Overall structure of $Au_{12}Ag_{60}(S\text{-}c\text{-}C_6H_{11})_{31}Br_9(Dppp)_6$: achieving stronger assembly of icosahedrons M_{13} units

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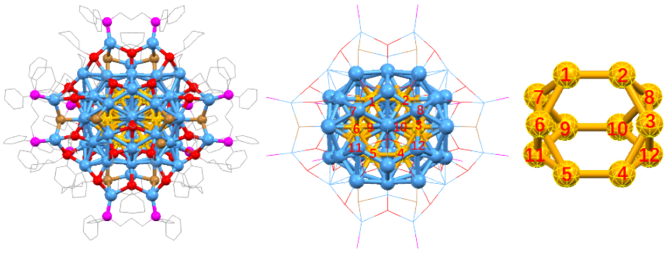


Figure S1. The overall structure of $Au_{12}Ag_{60}(S\text{-}c\text{-}C_6H_{11})_{31}Br_9(Dppp)_6$ and the 12 gold atoms are labeled Au-1 to Au-12 in order. Color label: sky blue = Ag; orange = Au; red = S; brown= Br; purple = P.

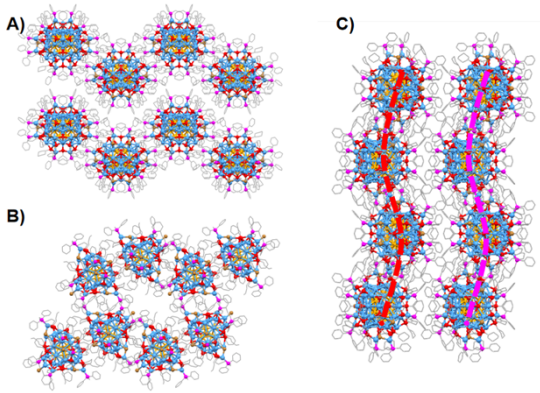


Figure S2. The packing mode of $Au_{12}Ag_{60}(S\text{-}c\text{-}C_6H_{11})_{31}Br_9(Dppp)_6$ defaulting from a, b and c.

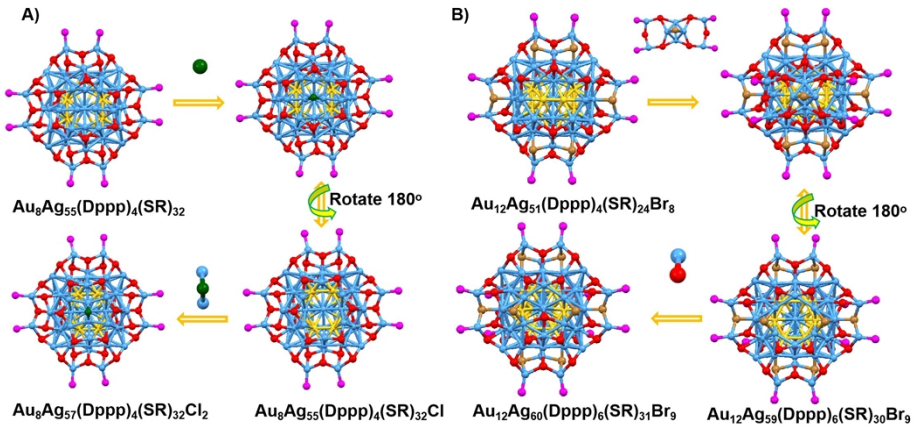


Figure S3. The similarities and differences between the frameworks of A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$.

