

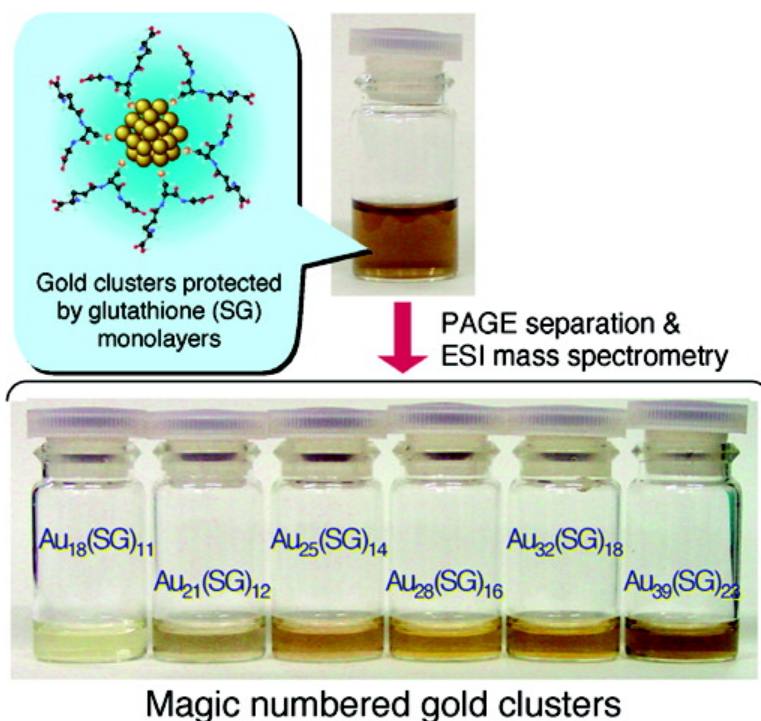
Communication

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Magic-Numbered Au_n Clusters Protected by Glutathione Monolayers (n = 18, 21, 25, 28, 32, 39): Isolation and Spectroscopic Characterization

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Monolayer-protected clusters (MPCs), especially with sub-nanometer-sized metal cores,^{1–6} provide us good opportunities to study evolution of electronic, optical, and chemical properties as a function of a core size as well as to develop novel building blocks for various nanoscale devices. To attain these ends, preparation of MPCs with well-defined compositions is of primary importance. Although one can control the average core size of the MPCs prepared by the conventional chemical route based on nucleation of zerovalent metal atoms in the presence of thiols,⁷ such a method inevitably produces a distribution in the core sizes due to statistical fluctuations in the nucleation process. Thus, development of size-selection and characterization techniques with atomic resolution^{1a,b,8} is indispensable in achieving this formidable task. Recently, Whetten and co-workers fractionated gold clusters protected by monolayers of glutathione (GSH = γ -Glu-Cys-Gly) by using polyacrylamide gel electrophoresis (PAGE) and identified the most abundant species as Au₂₈(SG)₁₆ by mass spectrometry.^{1a,b} In the present study, we extend mass spectrometric measurement to a wider range of PAGE-separated Au:SG clusters, demonstrating isolation of magic-numbered gold clusters: Au₁₈(SG)₁₁, Au₂₁(SG)₁₂, Au_{25±1}(SG)_{14±1}, Au₂₈(SG)₁₆, Au₃₂(SG)₁₈, and Au₃₉(SG)₂₃. Optical measurements illustrate that the electronic structures of these Au:SG clusters are molecular-like and are heavily dependent on their compositions.

The Au:SG clusters were prepared by the Himeji group by following the recipe reported previously.⁹ TEM observation of the Au:SG clusters thus prepared revealed that their core sizes appear to be ~1 nm (Supporting Information, Figure S1). The crude sample of the Au:SG clusters was further fractionated into six components by a high-resolution PAGE (Supporting Information, Figure S2).^{1a,b} These fractions are referred to as **1–6** in order of their mobility (Figure 1).

