Supporting Information:

Site-Specific Doping of Silver Atoms into Au_{25} Nanocluster as Directed by Ligand Binding Preference

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I. Characterization

Figure.

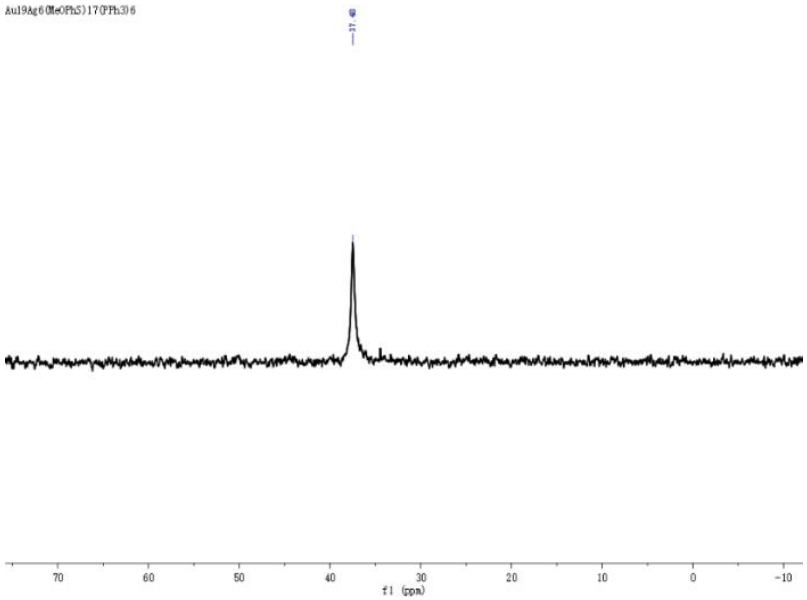

Fig. S1. ^{31}P-NMR spectrum of **$Au_{19}Ag_6$** in CD_2Cl_2.

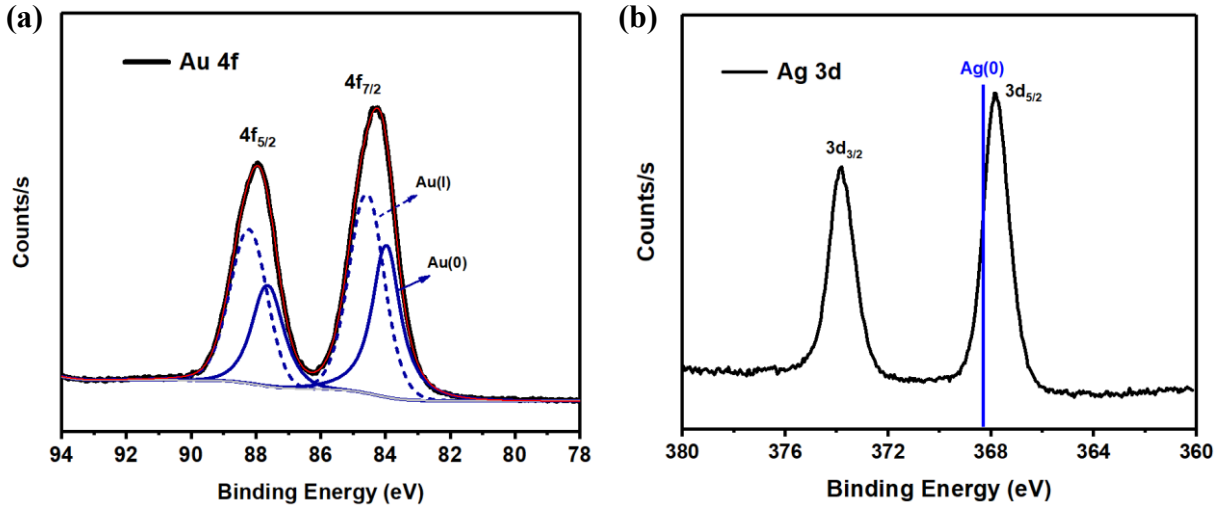

Fig. S2. (a) Au 4f XPS spectrum and (b) Ag 3d XPS spectrum of **$Au_{19}Ag_6$**.

Table S1. The transitions corresponding to the significant peaks of **$Au_{19}Ag_6$** calculated according to TDDFT method using the quantum chemistry program Gaussian 16.

Transition		*Coefficient*	*Contribution*[#]	*E (eV) / $\lambda_{cal.}$ (nm)*	*Oscillator Strength*	$\lambda_{exp.}$ *(nm)*
α (HOMO→LUMO+1)	434→437	-0.30943	19.149%	2.76 / 449	0.1891	463
	434→438	0.36975	27.343%			
	435→437	-0.35593	25.337%			
	435→438	-0.32524	21.156%			
	434→437	0.35640	25.404%	2.77 / 448	0.2036	
	434→438	0.32417	21.017%			
	435→437	-0.30905	19.102%			
	435→438	0.36809	27.098%			
β (HOMO→LUMO+2)	435→439	0.63482	80.599%	3.36 / 369	0.1492	390
	434→439	0.64224	82.494%	3.37 / 368	0.1509	

#: Contribution = (Coefficient)^2/0.5; 435: HOMO; 436: LUMO

Table S2. Crystal data and structure refinement for **$Au_{19}Ag_6$**.

Empirical formula	$C_{227}H_{209}Ag_6Au_{19}B_2F_8O_{17}P_6S_{17}$
Formula weight	8502.97
Temperature/K	172.98(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	20.4536(6)
b/Å	20.7898(7)
c/Å	33.6586(9)
α/ °	72.945(3)
β/ °	82.104(2)
γ/ °	63.917(3)
Volume/Å^3	12289.0(7)
Z	2
ρ_{calc}g/cm^3	2.298
μ/mm^{-1}	26.656
F(000)	7868.0
Crystal size/mm^3	0.1 × 0.03 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.268 to 128.994
Index ranges	-23 ≤ h ≤ 18, -24 ≤ k ≤ 23, -39 ≤ l ≤ 38
Reflections collected	77948
Independent reflections	39715 [R_{int} = 0.0992, R_{sigma} = 0.1322]
Data/restraints/parameters	39715/1743/2266
Goodness-of-fit on F^2	0.944
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0853, wR_2 = 0.2065
Final R indexes [all data]	R_1 = 0.1545, wR_2 = 0.2442
Largest diff. peak/hole / e Å^{-3}	2.25/-2.32