

Ligand Exchange Reactions Yield Subnanometer, Thiol-Stabilized Gold Particles with Defined Optical Transitions

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A convenient preparation is reported for a series of functionalized, thiol-stabilized gold particles with *subnanometer* core diameters ($d_{\text{CORE}} = 0.8 \pm 0.2$ nm). The preparation produces previously inaccessible materials through ligand exchange reactions of a phosphine-stabilized precursor, $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_3$, with ω -functionalized alkanethiols. Convenient access to these new materials is a prerequisite to the detailed study of the electronic and optical properties of subnanometer particles and the investigation of the utility of these building blocks in nanoscale devices. Preliminary investigations of the optical properties of these new materials by UV–vis spectroscopy revealed that the particles have defined optical transitions. These results confirm the presence of discrete energy levels in the electronic structure of these materials that might be expected due to quantum size effects. Initial studies also suggest that the optical properties depend on the nature of the stabilizing ligand shell. The ligand exchange method described is applicable for a diverse family of alkanethiols to produce both organic- and water-soluble particles that show increased stability over the phosphine-stabilized precursor. Extensive characterization indicates that the thiol-stabilized exchange products have well-defined core sizes and dispersities.

The size-dependent properties, for example, electronic and optical phenomena such as single-electron charging and quantum size effects, in metal and semiconductor nanoparticles are fundamentally interesting and, in many cases, useful in technological applications.^{1–5} Fundamental studies of metal nanoparticle properties have provided insight into the evolution of properties with increasing particle dimension, ranging from molecular compounds to metals.^{6–8} Recent applications that take advantage of the size-dependent properties of metal nanoparticle materials include catalysis,^{9,10} sensing,^{11–13} and electronics.^{4,14–16} However, nearly all of these studies employ metallic nanoparticles with core diameters greater than 1–2 nm. Although the properties and applications of particles with core diameters in the range of one to tens of nanometers have been extensively studied, the materials properties and applications of particles with subnanometer core diameters have not been widely investigated. Metal particles with core diameters smaller than 1 nm are of considerable interest because they are small enough to possess discrete electronic states^{17,18} (and thus may exhibit electronic quantum confinement^{9,19,20} useful for nanoelectronic, catalytic, or sensing applications) not found in larger particles.

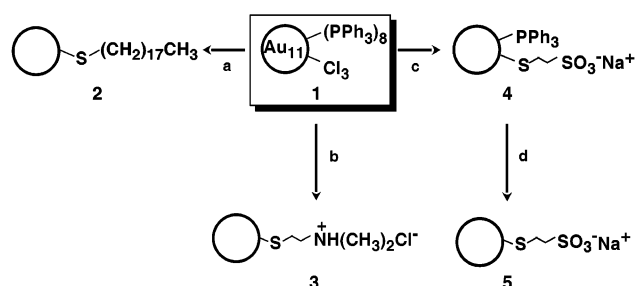
Although transition metal *clusters* (smaller than the widely studied nanoparticles, possessing typically less than 10–20 metal atoms) have been widely investigated as coordination complexes,^{21,22} potential homogeneous catalysts,^{23,24} and biotagants,^{25–28} convenient methods for their chemical modification and use as building blocks for nanoscale assemblies are virtually unexplored. This may be due, in some cases, to limited particle stability and because the vast majority of the known cluster compounds are stabilized by capping ligands that do not possess the functionality necessary to organize the particles through functional group directed assembly. Here, we describe a

convenient preparation of stable, externally functionalized, thiol-stabilized nanoparticles with an average core diameter of 0.8 nm based upon the undecagold (Au_{11}) core.

Phosphine-stabilized undecagold derivatives have been widely investigated because of their use as labeling reagent for biomolecules in electron microscopy.^{26–28} Peripherally functionalized undecagold derivatives have been reported, but the synthetic methods involve multistep syntheses, challenging purification, or both.^{29–31} In the case of the larger gold nanoparticles, thiol ligands have proven generally useful as ligands that can simultaneously stabilize and further functionalize the particles;^{5,32–36} thus, we have been exploring methods to prepare thiol-stabilized *undecagold* clusters. One can envision two approaches to preparing ω -functionalized, thiol-stabilized gold clusters with subnanometer cores⁵—direct synthesis of the core in the presence of a functionalized ligand or ligand exchange of a functional ligand for an inert capping ligand. Thus far, direct synthesis of thiol-stabilized subnanometer gold particles has not been possible. Ligand exchange, although a powerful method in the preparation of functionalized derivatives of larger particles,^{5,35,36} has been limited in the case of subnanometer clusters mostly to ligand exchange reactions that introduce functionalized phosphines in the place of inert ligands.³⁷

Given the large number of small transition metal clusters that have been prepared (and are therefore potentially ligand exchange precursors), development of general ligand exchange strategies that permit introduction of peripheral functionality would offer access to a wide range of new nanoparticle building blocks. The results of our initial attempts to extend the ligand exchange method that we previously described for 1.5 nm phosphine-stabilized gold nanoparticles to undecagold were surprising; there was no reaction under the same conditions. Apparently, the undecagold clusters are considerably less reactive than their larger analogues.

