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Research paper

Water-soluble Au_{13} clusters protected by binary thiolates: Structural accommodation and the use for chemosensing

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ABSTRACT

Here we report a successful synthesis of water-soluble 13-atoms gold clusters under the monolayer protection of binary thiolates, glutathione and penicillamine, under a molecular formula of $Au_{13}(SG)_5(PA)_7$. This monolayer-protected cluster (MPC) finds decent stability and is demonstrated to possess an icosahedral geometry pertaining to structural accommodation in contrast to a planar bare Au_{13} of local minima energy. Natural bond orbital (NBO) analysis depicts the interaction patterns between gold and the ligands, enlightening to understand the origin of enhanced stability of the Au_{13} MPCs. Further, the water-soluble Au_{13} MPCs are found to be a decent candidate for chemosensing and bioimaging.

1. Introduction

Gold clusters in recent decades have stimulated extensive research interest owing to their size-dependent properties and promising applications in nanoelectronics, catalysis, chemical sensing, optics and biomedicine, etc. [1–4]. In recent years, a series of monolayer-protected gold clusters (Au MPCs) with precise atomic-level structure have been reported, such as Au_{102} [5], Au_{60} [6], Au_{55} [7], Au_{38} [8], Au_{36} [9,10], Au_{30} [10,11], Au_{25} [12,13], Au_{20} [14,15], and Au_{18} [16], etc. Among others, reasonable research interest has been attracted upon ultrasmall gold clusters at n = 11–13 pertaining to a transition from 2D to 3D structures. In particular, 13-atoms metal clusters (such as Al_{13}^-) enable a minimal icosahedron structure and may fulfill a geometrical shell closing of 40 valence electrons known as a magic number [2,17]. In previously published investigations, gas-phase chemistry and topologies of Al_{13} [18,19], Pt_{13} [20], Ag_{13} [21,22], and Au_{13} clusters [17,23] have been established. According to these reports, icosahedral structures are found to be the most stable for Al_{13} and Pt_{13}, but Ag_{13} bears a bilayer triangular structure. In contrast, Au_{13} was found to have a planar geometry in its lowest-energy ground-state due to covalent bondings of gold atoms [24–28]. However, relativistic effect and electronegativity of the gold atoms perplex the interactions between ligands and gold cores in ligand-protected gold clusters [29–32], which also allows for an icosahedral innermost Au_{13} core for Au MPCs such as the aforementioned Au_{25} [12,13,33]. Therefore, it is important to rationalize the electronic and geometric structures of the typical small gold cluster—Au_{13} MPCs, hence furthering the understanding of the stability of such clusters in gas phase and in wet synthesis [34,35].

Along with the novel gold cluster stability, it's worth mentioning that the urgent demand of biocompatible use of such stable metal clusters has attracted many interests. However, the use of organic solvent as protecting ligand gives rise to poor water solubility of MPCs, which restricts the potential applications of gold clusters in biological systems and environmental analyses. This inconvenience can be overcome by using hydrophilic thiol molecules with diverse functional groups as the ligands to synthesize the water-soluble and biocompatible MPCs, such as glutathione (GSH), D-penicillamine (DPA), 1-thioglycerol, 2-mercaptoethylamine, etc. [36–39]. Among them, GSH is an important antioxidant (tripeptide) capable of preventing damage to cellular components by reactive oxygen species. DPA is a medication (L-penicillamine is toxic) of the chelator class and has also been found an efficient protection ligand in synthesizing nanoclusters with remarkable fluorescence. In addition to the combined consideration of biocompatibility, fluorescence and chelating

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effect, we are also motivated by noting that heterothiolate-protected nanoclusters could give rise to multifold properties [40,41].

Herewith we report a successful synthesis of water-soluble Au_{13} MPCs via the ligand-induced etching method by using a mixed thiolate protection (i.e., penicillamine and glutathione). The cluster structure $Au_{13}(SG)_5(PA)_7$ was determined via high resolution mass spectrometry along with first-principles optimization calculations. Considering the as-prepared Au_{13} MPCs bear decent red fluorescence at 690 nm, we have applied for chemo-sensing in ions detection and bioimaging. It is found that this water-soluble Au_{13} clusters protected by binary thiolates are highly efficient to detect and differentiate Fe^{3+} and Cu^{2+} ions in water and in living cells. This is an important promotion although such ion detection is not a fresh topic. Note that metal ions (such as Fe^{3+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions) may selectively cause health issues but accurate detection of them is actually not trivial, especially in vivo.

2. Experimental section

2.1. Chemicals

Hydrogen tetrachloroaurate(III), hydrate (49% Au) was purchased from Alfa Aesar. L-glutathione (reduced, 99%), penicillamine and sodium borohydride (99%) were obtained from J&K Scientific Ltd. (Beijing, China). Methanol (HPLC purity) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Ultrapure water (18.2 MΩ) was used in all experiments.

2.2. Synthesis of Au MPCs

All chemicals (analytical and spectroscopic grade) were commercially available and used as received without further purification. The monolayer-protected gold clusters were synthesized according to the following procedure. Firstly, the aqueous solution of H_4AuCl_3 (98.46 mg, 0.25 mM) and glutathione (GSH; 307.32 mg, 1.0 mM) were mixed together in the solution and kept at ~0 °C in an ice bath for 30 min. To this clear solution, a freshly prepared ice-cold aqueous $NaBH_4$ (94.58 mg, 12.5 mL) were slowly added dropwise under vigorous stirring condition. After removing the ice bath, the reaction was allowed to proceed under constant stirring for 1 h, and the products were precipitated with methanol. After filtration, black precipitate of Au nanoparticles (Au NPs) were obtained, and then washed with excessive methanol. Secondly, the as-prepared Au NPs were dissolved and stabilized in 12.5 mL H_2O. After penicillamine (PA, 74.6 mg, 0.5 mM) slowly added dropwise to the solution, the reaction was allowed to proceed under constant stirring for 12 h at 55 °C. The final gold clusters were precipitated and filtration with methanol.

