conditions. Their size distribution, however, is more disperse and particles protected by short chain branched thiols have low solubility and easily coagulate to larger particles. The dendrimer based thiol gave the best results as it
formed the smallest gold NPs in high yields and the NPs were stable as well as very soluble.

The bimodal size-distributions seen in TEM might be caused by the sample preparation. UV-VIS and XRD of these samples do not show any evidence of the presence of larger particles (>3 nm).

The gold NPs prepared in mixed solvent of poly(ethylene glycol)dimethyl ether and THF are smaller than those prepared in pure THF.

Small NPs prepared with branched alkylthiols might be stabilized in-situ by the addition of a thiol ligand that produces stable particles. The demonstrated ligand exchange of t-butylthiol to octadecanethiol resulted in an increase in NP size. However, Au-(tBu)-C18 was still of smaller average size than Au-C18 and optimized conditions might overcome this size increase.

Reference:


Chapter 4. Ligand Exchange of Pd-NPs

4.1 Introduction

A versatile and widely applied approach for derivatization and functionalization of monolayer protected metal nanoparticles is the partial or total exchange of the ligand molecules attached to previously prepared and characterized NPs by other ligand molecules. The Murray group and others could show that even comparatively strongly bond thiolates on Au-NPs are easily exchanged by other thiols. This exchange already occurs when a solution of thiol protected Au-NPs is stirred with another thiol.

The exchange is a statistical process and the relative exchange ratios depend on the structure of the thiol as well as their bonding sites. Thiols with higher surface packing density provide a better sterical protection of the thiolate and are generally more stable (e.g. bulky thiols are easily replaced by straight-chain thiols and octylthiol is easily replaced by dodecylthiol but not vice versa).

The binding site at the NP surface also influences the exchange kinetics and three separate exchange processes have been observed. This result was reasoned with terrace (100 and 111), ridge, and corner sites of a truncated octahedron. Thiols at terrace sites exchange as fast as thiols in 2D-SAMs while the ridge and corner thiols exchange much more readily.

Our aim was to turn NPs into amphiphilic building blocks by partially exchanging alkylthiol ligands with head-group and tail-group thiols that contain hydrophilic and long hydrophobic groups, respectively. Dithiols based on thioctic acid were chosen as exchange ligands (thioctObn(obnC18)2) as we expected two thiols per ligand to be more competitive in the exchange of dodecanethiol.
We use palladium NPs stabilized by dodecanethiol as parent NPs since they were smaller with a narrower size distribution and more soluble than Au NPs. The reduced thioctic acid was employed as polar head group ligand (a in Scheme 4.1) and the reduced thioctic acid ester (b in Scheme 4.1) as non-polar tail group. The syntheses of the ligands are discussed in Chapters 5 and 6.

![Scheme 4-1 Exchange for Palladium NPs a, thioctic acid dithiol; b, exchanged ligands](image)

**Scheme 4-1** Exchange for Palladium NPs a, thioctic acid dithiol; b, exchanged ligands

thioctObn(obnC18)2

4.2 Results and discussion

4.2.1 Synthesis and characterization of parent Pd NPs (Pd-C12)

Pd-C12 was prepared following the same conditions and amounts as for Au-C12 described in Chapter 2.1 except that Pd (II) acetate was used instead of HAuCl₄. TGA of Pd-C12 revealed an organic content of 17.8 w% and about 3.5 w% of inorganic impurities (Figure 4-1). Thus, Pd-C12 has a higher organic content and contained less inorganic salts than Au-C12 (10.5 w% and 8.6 w%, respectively).
A higher organic content agrees with a smaller average size of the Pd NPs, which was confirmed by TEM measurements (Figure 4-2). TEM also confirms a narrower size distribution of the Pd NPs when compared to Au-C12 (Chapter 2.2.2). XRD diffraction patterns also agree with a small particle size (Figure 4-3) as the (111) peak was very broad.

The UV-Vis absorption of Pd-C12 was shown in Figure 4-1. No plasmon band was observed in the visible wavelength range.

![UV-vis spectrum of Pd-NP stabilized by dodecanethiol in THF](image)

**Figure 4-1** UV-vis spectrum of Pd-NP stabilized by dodecanethiol in THF

Inorganic impurities attached to the Au NPs could be removed by an acid-wash procedure. Unfortunately, Pd-C12 was not stable to these conditions and formed larger NPs during the treatment. The thiolate is apparently less strongly bond to the Pd surface than to the Au surface. Light scattering suggests an increase from 2-3 nm to 3-4 nm but TEM investigations have not been completed.
Figure 4-2 TGA of palladium stabilized by dodecanethiol

**HR-TEM:**

Figure 4-3 TR-TEM images and size distribution of Pd-C12
4.2.2 Ligand Exchange of Pd-C12

First attempted was the exchange of some of the dodecylthiol ligands by thiocytic acid (a cyclic disulfide) by stirring a mixture of Pd-C$_{12}$ and thiocytic acid in THF. Surprisingly to us, no stable NPs with exchanged ligands could be isolated even though Au NPs have been prepared with thiocytic acid as ligand. In these cases, the cyclic disulfide opens up during the course of the reaction and generates two thiolate bonds.

