Supporting information for

Peculiar holes on checkerboard facets of trigonal prismatic $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$ cluster caused by steric hindrance and magic electron count

Lei Huang,‡ Juanzhu Yan,‡ Liting Ren, Boon K Teo*, and Nanfeng Zheng*

Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
*Emails: nfzheng@xmu.edu.cn; boonkteo@xmu.edu.cn
‡ L.H. and J.Y. contributed equally to this work.

Experimental Details

Reagents: Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$, 99.9%), Silver tetrafluoroborate ($AgBF_4$, A.R.), 2,4-dichloro-benzenethiol ($C_6H_4Cl_2S$, A.R.), Sodium borohydride ($NaBH_4$, 98%), dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.), and triethylamine ($(C_2H_5)_3N$, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd.(Shanghai, China).The water used in all experiments was ultrapure. All reagents were used as received without further purification.

Synthesis of $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$: 10 mg of $AuPPh_3Cl$ in dichloromethane, and 20 mg of $AgBF_4$ in methanol were mixed thoroughly in an ice bath. To the mixture was added 10 μL 2,4-dichloro-benzenethiol. After 20-min of stirring, 1 ml of $NaBH_4$ aqueous solution (45 mg ml^{-1}) and 20 ml triethylamine were added quickly under vigorous stirring. After aging for 12 hours at 0 ^oC, the aqueous phase was then removed, and the product was separated from the organic phase by precipitation with methanol and then washed several times with water and methanol. Black rod-like crystals were crystallized from CH_2Cl_2–hexane at 4 ^oC after 15 days. Yield: 30% based on Ag.

Single-Crystal Analysis: The diffraction data were collected on an Agilent SuperNova X-Ray single crystal diffractometer using Cu Kα (λ= 1.54184 Å) micro-focus X-ray sources at 100 K. The data were processed using CrysAlisPro [1]. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-

97 and SHELXL-97 [2] within OLEX2 [3]. Crystallographic data for $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$: monoclinic *P -1*, a = 22.2324(5) Å, b = 22.6794(4) Å, c = 39.9134(6) Å, α = 87.3105(13) °, β = 78.1561(15) °, γ = 62.729(2) °, V = 17481.5(6) Å^3, Z = 2, Cu Kα, T= 100 K, 2θ = 143.398°. 74362 reflections were measured, of which 47999 were unique with R_{int} = 0.0468. Final R_1 = 5.10%, wR_2 = 0.1366 for 3680 parameters and 58889 reflections with $I > 2\sigma(I)$.

Measurements of Optical Properties: Pure crystals of the title cluster were dissolved in dichloromethane for spectra measurements. Ultraviolet-visible (UV-Vis) spectra were recorded on a UV 2550 spectrophotometer.

References:

1) CrysAlis^{Pro}Version 1.171.35.19. (2011). Agilent Technologies Inc. Santa Clara, CA, USA.

2) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112.

3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.