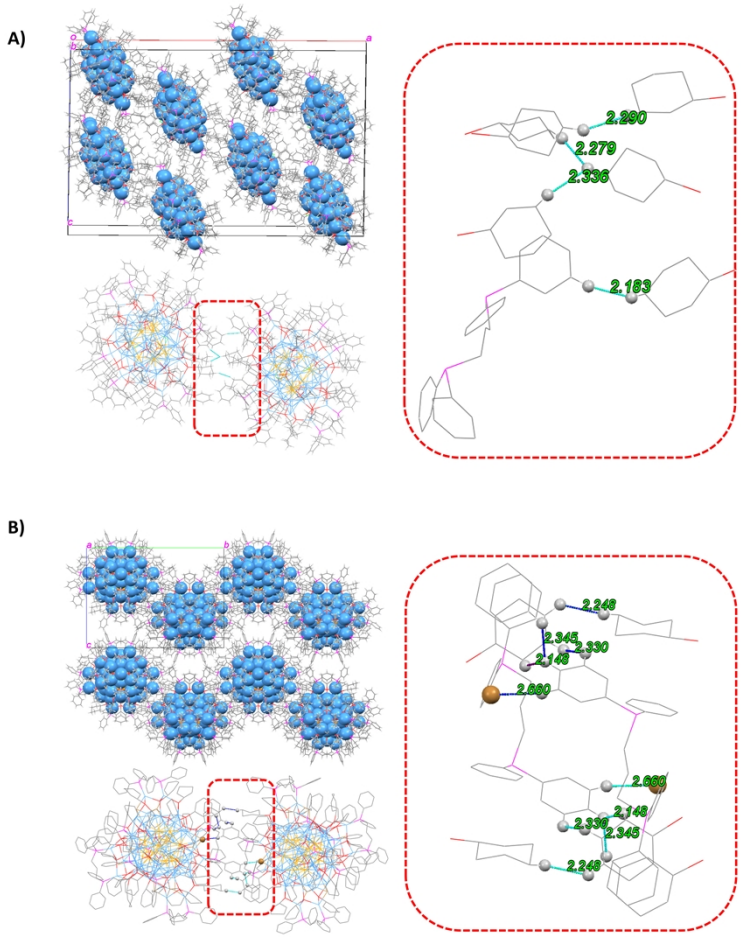


Figure S4. Crystalline packing and ligand-directed intercluster interactions of A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$ nanoclusters.

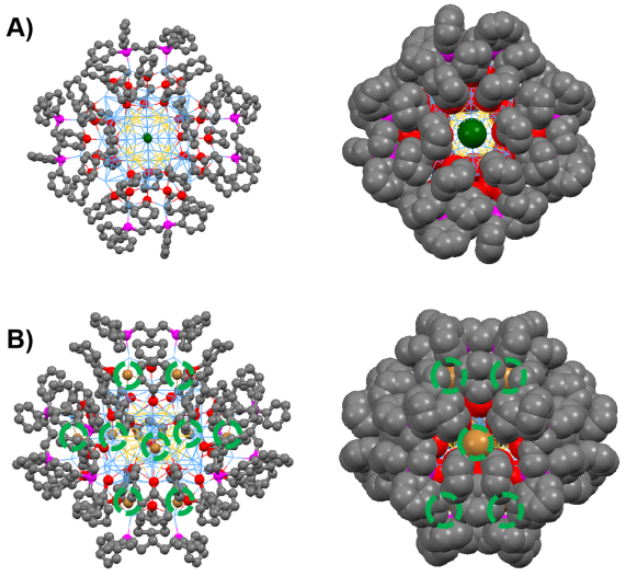


Figure S5. the arrangement of peripheral ligands in space fill mode for A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$.