What was observed was a change in solubility. The Pd NPs became soluble in the aqueous phase but this was apparently not based on a permanent exchange of dodecylthiol ligands by thiocytic acid ligands as the particles lost this property during workup.

Our second attempt started with the reduction of thiocytic acid to the open dithiol. Amphiphilic and stable Pd NPs that were stable in polar and non-polar organic solvents were prepared. The in-situ generated sodium dithiolate of thiocytic acid was apparently exchanging much more readily and non-reversibly as expected. Higher exchange ratios generated amphiphilic NPs that assembled at the ether water interface (Figure 4-5). Exchange ratios were estimated from FT-IR measurements as described below.
The FT-IR spectra were taken and analysed by Dr. Ramon A. Alvarez-Puebla in Dr. Ricardo Aroca’s group. Substitution of dodecylthiol by thioctic acid was quantified by integrating the $\nu$(C=O) band at 1706 cm$^{-1}$ and the $\nu$(C-H)$_{as}$ absorption centered at 2920 cm$^{-1}$. The carbonyl absorption is proportional to the content of thioctic acid while both ligands contribute to the C-H vibrational mode. The contribution of the thioctic acid to the C-H absorption was extracted from the FT-IR spectrum of the pure thioctic acid. Values used for the quantitative analysis are given in Table 4-1.

The relative amount of thioctic acid was determined to be 65.23 % (34.77% 1-dodecanethiol).
Figure 4-5 FT-IR a, dodecanthiol, b, thioctic acid dithiol, c, Pd exchanged NPs

Table 4-1 FT-IR calibration for the partial exchange of dodecylthiol by thioctic acid

<table>
<thead>
<tr>
<th></th>
<th>% acid</th>
<th>$\nu$ (C=O)</th>
<th>$\nu$ (C-H)$\text{as}$</th>
<th>$\nu$ (C=O)/$\nu$(C-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>100</td>
<td>0.9972</td>
<td>0.611</td>
<td>1.63207856</td>
</tr>
<tr>
<td>Acid: dodec</td>
<td>50</td>
<td>0.6842</td>
<td>0.9916</td>
<td>0.68999597</td>
</tr>
<tr>
<td>Pd-dodec</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(dodec +acid)</td>
<td>?</td>
<td>0.8755</td>
<td>0.8987</td>
<td>0.97418493</td>
</tr>
</tbody>
</table>
Some exploratory reactions were attempted in which two different ligands were introduced. A solution of Pd-C12, the reduced thiocytic acid, and a reduced thiocytic acid ester (thiocytic acid dithiol) in a biphasic chloroform and water mixture was stirred for three days and the NPs were isolated. The obtained Pd-NPs contained fractions of different solubility that were separated accordingly. The FT-IR spectrum of one fraction is shown below and qualitatively confirms that all three ligands are attached but a quantitative analysis is now more complex as at least two ligands contribute to any of the absorption bands. Further studies will have to quantify these exchange reactions and investigate the properties of all fractions.
4.3 Conclusion

Palladium NPs stabilized by dodecanethiol are smaller and more monodisperse than gold NPs stabilized by the same ligands that were synthesized at otherwise identical experimental conditions. The dodecylthiol layer of Pd-C12 can be partial substituted by reduced thiocytic acid (dithiol) and its esters. Exchange ratios can be quantified by IR measurements but these calculations become complex when three different ligands containing similar functional groups are attached.

Some Pd NPs show amphiphilic properties but a more detailed characterization of their properties and compositions is necessary.

Figure 4-6 FT-IR of thiocytic acid dithiol, exchanged ligands thioctObn(obnC18)2, and the Pd NPs containing both ligands and dodecanethiol.
References:


Chapter 5. Synthesis of Dendrimer Ligands

Two 1st-generation Freche type dendrimeric ligands (Sbn(obn)2 and thioctObn(obnC18)2) were synthesized roughly following published procedures (Schemes 5-1 and 5-2). The yields of all synthetic steps to Sbn(obn)2 was higher than 80 % except for the first step that yielded only 60 % of the product. The reason for the low yield in the first step was a non-optimized workup. Yields higher than 80 % might be obtained if the crude product is purified by flash column chromatography instead of recrystallization.

