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ARTICLE TYPE

Selective synthesis of organogold magic clusters $Au_{54}(C{\equiv}CPh)_{26}$†

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Organogold clusters $Au_{54}(C_2Ph)_{26}$ were selectively synthesized by reacting of polymer-stabilized Au clusters (1.2±0.2 nm) with excess phenylacetylene in chloroform.

Recent studies have shown that gold clusters protected by ligands (phosphines and thiolates) exhibit unique optical, electrochemical, magnetic, and catalytic properties.[1–7] Such ligand-protected Au clusters have poteintial applications in diverse fields including catalysis,[7–9] nanoscale electronics,[10–16] drug delivery,[17] molecular biology,[18–20] and surface patterning.[21,22] State-of-the-art precision synthesis, theoretical calculations, and single-crystal structure determination have shown that the novel properties of these clusters are associated with cluster substructures, namely the Au core, the ligands, and their interface. Therefore, to design and tune the properties of ligand-protected Au clusters, it is crucial to control the structures of individual substructures; specifically the number of constituent atoms and the geometric structure of the Au core, the interfacial structure between the Au core and the ligands, and the physicochemical properties of the ligands.

In this regard, an interesting challenge is to produce new properties by synergizing the properties of individual substructures. For example, Au clusters stabilized by Au–C covalent bonds (organogold clusters) are anticipated to exhibit novel charge transfer and photophysical properties that differ significantly from those of conventional thiolate-protected Au clusters. This is because, in organogold clusters, the Au core and the ligands are coupled more directly via the π–d interaction and the electronic conjugation can be easily extended via C=C and/or C≡C bonds. We recently synthesized the Au clusters stabilized by phenylacetylene (Au:C_2Ph) through Au–C covalent bonds.[23] Matrix-assisted laser desorption ionization (MALDI) mass spectrometry analysis revealed that as-prepared Au:C_2Ph clusters are a mixture of $Au_n(C_2Ph)_m$ with specific compositions, such as (n, m) = (43, 22), (46, 24), (52, 26), (54, 26), (59, 27), (71, 32), (90, 36), (94, 38), (101, 38), and (110, 40). We herein report selective synthesis and structural characterization of $Au_{54}(C_2Ph)_{26}$.

Au:C_2Ph clusters were prepared by mixing the hydrosol of polyvinylpyrrolidone (PVP)-stabilized Au clusters (Au:PVP) [mean diameter: 1.2±0.2 nm (**1a**), 1.4±0.2 nm (**1b**), and 1.8±0.3 nm (**1c**)][24] and an organic solution (toluene or chloroform) of PhC_2H.[23] The PhC_2H to Au molar ratio was 1000.[25] The reaction temperature was 333 K and reaction time was 3 h. The Au:C_2Ph clusters were purified by repeated washing out very small Au:C_2Ph clusters and excess PhC_2H with methanol followed by centrifugation.[25] MALDI mass spectrometry analysis of the thus-produced Au:C_2Ph revealed that that the extraction solvent employed and the Au:PVP size distribution greatly affect selective synthesis of $Au_{54}(C_2Ph)_{26}$.

We first show the effect of the extraction solvent on the size distribution of Au:C_2Ph. Figures 1a and 1b compare the appearances of ligand exchange in toluene and chloroform, respectively. Initially (i.e., at 0 h), the aqueous phases containing

