

Controlling Gold Nanoclusters by Diphospine Ligands

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S Supporting Information

ABSTRACT: We report the synthesis and structure determination of a new Au₂₂ nanocluster coordinated by six bidentate diphosphine ligands: 1,8-bis(diphenylphosphino) octane (L⁸ for short). Single crystal X-ray crystallography and electrospray ionization mass spectrometry show that the cluster assembly is neutral and can be formulated as Au₂₂(L⁸)₆. The Au₂₂ core consists of two Au₁₁ units clipped together by four L⁸ ligands, while the additional two ligands coordinate to each Au₁₁ unit in a bidentate fashion. Eight gold atoms at the interface of the two Au₁₁ units are not coordinated by any ligands. Four short gold–gold distances (2.64–2.65 Å) are observed at the interface of the two Au₁₁ clusters as a result of the clamping force of the four clipping ligands and strong electronic interactions. The eight uncoordinated surface gold atoms in the Au₂₂(L⁸)₆ nanocluster are unprecedented in atom-precise gold nanoparticles and can be considered as potential *in situ* active sites for catalysis.

There has been growing interest in gold nanoclusters with well-defined sizes over the past two decades due to their potential applications in catalysis, biology, and nanotechnology.^{1,2} Gold nanoparticles are generally synthesized in solution with thiolate ligands as a protection layer.^{3–7} The crystallization and X-ray structure determination of a 102-atom gold nanocluster⁸ have allowed the first atomic-level understanding of the ligand-cluster interface, stimulating the syntheses and structural determination of several atom-precise gold nanoclusters with thiolate ligands^{9–14} as well as a number of theoretical investigations.^{15–20} The thiolate-gold interface was observed to be rather complicated because the strong S–Au interactions were found to “lift” gold atoms out of the cluster surface to form RS–Au–SR types of staple motifs,^{8,21,22} which are the true protection layer for thiolate gold nanoparticles. Phosphines constitute another important class of ligands to stabilize gold nanoclusters. A number of gold clusters with phosphine ligands were known sometime ago,^{23–27} including the well-characterized undecagold Au₁₁ cluster and the icosahedral Au₁₃ cluster coordinated by phosphine and halide ligands.^{28,29} The [Au₃₉(PPh₃)₁₄Cl₆]Cl₂ cluster represents the largest phosphine-coordinated gold clusters to be synthesized and characterized by X-ray crystallography.³⁰ A larger Au₅₅(PPh₃)₁₂Cl₆ cluster was synthesized,³¹ but its crystal structure was not obtained. Recently, a phosphine-coordinated Au₂₀ cluster was reported, which is composed of two edge-shared Au₁₁ units.³² A Au₂₄ cluster protected by mixed phosphine/thiolate ligands³³ and a Au₁₄ cluster coordinated by phosphine/NO₃[−] ligands³⁴ have also been synthesized and characterized by X-ray crystallography

recently. Phosphine is a neutral ligand and prefers to coordinate to the atop sites on the gold cluster surface, yielding a simple cluster-ligand interface. Diphosphine-protected Au₁₃ icosahedral clusters and other smaller gold clusters have also been reported.^{28,29,35,36}

In all the prior gold clusters that have been structurally characterized, the surface atoms are all coordinated. In order for these complexes to function as catalysts, ligands have to be removed first, which can modify the cluster core and induce instability. Atom-precise gold clusters with uncoordinated surface sites would allow them to function potentially as *in situ* catalysts without any postsynthetic treatments. A tetrahedral Au₂₀ cluster was found previously to be highly stable in the gas phase with all 20 Au atoms on the cluster surface.³⁷ Preliminary studies showed that it could be stabilized by four phosphine ligands in solution,³⁸ leaving 16 uncoordinated surface sites. Further efforts to synthesize this unique gold cluster using diphosphine ligands, Ph₂P(CH₂)_MPPh₂ or L^M for short, uncovered a size-selectivity as a function of the ligand chain length.³⁹ This finding has been investigated in more detail recently.^{40–42} However, the prior studies have been limited up to L⁶, the longest diphosphine ligands available then, and the gold cluster cores synthesized are all smaller than 13 atoms.^{39–41} To increase and control the gold cluster size, longer diphosphine ligands are required. Here we report the synthesis and X-ray structural determination of a new Au₂₂ cluster coordinated by six long-chain L⁸ ligands, i.e., Au₂₂(L⁸)₆ [L⁸ = 1,8-bis(diphenylphosphino) octane]. The Au₂₂ cluster core consists of two Au₁₁ units clipped together by four L⁸ ligands and contains 8 uncoordinated surface gold atoms.

Details of the synthesis are provided in the Supporting Information (SI). Briefly, the starting reagent for the synthesis was Au₂L⁸Cl₂. A dichloromethane solution of Au₂L⁸Cl₂ was reduced by NaBH₄. The product was purified by column chromatography and used to grow single crystals suitable for X-ray analyses, which was performed at the Advanced Light Source at Lawrence Berkeley National Laboratory (see SI and Table 1). The new cluster was found to be neutral with an Au₂₂ core and six L⁸ ligands. The crystal structure of Au₂₂(L⁸)₆, shown in Figure 1,⁴³ was found to have a triclinic space group *P*-1 (Table 1).