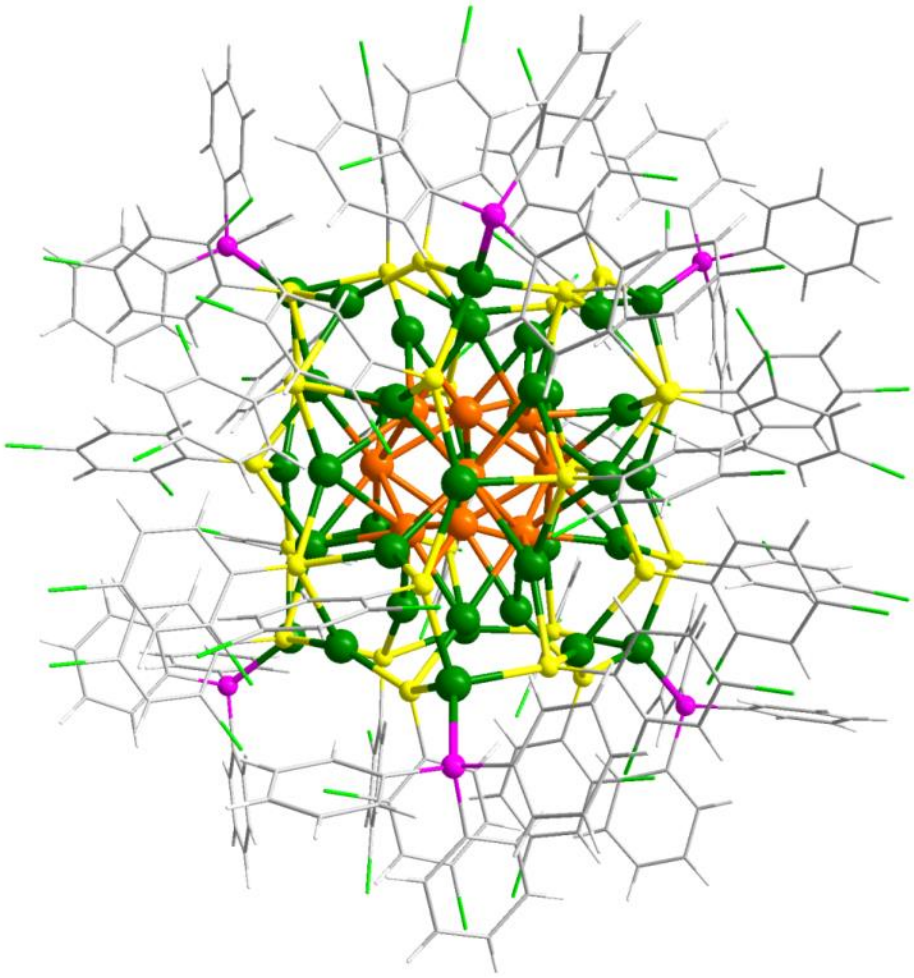

Figure S1. Molecular structure of $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$ nanoclusters. Color legend: Au, orange; Ag, green; S, yellow; P, pink; C, grey, Cl, light green, H, white.

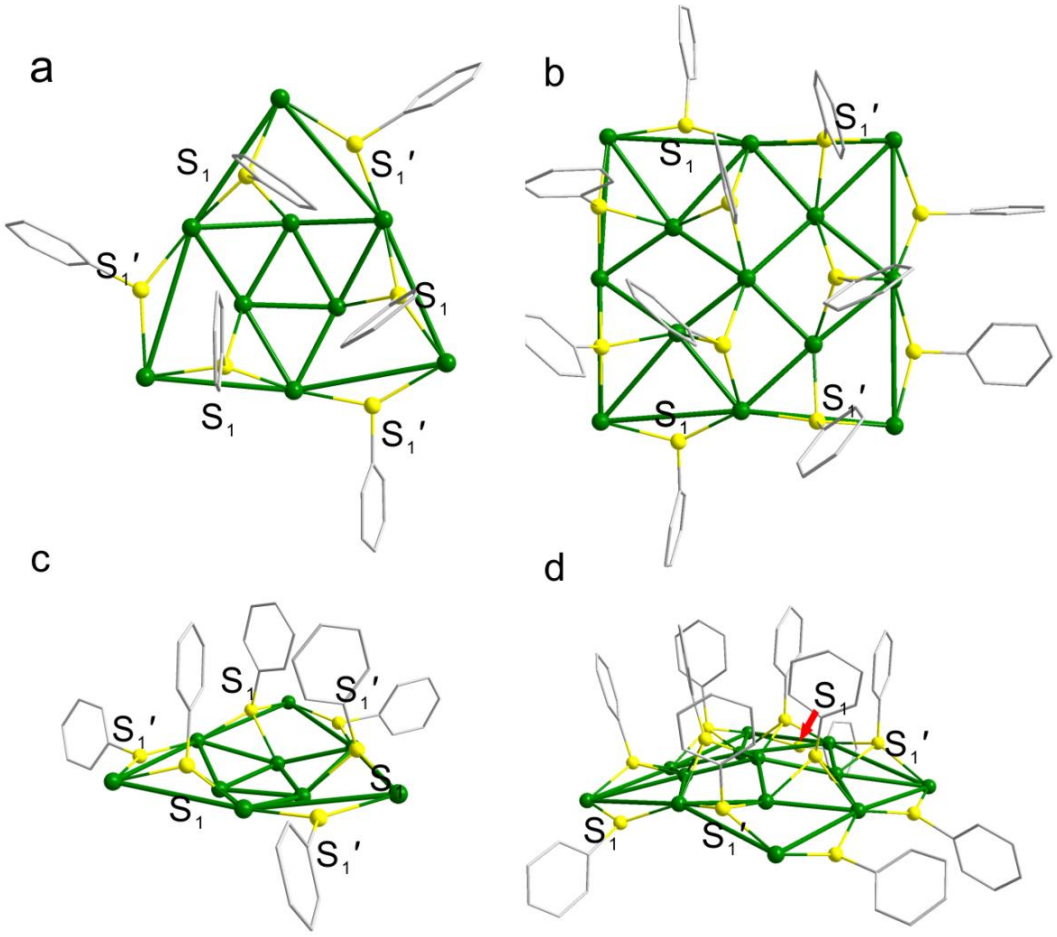

Figure S2. The two kinds of S_1 mercaptides associated with Ag. Color legend: Au, orange; Ag, green; S, yellow; P, pink; C, grey. Chlorine and hydrogen atoms are omitted for clarity.

