Electronic Supplementary Information for

$[Au_9Ag_6(C{\equiv}CR)_{10}(DPPM)_2Cl_2](PPh_4)$: A Four-Electron Cluster with a Bi-decahedral Twisted Metal Core

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Fig. S1 A photograph of the single crystal of the **Au_9Ag_6** cluster.

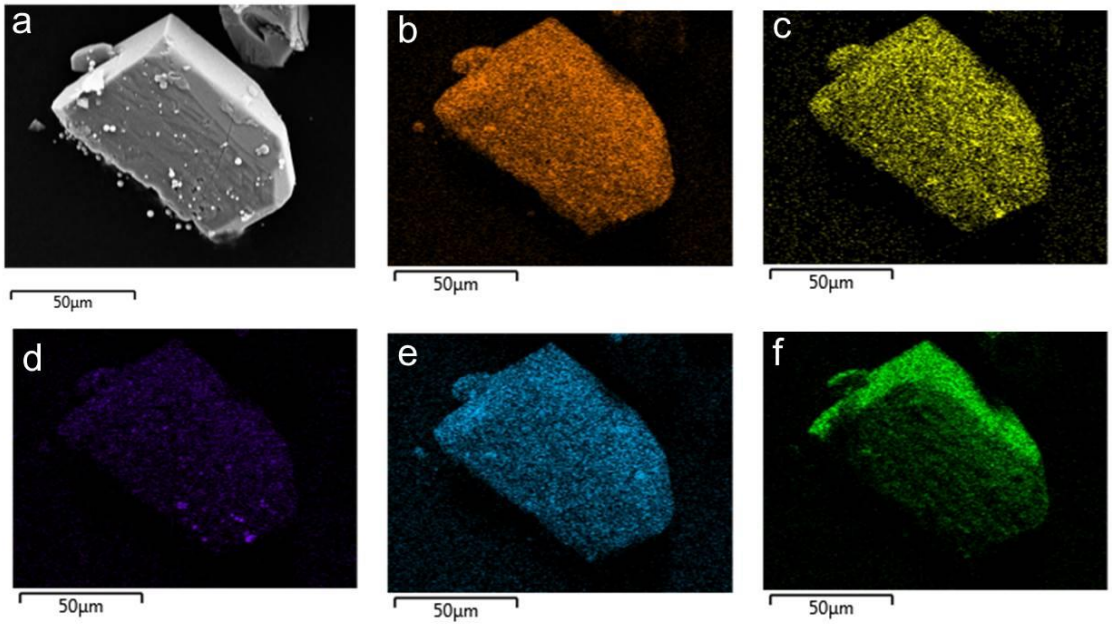

Fig. S2 (a) SEM image of a crystal of the **Au_9Ag_6** cluster. (b-f) Elemental mapping images of Au, Ag, Cl, P and F, respectively, of the **Au_9Ag_6** crystal.

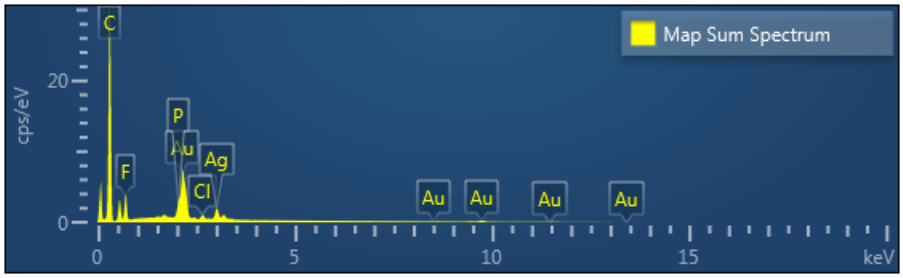

Fig. S3 SEM EDS spectrum of the $\mathbf{Au_9Ag_6}$ crystal.