The preparation of thioctObn(obnC18)2 followed basically the same route but the long aliphatic side-chains suppressed crystallization and trapped impurities, which complicated the workup at times. The added excess of BrC18H37 also likes to stick to the product and is UV-invisible on TLC. It, however, could be visualized by the spary reagent. The concentration of the developing agent as well as the heating time and temperature (about 5 minutes at 110 °C) was found to be crucial for the quality of the stained TLC plate. It is advisable to run octadecylbromide as a reference on every TLC separation.

Octadecylbromide needs to be removed quantitatively as it interferes with the alkylation of the benzenediol to generate the 1st-generation dendrimer. It can be washed by the silica column with hexane as first fraction while the product does not run in hexane.

Column chromatography of HObn(obnC18)2 and its thiocic acid ester was complicated by their low solubility in DCM and toluene, the two solvents that gave optimal separations.
The cyclic disulfide of thioctObn(obnC18)2 did not easily involve in ligand exchange reactions and we therefore decided to reduce thioctObn(obnC18)2 to the open dithiol. This ring opening could be monitored visually as the disulfide is pale yellow and the dithiol is colourless. The reaction is also easily monitored by TLC and proves the complete conversion of all the starting material. Unfortunately, the dithiol is very easily oxidized back to the disulfide and can not be easily isolated. Instead of excluding all potential oxidants, especially
oxygen, we decide to reduce \textit{thioctObn(obnC18)2} in-situ during the ligand exchange reaction as described in Chapter 4.

\textbf{Scheme 5-2 Synthesizing exchange ligands:}

\begin{align*}
\text{CH}_2\text{OH} & \xrightarrow{\text{2CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{Br},\text{Cs}_2\text{CO}_3} \text{H}_3\text{C}(\text{H}_2\text{C})_{17}\text{O-O-(CH}_2\text{)}_{17}\text{CH}_3 \\
\text{CBr}_4, \text{PPh}_3 & \xrightarrow{\text{rt}} \text{H}_3\text{C}(\text{H}_2\text{C})_{17}\text{O-O-(CH}_2\text{)}_{17}\text{CH}_3 \\
& \quad \downarrow \text{DMF, 70°C} \\
& \quad \downarrow \text{Cs}_2\text{CO}_3, \text{DMF, 70°C} \\
\text{H}_3\text{C}(\text{H}_2\text{C})_{17}\text{O-O-(CH}_2\text{)}_{17}\text{CH}_3 & \xrightarrow{\text{DIC, DMAP, DCM}} \text{COOH} \\
& \quad \downarrow \text{PPh}_3, \text{H}^+ \\
& \quad \downarrow \text{H}_3\text{C}(\text{H}_2\text{C})_{17}\text{O-O-(CH}_2\text{)}_{17}\text{CH}_3 \\
& \quad \downarrow \text{86%} \\
& \quad \text{over} \\
& \quad \text{86%} \\
\end{align*}
Reference:


Chapter 6. Experiment Part

6.1 Measurements

X-ray diffraction

X-ray diffraction was performed on a Bruker D8 Discover diffractometer system with GADDS 2D-detector. The X-ray generator was operated at 40 kV and 40mA and the initial beam diameter was 0.5 mm. Cu Kα1 radiation (λ=1.54184Å) was used for the experiments. Samples were sealed in X-ray glass tubes of 0.7 to 1.5 mm diameter [X-ray glass capillaries (wall thickness 10 microns) supplied by Charles Supper Company] and run for 30 min at angles of 0°, 33° and 65°. The obtained 2D diffraction patterns were integrated and analyzed with the software package EVA.

High-Resolution Transmission Electron Microscopic Measurements

High resolution transmission electron microscopy (TEM) micrographs were taken by Fred Pearson at McMaster University on a JEOL 2010F FEG TEM/STEM at 200 eV. The TEM samples were prepared by dropping a dilute THF solution of the nanoparticles onto a carbon-coated copper grid and allowing the solvent to evaporate. Samples of nanoparticles Au-iC4, Au-Bn, Au-Ph, Au-C12(M) were treated in a plasma beam prior to the measurement to remove organic impurities of unknown origin. This treatment, however, probably caused coagulation of some particles.

TGA-MS measurements

Thermal gravimetric analysis (TGA) analysis was performed on a Mettler Toledo TGA/SDTA 851e) that was attached to a Pfeiffer Vacuum ThermostarTM mass spectrometer (mass range 1-300 amu) via a thin glass capillary. Helium (99.99) was used
as purge gas at a flow rate of 70mL/min. The applied heating method was as follows: isothermal at 30 °C for 15 min, heating from 30 °C to 500 °C at a rate of 10 °C/min, and heating from 500 °C to 1000 °C at a rate of 20°C/min. Samples of 3-5 mg were run in Alumina crucibles 70 micro L Mettler (PN ME-00024123).