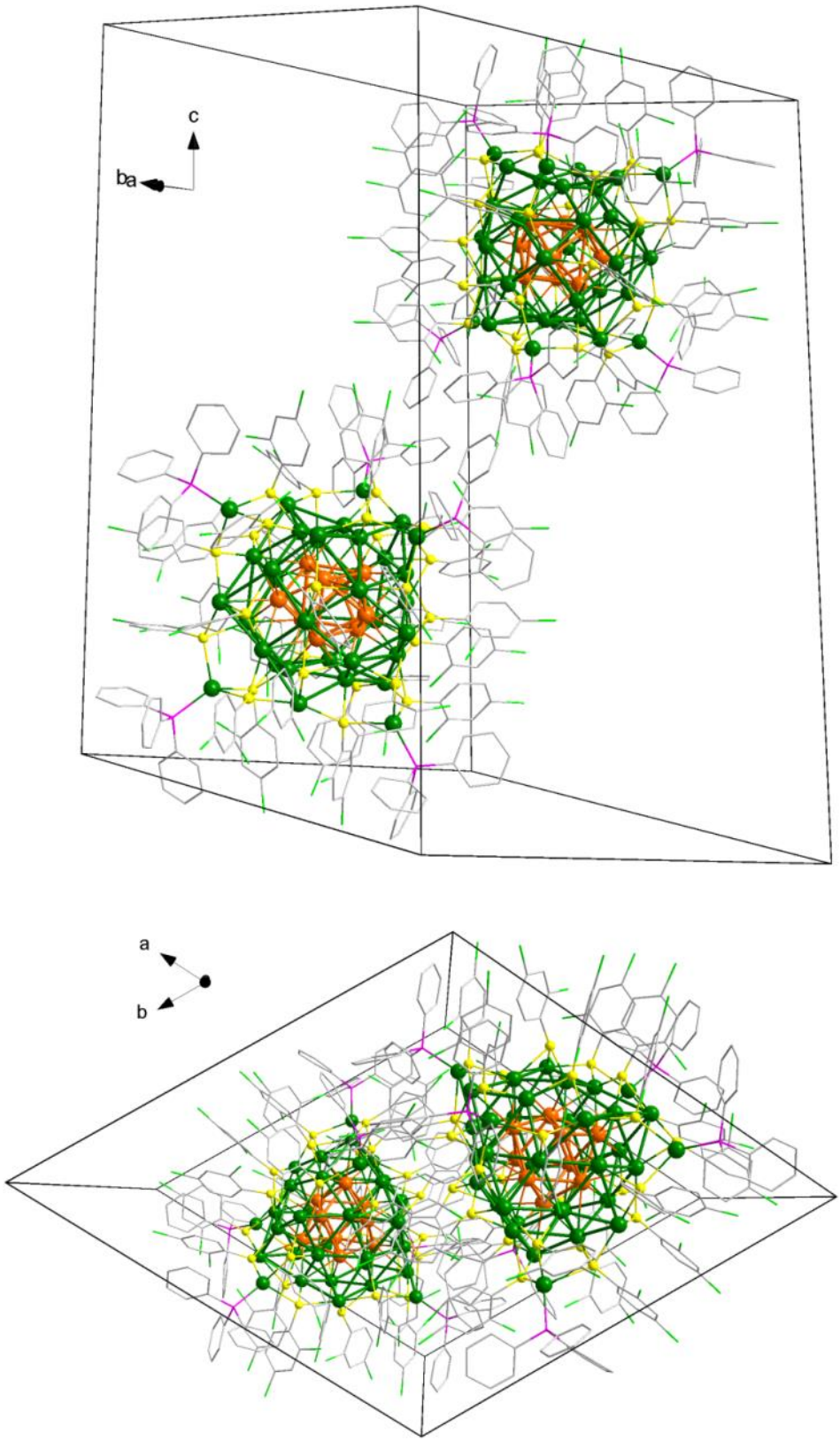

Figure S3. The packing diagram of $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$ crystal. Color legend: Au, orange; Ag, green; S, yellow; P, pink; C, grey, Cl, light green. All hydrogen atoms are omitted for clarity.