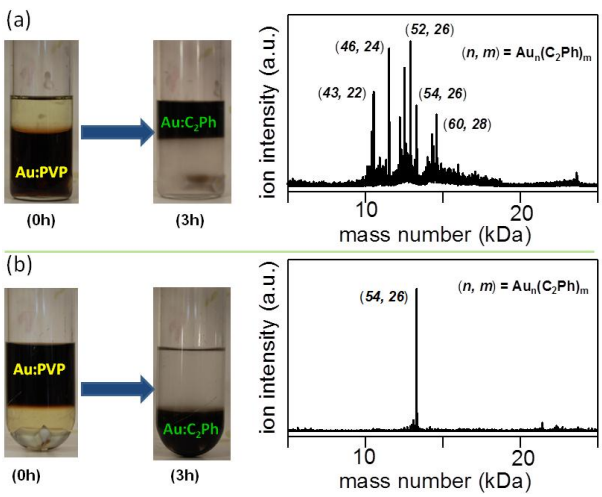

Figure 1. Photographs of the phase transfer reaction for Au:C_2Ph synthesis and negative-ion MALDI mass spectra of Au:C_2Ph prepared using (a) toluene and (b) chloroform.

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Au:PVP were brown and the organic phases containing PhC_2H were colourless. After 3 h, the water phases became colourless and the organic phases turned deep brown, indicating completion of ligand exchange. The Au:C_2Ph yield was higher when using chloroform (~90%) than when using toluene (~60%). The Au:C_2Ph size distributions obtained using toluene and chloroform differed remarkably. MALDI mass spectrometry analysis indicated that $Au_{54}(C_2Ph)_{26}$ was selectively formed when using chloroform (Figure 1b), whereas Au:C_2Ph prepared using toluene contained clusters with different compositions (Figure 1a).

We next show the effect of the initial size of Au clusters in PVP on the size distribution of Au:C_2Ph. Figure 2 shows MALDI mass spectra of Au:C_2Ph obtained from Au:PVP (**1a**–**1c**) under chloroform–water biphasic condition. The smallest Au:PVP (**1a**) gave the highest selectivity to $Au_{54}(C_2Ph)_{26}$, whereas the selectivity was lower for larger Au:PVP (**1b** and **1c**). Under optimized conditions, we could produce ~5 mg of $Au_{54}(C_2Ph)_{26}$ from **1a** in a single synthesis.[25]

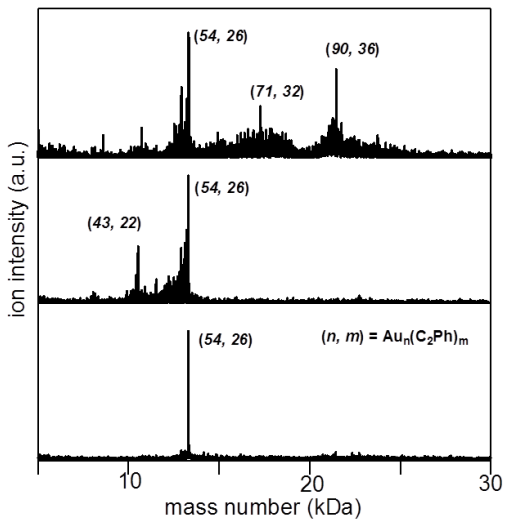

Figure 2. Negative ion MALDI mass spectra of Au:C_2Ph produced from **1a** (below), **1b** (middle), and **1c** (above) using chloroform as the extraction solvent.

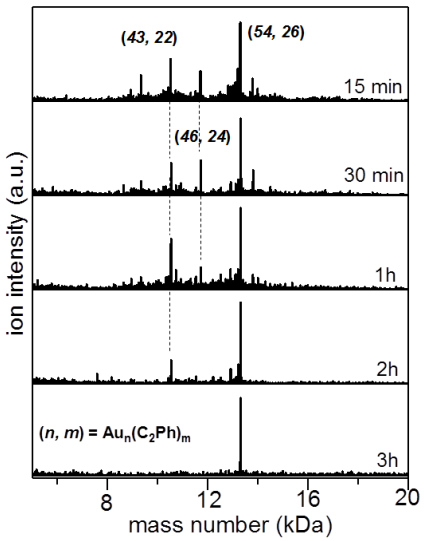

Figure 3. Negative–ion MALDI mass spectra of Au:C_2Ph obtained from Au:PVP (**1a**) for five different reaction times.