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SCHEME 1^a

^a Conditions: (a) ligand exchange of **1** in CHCl_3 at 55°C with excess octadecanethiol produces the thiol-stabilized particle **2**; (b) interfacial ($\text{CHCl}_3/\text{H}_2\text{O}$) ligand exchange of **1** at 55°C with (*N,N*-dimethylamino)ethanethiol hydrochloride produces the cationic thiol-stabilized particle **3** in a single step; (c) interfacial ($\text{CHCl}_3/\text{H}_2\text{O}$) ligand exchange of **1** at 55°C with sodium 2-mercaptoethanesulfonate (MESA) produces the anionic particle **4**, which contains a mixed ligand shell; (d) treatment of **4** with excess MESA in 1:1 THF/ H_2O yields particle **5** containing only MESA in the ligand shell.

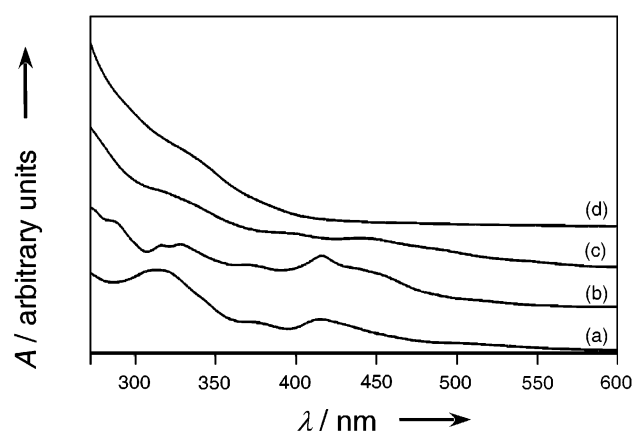


Figure 1. UV-visible spectra of (a) triphenylphosphine-stabilized undecagold particle **1**, (b) octadecanethiol-stabilized undecagold particle **2**, (c) (*N,N*-dimethylamino)ethanethiol-functionalized undecagold particle **3**, and (d) fully 2-mercaptoethanesulfonate-stabilized undecagold particle **5**.

Herein, we demonstrate a general method to exchange phosphine-stabilized undecagold precursors with thiols to convert “inert” (i.e., without peripheral functionalization) particles into functionalized subnanometer building blocks. These can be used to make materials via functional group directed assembly processes. The ligand exchange strategy provides convenient access to a diverse family of previously inaccessible thiol-stabilized Au particles (Scheme 1) from a single, easily prepared precursor, $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_3$ (**1**). The products of these exchange reactions possess the same core size yet are considerably more stable than the phosphine-stabilized parent.

Precursor **1**, prepared using a modification of the procedure described by Bartlett et al.,²⁵ is a molecular and thus monodisperse species. The chemical composition and purity of **1** was established using an array of analytical techniques.³⁸ UV-visible spectroscopy showed the signature peaks of a Au_{11} core (Figure 1, trace a), and transmission electron microscopy (TEM) confirmed a metal core diameter of 0.8 ± 0.2 nm.³⁸

Particle **1** undergoes controlled ligand exchange with a variety of thiols to produce both organic- and water-soluble nanoparticles. Three representative examples that demonstrate the scope of the method are shown in Scheme 1, including an exchange with octadecanethiol (ODT) to form the organic-soluble particle **2** and with *N,N*-dimethylaminoethanethiol (DMAT) and mer-

captoethanesulfonic acid (MESA) to form water-soluble particles **3** and **5**, respectively.

Ligand exchange is achieved by stirring **1** in the presence of excess thiol in either a single organic phase or a biphasic system. The undecagold/thiol ratio is important because high thiol concentrations (more than 30 equivalents relative to the number of phosphine ligands) result in decomposition of the particles (indicated by the formation of an insoluble white material) and low thiol concentrations (less than 5 equivalents/phosphine) result in incomplete exchange (producing particles with a mixed ligand shell).