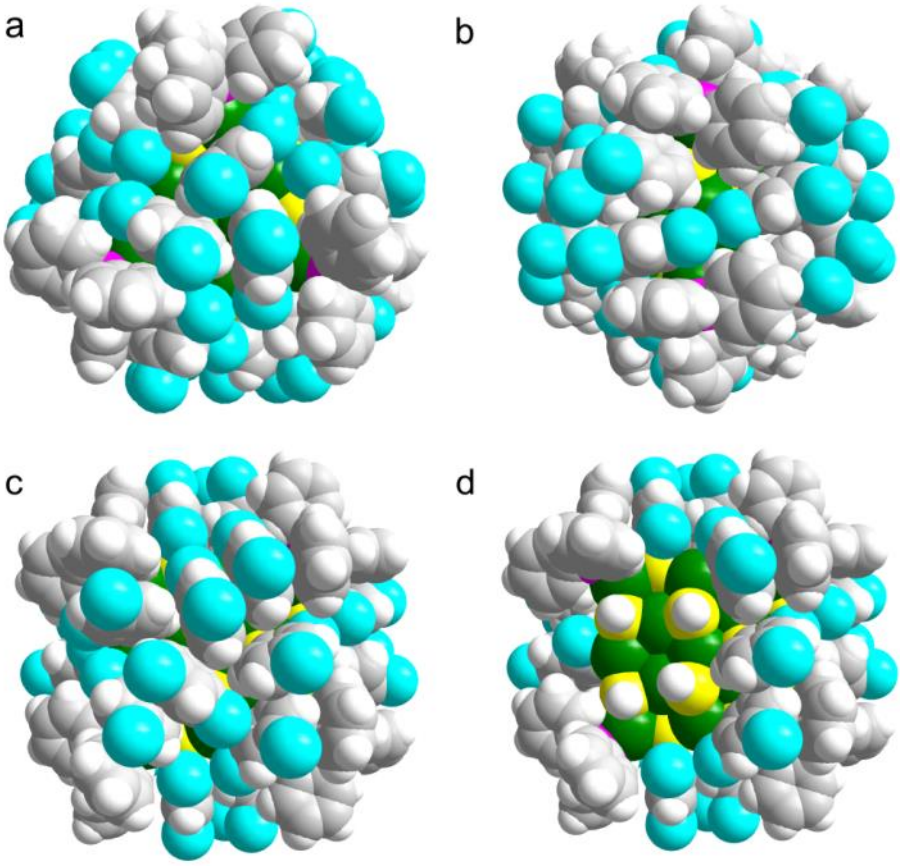

Figure S4. The space filling model of $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$ nanoclusters in the view along different direction, (a) is along the view of Fig. 4c, (b) is along the view of Fig. 4e, and (c) is along the view of Fig. 4f. (d) is the same as (c) with the exception that the four $SPhCl_2$ ligands ($2S_2$ and $2S_3$) surrounding the "hole" have been changed to SH to expose the "hole". Color legend: Au, orange; Ag, green; S, yellow; P, pink; C, grey, H, white, Cl, light blue.

Table S1. Average metal-metal distances of different types in $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$ **.**

Connectivity	Average length [Å]
On quasi-(111) plane (Fig. 4 a-c)	
$A_1 – A_1$	2.9102
$B_1 – B_2$	3.1015
$B_2 – B_2$	3.0404
$C – B_1$	4.8143
$C – B_2$	3.8714
On quasi-(100) plane (Fig. 4 d-f)	
$A_1 – A_1$	3.0041
Around S_1 and the ligand hole	
$C – B_4$	3.8440
$B_1 – B_4$	3.4229
$B_3 – B_4$	3.0318
$B_c – B_4$	3.1796
Around S_1' and S_4	
$C – B_4$	3.7044
$B_1 – B_4$	3.1572
$B_3 – B_4$	3.1142
$B_c – B_4$	3.3688
Inter-shell distances	
$A_1 – B_1$	3.3384
$A_1 – B_2$	2.7371
$A_c – B_2$	3.7372
$A_c – B_3$	3.5764
$A_c – B_4$ (near the hole)	2.7599
$A_c – B_4$	2.8170

Table S2. Ag-S bond distances in $Au_9Ag_{36}(SPhCl_2)_{27}(PPh_3)_6$.

Connectivity	Number	Range [Å]	Average length [Å]
S_1 - B_1	6	2.453 - 2.502	2.480
S_1'- B_1	6	2.475 - 2.505	2.494
S_1 - C	6	2.571 - 2.649	2.620
S_1'- C	6	2.637 - 2.690	2.672
S_1 - B_2	6	2.464 - 2.483	2.476
S_1'- B_4	6	2.489 - 2.511	2.500
S_2 - B_1	6	2.638 - 2.766	2.693
S_2 - B_3	6	2.508 - 2.571	2.543
S_2 - B_4	6	2.546 - 2.600	2.573
S_3 - B_2	6	2.503 - 2.527	2.515
S_3 - B_4	6	2.478 - 2.518	2.500
S_3 - C	6	2.562 - 2.600	2.579
S_4 - B_4	6	2.530 - 2.673	2.589
S_4 - B_c	3	2.554 - 2.646	2.592