Gold Nanoclusters

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A Chiral Gold Nanocluster Au_{20} Protected by Tetradentate Phosphine Ligands**

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Dedicated to Professor Xin-Tao Wu on the occasion of his 75th birthday

Abstract: *The chirality of a gold nanocluster can be generated from either an intrinsically chiral inorganic core or an achiral inorganic core in a chiral environment. The first structural determination of a gold nanocluster containing an intrinsic chiral inorganic core is reported. The chiral gold nanocluster $[Au_{20}(PP_3)_4]Cl_4$ (PP_3 = tris(2-(diphenylphosphino)ethyl)phosphine) has been prepared by the reduction of a gold(I)–tetraphosphine precursor in dichloromethane solution. Single-crystal structural determination reveals that the cluster molecular structure has C_3 symmetry. It consists of a Au_{20} core consolidated by four peripheral tetraphosphines. The Au_{20} core can be viewed as the combination of an icosahedral Au_{13} and a helical Y-shaped Au_7 motif. The identity of this Au_{20} cluster is confirmed by ESI-MS. The chelation of multidentate phosphines enhances the stability of this Au_{20} cluster.*

Ligand-protected gold nanoclusters of atomic precision have attracted increasing attention owing to their potential applications in catalysis, sensing, or in biology.[1–5] Some gold nanoclusters can bear intrinsically chiral features. The chirality of a gold nanocluster can be generated from two origins: an intrinsically chiral inorganic core or an achiral inorganic core in a chiral environment.[6] The environment can be chiral organic ligands or asymmetric arrangements, such as RS-Au-SR-Au-SR staples. A large number of ligand-protected gold nanoclusters have been prepared, but only a few have been structurally determined.[7] $Au_{38}(SR)_{24}$ is chiral owing to the asymmetric arrangement of staples, although it has a high symmetric gold kernel.[8] $Au_{28}(SR)_{20}$[9] and $Au_{102}(SR)_{44}$[10] are also chiral for the same reason. However, $Au_{25}(SR)_{18}$, having a structure with a Au_{13} core surrounded by RS-Au-SR-Au-SR staples, is not chiral.[11] $Au_{36}(SR)_{24}$ is not chiral either.[12] To date, there is no structural evidence showing a ligand-protected gold nanocluster with a chiral inorganic core, although a theoretical study confirmed a bare gold cluster Au_{34}^- to be intrinsic chiral.[13]

Both phosphines and thiolates have been used in the preparation of ligand-protected gold nanoclusters.[14] Phosphine-protected gold nanoclusters have a stability issue, because of the weaker Au–P bond in comparison with gold–thiolate bonding. Our strategy to solve this problem is the use of multidentate phosphines, and the attempt with tetradentate phospine tris(2-(diphenylphosphino)ethyl)phosphine (PP_3) led to the isolation of a chiral gold nanocluster $[Au_{20}(PP_3)_4]Cl_4$ (**1**) with a chiral 20-gold-atom core. Herein, we present this unprecedented structurally determined Au_{20} nanocluster with an intrinsic chiral inorganic core. The C_3 Au_{20} core can be viewed as the combination of a centered icosahedral Au_{13} and a helical Y-shaped Au_7 motif.

The preparation of **1** started with the reduction of $[PP_3Au_4Cl_4]$ by $NaBH_4$ in CH_2Cl_2 solution. Solvents were removed to give a black solid, which was recrystallized in CH_2Cl_2/CH_3OH/pentane to afford black crystals of **1** in a typical yield of about 20%.

Single-crystal structural analysis[15] revealed that **1** comprises a tetracationic cluster $[Au_{20}(PP_3)_4]^{4+}$ and chloride counterions. As shown in Figure 1a, the structure has a Au_{20} core wrapped by four PP_3 ligands. It has a C_3 symmetry with a threefold axis passing through atoms P1, Au1 and Au8. Geometrically, the Au_{20} core can be described as a centered icosahedron Au_{13} combined with a Au_7 motif. The Au_{20} core has 16 surface and four interstitial gold atoms. Each surface gold atom is coordinated by a phosphorus donor of PP_3. The PP_3 ligands are of two types: the one on the top bridges four Au atoms symmetrically; the other three are of the same type, each connects one Au_3 triangle and a neighboring Au atom (Figure 1b).

