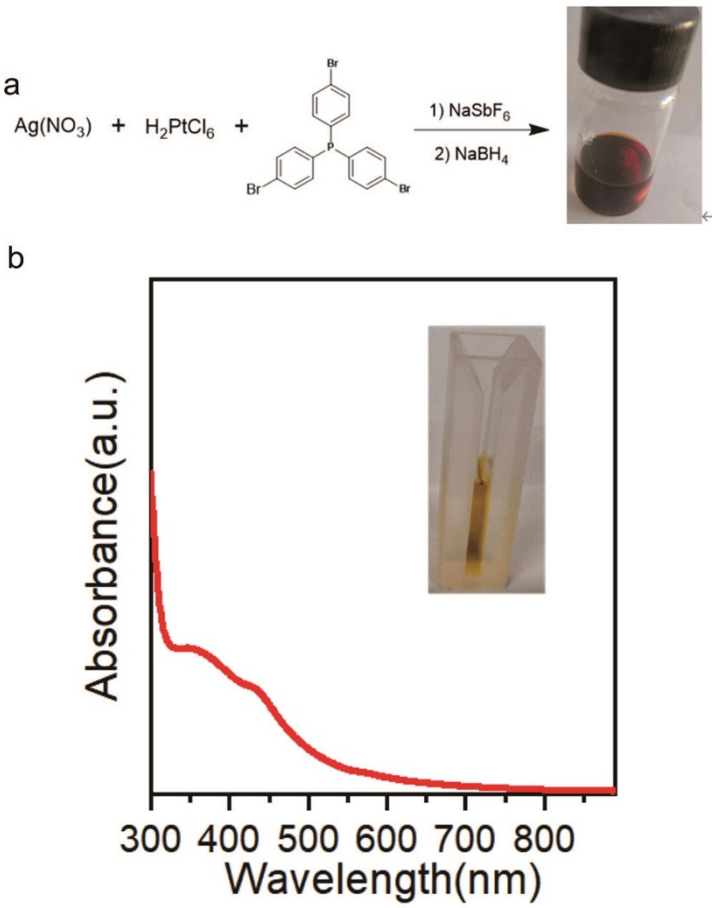

Figure S1. (a) Synthetic protype and (b) characterization of raw product of $PtAg_9$ clusters.

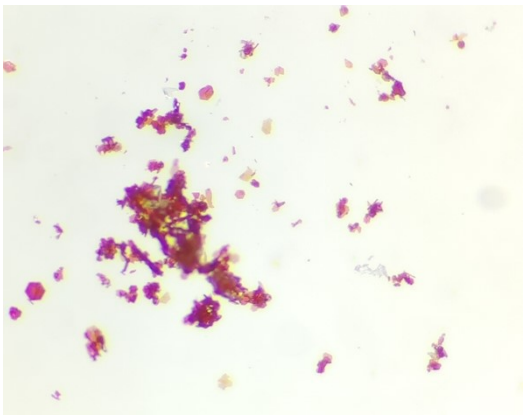

Figure S2. Photographs of single crystals of $PtAg_9$ clusters.

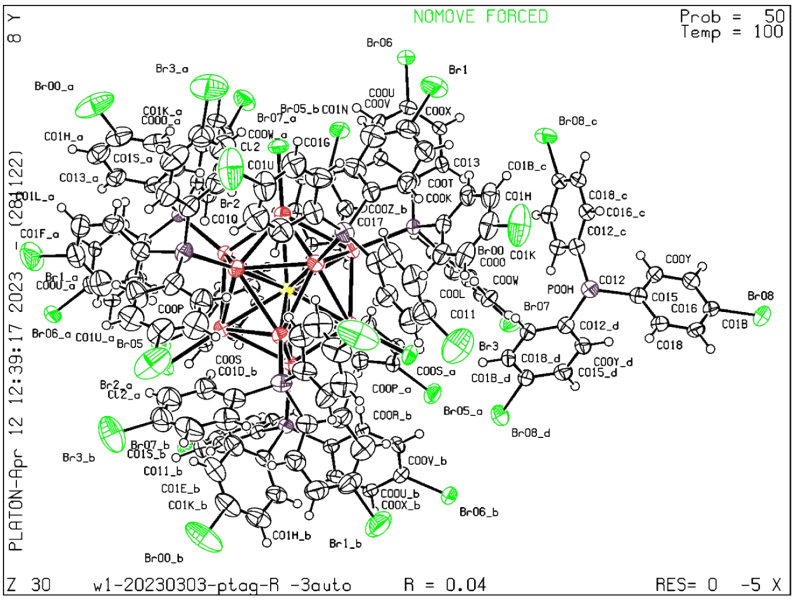

Figure S3. The thermal ellipsoids of the ORTEP diagram of $PtAg_9$ clusters at 50% probability.

