Communication

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Au$_{42}$: An Alternative Icosahedral Golden Fullerene Cage

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Gold nanoclusters have attracted much attention over the past two decades due to their wide applications toward biology, catalysis, and nanotechnology.[1−3] Many earlier studies have shown that planar trigonal raft structures attain the lowest energies for neutral gold cluster Au$_n$ up to $n = 7$, whereas a large number of amorphous compact structures with almost the same energy are found for $n \geq 13$.[1c,4−6] Cleveland et al. analyzed three classes of gold nanoclusters with diameter of 1−2 nm using X-ray powder diffraction and suggested a truncated-decahedral motif.[5d] Later, Koga et al. studied larger gold nanoclusters of 2−3 nm and arrived at a similar conclusion.[5e] Häberlen et al. performed scalar relativistic all-electron density functional theory (DFT) calculations for several highly ordered clusters with icosahedral, octahedral, and cuboctahedral symmetries and size up to $n = 147$.[6a] Recently, Li et al. revealed a new structure of Au$_{20}$ with a remarkably large HOMO−LUMO gap and electron affinity based on their photoelectron spectroscopy experiments.[7] Their DFT studies also showed that this new cluster adopts a tetrahedral structure that is a fragment of the face-centered cubic lattice. Despite these major advances, medium-sized gold clusters observed thus far are all space-filled compact structures, and no cagelike structures have been synthesized in laboratory. Highly symmetrical gold clusters with a hollow cage would be of both fundamental and practical interests because of their larger surface area (compared to their compact-structure counterparts) as well as their potential applications as golden cages to accommodate other atoms or molecules, or as structural motifs to build highly stable or even possibly magic-number core−shell nanoclusters[8a,b] and novel cluster-assembled materials.[8c]

As mentioned above, to date, it is still an open question whether the cagelike gold clusters exist. The closest match of cagelike cluster is bimetallic icosahedron W@Au$_{12}$, which was first predicted by Pyykkö and Runeberg[9] and later synthesized by Li et al.[10] However, the pure icosahedral form of Au$_{12}$ is unstable and must be stabilized by the endohedral W atom. Theoretical studies of gold fullerenes are also scarce.[7] Recently, Johansson et al. predicted, for the first time, a highly stable icosahedron Au$_{32}$ fullerene based on DFT calculations.[11] This I_h symmetrical gold fullerene can be constructed using the carbon fullerene C$_{60}$ as a template. Remarkably, the Au$_{32}$ fullerene exhibits perhaps the largest HOMO−LUMO gap among medium-sized gold clusters. Moreover, the Au$_{32}$ fullerene is consistent with the $2(N + 1)^2$ aromatic rule, introduced by Hirsch and co-workers, and has strong aromaticity (NICS: −100).[12] A recent theoretical study suggested that the Au$_{32}$ fullerene cage could incorporate up to three Au atoms inside without showing major structural deformation.[13] Except for these previous works, no other gold fullerenes have been reported. In this communication, we report another highly stable and closed-shell I_h symmetrical fullerene Au$_{42}$, as shown in Figure 1, based on DFT calculations. Two DFT methods were employed, that is, the generalized gradient approximation (GGA) functional BP86[14] and Becke's three parameter hybrid functional with the Lee−Yang−Parr correlation functional B3LYP.[15] The effective core potential (ECP) of LANL2DZ basis
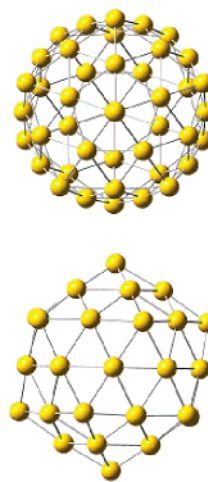

Figure 1. Top view (top) and side view (bottom) of the calculated icosahedral I_h geometry of Au$_{42}$ using the BP86/LANL2DZ method. The Au−Au bond lengths vary between 2.786 and 2.870 Å.

Table 1. Calculated Properties of Au$_{42}$ versus Au$_{32}$ Fullerene[11]

property	Au$_{32}$ (ref 11)	Au$_{42}$
diameter (nm)	∼0.9	∼1.1
symmetry point group	I_h	I_h
HOMO/LUMO gap (eV)	1.7/2.5^a	0.4/0.9^c
frontier orbital configuration	$(t_{2u})^6(g_u)^8(g_g)^0$	$(a_u)^2(h_g)^{10}(g_g)^0$
vibrational freqency (cm^{-1})		
lowest	30/37^a	12/7^c
highest	145/147^a	156/143^c
HOMO (eV)	−6.04^b	−5.75/−5.82^c
binding energy per atom (eV)	2.25^b	2.25/1.82^c
NICS at center of cage	−100^b	116/140^c

^{a} BP86/PBE0 value.[11] ^{b} BP86 value. ^{c} BP86/B3LYP value.

sets[16] was adopted for the gold atom. The harmonic-frequency calculations were performed based on the optimized geometries. All calculations were performed with the Gaussian03 program package.[17]

