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Faradaurate Nanomolecules: A Superstable Plasmonic 76.3 kDa Cluster

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Supporting Information

ABSTRACT: Information on the emergence of the characteristic plasmonic optical properties of nanoscale noble-metal particles has been limited, due in part to the problem of preparing homogeneous material for ensemble measurements. Here, we report the identification, isolation, and mass spectrometric and optical characterization of a 76.3 kDa thiolate-protected gold nanoparticle. This giant molecule is far larger than any metal-cluster compound, those with direct metal-to-metal bonding, previously known as homogeneous molecular substances, and is the first to exhibit clear plasmonic properties. The observed plasmon emergence phenomena in nanomolecules are of great interest, and the availability of absolutely homogeneous and characterized samples is thus critical to establishing their origin.

During experiments aimed at determining the thermo-chemical stability of small metal crystallites, reduced gold has been treated with excess thiolate at elevated temperatures for extended periods, ultimately producing a remarkably stable nanomolecule that was isolated and then studied by matrix assisted laser desorption and electrospray ionization mass spectrometry. Among the properties of this unique structure are: it has a metallic electronic structure, as evidenced by an optical plasmon band centered near 500 nm; it forms true solutions in several solvents; and it has already been obtained with two distinct thiolate groups. Its stability along with these characteristics make it a highly suitable nanomolecular platform for a range of applications in optics, electronics, chemical sensors, and biomedicine.

The technique used to produce and identify this unusual molecule involves¹ (i) the solution-phase reduction of a Au(III) salt by thiolate and by borohydride; followed by (ii) a variable-length thermo-chemical treatment (60 °C, excess thiol, air); and (iii) detection at each stage of the resulting distribution of clusters by mass spectrometry. Upon completion of the etching-annealing treatment, the mass spectrum reveals the presence exclusively of the superstable cluster compounds. Isolation of the title compound is then achieved by recrystallization from solution. Finally, the molecular weight of the purified compound is established by mass spectrometry (Figure 1), along with further characterization of its properties. These general procedures have been fully described elsewhere¹ and can be extended to even larger 76.3, 114, and 207 kDa superstable sizes, as indicated in Figure 1a.

Earlier attempts² to identify and isolate larger thiolate-protected gold clusters suffered from inadequate analytical methodology. In that work, clusters of up to 500 metal atoms were

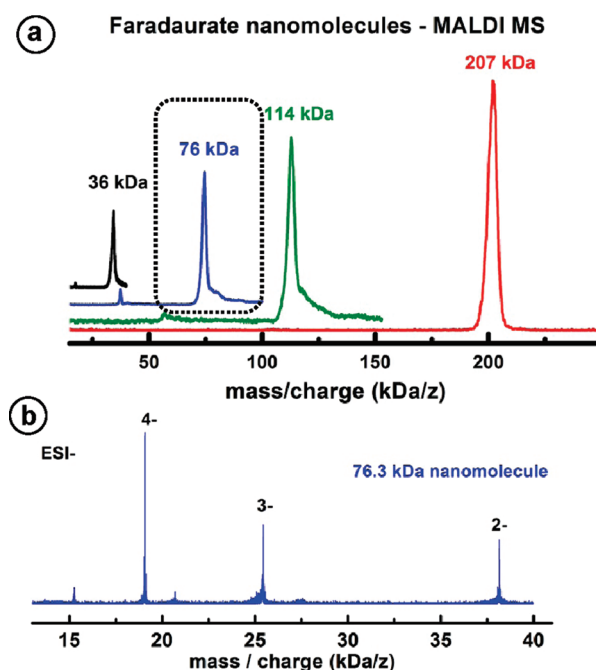


Figure 1. (a) MALDI TOF MS of 76.3 kDa (blue) along with 36 (black), 114 (green), and 207 kDa (red) nanomolecules. (b) Electrospray Ionization of purified 76.3 kDa nanomolecules showing 2[−], 3[−], and 4[−] ions. ESI was obtained by spraying from a toluene/CH₃CN mixture in the presence of cesium acetate electrolyte.¹¹ DCTB matrix was used to obtain the MALDI spectrum.¹²

observed, and it was noted that the distribution of abundance has several pronounced maxima, including one ~314 Au atoms, although it was never completely dominant. More recently, improved methods have established a superstable cluster comprising 144 metal atoms and 60 symmetry-equivalent thiolates (Au₁₄₄(SCH₂CH₂Ph)₆₀),^{3–5} with a total mass of 36.6 kDa. It has been isolated in pure form (various thiolates) and studied extensively for its special structural and electronic properties, as well as for many applications. Up to ~60 of the Au atoms can be replaced by Ag, without compromising the special (144,60) composition.¹ In this form its optical absorption spectrum, normally nonplasmonic, exhibits strong broad peaks which might indicate an emergent surface plasmon resonance (SPR) of metallic Au–Ag nanoparticles. Its internal and surface structure⁶ is related to that determined for a smaller (102,44) homologue,⁷ and also to the earlier Pd₁₄₅ and (PtPd)₁₆₅ ones,^{8–10}

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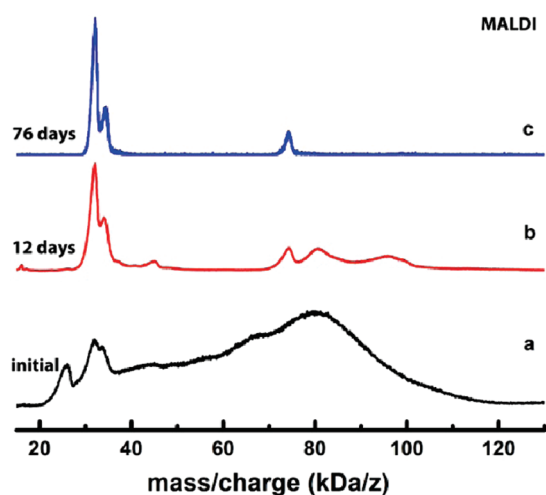


Figure 2. MALDI mass spectra of gold phenylethane thiolate cluster distributions evolving (a–c) under etching conditions (excess thiol, 60 °C, air) from a broad polydisperse mixture leading up to homogeneous nanomolecules at 76 kDa. Purification to obtain homogeneous 76 kDa cluster was performed by fractional recrystallization using toluene–methanol solution.²

which are the largest metal–cluster compounds isolated in compositionally pure forms. Described below is an advance—a leap to unprecedented large sizes—both in these methods and in the resultant nanomolecular noble-metal materials.