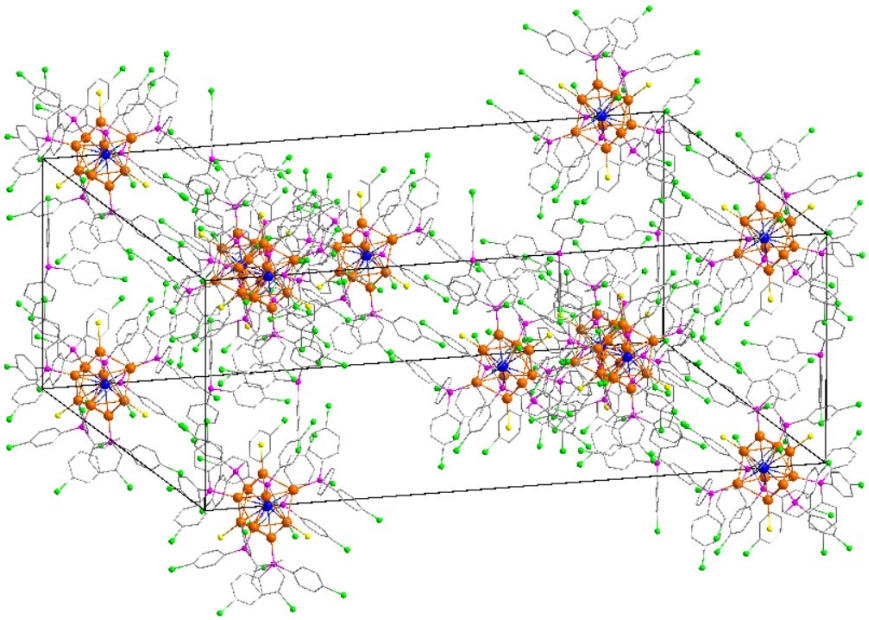

Figure S4. The packing structure of $PtAg_9$ clusters in their single crystals. Color legend: orange spheres, Ag; green spheres, Pt; pink spheres, P; yellow spheres, Cl; gray spheres, C; bright green spheres, Br. All hydrogen atoms are omitted for clarity.

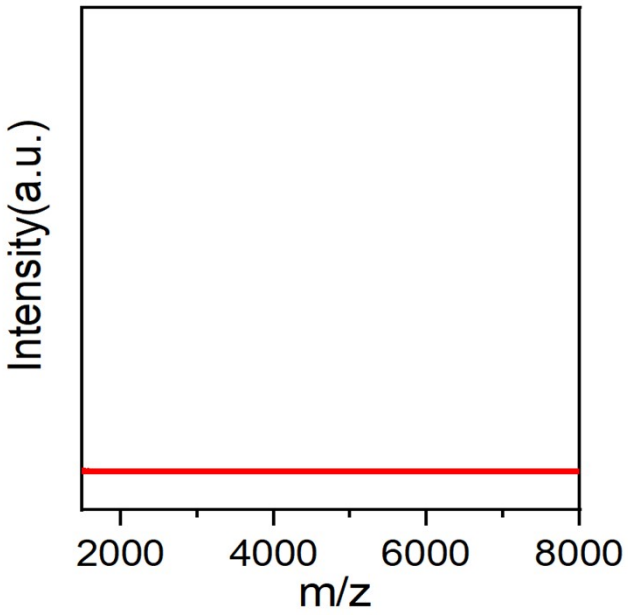

Figure S5. ESI-MS of $PtAg_9$ in the positive mode.

