



Communication

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Structural Evolution of Atomically Precise Thiolated Bimetallic $[Au_{12+n}Cu_{32}(SR)_{30+n}]^{4-}$ (n = 0, 2, 4, 6) Nanoclusters

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All-thiol-stabilized Ag_{44} and Au_{12}Ag_{32} nanoparticles with single-crystal structures

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Structure of $Ag_{44}(4-FTP)_{30}$ cluster







Background

Ligand-Stabilized Au₁₃Cu_x (x = 2, 4, 8) Bimetallic Nanoclusters: Ligand Engineering to Control the Exposure of Metal Sites

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Crystal structures of $[Au_{13}Cu_2(PPh_3)_6(SPy)_6]^+$ (a,b) and $[Au_{13}Cu_4(PPh_2Py)_4(SC_6H_4$ -tert- $C_4H_9)_8]^+$ (c,d) clusters. (b,d) Structures showing only metal atoms.

In this paper.....

Experimental

Cluster	Gold precursors	Counter ions
Au ₁₂ Cu ₃₂ (SPhCF ₃) ₃₀ -4PPh ₄	AuPPh ₃ Cl	PPh ₄ Br
Au ₁₄ Cu ₃₂ (SPhCF ₃) ₃₂ ·4PPh ₄	AuPPh ₃ Cl	NBu ₄ Br
Au ₁₆ Cu ₃₂ (SPhCF ₃) ₃₄ -4PPh ₄	AuPPh ₂ PyCl	PPh ₄ Br
Au ₁₆ Cu ₃₂ (SPhCF ₃) ₃₄ -4PPh ₄	AuPPh ₂ PyCl	NBu ₄ Br

$$[Au_{12+n}Cu_{32}(SR)_{30+n}]^{4-}$$
 (n = 0, 2, 4, 6)





The average Cu···Cu distance in six $Cu_2(SR)_5$ units is 2.763 Å (2.761–2.781 Å), 8% I onger than the sum of Cu atomic radii (1.28 Å),

Ag···Ag distance in $[Au_{12}Ag_{32}(SR)_{30}]^{4-}$ was averaged as 2.978 Å, only 3% longer than the sum of Ag atomic radii (1.44 Å).

Crystal structure of the $[Au_{12}Cu_{32}(SR)_{30}]^{4-}$ cluster. (a) Overall structure of the $[Au_{12}Cu_{32}(SPhCF_3)_{30}]^{4-}$ cluster. All hydrogen and trifluoromethyl groups are omitted for clarity. (b) Two-shell $Au_{12}@Cu_{20}$ core of the cluster. (c) Structure of the cluster with the $Au_{12}@Cu_{20}$ two-shell cores in the space-filling style. (d) Structure of the surface $[Cu_2(SPhCF_3)_5]$ motif. Color legend: orange spheres, Au; blue spheres, Cu; yellow spheres, S; gray sticks/spheres, C.





Surface structures of $Au_{12}Cu_{32}@Aux$ (x = 0, 2, 4, 6) nanoclusters: (a) $[Au_{12}Cu_{32}(SR)_{30}]^{4-}$. (b) $[Au_{12}Cu_{32}Au_2(SR)_{32}]^{4-}$. (c) Schematic diagram of the formation of the $Cu_2Au(SR)_6$ unit from $Cu_2(SR)_5$ unit. (d) $[Au_{12}Cu_{32}Au_4(SR)_{34}]^{4-}$. (e) $[Au_{12}Cu_{32}Au_6(SR)_{36}]^{4-}$. Color legend: gold spheres, Au; blue spheres, Cu; yellow spheres, S. All hydrogen, fluorine, and carbon atoms are omitted for clarity.



Figure S5. Top: Projection of the Kohn-Sham electron states to spherical harmonics in the $Au_{12}Cu_{20}$ core of $[Au_{12}Cu_{32}(SCPhCF_3)_{30}]^4$. The HOMO-LUMO gap is centered around zero energy. The HOMO manifold has superatomic 1D-symmetry and the LUMO manifold 1F-symmetry (note that the 2S state is found in the middle of the 1F-states). Bottom: analysis of angular momentum character of the states localized to Au atoms in the core, Cu atoms in the core and Cu atoms in the ligand layer. The electronic structure of the other $[Au_{12+n}Cu_{32}(SCPhCF_3)_{30+n}]^{4-}$ (n = 2, 4, 6) clusters is similar and is not shown here