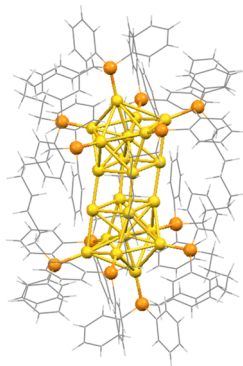
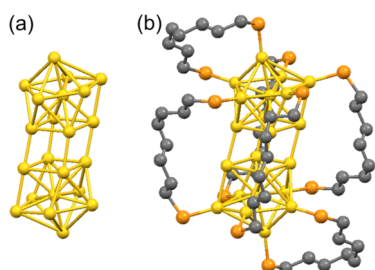
The Au₂₂ core (Figure 2a) is composed of two icosahedron-based Au₁₁ units joined together through a square face with inversion symmetry. The interface between the two Au₁₁ units is characterized by a distorted cubic Au₈ motif. The detailed Au–Au distances are given in Figure S7 and Table S1. The total length of the cluster measured between the two apex gold atoms is 11.54 Å, resulting in an overall cluster dimension of about 1.4

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Table 1. Crystal Data and Structure Refinement for the Au₂₂(L⁸)₆ Cluster

identification code	Au ₂₂
empirical formula	C ₉₆ H ₁₀₈ P ₆ Au ₁₁
formula weight	3614.27
temperature	123.(2) K
wavelength	0.77490 Å
crystal system	triclinic
space group	P-1
unit cell dimensions	$a = 15.493(4)$ Å, $\alpha = 82.13(3)^\circ$ $b = 17.157(4)$ Å, $\beta = 73.24(3)^\circ$ $c = 21.556(5)$ Å, $\gamma = 64.98(3)^\circ$
volume	4971.31(2) Å ³
Z	2
density (calculated)	2.415 g/cm ³
absorption coefficient	20.185 mm ⁻¹
F(000)	3282
Crystal size	0.03 × 0.025 × 0.005 mm ³
θ range for data collection	1.68° to 28.97°
index ranges	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -26 ≤ l ≤ 26
reflections collected	51286
independent reflections	20278 [R(int) = 0.1215]
completeness to $\theta = 28.97^\circ$	99.7%
absorption correction	multiscan (SADABS v 2012/1)
max. and min transmission	0.906 and 0.583
refinement method	SHELXL 2013 (Sheldrick, 2013)
data/restraints/parameters	20270/0/1018
goodness-of-fit on F ²	0.973
final R indices [$I > 2 \sigma(I)$]	R1 = 0.0880, wR2 = 0.2224
R indices (all data)	R1 = 0.1473, wR2 = 0.2645
largest diff. peak and hole	2.996 and -3.107 e.Å ⁻³

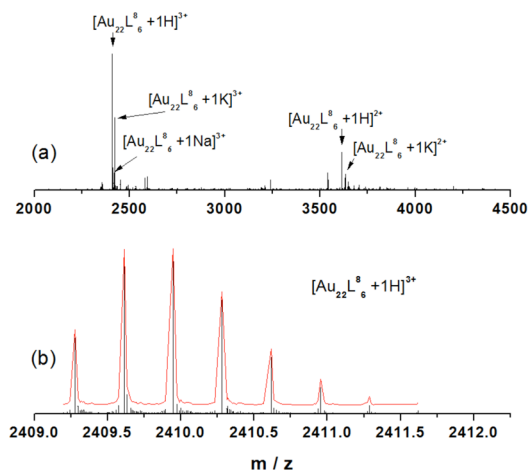
**Figure 1.** Total structure of the Au₂₂(L⁸)₆ cluster (color labels: yellow = Au; orange = P; gray = C).**Figure 2.** Core structure of the Au₂₂(L⁸)₆ cluster (colors are same as specified in Figure 1).

nm if a 1.5 Å covalent radius is taken for gold atoms. The coordination environment of the Au₂₂ core is highly unique, as

shown more clearly in Figure 2b. The two Au₁₁ units can be viewed as being clipped together by four L⁸ diphosphine ligands, while the additional two ligands each coordinate to an Au₁₁ unit in a bidentate fashion. Significantly, the eight gold atoms at the interface between the two Au₁₁ units are not coordinated at all.