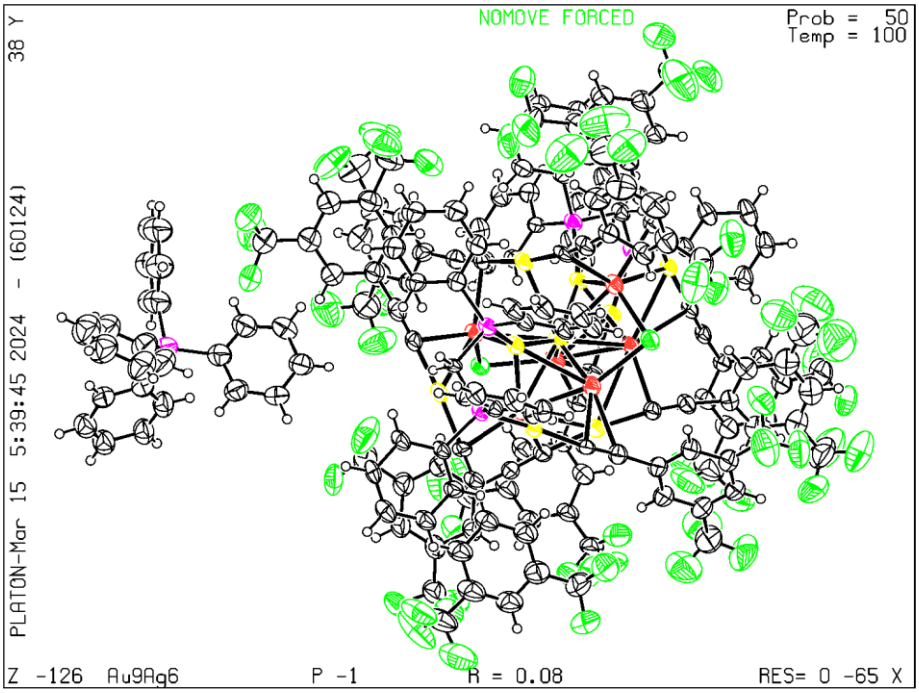

Fig. S4 ORTEP diagram of the $\mathbf{Au_9Ag_6}$ cluster with 50% probability thermal elipsoids.

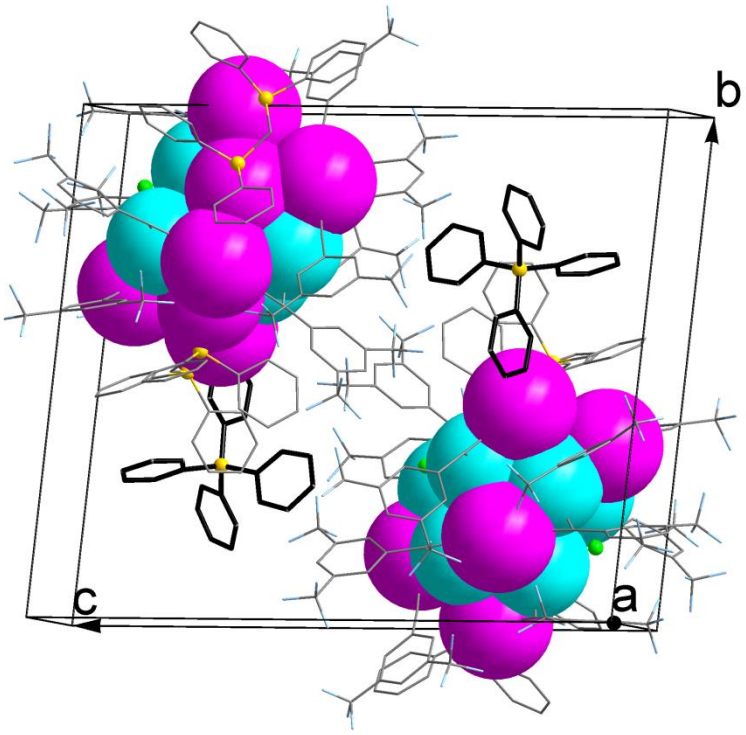

Fig. S5 The packing diagram of **Au_9Ag_6**. Color legend: magenta, Au; turquoise, Ag; yellow, P; green, Cl; pale blue, F; and gray, C. All hydrogen atoms are omitted for clarity.