For clarity, the Au_{20} core is illustrated in Figure 1c with Au atoms highlighted in different colors. The Y-shaped Au_7 motif is in green and the Au_{13} icosahedron is in orange. A side view of the core is illustrated in Figure 1d to show the asymmetric arrangement of gold atoms. As shown in Figure 1e, the 16 surface gold atoms can be classified into six types (from type A to type E). Accordingly, the ^{31}P NMR should display six peaks at a ratio of 1:3:3:3:3:3 based on the number of atoms of each type. Experimentally, five peaks at $\delta = 39.78$, 41.32, 48.56, 57.05 and 66.26 ppm in a ratio of 1:3:3:6:3 were observed (Supporting Information, Figure S1). The ^{31}P NMR data match the expected, because the peak at $\delta = 57.05$ ppm actually contains the contribution from phosphorous donors linked to two types of Au atoms (types D and E) with similar coordination environments. The Au–Au distances are in the range of 2.572(2)–3.216(2) Å, and the 2.572(2) Å bond length is among the shortest ones observed for gold clusters. A very

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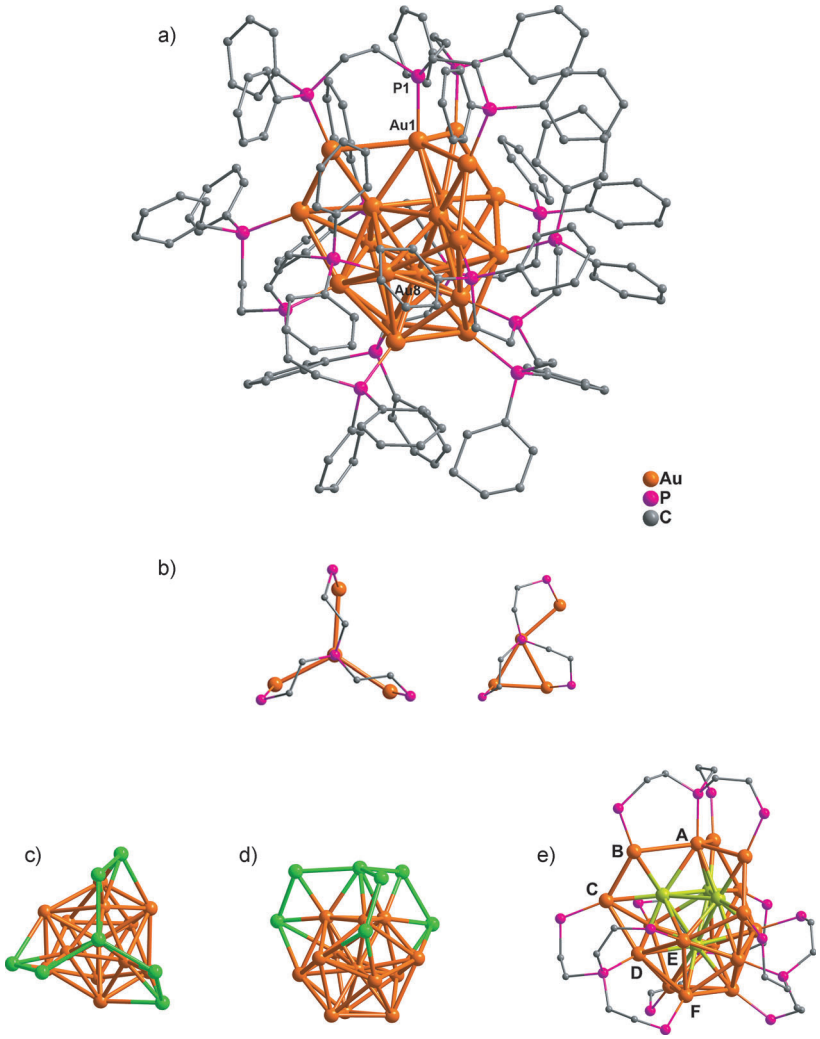

Figure 1. a) The structure of the tetracationic $[Au_{20}(PP_3)_4]^{4+}$ cluster in **1**. b) Two types of bridging modes of PP_3 ligands. c) Top view of the Au_{20} core structure in **1**; green atoms denote the Au_7 unit, and the Au_{13} icosahedron is shown in orange; d) side view. e) The bridging mode of PP_3 in **1**; the 16 surface gold atoms are of six types (from A to F), the four interstitial Au atoms are shown in green, and phenyl groups have been omitted for clarity.

short Au-Au distance of 2.5817(7) Å was found recently in $[Au_{14}(PPh_3)_8(NO_3)_4]$.[16]

The Au_{20} core is chiral. The C_3 symmetry is clearly shown in Figure 1c, where the cluster is viewed down the threefold axis. The helical arrangement of the Au_7 motif lowers the symmetry of the Au_{20} cluster. This is the first structural evidence on a gold nanocluster bearing an intrinsic chiral inorganic core. Previous structurally determined chiral gold nanoclusters all contain achiral inorganic cores in chiral environments, and the origin of the chirality is either the chiral organic ligand or the asymmetric arrangement of staples.