UV-Visible Spectrophotometry

UV-visible absorption spectra were taken of THF and hexane solution of nanoparticles in quarts cuvettes on Agilent-A453 spectrophotometers. The reported spectral data were corrected for THF background absorption. Concentrations of the solutions depended on the solubility and were between 1g/10mL to saturated solution.

Elemental analyses

C, H, N were conducted using standard techniques. For accuracy, every sample was analyzed at least twice.

Infrared Spectroscopy (IR)

Approximately 3mg of the gold nanoparticles was mixed with approximately 100 mg of potassium bromide, and the resulting mixture was ground into a fine powder with mortar and pestle. A portion of this material was pressed into a transparent disk at 20,000 psi. The infrared spectra for quantitative measurements on ligand exchanged nanoparticles were collected in the transmission mode by Ramon.Alvarez in Dr.Ricardo Aroca’s group. The spectra were acquired over 32 scans (30secs) from which a background spectrum was subtracted. The infrared spectra of gold nanoparticles (KBr pellets) were collected over the range 400-4000cm⁻¹.
6.2 Experiments:

Chemicals

The following chemicals were used as obtained: 1-Octanethiol (Aldrich, 98.5+ %), 1-dodecanethiol (Aldrich, 98+ %), 1-octadecanethiol (Aldrich, 98 %), 2-methyl-1-propanethiol (Aldrich, 92 %), 2-methyl-2-propanethiol (Aldrich, 99 %), cyclohexanethiol (Aldrich, 97 %), thiophenol (Aldrich, 99+ %), benzylmercaptan (Aldrich, 99 %), 2-phenylethanethiol (Aldrich, 98 %), lithium triethylborohydride (Super-Hydride® Aldrich, 1.0 M in THF), hydrogen tetrachloroaurate(III)hydrate (Strem Chemicals, Inc. 99.9 %), 5-hydroxymethylbenzene-1,3-diol (Aldrich, 97 %), benzylchloride (Aldrich, 98 %), carbontetrambride (Aldrich, 98 %), thioacetic acid (Aldrich, 99 %), triphenylphosphine (Aldrich, 98 %), cesium carbonate (Aldrich, 98 %). All solvents were used as received except of THF, which was freshly distilled from sodium under nitrogen.

Synthesis and purification of nanoparticles (NPs)

The single-phase synthesis of gold and palladium NPs developed in this thesis was based on previously reported procedures.[1,2] Hydrogen tetrachloroaurate(III) hydrate (0.306 g, 1mmol) or palladium(II) acetate (0.224g, 1mmol) were dissolve in 15 mL of dry THF and stirred under Ar for 15 min. 2.53 eq. of thiol were added and the mixture was stirred for another 30 min. Superhydride® solution (1 M in THF, 15 mL, 15mmol of Superhydride) was added in 30 min via a syringe pump. The mixture was stirred for another 2 hours before the mixture was quenched by the addition of anhydrous ethanol (Aldrich, 30 mL, later 95 % ethanol or even 50 % ethanolaq was used). The sample was refrigerated for 12 hours and filtered through a 0.2 μm teflon filter. The precipitated NPs
were washed with ethanol, dissolved in THF (5 mL), and again precipitated by the addition of ethanol (30 mL). The final precipitate was collected on the filter, dried in house vacuum for 24 hours.

Alternatively, the NPs could be separated from the THF reaction solution without the addition of ethanol by ultracentrifugation. Samples were transferred into 10 mL centrifuge tubes [Beckman centrifuge tubes polyallomer (10 mL, PN:355646)] and run in a Beckman Coulter Optima TM MAX E ultracentrifuge at 45,000 rpm at 12 °C for 20 minutes. The solvent was decanted off and the pellet was dissolved in THF and centrifuged again. This procedure was repeated with deioniced water and ethanol. The final pellet was dried in house vacuum for 24 hours.

Synthetic details and deviations from the general procedure described above are given below.

**Au-C_{12} (J1)** gold NP with 1-dodecanethiol ligand (length of ligand in all trans-configuration 15.109Å)

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in 1-dodecanethiol, the solution became brown; and then added in super hydride, the solution became dark. And then precipitated from THF solution by adding ethanol. The process was repeated for three times. Yield: 72%.

**Pd-C_{12} (J2): Ligand**: 1-dodecanethiol, Palladium

After palladium (II) acetate was dissolved in THF, the solution was red; then add in 1-dodecanethiol, the solution became brown; and then added in super hydride, the solution became dark. And then precipitated from THF solution by adding ethanol. The process was repeated for three times. Yield: 94%.
Au-C₄ (J3): Ligand: 2-methyl-2-propanethiol (L=4.852Å)

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in thiol, the solution became pale yellow and opaque brown; and then added in super hydride, the solution became dark. And then precipitated in ethanol three times. Yield: 31%.