Particle **1** is less reactive toward thiol ligand exchange than the larger ($d_{\text{CORE}} \approx 1.5$ nm) triphenylphosphine-stabilized nanoparticles³⁴ that undergo ligand exchange readily at room temperature. For **1**, thiol ligand exchange is only observed for longer reaction times (1 to 24 h) and at elevated temperatures ($\sim 55^\circ\text{C}$). Under these conditions, complete exchange of the phosphine ligands by the incoming thiols is observed as indicated by the disappearance of aromatic signals in the ^1H NMR spectrum and by the absence of phosphorus in X-ray photoelectron spectroscopy (XPS).³⁸ In some cases (if insufficient excess of thiol is used or in the case of **4**), a stable intermediate with a mixed ligand shell is formed. Both ^1H NMR spectroscopy and XPS³⁸ confirm the presence of thiol and phosphine ligands in the products of these exchanges. Complete exchange can be achieved by treating these intermediates with additional thiol as was reported earlier for ligand exchanges involving larger particles.³⁶

Once the solvent has been removed, purification of the resultant clusters is accomplished by precipitation, trituration, or column chromatography.³⁸ Determination of the elemental composition of the exchange products by XPS (in the case of **3** and **5**) and elemental analysis (in the case of the free-base form of **3**) confirms that the undecagold core is preserved during the exchange reaction.³⁸

Optical spectra of the precursor and the exchange products are shown in Figure 1. The spectrum of **1** (Figure 1, trace a) shows two absorbances centered at 309 and 416 nm characteristic of phosphine-stabilized undecagold.^{25,30,31} The UV-vis spectrum of **2** (Figure 1, trace b) shows the same two main absorbances; however, there appears to be more structure within each of these bands. Although similar features are observed in the water-soluble products, the bands are significantly broadened in these spectra (Figure 1, traces c and d) likely because of differences in solvation of the ionized headgroups in aqueous solution or perhaps because of differences in ligand chain length.

Quantitative core size analysis for each new particle, obtained using TEM,³⁹ also suggests that the Au_{11} core is present in all of the products. By use of the same technique, cluster **1** shows a core diameter of 0.8 ± 0.2 nm, in good agreement with core diameters ($d_{\text{CORE}} = 0.8$ nm) of similar undecagold clusters calculated from single-crystal X-ray diffraction data.⁴⁰ Size analysis of TEM images of the ligand exchange products **2** (Figure 2a) and **5** (Figure 2b) reveals average core sizes for both particles of 0.8 ± 0.2 nm, the same as that found in **1**.⁴¹

The ligand exchange products show remarkably increased thermal stability compared to precursor **1**. Once excess ligand is removed, the thiol-stabilized particles can be stored in solution for several weeks without any observable degradation as shown by UV-visible spectroscopy. Even at elevated temperature ($\sim 55^\circ\text{C}$), **2** and **5** are stable for at least 3 days, whereas **1** decomposes after only 3 h under the same conditions. Moreover, particles **3** and **5** showed no observable decomposition or aggregation at extremes of pH and high salt concentrations.⁴²

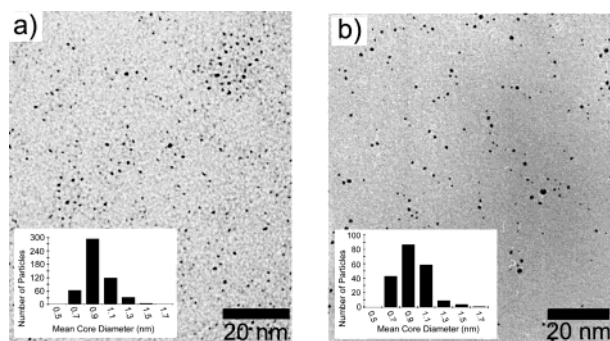


Figure 2. Representative TEM images with inset histograms of (a) octadecanethiol-stabilized particle **2** and (b) sodium 2-mercaptoethane-sulfonate particle **5**.

The convenient synthesis and purification methods described allow the rapid production of diverse collections of stable, highly functionalized, and monodisperse subnanometer gold particles suitable for biological or materials applications. These findings extend the use of ligand exchange chemistry for the preparation of highly functionalized nanoparticles and suggest a broader applicability of the method. Further, initial optical studies confirm that these particles possess discrete electronic levels. Given their ease of functionalization and subnanometer dimensions, these materials offer an entry into the detailed exploration of the electronic properties of nanoassemblies in which the metal particles have defined electronic states. Systematic studies of the optical and electronic properties of this class of particles and the influence of variations in the ligand shell on these properties are underway.

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Supporting Information Available: Experimental details of the synthesis of **2**, **3**, **4**, and **5**, ^1H NMR spectra, XPS data of **2**, **3**, **4**, and **5** and TEM data of **1**, **3**, and **4**. This material is available free of charge via Internet at <http://pubs.acs.org>.

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- See Supporting Information.
- Images were taken on a Phillips CM-200 at 200 kV accelerating voltage or on a Phillips CM-12 at 100 kV.
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- Particle count for **2** was $N = 511$; particle count for **5** was $N = 203$.
- Several samples were stored for 15 days under pH 0.5 and pH 12 and in saturated NaCl solutions and monitored by UV–vis spectroscopy.