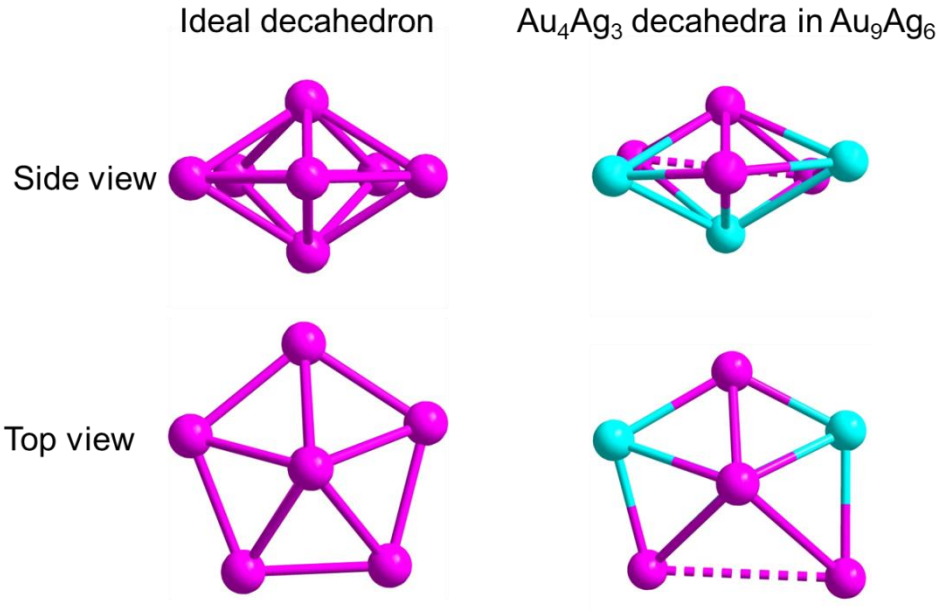

Fig. S6 Comparison of Au_4Ag_3 decahedron in **Au_9Ag_6** cluster with ideal decahedron. Color legend: magenta, Au; turquoise, Ag.

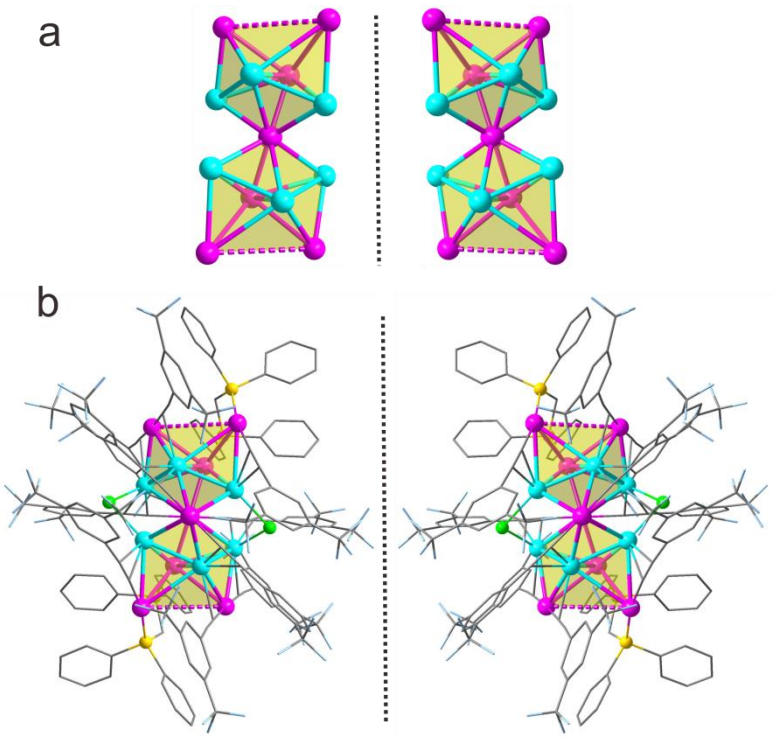

Fig. S7 (a) The chiral bi-decahedral core of **Au_9Ag_6**. (b) Racemate of chiral **Au_9Ag_6** in the unit cell. Color legend: magenta, Au; turquoise, Ag; yellow, P; green, Cl; pale blue, F; and gray, C. All hydrogen atoms are omitted for clarity.