3. Results and discussion

We used high-resolution electrospray ionization mass spectrometry (ESI MS) to monitor and optimize the synthesis of the as-prepared gold clusters, as shown in Fig. 1A, where an intense peak at $m/z = 2562.68359$ was observed (marked as peak No. 1), exclusively assigned to $[Au_{13}(SG)_5(PA)_7)]^{2-}$ along with identical isotopic distributions comparing with simulated pattern (Fig. 1A inset). This specific isotope pattern ensures exclusive identification of the as-prepared cluster. There are also a few other sodium-involved [1,42,43] and MeOH-attached peaks showing reasonable intensity due to the mobile phase molecules, such as $[Au_{13}(SG\text{-}H)_5(PA)_7Na]^{2-}$ (No. 2, 2573.67682), $[Au_{13}(SG\text{-}2H)_5(PA)_7Na_2(CH_3OH)]^{2-}$ (No. 3, 2601.25619), $[Au_{13}(SG\text{-}3H)_5(PA)_7Na_3(CH_3OH)]^{2-}$ (No. 4, 2601.25619) and $[Au_{13}(SG\text{-}2H)_5(PA)_7Na_2(CH_3CN)(CH_3OH)]^{2-}$ (No. 5, 2637.21145), evidencing the Au_{13} motifs synthesized in our procedure. More characterization details (UV–Vis adsorption, TEM, XPS and fluorescence spectrum) as well as the expanded and simulated spectra of these fragment peaks are given in Figs. S1–S3 (ESI). The polyacrylamide gel electrophoresis (PAGE) analysis reveals high grade of purity of the Au_{13} MPCs (Fig. S2d, ESI).

Fig. 1B presents a FT-IR spectrum of the Au_{13} MPCs comparing with that of glutathione and penicillamine respectively. It is worth noting that the infrared-active mode assigned to S—H bond vibration disappears in the Au_{13} MPCs, indicating a substitute of the S—H bond by corresponding Au—S bond in forming the protected monolayer. To further investigate the ligand binding mode on the surface, 2D-NMR correlation (^1H-^1H COSY) experiment was conducted, as shown in Fig. 1C, where the peaks are assigned as the proton signals H_a, H_b, H_c on —PA ligands, and H_1-H_6 on —SG ligands. The peaks of H_3 and H_4 proton signals split into two pairs of peaks (labeled as 3, 3′ and 4, 4′). The NMR spectrum shows that —PA and —SG ligands adopt two binding modes on the Au_{13} MPCs surface as the inset shows.

Having measured the formula weight and composition of the Au_{13} MPCs, we then endeavor to fully demonstrate the packing structure of this cluster. Extensive investigations of thiolate-protected metal clusters have ascertained two favorable forms of the lowest-energy structures, i.e., in the form of RS-Au and RS–Au–SR motifs. Furthermore, previously published work has found four lowest-energy geometrical structures for a bare Au_{13}: planar, flake, cuboctahedral, and icosahedral, as shown in Fig. 2A [24–28]. Our calculation results based on both DFT with Gaussian and VASP packages (details of calculation methods in ESI) confirmed that the planar structure of Au_{13} possess a local minimum energy with the others in the following order: E(planar) < E(flake) < E(cuboctahedron) < E(icosahedron), which is in agreement with previous studies [24–28]. However, it is found that the local minimum energy structure of $Au_{13}(SCH_3)_{12}$ belongs to the icosahedral geometry (i.e., one center Au atom and the other 12 Au atoms forming an icosahedral structure). This is consistent with the previous findings of ligand-protected Au_{13} clusters as determined by single-crystal analysis [44,45], indicating the 12 surface sites of an icosahedral Au_{13} are equally favorable for the monolayer protection [46]. It is also evidenced that, from the IR spectroscopic analysis as mentioned above, IR-active mode assigned to S—H bond vibration disappeared, revealing that the 12 ligands chemisorb on the gold core with end-on orientation of the S atoms by forming 12 Au—S bonds. Note that, the average Au—Au bond length of each $Au_{13}(SCH_3)_{12}$ increases comparing to that of a bare Au_{13} (Table S1 in ESI). Furthermore, the UV–Vis absorption spectrum in aqueous solution is reproduced (with identical spectral profile and peak positions) through TD-DFT calculations by using the icosahedral structure of $Au_{13}(SCH_3)_{12}$ as the model system (Fig. S4a, ESI). The theoretical absorption spectrum shows a broad weak absorption band, which appears to be in good agreement with the experimental results, and validates the icosahedral structure of Au_{13} MPCs in the form of RS–Au.

We have also investigated the surface charge distributions typically for cuboctahedral and icosahedral isomers, and find that the charge-density becomes more positively addressed for the core Au atom and more negatively for the surface Au atoms when linked with the ligands (Fig. S5 in ESI). This seems contradictory with the aforementioned lengthening of Au—Au bond when considering that positive and negative charges between the Au atoms might make bonds shorter under coulomb attraction. However, the fact is that, within such an Au—Au—S system, the bond strength of Au—S bond (4.34 eV) is even more intensive than the Au—Au bond (~2.27 eV). NBO analysis shows that it is the electron transfer from ligands to Au—Au bonds that creates strong Au—S covalent bonds