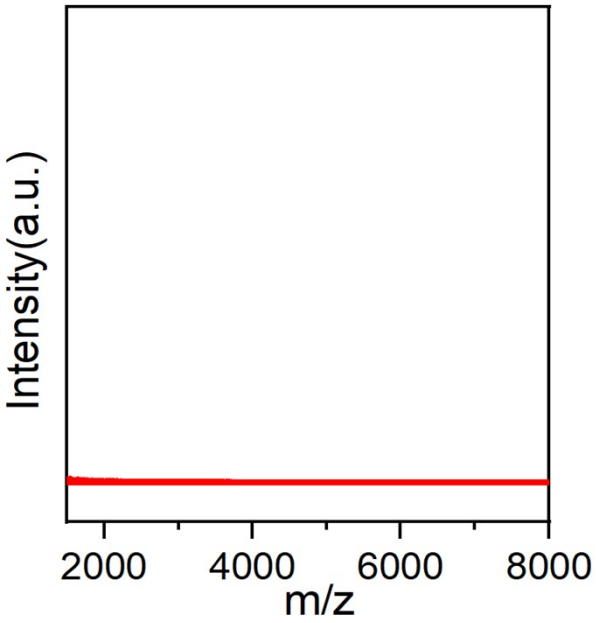

Figure S6. ESI-MS of $PtAg_9$ in the negative mode.

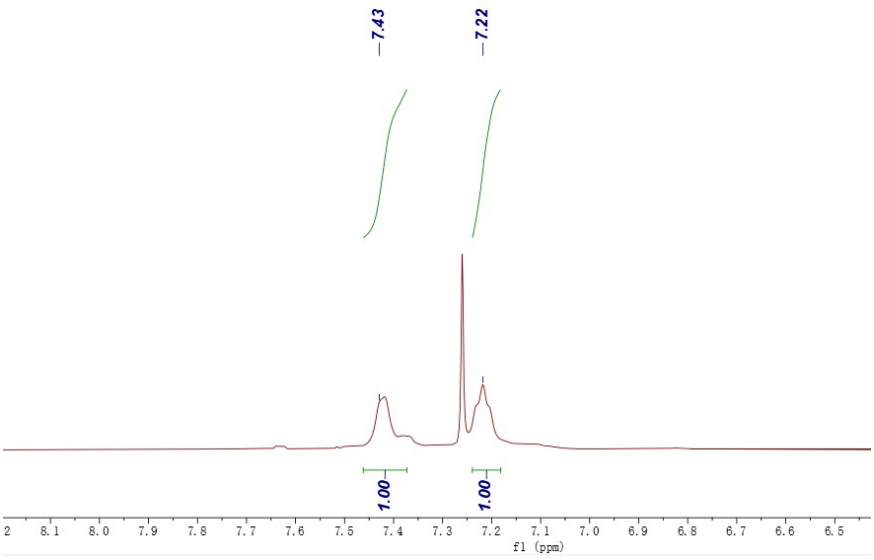

Figure S7. ^{1}H NMR of $PtAg_9$ in $CDCl_3$.

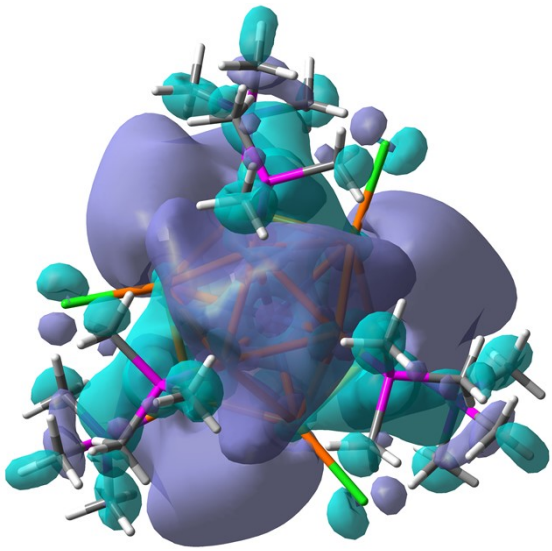

Figure S8. The electronic diagrams of LUMO+2 of $PtAg_9$.