In comparison to the structure of the well-known undecagold Au₁₁,^{25,28,35} the Au₁₁ units in the new Au₂₂ cluster exhibit some significant structural distortions as a result of the unique coordination environment. The internal Au atom in each Au₁₁ unit is pushed closer to the apex atom as a result of the clamping ligation that pulls the two units tightly together. The apex atom is distorted toward the atom that is coordinated by the same ligand (Figure 2b). For phosphine-coordinated gold clusters, radial-type Au–Au distances between a central gold atom and its first coordination shell are usually much shorter than Au–Au distances between surface atoms, such as the cases in the undecagold Au₁₁, Au₁₃, Au₁₄, Au₂₀, and Au₂₄ clusters.^{27–29,32–34} In the current Au₂₂ cluster, the Au–Au distances (2.64–2.65 Å) at the interface of the two Au₁₁ units are also fairly short, probably as a result of the clamping effects of the four ligands linking the two units and the strong electronic interactions between the two Au₁₁ units. The well-known undecagold Au₁₁ carries three positive charges (Au₁₁³⁺) with eight valence electrons, consistent to a major shell closing in the electron shell model.⁴⁴ The current Au₂₂ cluster core is neutral with 22 electrons, which does not correspond to a shell closing. Hence each Au₁₁ unit can be viewed as contributing three electrons for the bonding between the two units, resulting in the short Au–Au distances at the interface. The recently reported Au₁₄ cluster, which carries four positive charges with 10 valence electrons,³⁴ is also found not to correspond to any major shell closing.

Further characterization of the new Au₂₂ cluster was carried out using electrospray ionization mass spectrometry (ESI-MS) in the positive ion mode, as shown in Figure 3. The intense peak at

**Figure 3.** (a) Mass spectrum of the Au₂₂ cluster. (b) The measured (black) and simulated (red) isotopic patterns of [Au₂₂(L⁸)₆ + 1H]³⁺.

$m/z = 2410$ corresponds to [Au₂₂(L⁸)₆ + 1H]³⁺. Our X-ray structural refinement found no evidence of counterions (Table 1), and the Au₂₂(L⁸)₆ nanocluster is clearly neutral. Thus, all the charged species observed in the mass spectrum were produced during the ESI. The observed isotopic pattern agrees with the simulated spectrum (Figure 3b). The UV–vis absorption spectrum of the Au₂₂ cluster in dichloromethane is shown in Figure 4, exhibiting one prominent band at 456 nm. The optical

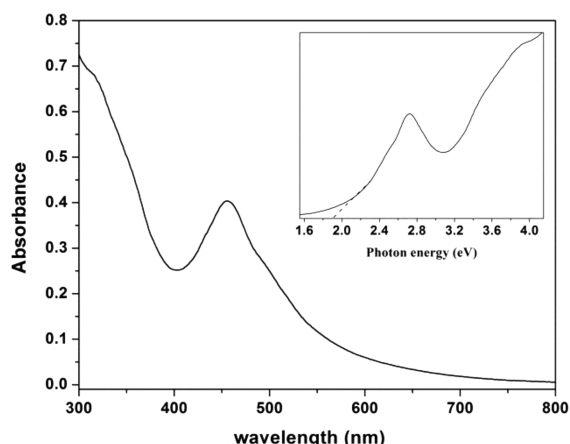


Figure 4. Optical absorption spectrum of the Au₂₂ cluster in methylene dichloride. (Insert) The spectrum on the energy scale (eV); the estimated optical gap is 1.9 eV.

energy gap was determined to be ~ 1.9 eV (see inset of Figure 4), which is lower than the 2.24 eV gap found in the recently reported phosphine-protected Au₂₀ cluster³² and higher than the 1.35 eV gap found in the Au₂₄ cluster.³³ We also investigated the fluorescence properties of the Au₂₂ cluster and found that it was luminescent, displaying visible to near-infrared emissions at room temperature. Figure 5 shows the photoluminescence

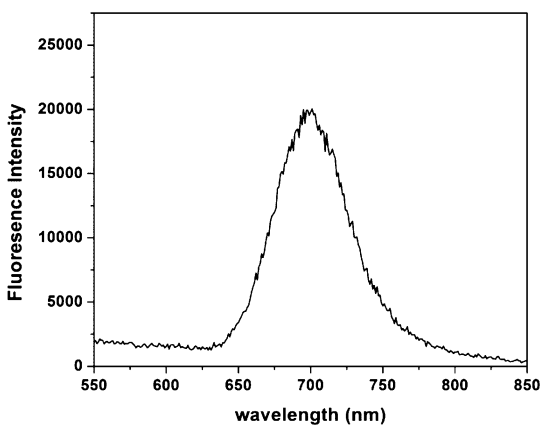


Figure 5. The fluorescence spectrum of the Au₂₂ cluster in methylene dichloride. ($\lambda_{\text{ex}} = 456$ nm).

spectrum of the Au₂₂ cluster dissolved in dichloromethane upon excitation at 456 nm. A band centered around 700 nm was observed with a quantum yield of $\sim 0.1\%$ relative to the [Ru(bpy)₃]²⁺ metal complex.⁴⁵

The new Au₂₂(L⁸)₆ nanocluster reported here is unprecedented both in its coordination environment and the core structure. It represents the first ligand-protected atom-precise cluster with uncoordinated gold sites, which may be used as *in situ* catalytic active sites. The observation of ligand control of the cluster size is an important finding. It is expected that other diphosphine ligands with different chain lengths (L^M) may yield a series of atom-precise gold clusters with tunable sizes, giving rise to a new strategy for controlling and tuning gold nanoclusters by ligands.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis details and crystallographic analysis. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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