Results and discussion

Table S2. Comparison of PBE-relaxed theoretical structures and the crystal data for $[Au_{12+n}Cu_{32}(SPhCF_3)_{30+n}]^4$ - clusters. Average bond lengths given in Å.

n		Au-Au (1 st shell)	Cu-Cu (2 nd shell)	Au-Cu	Cu-S	Au-S
0	exp.	2.788	3.050	2.699	2.326	-
0	calc.	2.878	3.092	2.723	2.352	-
2	exp.	2.786	3.048	2.697	2.308	2.253
2	calc.	2.877	3.096	2.727	2.341	2.341
4	exp.	2.779	3.044	2.694	2.292	2.299
4	calc.	2.882	3.099	2.730	2.338	2.339
6	exp.	2.784	3.065	2.721	2.295	2.276
6	calc.	2.874	3.096	2.727	2.330	2.336





Optical absorption spectra of $[Au_{12}Cu_{32}(SPhCF_3)_{30}] \cdot 4PPh_4+$, $[Au_{14}Cu_{32}(SPhCF_3)_{32}] \cdot 4NBu_4+$, $[Au_{16}Cu_{32}(SPhCF_3)_{34}] \cdot 4PPh_4+$, and $[Au_{18}Cu_{32}(SPhCF_3)_{36}] \cdot 4NBu_4+$ in CH_2CI_2 and the computed absorption spectrum for $[Au_{12}Cu_{32}(SR)_{30}]^{4-}$. In the theoretical spectrum, the individual optical transitions have been folded into a smooth curve by using a Gaussian width of 0.1 eV.



Figure S8 Optical absorption spectra of CH_2Cl_2 solutions of (a) $Au_{12}Cu_{32}(SPhCF_3)_{30} \cdot 4PPh_4^+$, (b) $Au_{14}Cu_{32}(SPhCF_3)_{32} \cdot 4NBu_4^+$, (c) $Au_{16}Cu_{32}(SPhCF_3)_{34} \cdot 4PPh_4^+$, and (d) $Au_{18}Cu_{32}(SPhCF_3)_{36} \cdot 4NBu_4^+$ at room temperature for different times under N_2 atmosphere.



> UV-Vis spectra of DMF solutions of (a)Au₁₂Cu₃₂(SPhCF₃)₃₀·4PPh₄⁺, (b)Au₁₄Cu₃₂(SPhCF₃)₃₂·4NBu₄+,(c)Au₁₆Cu₃₂(SPhCF₃)₃₄·4PPh₄+, and (d) Au₁₈Cu₃₂(SPhCF₃)₃₆.4NBu₄+ heated in air at 50°C for different times.



The comparative change of the absorption at 504 nm with heating time.





Crystal structure of the $[Au_{13}Cu_{12}(SPhCF_3)_{20}]^{4-}$ cluster. (a) Overall structure of the cluster. (b) Side view of the capping of two $Cu_6(SR)_{10}$ units on the Au_{13} core. (c) Top view showing how $Cu_2Au(SR)_6$ is sitting on the Au_6 unit of the Au_{12} shell. Color legend: gold spheres, Au; blue spheres, Cu; yellow spheres, S. All hydrogen atoms and trifluoromethyl groups in (a) and fluorine and carbon atoms in (b) and (c) are omitted for clarity.



- A series of all-thiol capped bimetallic Au–Cu nanoclusters, [Au_{12+n}Cu₃₂(SR)_{30+n}]^{4–} (n = 0, 2, 4, 6), have been successfully prepared.
- The metal distribution and the surface structure of the bimetallic nanoclusters were found to be highly sensitive to the Au precursors and countercations.
- Each [Au_{12+n}Cu₃₂(SR)_{30+n}]⁴⁻ (n = 0, 2, 4, 6) cluster consists of a Keplerate two-shell Au₁₂@Cu₂₀ core protected by (6 - n) units of Cu₂(SR)₅ and n units of Cu₂Au(SR)₆ (n = 0, 2, 4, 6) on its surface.
- Structural determination of the degradation product of the [Au_{12+n}Cu₃₂(SR)_{30+n}]⁴⁻ clusters clearly indicated that the poor stability of thiolated Au–Cu bimetallic nanoclusters was mainly due to the easy oxidation of zerovalent Cu by air.