After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in thiol, the solution became yellow and then brown; and then added in super hydride, the solution became dark. And then precipitated in ethanol three times. Yield: 42%.


After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in thiol, the solution became brown; and then added in super hydride, the solution became dark. And then precipitated in ethanol three times. Yield: 93%.


After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in thiol, the solution became brown; and then added in super hydride, the solution became dark. And then precipitated in ethanol three times. Yield: 89%.

Au-C₆ (J7): Ligand: Cyclohexanethiol (4.708Å).

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in cyclohexanethiol, the solution became brown yellow; and then add in super hydride, the solution became dark. And then precipitated in ethanol three times. Yield: 35%.
**Au-Bn (J9):** Ligand: Benzyl mercaptan (4.655Å)

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in benzyl mercaptan, the solution became yellow (opaque); and then add in super hydride, the solution became yellow-white yellow-brown, dark brown-dark. And then precipitated in ethanol three times. Yield:56%.

**Au-Ph (J10):** Ligand: 2-Phenylethanethiol (5.224Å)

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then add in 2-Phenylethanethiol the solution became yellow (opaque); and then add in super hydride, the solution became yellow-white yellow-brown-brown dark-dark. And then precipitated in ethanol three times.

**Au-C_{12}(M) J11:** Ligand: dodecanthiol

The solvent is prepared by mixing 4.5 g THF and 12.5 g polyether, stirred while heated until all polyether melt to form solution. Weight about 1mmol HAuCl₄ in, and then add 2.53 dodecanthiol then from opaque brown mixture, And then added 15ml superhydride, then form much bubbles, then the mixture turned to brown black mixture, followed to neutron to PH=6. Then put in ethanol, precipitate three times.

**Au-Den (J12):** Ligand, self-synthesized dendrimer (3, 5-Bis-benzyloxy-phenyl)-methanethiol

After hydrogen tetrachloroaurate (III) hydrate was dissolved in THF, the solution was golden; then added in dendrimer, the solution became brown, and then added in super hydride, the solution became dark. And then precipitated in ethanol three times.

**Au-tC₄, (J13):** Ligand, tert-butylthiol
The solvent is prepared by mixing 4.5 g THF and 12.5 g polyether, stirred while heated until all polyether melt to form solution. Weight about 1mmol HAuCl₄ in, and then add 2.53 tert-butylthioil then from opaque brown mixture, And then added 15ml superhydride, then form much bubbles, then the mixture turned to brown black mixture, followed to neutron to pH=6. Then put in ethanol, precipitate three times.

J14, exchange tert-butylthiol with octadecanethiol.

50 mg of “as-prepared” nanoparticles and the appropriate amount of incoming ligands were co-dissolved in 25 mL of distilled THF and stirred for 72 h. The place-exchanged nanoparticles were purified by centrifuge and precipitation.

Purification process:

50 mg of “as-prepared” gold NPs was dissolved in 10ml THF, stir for a moment, and then add 30ml 50% ethanol, add dilute hydrochloride acid (0.5M) until PH~6.

Place-Exchange Reactions

In a typical place-exchange reaction, 50 mg of nanoparticles and the appropriate amount of incoming ligands were co-dissolved in 25 mL of distilled THF and stirred for 72 h. The ligands exchanged nanoparticles were purified by centrifuge and precipitation. Different reaction solvents are tried. 50 mg of NPs was dissolved in chloroform, the appropriate amount of incoming ligands was dissolved in NaHCO₃ (10% aq), and then added to the NPs solution.

6.3 Synthesis of dendritic thiol ligands

Dentrimer:

(3, 5-bis-benzylxy-phenyl)methanol
To a flask with a mixture of 5-hydroxymethyl-benzene-1,3-diol (3 g, 0.0214 mol) and potassium carbonate (7.39 g, 0.0535 mol) in 100 mL dry DMF was added benzyl chloride (6.23 g, 0.04922 mol). The reactant mixture was heated at 60 °C under argon for 20 hours. Insoluble products such as KCl were filtered off and washed with toluene (3 x 10 mL). The combined organic phase was extracted with water (3 x 40mL) to remove DMF and salts and then dried over MgSO₄. Evaporation of the solvent in vacuum yielded the crude product as a yellow solid, which was subject to flash column chromatography (silica gel 60 Å, 230-400 mesh) using toluene as eluant to afford the pure product as a white solid? (4.11 g, 61 % yield).