The selective formation of $Au_{54}(C_2Ph)_{26}$ in chloroform from Au:PVP (**1a**) can be explained in terms of thermodynamic stability of $Au_{54}(C_2Ph)_{26}$ as well as kinetic factors. Figure 3 shows MALDI mass spectra of the products obtained from **1a** at different stages of the reaction in chloroform. Initially formed $Au_{43}(C_2Ph)_{22}$, $Au_{46}(C_2Ph)_{24}$ and some others disappeared and only $Au_{54}(C_2Ph)_{26}$ remained after 3 h. This observation clearly indicates that complete selectivity to $Au_{54}(C_2Ph)_{26}$ was achieved by disappearance of all the other metastable species which are concomitantly populated just after the completion of the ligation to the Au clusters. Chemical etching of the Au core was proposed as a decomposition route of metastable Au clusters in the selective formation of $Au_{25}(SG)_{18}$ via the ligand exchange of glutathione (GSH) and GS-protected Au clusters.[26] More efficient conversion in chloroform than in toluene (Figure 1) is ascribed to more efficient core etching of Au:C_2Ph in chloroform due to their higher solubility. Whatever the mechanism of the selective decomposition might be, a proper size distribution of the nascent Au:C_2Ph clusters is a key for the selective and high-yield synthesis of thermodynamically and chemically stable $Au_{54}(C_2Ph)_{26}$.

To obtain information about the Au core structure of $Au_{54}(C_2Ph)_{26}$, Au:C_2Ph produced from **1a** using chloroform was characterized by transmission electron microscopy (TEM), UV–visible spectroscopy, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) spectroscopy, and extended X-ray absorption fine structure (EXAFS) spectroscopy. The TEM image (Figure 4a) clearly shows that the clusters are monodisperse (mean diameter: 1.3±0.2 nm) and do not contain impurities of larger nanoparticles. The UV–visible spectrum (Figure 4b) exhibits an exponential-like profile without the surface plasmon peak. The Au 4f XP spectrum (Figure 4c) shows that Au $4f_{7/2}$ has a binding energy of 84.3 eV, which is slightly higher than that of bulk gold (84.0 eV). This suggests that electron transfer occurs from the Au cores to the PhC_2 ligands. The XRD pattern shows diffraction peaks from the Au lattice

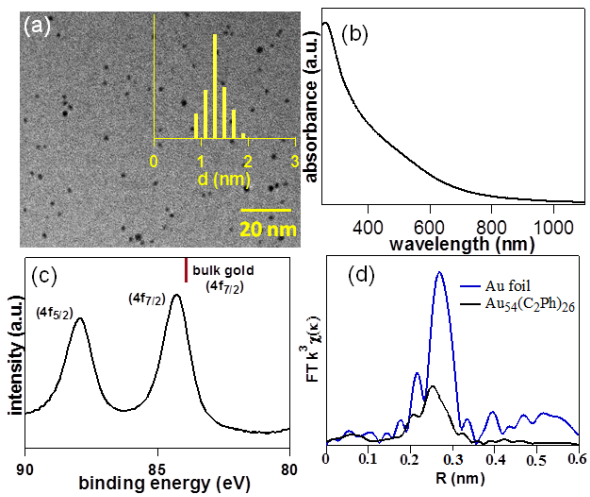

Figure 4. (a) TEM image and size distribution; (b) UV–visible spectrum in chloroform; (c) XP spectrum in the vicinity of Au 4f, (d) Fourier-transform EXAFS spectrum of $Au_{54}(C_2Ph)_{26}$.

planes with a smaller lattice constant.[25] The XANES spectrum indicates that absorption onset for $Au_{54}(C_2Ph)_{26}$ (11920.38 eV) was the same as that of an Au foil (11920.38 eV).[25] Figure 4d shows a k^3-weighted Fourier-transform EXAFS spectrum of $Au_{54}(C_2Ph)_{26}$. The peak in the range of 0.221–0.313 nm is assigned to the Au–Au shell. From a curve-fitting analysis,[25] the Au–Au distance was determined to be 0.279 nm, which is significantly smaller than that in the bulk (0.289 nm). The Au–Au coordination number (CN) for $Au_{54}(C_2Ph)_{26}$ was calculated to be 7.3±1.6 by assuming that the electron mean free path is 0.5 nm.[27] This CN value is comparable to that (7.9) of cuboctahedral Au_{55}. These results clearly show the formation of small Au cores in $Au_{54}(C_2Ph)_{26}$.