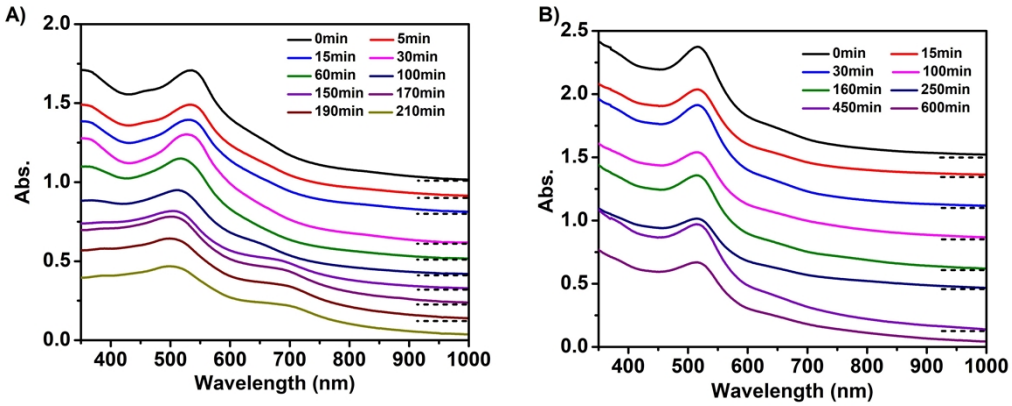


Figure S6. Stability test of A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$ nanoclusters dissolved in $CHCl_3$ at 50°C in contact with the air.

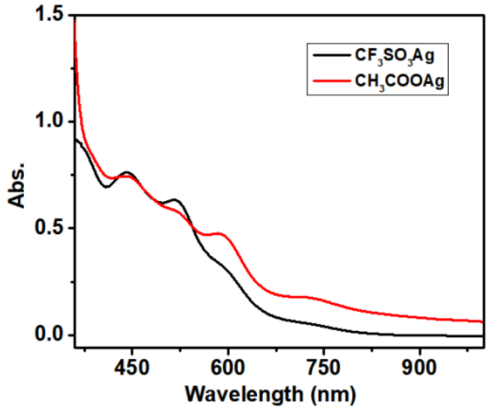


Figure S7. The UV-vis spectra of products synthesized via other silver sources (CF_3SO_3Ag/ CH_3COOAg).

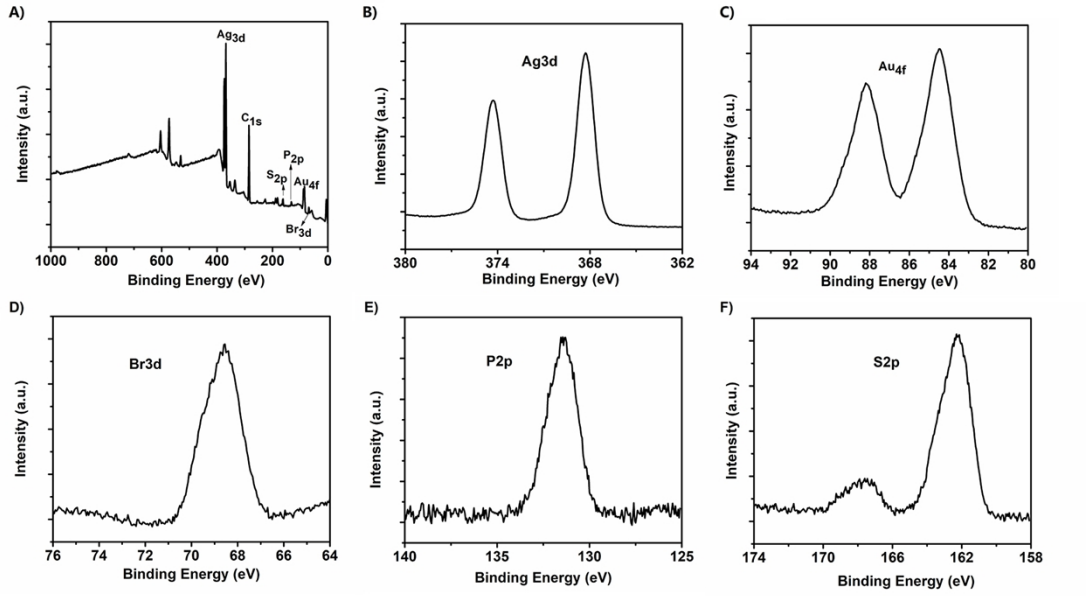


Figure S8. X-ray photoelectron spectroscopy (XPS) data of $Au_{12}Ag_{60}(S\text{-}c\text{-}C_6H_{11})_{31}Br_9(Dppp)_6$