Au$_{42}$ has a perfect I_h structure since it is constructed from the carbon fullerene C$_{80}$ (with I_h symmetry) as a template. C$_{80}$ fullerene has 42 surfaces: 12 pentagons and 30 hexagons. To build the Au$_{42}$ fullerene, we first place an Au atom at the center of each pentagon and hexagon of C$_{80}$. We then adjust the Au−Au bond length to obtain an initial icosahedron Au$_{42}$. Last, full geometry optimizations with DFT methods (without symmetry constraint) give rise to the final structures (Figure 1). The calculated properties of icosahedral Au$_{42}$ are collected in Table 1. The diameter of icosahedral Au$_{42}$ is 1.1 nm, about 0.2 nm larger than the icosahedral Au$_{32}$ fullerene. The Au$_{42}$ cage is composed of 12 vertexes, 30 edges, and 20 carats. Each edge has three gold atoms, and each surface has six gold atoms to form a trigonal-planar D_{3h} geometry, which has been widely verified as the lowest energy isomer of Au$_6$ by the DFT, MP2, and even the CCSD(T) calculations.[4b,18] The Au−Au bond lengths are

2.819 and 2.920 Å with B3LYP and 2.786 and 2.870 Å with BP86 calculation. These calculated bond lengths are slightly shorter than the corresponding bond lengths calculated from the local-density approximation (2.89 Å) and GGA (2.97 Å),[6a] but are in accordance with the results from recent density functional studies for clusters such as W@Au$_{12}$, Au$_{20}$, and Au$_{32}$.[7,9,11] The Au$_{42}$ fullerene has a modest energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), that is, 0.4 eV with BP86 and 0.9 eV with B3LYP calculation. Moreover, the HOMO is 5-fold and the LUMO is 4-fold degenerate. Note that these calculated HOMO−LUMO gaps are much smaller than the icosahedral Au$_{32}$ (BP86: 1.7 eV, PBE0: 2.5 eV),[11] indicating that the Au$_{42}$ fullerene is not as chemically stable as the icosahedral Au$_{32}$, even though both fullerene structures have the same binding energy per atom (Table 1). In addition, unlike the Au$_{32}$ fullerene, the Au$_{42}$ fullerene does not satisfy the $2(N + 1)^2$ aromatic rule.[12] In particular, the nucleus-independent chemical shift (NICS) value at the center of Au$_{42}$ exhibits a large positive number (Table 1). Although the NICS value is generally considered as an index to measure the aromaticity of fullerene cages, we note that recent works of Aihara et al. show that the NICS value at the cage center may not always correlate with the aromaticity (e.g., for C$_{86}$ fullerene).[19] Thus, the large positive NICS value at the center of the Au$_{42}$ cage may stem from the modest HOMO−LUMO gap, following the explanation of Aihara and co-workers.

The harmonic vibrational frequencies, calculated from both DFT methods (BP86 and B3LYP) for the optimized icosahedral Au$_{42}$, show that the Au$_{42}$ fullerene is a local minimum on the potential energy surface. No imaginary frequencies are found. To determine relative stability of this geometry, we compared the Au$_{42}$ fullerene with two compact structures of Au$_{42}$ suggested earlier. Darby et al. reported a compact C_1 structure as the global minimum based on many-body Gupta potential.[6c] Doye and Wales suggested another compact C_s global-minimum structure based on the Sutton−Chen potentials.[20] Full geometry optimizations were applied to both compact structures using the BP86/LANL2DZ method (both structures were assumed to be closed-shell singlet). The icosahedral Au$_{42}$ fullerene is found slightly higher in energy (ca. 0.7 eV or 70 kJ/mol) than the two compact structures, indicating that the I_h fullerene geometry of Au$_{42}$ is definitely not the global minimum, but nevertheless a low-lying stable structure. In contrast, the Au$_{32}$ fullerene not only satisfies the $2(N + 1)^2$ aromatic rule but also is most likely the global minimum. Note that the icosahedral Au$_{42}$ cage might also be thermodynamically competitive in comparison to its compact counterparts, assuming that the fullerene cage is also as fluxional as the icosahedral cage of the W@Au$_{12}$ cluster.[1c]

Finally, to investigate relative chemical stability of the Au$_{42}$ fullerene, we calculated the HOMO−LUMO gap of the two compact Au$_{42}$ structures mentioned above using the BP86 functional. Indeed, we found that the HOMO−LUMO gap of the icosahedral Au$_{42}$ is appreciably larger than those of the two compact structures (I_h: 0.4 eV; C_1 and C_s: 0.2 eV), suggesting that the fullerene cage structure is likely more chemically stable than the compact structures.

In conclusion, we have shown a new icosahedral fullerene cage structure, Au$_{42}$, which is competitive energetically with respect to the compact structures. More importantly, this fullerene cage structure possesses very high symmetry (I_h) and a hollow space that can hold up to 13 Au atoms (which gives Au$_{55}$ icosahedral compact structure[5,6a]) as well as a larger HOMO−LUMO gap than compact counterparts. Unlike the known gold fullerene Au$_{32}$, the Au$_{42}$ fullerene does not satisfy the $2(N + 1)^2$ aromatic rule. With their apparently dissimilar chemical characteristics, the two gold fullerenes can be used to accommodate other atoms or molecules for the purpose of studying fundamental chemistry.

Supporting Information Available: Data of Cartesian coordinates, harmonic vibrational frequencies, electronic energies for Au$_{42}$, and the complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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