Rᵣ = 0.4 (toluene). ¹H-NMR (CDCl₃, 500 MHz), δ (ppm): 1.7 (1H, t, OH), 4.64 (2H, d, H-a), 5.05 (4H, s, H-b), 6.63 (1H, s, H-d), 6.64 (2H, s, H-c), 7.26-7.42 (10H, m, H-g, h, i),

\[
\begin{align*}
\text{1,3-Bis-benzyloxy-5-bromomethyl-benzene:} \\
(3,5-\text{Bis-benzyloxy-phenyl})\text{methanol (1.5 g, 3.91 mmol), carbon tetrabromide (1.62 g, 4.89mmol), and triphenylphosphine (1.28 g, 4.89 mmol) were dissolved in dried THF (30 mL) and stirred at room temperature under argon for 1hour. Solid precipitate was filtered off and washed with THF. The combined organic phase was evaporated in vacuo to give}
\end{align*}
\]
the crude product as yellow solid which was subject to flash column chromatography (silica gel 60 A, 230-400 mesh) using toluene as an eluant to afford the pure product as a white solid? (1.24 g, 91% yield).

\[ R_f = 0.65. \]

\[ ^1H \text{NMR (CDCl}_3, 500MHz), \delta \text{ 4.42 (2H, s, H-a), 85.04 (4H, s, H-b), } \delta \text{ 6.65(2H, s, H-c), } \delta \text{ 6.56 (1H, s, H-d), } \delta=7.26-7.43 \text{ (10H, m, H-g, h, i); } ^{13}C \text{NMR (CDCl}_3, 833.737 \text{ (C-a), 70.388} \text{ (C-b), 102.421} \text{ (C-d), 108.390 (C-c), 127.742} \text{ (C-g), 128.810(C-h), 128.264(C-i), 136.837 (C-e), 139.980 (C-j), 160.289 (C-f),} \]

\[ \text{Thioacetic acid 3,5-bis-benzyloxybenzyl ester} \]

To a solution of 1,3-bis-benzyloxy-5-bromomethyl-benzene (1 g, 2.61 mmol) in dry DMF (20mL) was added thioacetic acid (0.30g, 3.91 mmol), and then cesium carbonate (1.27g, 3.91mmol). The reaction mixture was stirred at 60 °C under argon for 3 hours. Insoluble solid was filtered off, washed with toluene (3 x 10mL), and the combined organic phase was extracted with water (3 x 40mL). The organic phase was dried over MgSO$_4$, the solvent was removed in vacuum to yield the crude product as a yellow solid/oil?, which was subject to flash column chromatography (silica gel 60 A, 230-400 mesh) using toluene as an eluant to afford the pure product as yellow oil.( 0.78 g, 80 % yield ).
H-NMR (CDCl₃), δ 2.35 (3H, s, H-a), δ 4.06 (2H, s, H-b), δ 5.01 (4H, s, H-c), δ 6.55 (2H, s, H-d), δ 6.54 (1H, s, H-e), δ 7.39-7.41 (10H, m, H-f);

(3, 5-Bis-benzyloxy-phenyl)-methanethiol

To a flask with thioacetic acid 3, 5-bis-benzyloxy-benzyl ester (0.5g, 1.32mmol) was added dropwise lithium aluminum hydride solution (concentration, solvent, 0.060g, 1.58 mmol) in 10mL of dry ether via syringe over 10 min. The reactant mixture was further stirred for 30min. The insoluble solid was filtered off and the organic phase was concentrated through rotary evaporator in vacuo. The crude product residue was subject to flash column chromatography (silica gel 60A, 230-400 mesh) using toluene as an eluant to afford the pure product (0.41g, 92% yield). Rf = 0.8. ¹H NMR (CDCl₃),
δ1.75-1.80 (1H, t, H-a), δ3.67, 3.70 (2H, d, H-b), δ5.04 (4H, s, H-c), δ6.60 (2H, s, H-d), δ6.53 (1H, s, H-e), δ7.32-7.45 (10H, m, H-f). ¹³C NMR (CDCl₃), δ 29.286 (C-a); 70.174 (C-e); 100.803 (C-d); 107.297 (C-c); 127.616 (C-g); 128.658 (C-h); 128.087 (C-i); 136.853 (C-j) 143.509 (C-b); 160.184 (C-f).

ESI-MS calcd: 336, found: 336.05, 30%; 181.10, 22.5%; 91.10, 97.5%; 65.00, 12.5%.

**Exchange ligands synthetic procedures:**

**3,5-bis-octadecyloxy-phenyl) methanol**

To a flask with 5-hydroxymethyl-benzene-1, 3-diol (1.34g, 9.56mmol), bromooctadecane (7.97g, 0.023mmol), Cs₂CO₃ (7.79g, 0.023mol) was added dry 30mL of DMF; the reaction mixture was heated at 100°C for 24 hours under the protection of argon. The insoluble solid was filtered off and washed with toluene (10mL) for three times. The organic phase was collected and then washed by water (40mL) for three times, dried by anhydrous MgSO₄. The solvent was removed by rotary evaporation and the crude product residue was subject to flash column chromatography (silica gel 60A, 230-400 mesh) using hexane and ethyl acetate (v/v =7:1) as an eluant to afford the pure product (4.81 g, 78% yield). Excess of bromooctadecane was first removed by washing the column with hexane.