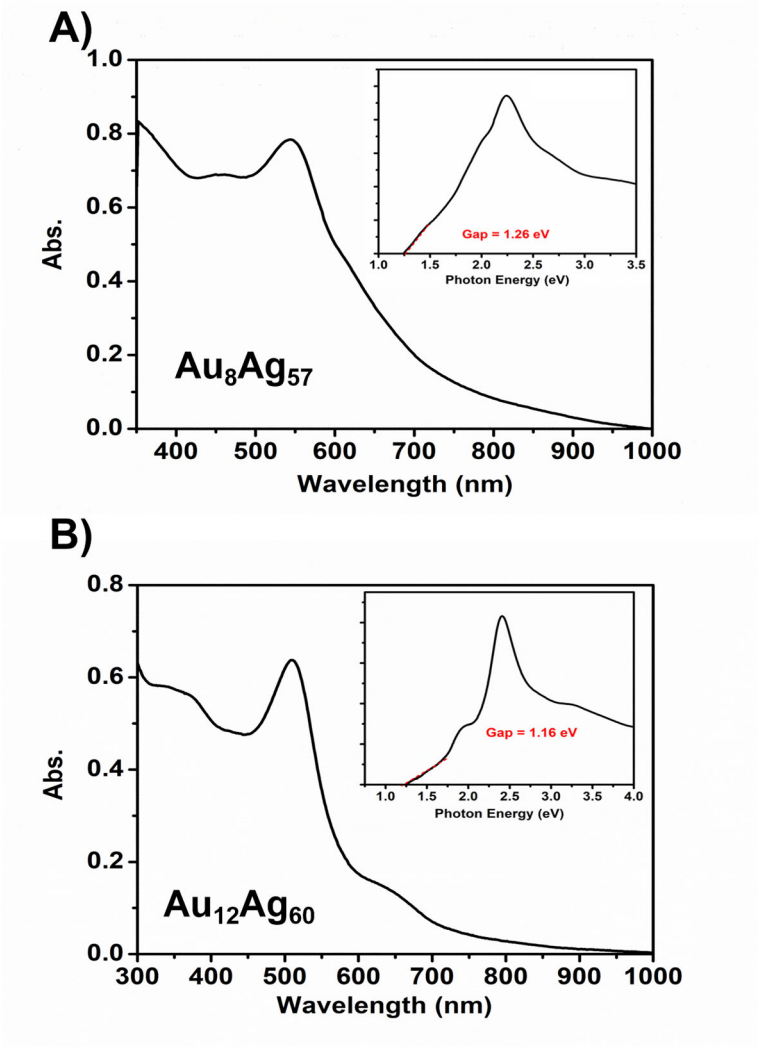


Figure S9. The UV-vis spectra and the optical energy gaps of A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$.

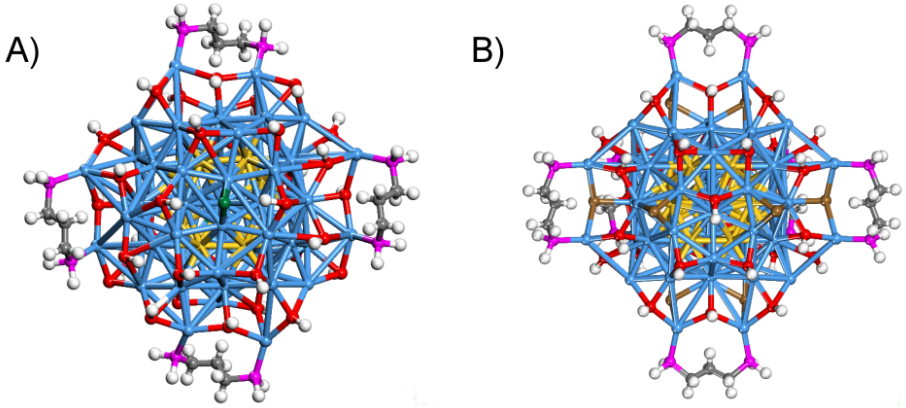


Figure S10. DFT geometry optimization of A) Au_8Ag_{57} and B) $Au_{12}Ag_{60}$.