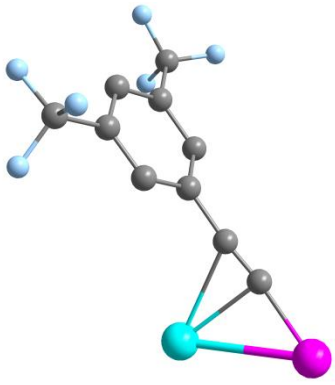

Fig. S8 The coordination mode of -C≡CR ligands on **Au_9Ag_6**. Color legend: magenta, Au; turquoise, Ag; pale blue, F; and gray, C.

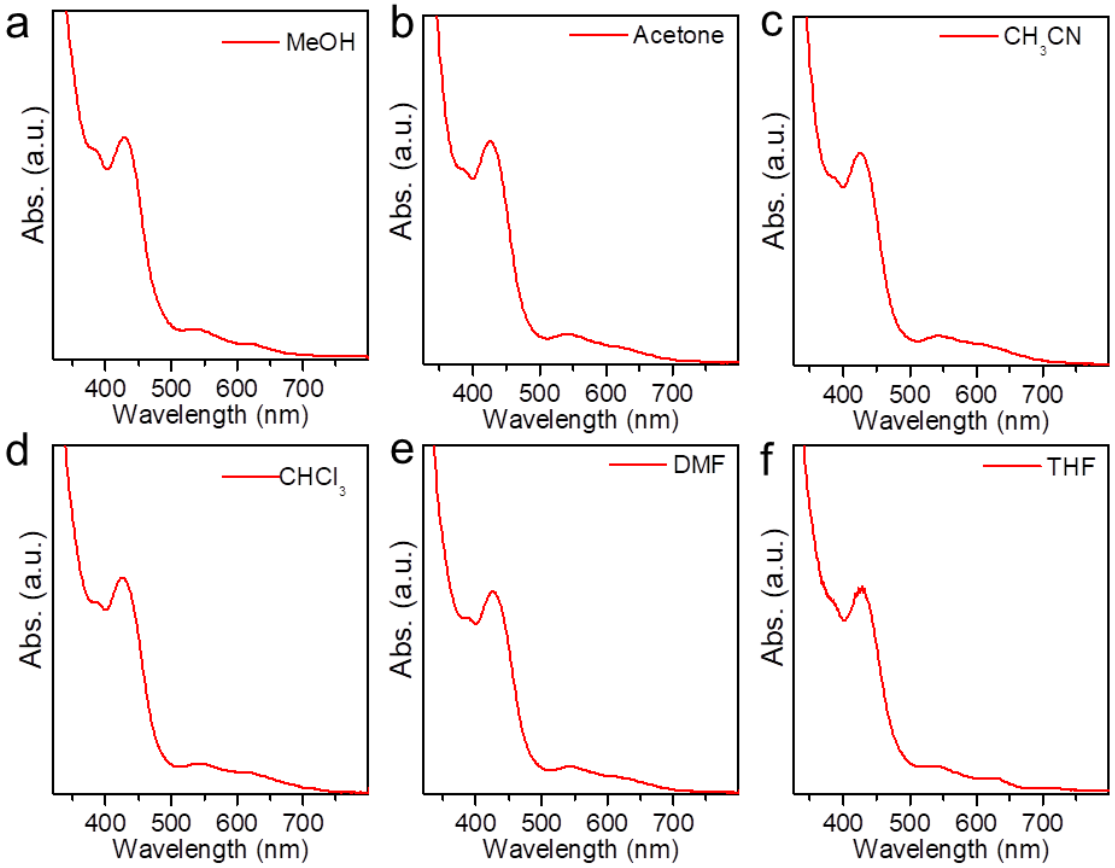

Fig. S9 UV/vis absorption spectra of single crystals of **Au_9Ag_6** in various commonly used organic solvents: (a) methanol (MeOH); (b) acetone; (c) acetonitrile; (d) chloroform ($CHCl_3$); (e) *N*,*N*-dimethylformamide (DMF); and (f) tetrahydrofuran (THF).