Rₜ = 0.05 (hexane:ethyl acetate = 5:1 V/V).
$^1$H NMR (CDCl₃, 500Hz), δ 0.86-0.90 (6H, m, H-h), δ 1.23-1.31 (56H, m, H-e), δ 3.90-3.95 (4H, t, H-b), δ 4.19 (4H, m, H-d), δ 4.41 (2H, s, H-a), δ 4.32 (4H, H-c), δ 6.52 (2H, m, H-f), δ 6.38 (1H, H-g); $^{13}$C NMR (CDCl₃), δ 14.80 (C-h), 25.71 (C-d), 29.11 (C-c), 30.29 (C-e), 69.1 (C-a), 73.01 (C-b), 98.8 (C-j), 104.46 (C-f), 142.84 (C-i), 159.6 (C-g).

1-Bromomethyl-3,5-bis-octadecyloxy-benzene

To a round bottom flask with (3, 5-bis-octadecyloxy-phenyl) methanol (2g, 3.1mmol), carbon tetrabromide (1.39g, 4.18mmol) and triphenylphosphine (1.10g, 4.18mmol) was added dried THF (30mL), the mixture was stirred at room temperature for 1 hour under argon. The solid was filtered off and washed with THF. The organic phase was combined. The solvent was removed by rotary evaporation in vacuo. The crude product residue was subject to flash column chromatography (silica gel 60A, 230-400 mesh) using hexane and ethyl acetate (V/V=7:1) as an eluant to afford the pure product (1.97 g, 90% yield). Rf = 0.7 (hexane: ethyl acetate = 7:1 V/V). $^1$HNMR (CDCl₃, 500Hz),

![Diagram of 1-Bromomethyl-3,5-bis-octadecyloxy-benzene](image)

δ 1.26-1.33 (60H, m, H-d), δ 3.90 (4H, t, H-b), δ 4.41 (2H, s, H-a), δ 4.27 (4H, H-c), δ 6.52 (2H, H-f), δ 6.38 (1H, H-g); $^{13}$C NMR (CDCl₃), δ 14.80 (C-h), δ 26.37 (C-d), δ 29.90 (C-c), 68.806 (C-a), δ 77.26 (C-b), δ 98.76 (C-g), δ 105.79 (C-f), δ 140.28 (C-i), δ 161.110 (C-j),

3,5-Bis-(3,5-bis-octadecyloxy-benzyloxy)-phenyl-methanol
To the flask with 1-bromomethyl-3, 5-bis-octadecyloxy-benzene (1.5g, 2.1mmol), 1-bromomethyl-3, 5-bis-octadecyloxy-benzene (0.15g, 1mmol) and Cs$_2$CO$_3$ (7.05g, 2.1mol) was added dry DMF (30mL). The reaction mixture was heated at 100°C for 72 hours under argon. The insoluble inorganic salts was filtered and washed with 10mL of toluene for three times. The organic phase was collected and washed with 40mL water for three times, dried by anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the residue was subject to flash chromatographic column first using hexane/DCM (3:1) to wash away the bromo-generation 1 and PPh$_3$. And then toluene/ethyl acetate (8:1) as eluants to afford the pure product (1.17g, 70% yield). $R_f = 0.86$ (toluene/ethyl acetate = 8:1, V/V). ^1HNMR (CDCl$_3$, 500 Hz),

$$
\begin{align*}
\delta & 0.89 (12H, t, H-k), \delta 1.31 (112H, m, H-f), \delta 1.44 (8H, m, H-e), \delta 1.78 (8H, t, H-d), \delta 3.92-3.95 (8H, t, H-c), \delta 4.71 (2H, d, H-a), \delta 4.95 (4H, s, H-b), \delta 6.45 (3H, m, H-h), \\
& \delta 6.55 (4H, s, H-g), \delta 6.61 (2H, m, H-i),
\end{align*}
$$

4, 5-[1, 2] dithiolan-3-yl-pentanoic acid 3, 5-bis-(3,5-bis-octadecyloxy-benzyloxy)-benzyl ester