Recently, Chen and co-workers reported formation of two types of bonding of carbon of the ligands to Ru nanoparticles; Ru-alkynide (Ru–C≡C–)[28] and Ru-vinylidene (Ru=C=CH–).[29] Our mass analysis supported the formation of $Au_{54}(–C≡C–Ph)_{26}$ rather than $Au_{54}(=C=CH–Ph)_{26}$.[25] To obtain further insight into the interfacial structure of $Au_{54}(C_2Ph)_{26}$, we measured the Fourier-transform infrared (FTIR) and Raman spectra (Figure 5). Absence of C–H vibrational peak in the FTIR spectrum[25] indicates the direct bonding between carbon and gold in $Au_{54}(C_2Ph)_{26}$. Figure 5 shows that the peak for the –C≡C– stretching mode of PhC_2H (2110 cm^{-1})[30] is red shifted to 2028 cm^{-1} for the ligands of $Au_{54}(C_2Ph)_{26}$. This suggests that alkynyl carbon binds covalently with gold and that the –C≡C– bond is weakened by electron transfer from the Au core to the π* orbital of the PhC_2 ligands.

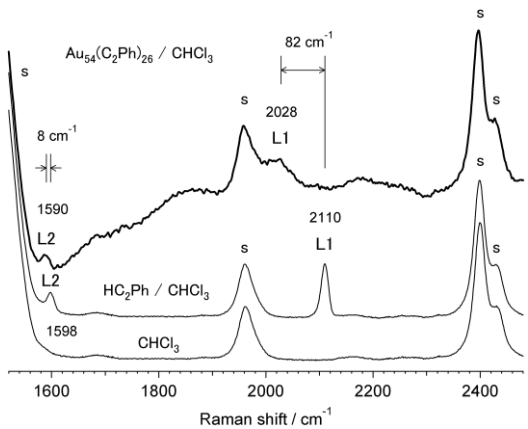

Figure 5. Raman spectra of $Au_{54}(C_2Ph)_{26}$ (top) and PhC_2H (middle) in chloroform with 532 nm excitation. The spectrum of chloroform is shown for comparison (bottom). Peaks indicated by L1 and L2 correspond to the stretching mode of C≡C and in-plain stretching mode of the phenyl group of PhC_2H (L2), respectively. The peaks due to the solvent are indicated by "s".

In summary, we have developed a selective and high yield synthetic method of $Au_{54}(C_2Ph)_{26}$ by controlling the initial cluster sizes of Au:PVP and the solvents for the ligand exchange. Large-scale synthesis of a new magic cluster $Au_{54}(C_2Ph)_{26}$ will open up the possibility of gaining a deeper understanding of the structure and properties as well as realizing practical applications.

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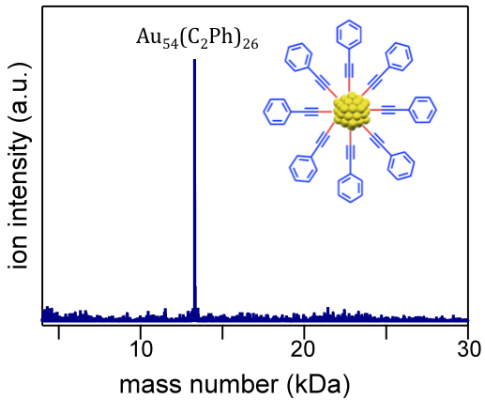

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