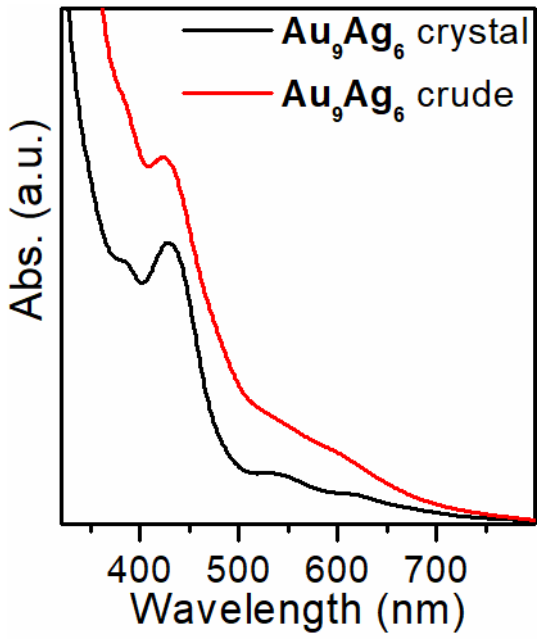

Fig. S10 Comparison of UV/vis absorption spectra of single crystals and crude product of **Au_9Ag_6**.

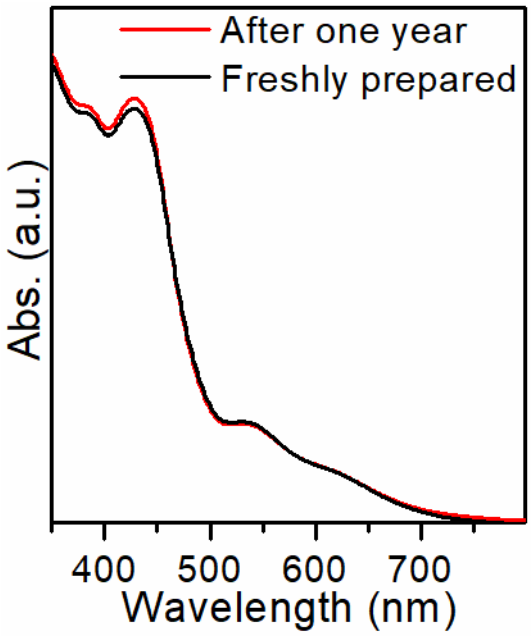

Fig. S11 Comparison of UV/vis spectra of the crystals after exposure to air for one year and freshly prepared crystals of **Au_9Ag_6**.

Table S1. The crystal data and structure refinement for the **Au_9Ag_6** cluster.

Identification code	**Au_9Ag_6**
Empirical formula	$C_{174}H_{94}Ag_6Au_9Cl_2F_{60}P_5$
Formula weight	5970.15
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	19.1458(2)
b/Å	22.7805(4)
c/Å	23.8161(2)
α/°	91.2230(10)
β/°	94.2580(10)
γ/°	114.0090(10)
Volume/Å ^{3}	9447.4(2)
Z	2
ρ_{calc}g/cm^3	2.099
μ/mm^{-1}	19.238
F(000)	5560.0
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.846 to 133.202
Index ranges	$-19 \leq h \leq 22$, $-27 \leq k \leq 20$, $-28 \leq l \leq 28$
Reflections collected	92935
Independent reflections	32753 [R_{int} = 0.0653, R_{sigma} = 0.0623]
Data/restraints/parameters	32753/1599/2293
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0771, wR_2 = 0.1980
Final R indexes [all data]	R_1 = 0.0924, wR_2 = 0.2091
Largest diff. peak/hole / e Å $^{-3}$	4.49/-2.75