Figure 2 shows a series of distributions evolving from an initial polydisperse mixture (a–c) in which a single peak, centered near 76 kDa, totally dominates the high-mass region (40–200 kDa). The peak centered around 36 kDa is Au_{144} species. The resulting cluster distribution (>40 kDa) is now dominated by this 76 kDa feature, to the complete exclusion of other smaller and larger features. At this stage, the thermo-chemical treatment is discontinued, and the superstable compound is isolated in high yield by recrystallization. The MALDI mass spectrum of the purified substance (Figure 1, blue curve) confirms the complete removal of the much smaller (<40 kDa) species. The precise molecular weight (76.3 kDa) could be determined using electrospray ionization (ESI) mass spectrometry (Figure 1, blue curve and Figure S2 and S3) from a toluene–acetonitrile solution. Similar results were obtained with hexane thiol.

We briefly describe a few salient properties of this new compound and its variants: It can be obtained in ~5 mg quantity already and the preparation and separation can be scaled easily. It is stable in air, under light, and moisture. This compound is also obtained with hexane thiol. It is soluble in several common solvents such as toluene, methylene chloride, and chlorobenzene; insoluble in acetonitrile and methanol. The color of the dilute solution appears red to magenta and it is black as a dry powder or film. Its optical absorption spectra in dilute solutions exhibits an emergent plasmonic response, the surface plasmon resonance (SPR) band being slightly enhanced and shifted in more refractive solvents. Such plasmon emergence phenomena in nanometer scale metal crystallites are of great interest, as they are not presently understood in terms of any microscopic theory;¹³ the availability of absolutely homogeneous and characterized samples is thus critical. One open question is whether SPR band emergence indicates a true insulator-to-metal transition, occurring within individual clusters,¹⁴ which could be

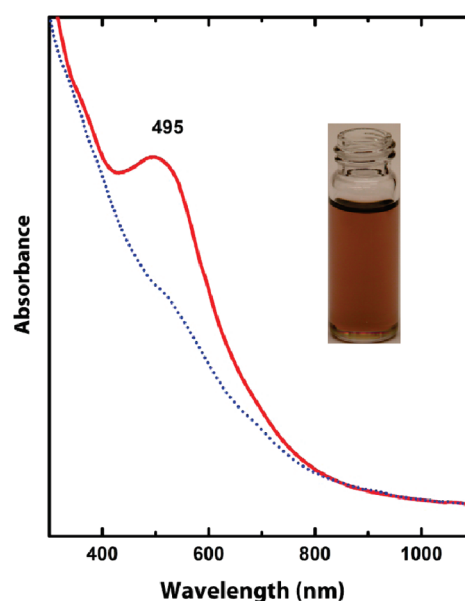


Figure 3. Plasmonic UV–vis spectrum of the 76.3 kDa nanomolecules (red curve) in toluene in contrast to the nonplasmonic $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$ (dotted). Inset shows a photograph of the toluene solution of the nanomolecule.

sensitive to external conditions. It goes without saying that these enhanced properties are obviously favorable for various applications, particularly those requiring or benefiting from a molecular level of homogeneity. With regard to applications in solid-state chemistry and physics, the combination of large metallic (plasmonic) cores and perfect homogeneity will be crucial to establishing the (macroscopic) insulator–metal transition¹⁵ in crystalline solids of metallic nanocrystal molecules, which in turn may lead to other broken symmetry ground states including superconductivity. With regard to bioconjugation (or labeling) applications, it is notable that a mere 0.23-nm increase in nanoparticle radius (or ‘standoff’ distance from the labeled center) accompanies a more than doubling of the X-ray (or electron-beam) scattering intensity or enhancement in the case of diffraction, and a quadrupling of the optical intensity in the green region (Figure 3).

In conclusion, we have reported the identification, isolation, and characterization of a 76.3 kDa phenylethane thiolate protected metal cluster compound far beyond any previously known in homogeneous molecular form and the first such compound to exhibit clear plasmonic properties. Further structural characterization by advanced electron microscopy (STEM) and X-ray scattering is underway. This series of compounds and higher homologues and their many potential variants of definite and homogeneous composition and structure will be crucial to establishing the emergence and evolution of the metallic (plasmonic) state of matter.

For such a unique and centrally important structure, a concise name would be useful. It was Michael FARADAY¹⁶ (1857) who first explored the small-size limit of the optical properties of metallic gold (and other elements), and who marveled at the extraordinary stability of his thiocarbonate-protected gold sols (prepared by combining P_4/CS_2 and $\text{NaAuCl}_4/\text{H}_2\text{O}$ solutions), asking whether these “be considered... as molecules of gold.” The nomenclature proposed herein combines this name with the

cognate for compounds of gold (farad-aurates, -argentates, etc.), to which various descriptor (Faradaurate Au₁₄₄, Faradaurate 76, 114, and 207 kDa, ...) can be added.¹⁷

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic conditions, optical spectra (dilutions), expanded ESI mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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