The absolute configuration of **1** is related to the conformation of PP_3. Because the flexible PP_3 can adopt two types of conformations, both enantiomers of **1** are present in the crystal (Supporting Information, Figure S6). Cluster **1** crystallized in a non-centrosymmetric space group, but racemic twinning occurred as suggested by Flack parameter of 0.36(6). The sample is silent in CD spectroscopy because it is a racemic mixture.

The sample was further characterized by an ESI-TOF mass spectrometer with an electrospray ionization source in positive mode (Figure 2a). The spectrum is quite clean, with the molecular ion peak $[Au_{20}(PP_3)_4]^{4+}$ at $m/z = 1655.30$ being dominant. A minor peak at $m/z = 2219.06$ was observed, which corresponds to $[Au_{20}(PP_3)_4Cl]^{3+}$ derived from the binding of a chloride to $[Au_{20}(PP_3)_4]^{4+}$. The observed isotopic patterns of $[Au_{20}(PP_3)_4]^{4+}$ and $[Au_{20}(PP_3)_4Cl]^{3+}$ are perfectly in agreement with the simulated (Figure 2b,c). To fulfill the requirement of charge balance, 16 of the 20 gold atoms should have a valency of zero. The bonding energy of Au $4f_{7/2}$ was determined to be 84.3 eV by XPS (Supporting Information, Figure S2), which are characteristic of Au^0. Because the Au atoms are largely Au^0 in the nanocluster, the band at 84.9 eV for Au^I could hardly be observed.

Nanoclusters with 20 gold atoms fall in a special category. Wang et al. reported that the most stable form of a bare Au_{20} is a tetrahedral (T_d) structure.[17] They also synthesized ligand-protected Au_{20} using a two-phase system, and the product was identified as $Au_{20}(PPh_3)_8^{2+}$ by mass spectrometry, which was computed to have a tetrahedral structure.[18] Jin et al. reported a thiolate-protected Au_{20} cluster, and its composition $Au_{20}(SCH_2CH_2Ph)_{16}$ was determined by mass spectrometry.[19] Zen et al. theoretically predicted that this thiolate-protected Au_{20} cluster has a prolate Au_8 core with four -RS-Au-RS-Au-RS-Au-RS- extended staples.[20] Recently, we reported the first structural determination of a phosphine-protected Au_{20} cluster $[Au_{20}(PhPpy_2)_{10}Cl_2]Cl_4$, which has a bivertex-shared double incomplete icosahedral structure.[21] The present work represents an unprecedented chiral arrangement of Au_{20}.

The UV/Vis absorption spectrum of **1** in CH_2Cl_2 shows three prominent absorption bands at 370, 495, 550 (shoulder), and a broad band around 833 nm tailing to 1000 nm (Figure 3). The optical energy gap was determined to be 1.33 eV (Figure 3 inset), which is much lower than 1.77 eV found in bare Au_{20}, 2.15 eV in $Au_{20}(SCH_2CH_2Ph)_{16}$, and 2.24 eV in $[Au_{20}(PhPpy_2)_{10}Cl_2]Cl_4$. Cluster **1** and $[Au_{20}(PhPpy_2)_{10}Cl_2]Cl_4$[21] each contains a phosphine-protected Au_{20} core, but they have quite different HOMO–LUMO gaps. This fact shows that the core structures affect the optical properties of gold nanoclusters containing the same number of gold atoms.