The chemical compositions of **1–6** were investigated by using an electrospray ionization (ESI) mass spectrometer constructed at IMS (Supporting Information, Figure S3). Figure 2 displays the negative-ion ESI mass spectra of **1–6**. Note that the extensive fragmentation into low-mass ions such as (AuSG)₄²⁻ and Au(SG)₂⁻ reported previously^{1a,b} is significantly suppressed under an optimized condition for desolvation. Each spectrum is composed of a series of multiply charged anions originated from deprotonation of the carboxyl moieties of the GS ligands. The molecular weights determined from the deconvoluted spectra (Figure 2) are well reproduced by combinations of Au atoms, GS ligands, and Cl atoms: clusters **1**, **2**, **4**, **5**, and **6** are formulated as Au₁₈(SG)₁₁Cl_x, Au₂₁(SG)₁₂Cl_x, Au₂₈(SG)₁₆Cl_x, Au₃₂(SG)₁₈Cl_x, and Au₃₉(SG)₂₃Cl_x,



Figure 1. Appearance of gels containing fractionated clusters **1–6**.

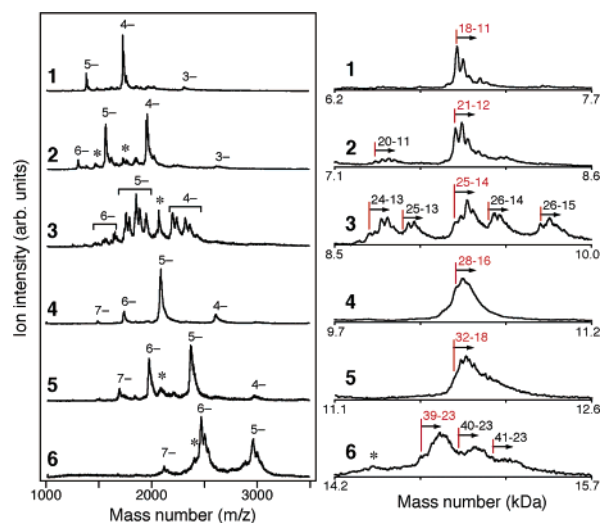


Figure 2. Negative-ion ESI mass spectra of clusters **1–6** (left). Mass peaks marked by asterisks are due to impurities from adjacent fractions. The right panels show the deconvoluted spectra. The red bars indicate the molecular weights of Au_n(SG)_m clusters with *n–m* values designated on the envelopes.

respectively.¹⁰ Fraction **3** is dominated by Au₂₅(SG)₁₄Cl_x but is contaminated appreciably by Au₂₄ and Au₂₆ clusters. The Cl constituents, originated from HAuCl₄, the starting material for the cluster preparation, will not be denoted explicitly hereafter for simplicity. The most important finding is that a series of nearly single-sized Au_n(SG)_m clusters is isolated by the PAGE method.

Preferential formation of the Au_n(SG)_m clusters with *n* = 18, 21, 25, 28, 32, and 39 indicates that they are relatively stable as compared with other-sized clusters. The most plausible explanation for their marked stability is the intrinsic stability of the Au cores arising from closing of geometrical and/or electronic shells. Indeed, truncated octahedral fcc structure has been theoretically suggested for the Au core of Au₃₈(SCH₃)₂₄.¹¹ However, sequential completion of polyhedral shell structures does not explain the whole sequence of the Au core sizes observed here. Moreover, other computational studies suggest that the core structures of Au₂₈(SCH₃)₁₆ and

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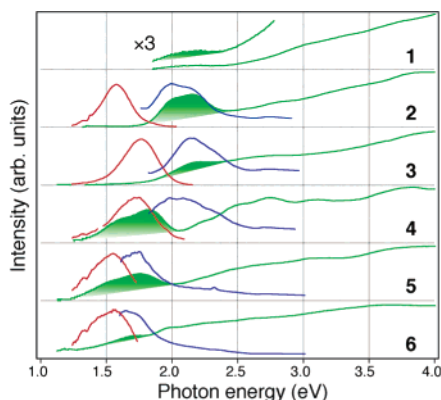


Figure 3. Optical absorption (green), photoemission (red), and photoexcitation (blue) spectra of aqueous solutions of **1–6** (300 K).²⁰ The PL spectrum of **1** could not be obtained probably due to the small yield.