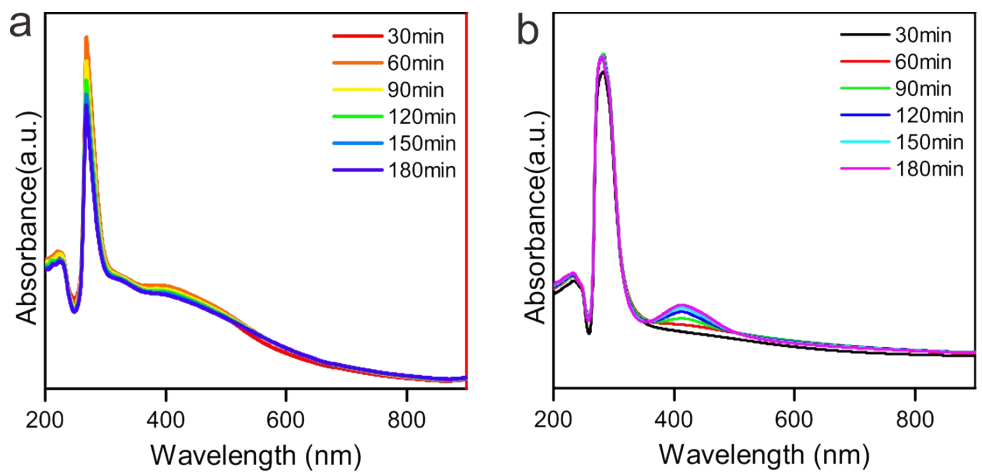

Figure S9. Time-dependent UV-Vis spectra of $[PtAg_9(C_{18}H_{12}Br_3P)_7Cl_3](C_{18}H_{12}Br_3P)$ (a) and the previously reported $Pt_1Ag_9[P(Ph\text{-}F)_3]_7Cl_3$ (b) under ambient atmosphere.

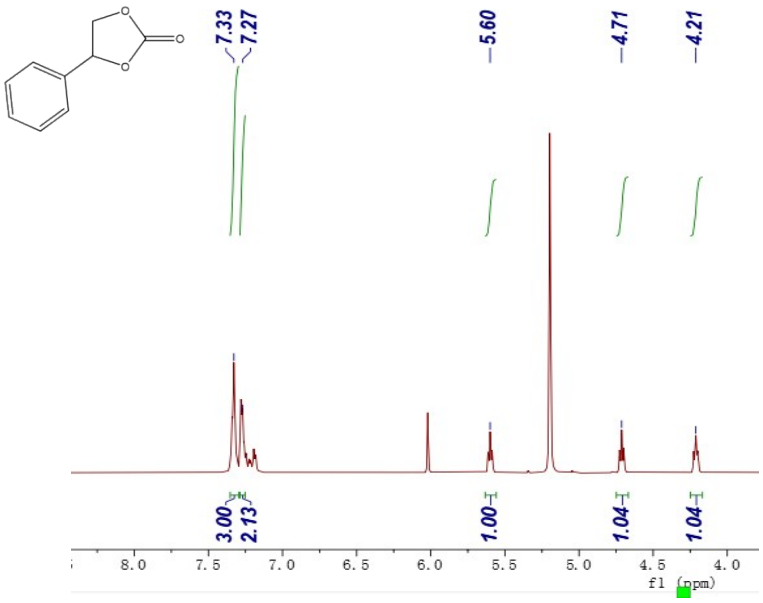

Figure S10. The ^1H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one ($CDCl_3$).

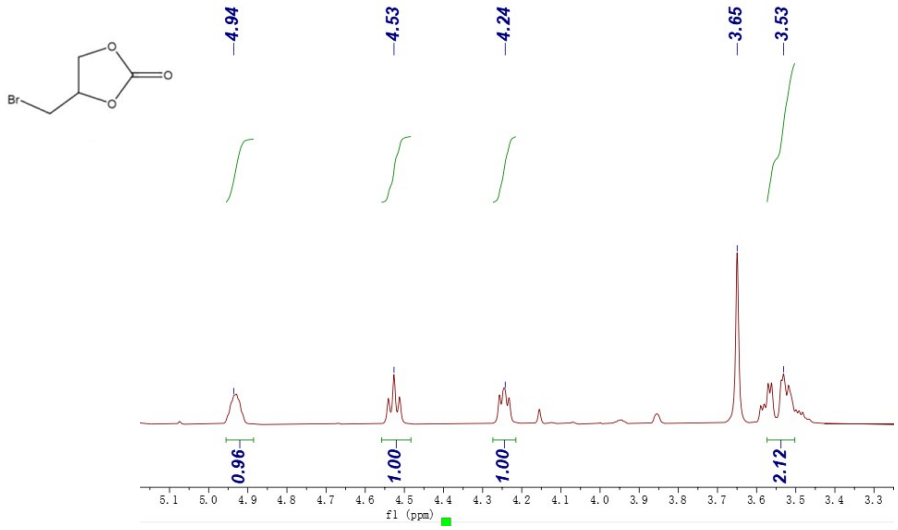

Figure S11. The ^{1}H NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one ($CDCl_3$).