To a flask with a mixture of 3, 5-bis-(3,5-bis-octadecyloxy-benzyloxy)-phenyl]-methanol (0.5g 0.36mmol) and thiocic acid (5-[1,2]Dithiolan-3-yl-pentanoic acid)
(0.088g, 0.43mmol) in dry DCM was added 1,3-diisopropyl carbodiimide (DIC) (0.027g mmol) and then 4-(dimethylamino)-pyridine (DMAP) (trace). The reactant mixture was stirred at room temperature for 1 hour. The insoluble solid was filtered off and the solvent of organic phase was removed by rotary evaporation and the residue was subject to flash chromatographic column using hexane and dichloromethane (V/V = 2:1) to afford pure product (0.46 g, 86% yield). R<sub>f</sub> = 0.5 (hexane/dichloromethane=2:1, V/V),<sup>1</sup>H-NMR (CDCl<sub>3</sub>), δ 0.88 (12H, t, H-f), δ 1.34 (120H, m, H-e), δ1.44 (8H, m, H-d), δ 1.56 (6H, m, H-k, m, l), δ 2.23 (2H, t, H-j), δ 2.45 (4H, m, H-o, j), δ 3.156 (2H, m, H-p), δ 3.56 (1H, H-n), δ 3.94 (8H, t, H-c), δ 4.94 (4H, s, H-b), δ 5.04 (2H, s, H-a), δ 6.40-6.58 (9H, m, H-g, h, i);

<sup>13</sup>C NMR (CDCl<sub>3</sub>),
δ 22.681 (C-t), δ 24.667 (C-k), δ 26.081 (C-l), δ 29.692 (C-d), δ 31.925 (C-s), δ 32.692 (C-e, f), δ34.053 (C-j), δ 34.579 (C-m), δ 38.470 (C-p), δ 40.170 (C-o), δ 56.291 (C-n), δ 60.574 (C-q), δ66.00 (C-c), δ 68.134 (C-b), δ 70.234 (C-a), δ 101.783 (C-g), δ 100.912 (C-g), δ 105.806 (C-i), δ 138.884 C-w), δ 160.134 (C-r), δ 173.178 (C-v).
6,8-Dimercapto-octanoic acid 3,5-bis-(3,5-bis-octadecyloxy-benzyloxy)-benzyl ester

To a flask with a mixture of 5-(1, 2) dithiolan-3-yl-pentanoic acid 3,5-bis-(3,5-bis-octadecyloxy-benzyloxy)-benzyl ester (0.3g), triphenyl phosphine (0.067g) in 1,4-dioxane and water (V/V = 1:1) was added one drop of concentrated hydrochloric acid. The reactant mixture was stirred for 2 hours at room temperature. The solvent was partly removed by rotary evaporation and ether was added to extract the product for two times. The organic phase was combined and washed with water for two times, dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporation in vacuo. The crude product residue was subject to flash column chromatography (silica gel 60A, 230-400 mesh) using dichloromethane, and then ethyl acetate and dichloromethane (V/V=3:2) as an eluant to afford the pure product. Rf = 0.3 (acetate/dichloromethane = 3:2, V/V). The product is easily oxidized back to the disulfide and no clean NMR spectrum was obtained. The \(^1\text{H}\) NMR 3-4 multi-peaks of starting materials will disappear when it turned to be dithiol.

Thioctic acid dithiol (6,8-dimercapto-octanoic acid):

The reduction of thiotic acid to dithiol:

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} \\
\text{\textbullet 4 SH} & \quad \text{\textbullet 4 SH} \\
\text{dioxane, } \text{H}_2\text{O} & \quad \text{dioxane, } \text{H}_2\text{O}
\end{align*}
\]

To a flask with a solution of thioctic acid (0.412g, 0.002mol) in dioxane (10mL) and H\(_2\)O (10mL) was added, triphenyl phosphine (0.786g, 0.004mol) and a drop of concentrated hydrochloric acid. The reactant mixture was stirred for 3 hours at room
temperature under argon. The solvent was partly removed by rotary evaporation and then ether was added to extract the product for two times. The ether phase was collected and combined, washed with water for two times, dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporation in vacuo. The crude product residue was subject to flash column chromatography (silica gel 60A, 230-400 mesh) using dichloromethane, and then ethyl acetate and dichloromethane (V/V=3:2) as an eluant to afford the pure product (72 % yield). Rf = 0.3 (acetate/dichloromethane = 3:2, V/V).

$^1$HNMR (CDCl$_3$), δ 1.29 (2H, m, H-c), δ 1.59 (6H, m, H-b, d, h), δ 1.86 (2H, m, H-f), δ 2.3 (2H, t, H-a), δ 2.93 (1H, m, H-e), δ 2.57 (2H, m, H-g);

$^{13}$CNMR (CDCl$_3$), δ 22.456 (C-g), δ 24.491(C-b), δ 26.636 (C-c), δ 34.094 (C-a), δ 38.864(C-d), δ 39.472(C-e), δ 42.094(C-f), δ 179.968 (C-h).
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