Table 1. Spectroscopic Features of **1–6**

fraction	formula	E_{gap} (eV) ^a	E_{emis} (eV) ^b	E_{ss} (eV) ^c	ϕ^d
1	Au ₁₈ (SG) ₁₁	1.8			
2	Au ₂₁ (SG) ₁₂	1.7	1.6	0.4	1×10^{-3}
3	Au _{25±1} (SG) _{14±1}	1.5	1.8	0.4	3×10^{-3}
4	Au ₂₈ (SG) ₁₆	1.3	1.7	0.3	7×10^{-4}
5	Au ₃₂ (SG) ₁₈	1.2	1.6	0.2	6×10^{-4}
6	Au ₃₉ (SG) ₂₃	<1.2	1.6	0.1	4×10^{-4}

^a Absorption onset. ^b Emission maximum. ^c Stokes shift. ^d PL quantum yield.

Au₃₈(SCH₃)₂₄ are distorted considerably by thiolate passivation.¹² An alternative to account for the core stability is the closing of electronic shells with given numbers of 6s valence electrons (8, 18, 20, 34, and so on).¹³ The electronic shell model well explains, for example, preferential formation of Au₈ within a dendrimer¹⁴ and intensity distributions of the gas-phase Au cluster ions,^{15,16} but not the series of the core sizes of the Au:SG clusters. These considerations lead us to conclude that the GS monolayers play a crucial role in stabilizing the series of gold clusters. Because our research project is at the initial stage, we can only propose plausible roles of thiolate ligation in the formation of the particular-sized clusters: (1) the thermodynamic stabilities of some of the isolated Au:SG clusters may be explained in terms of an electron counting scheme in which partial electron transfer at the Au–S interfaces^{11,17} is taken into account; (2) nucleation of the Au cores may be kinetically hindered each time the GS protecting shells are completed, resulting in the formation of a series of metastable Au:SG clusters. We note that lateral hydrogen bonding (–NH···O=C–) may afford the GS monolayer’s enhanced stability.

The optical absorption spectra of **1–6** are summarized in Figure 3. There appear clear absorption onsets followed by humps in the range of 1.5–2.5 eV. The lowest-energy absorption bands, colored in green, are ascribed to optical transitions between quantized levels associated mostly with the gold cores, since they are observed only in the small clusters and evolve with the core sizes. This assignment is in parallel with recent DFT results on Au₁₃(SCH₃)₈³⁺, a smaller analogue of the systems studied here.¹⁸ The molecular-like properties of these small Au clusters^{1–6} also manifest themselves in the photoluminescent (PL) behavior, as shown in Figure 3. Table 1 summarizes the PL properties of **2–6**. The PL quantum yields, ϕ , are remarkably larger than that of the bulk gold ($\phi = 10^{-10}$), showing an enhanced contribution of the radiative process in the decay of the photoexcited states for these small systems.^{1c,d,3b,4c,19} The relatively small Stokes shifts and the excitation profiles suggest that the PL originates from vibrationally relaxed states of the first

electronically excited state. We must await theoretical studies for detailed assignment of the optical and PL spectra reported here.

To summarize, we report herein mass spectrometric characterization of electrophoretically fractionated Au:SG clusters. The main contribution of the present work has been to isolation of a series of magic-numbered clusters, Au₁₈(SG)₁₁, Au₂₁(SG)₁₂, Au_{25±1}(SG)_{14±1}, Au₂₈(SG)₁₆, Au₃₂(SG)₁₈, and Au₃₉(SG)₂₃. The results provide basic guidelines for further experimental and theoretical studies on structures, stabilities, and optical properties of small gold MPCs as well as for development of new cluster-based materials.

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Note Added after ASAP. The abscissa units on the left side of Figure 2 were incorrect in the version published 5/6/2004. The final version published 5/7/2004 and the print version are correct.

Supporting Information Available: Experimental procedures and TEM data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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