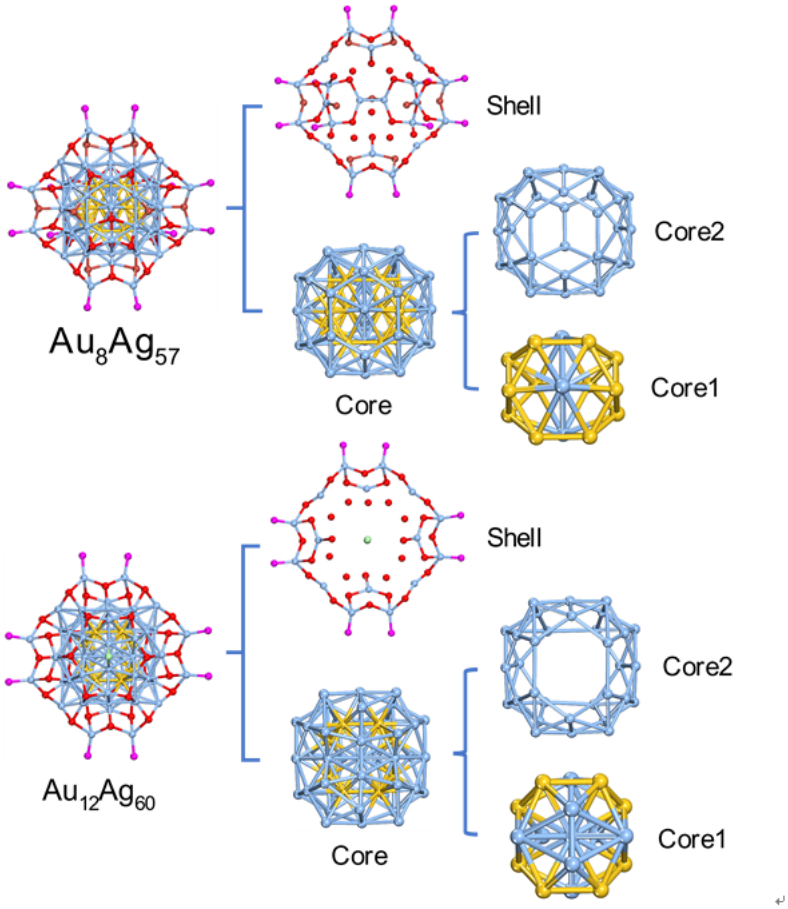


Figure S11. Structural analysis of Au_8Ag_{57} and $Au_{12}Ag_6$ based on core-shell form.