Although the optical energy gap of **1** is not high, this Au_{20} cluster is quite stable. It is confirmed by UV/Vis spectra that no decomposition was observed after its solution had been

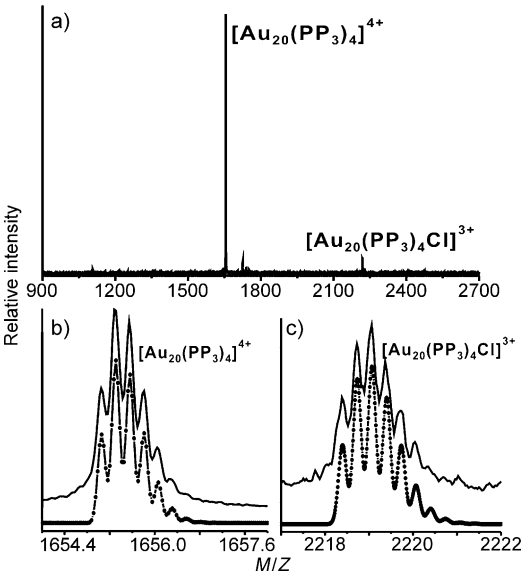

Figure 2. a) Mass spectrum of the Au_{20} cluster. b), c) The measured (solid trace) and simulated (dotted trace) isotopic patterns of b) $[Au_{20}(PP_3)_4]^{4+}$ and c) $[Au_{20}(PP_3)_4Cl]^{3+}$.

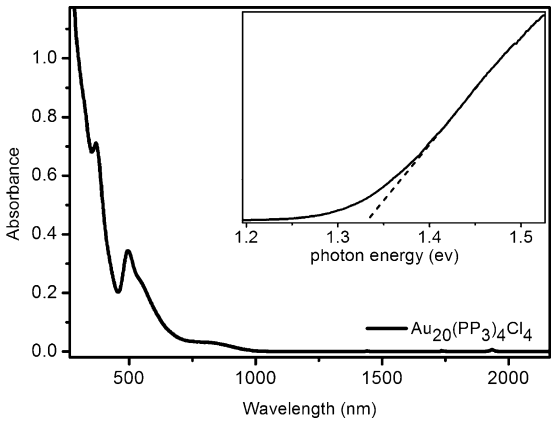

Figure 3. The optical absorption spectrum of **1** in dichloromethane. Inset: the spectrum on the energy scale (eV); the HOMO–LUMO gap is 1.33 eV.

stored under ambient conditions in the absence of light for three weeks (Supporting Information, Figure S3). The total number of valence electrons of $[Au_{20}(PP_3)_4]^{4+}$ is calculated to be 16 ($n = 20–4$). It does not match either the case of shell closure (18 electrons)[22] or the 2D electron-counting requirement (12 electrons).[23] The valence electron number of $Au_{38}(SR)_{24}$ with a face-fused bi-icosahedral Au_{23} core is 14, which is not a magic number as required by the superatom model; this can be explained with an ellipsoidal shell model.[24,25] Cluster **1** with a nonspherical structure might also fall in this category. The stability of **1** comes from both electronic and geometrical factors. Furthermore, the chelation of the tetraphosphine PP_3 provides additional stabilization contribution.

In summary, this work presents important structural evidence on the existence of a chiral gold cluster core. Compound **1** has a new type of Au_{20} configuration. The chelating ability of multidentate phosphines enhances the stability of the Au_{20}. The chiral arrangement of the Au_{20} core structure indicates that the protecting ligands can impose intense influence on the structure of the resulted gold clusters. We expect that homochiral gold nanoclusters with a chiral inorganic gold core could be prepared with the use of chiral multidentate protecting ligands. Further work on modulating the structures of gold nanoclusters with various bridging ligands is in progress.

Experimental Section

Synthesis of **1**: A freshly prepared solution of $NaBH_4$ (22.1 mg, 0.585 mmol) in ethanol (3.0 mL) was added dropwise under vigorous stirring to a solution of $PP_3Au_4Cl_4$ (93.4 mg) in CH_2Cl_2 (80 mL). The solution color changed from colorless to brown and finally to black. The reaction mixture was stirred for 10 h at 30 °C in air in the absence of light. Solvent was removed under reduced pressure to give a black solid. This solid was then dissolved in CH_2Cl_2 (3.0 mL) and CH_3OH (0.1 mL), and the solution was centrifuged for 4 min at 8000 r min^{-1}. The brown supernatant was collected and subjected to the diffusion of pentane, black crystals of **1** deposited after about 5 days (17.8 mg, yield 23.2% based on Au).

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[15] Crystal data for **1**: $C_{168}H_{168}Cl_4P_{16}Au_{20}$, $a = b = c = 36.0125(2)$ Å, $V = 46704.6(4)$ Å^3, cubic, space group $P\bar{4}3n$, $Z = 8$, $T = 100$ K, 31285 reflections measured, 10933 unique ($R_{int} = 0.0741$), final $R1 = 0.1010$, $wR2 = 0.1276$ for 8956 observed reflections [$I > 2\sigma(I)$]. CCDC 959621 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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