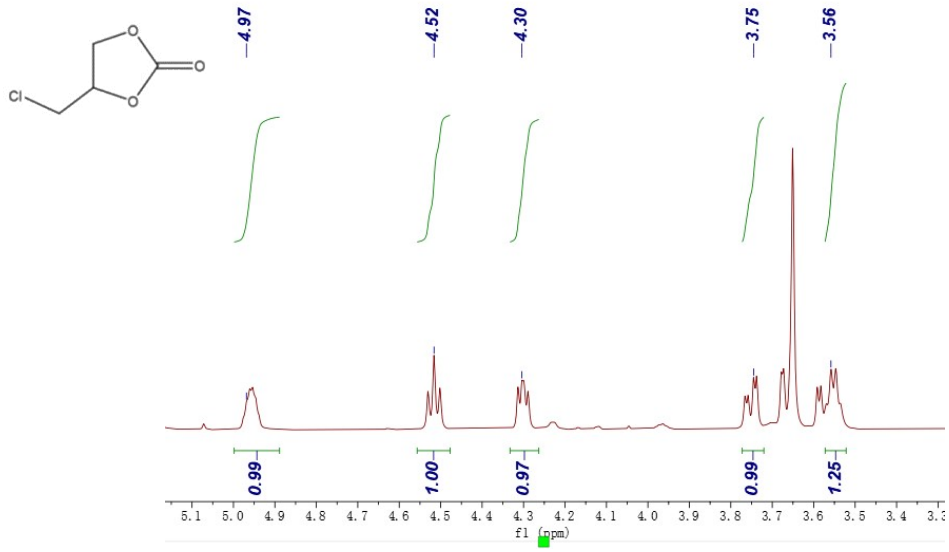

Figure S12. The ^{1}H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (CD Cl_3).

Table S1. Crystal data and structure refinement for $PtAg_9P_8C_{144}H_{96}Br_{24}Cl_3$.

Identification code	W1-20230303-PtAg-P28_auto
Formula	$C_{144}H_{96}Ag_9Br_{24}Cl_3P_8Pt$
Formula wight	5264.07
Temperature/K	100.00(10)
Crystal system	trigonal
Space group	R-3
a (Å)	19.1020(3)
b (Å)	19.1020(3)
c (Å)	90.1075(13)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	28474.0(10)
Z	6
D_c / (g·cm^{-3})	1.842
Radiation	Cu Kα (λ=1.54184 Å)
Theta (°) range	5.432 to 129.126
Index ranges	-22 ≤ h ≤22, -22≤ k ≤ 22, -90≤ l ≤ 104
Refls. Total	88547
Restraints	95
Parameters	568
R_{int}	0.0866
R1/wR2 [I>2σ(I)]	0.0398 0.0945
R1/wR2 (all data)	0.0596 0.1008
GooF	1.076

Table S2. Selected bond lengths (Å) for cluster $PtAg_9$.

Parameter	value	Parameter	value
Pt01-Ag02	2.6988(4)	Ag02-Ag03	2.8519(6)
Pt01-Ag02	2.6988(5)	Ag02-Ag03	2.8925(6)
Pt01-Ag03	2.7497(5)	Ag02-Ag04	2.8363(6)
Pt01-Ag03	2.7498(5)	Ag02-P00E	2.4078(17)
Pt01-Ag04	2.7402(6)	Ag03-Ag04	2.8981(7)
Pt01-P00D	2.283(3)	Ag03-Ag04	2.7985(7)

Table S3. Frontier molecular orbital compositions (%) in the ground state for cluster $PtAg_9$ at the PBE0/6-31G* & LANL2DZ level.

orbital	Contribution (%)			
	Pt	Ag_9	Cl	Phosphine
HOMO-1	27.23	42.34	4.21	26.21
HOMO	12.74	60.56	9.62	17.06
	12.74	60.56	9.62	17.06
LUMO	10.61	56.96	1.99	30.44
LUMO+1	7.34	61.14	5.63	25.87
	7.34	61.14	5.63	25.87
LUMO+2	1.85	42.33	2.15	53.67