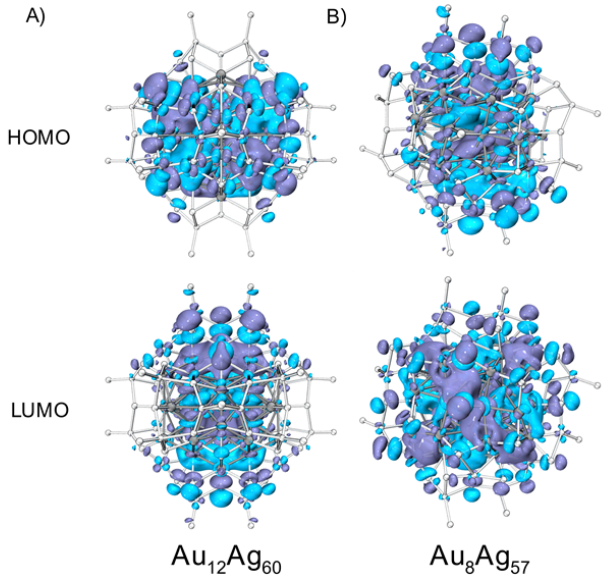
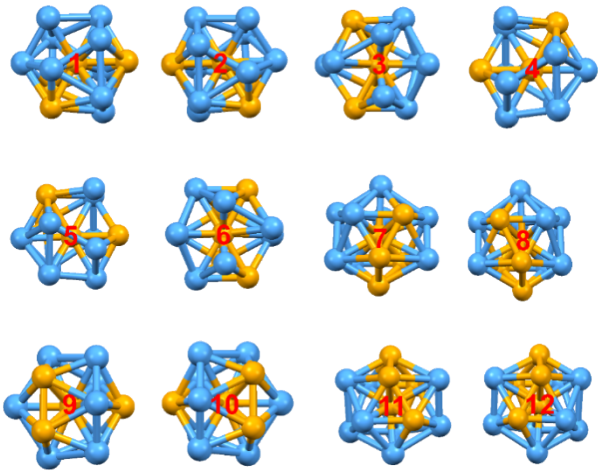


Figure S12. Frontier orbitals of A) $Au_{12}Ag_{60}$-H and B) Au_8Ag_{57}-H.

Table S1. The bond lengths from the central metal atom of the icosahedron to the surface atoms.



Au-1	Au-2	Au-3	Au-4	Au-5	Au-6	Au-7	Au-8	Au-9	Au-10	Au-11	Au-12
2.741	2.741	2.83	2.785	2.785	2.83	2.74	2.74	2.683	2.683	2.729	2.729
2.707	2.707	2.784	2.713	2.713	2.784	2.741	2.741	2.74	2.74	2.802	2.802
2.784	2.784	2.785	2.74	2.74	2.785	2.83	2.83	2.729	2.729	2.809	2.809
3.074	3.074	2.809	3.091	3.091	2.809	2.802	2.802	2.994	2.994	2.74	2.74
3.094	3.094	3.171	3.089	3.089	3.171	2.757	2.757	3.088	3.088	3.19	3.19
2.895	2.895	2.924	3.317	3.317	2.924	2.808	2.808	2.726	2.726	3.017	3.017
2.819	2.819	2.755	2.783	2.783	2.755	2.844	2.844	2.868	2.868	2.806	2.806
2.809	2.809	2.683	2.796	2.796	2.683	2.613	2.613	2.935	2.935	2.749	2.749
2.92	2.92	2.895	2.784	2.784	2.895	2.916	2.916	2.836	2.836	2.806	2.806
2.807	2.807	2.714	2.863	2.863	2.714	2.825	2.825	3.019	3.019	2.883	2.883

2.886	2.886	2.888	2.831	2.831	2.888	3.157	3.157	2.851	2.851	2.804	2.804
2.825	2.825	2.993	2.796	2.796	2.993	2.978	2.978			2.743	2.743

Table S2. Crystal data and structure refinement for AuAg)72

Empirical formula	$C_{348}H_{497}Ag_{60}Au_{12}Br_{11}P_{12}S_{31}$
Formula weight	15760.73
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	24.2837(13)
b/Å	36.2599(15)
c/Å	28.6687(14)
α/°	90
β/°	113.087(4)
γ/°	90
Volume/Å^3	23222(2)
Z	2
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	3.35 to 140.056
Index ranges	$-29 \leq h \leq 21$, $-24 \leq k \leq 44$, $-33 \leq l \leq 34$
Reflections collected	345262
Independent reflections	43360 [R_{int} = 0.0286, R_{sigma} = 0.0612]
Data/restraints/parameters	43360/9/2179
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.0784
Final R indexes [all data]	R_1 = 0.0481, wR_2 = 0.0795
Largest diff. peak/hole / e Å^{-3}	1.32/-1.28