Supporting Information

$[Au_7Ag_9(dppf)_{3(}CF_3CO_2)_7BF_4]_n$: A Linear Nanocluster Polymer from Molecular Au_7Ag_8 Clusters Covalently Linking by Silver Atoms

Zhao-Rui Wen,[a] Zong-Jie Guan,[a] Ying Zhang,[a] Yu-Mei Lin*[a] and Quan-Ming Wang [ab]

a Department of Chemistry, College of Chemistry and Chemical Engineering Xiamen, 361005, P. R. China.

b Department of Chemistry, Tsinghua University, China

E-mail: linyum@xmu.edu.cn

Contents

I. Physical measurements

UV-Vis absorption spectrum was recorded on a Shimadzu UV-2550 spectrophotometer. Mass spectra were recorded on an Apex Ultra 7.0T FTICR-MS. IR spectrum was recorded on a Nicolet iS50 FT-IR instrument. X-ray photoelectron spectroscopy (XPS) was recorded on PHI Quantum-2000 XPS. The sample was put under UHV to reach the10^{-8} Pa range. The non-monochromatized Al Kα source was used at 10 kV and 10 mA. All binding energies were calibrated using the C(1s) carbon peak (284.8 eV), which was applied as an internal standard. High resolution narrow-scan spectra were recorded with the electron pass energy of 50 eV and take off angle of 55° to achieve the maximum spectral resolution.

X-ray Crystallography

Intensity data of compound **1** was collected on an Agilent SuperNova Dual system(Mo Kα, 100K). Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved by direct methods, and non-hydrogen atoms except solvent molecules and counteranions were refined anisotropically by least-squares on F^2 using the SHELXTL program.

Materials and reagents.

Silver tetrafluoroborate ($AgBF_4$, 98%) and Silver trifluoroacetate ($AgCF_3CO_2$, 98%) were purchased from *J&K*; 1,1'-Bis(diphenylphosphino)ferrocene, $((C_6H_5)_2PC_5H_4FeC_5H_4P(C_6H_5)_2$, 99%) was purchased from Shanghai Boka Chemical Technology Co. Ltd. (Shanghai, China); Sodium borohydride ($NaBH_4$, 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification.

II. Characterization

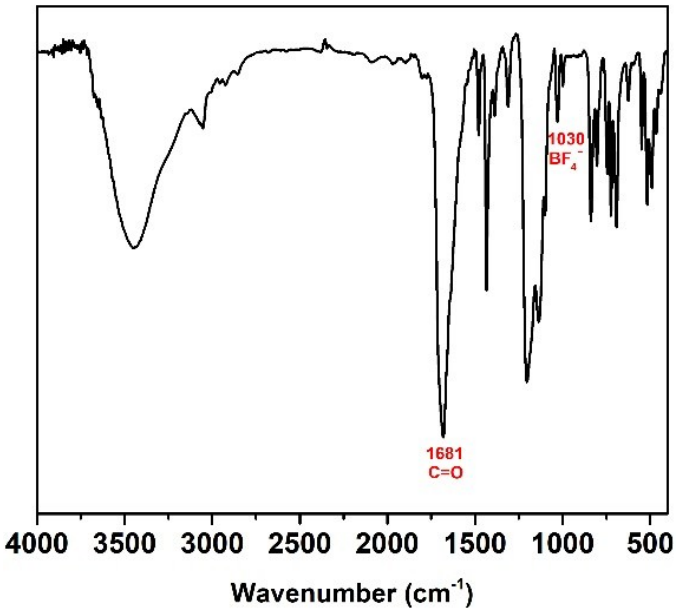

Fig. S1. IR spectrum of $[Au_7Ag_9(dppf)_{3(}CF_3CO_2)_7BF_4]_n$ (KBr pellet).

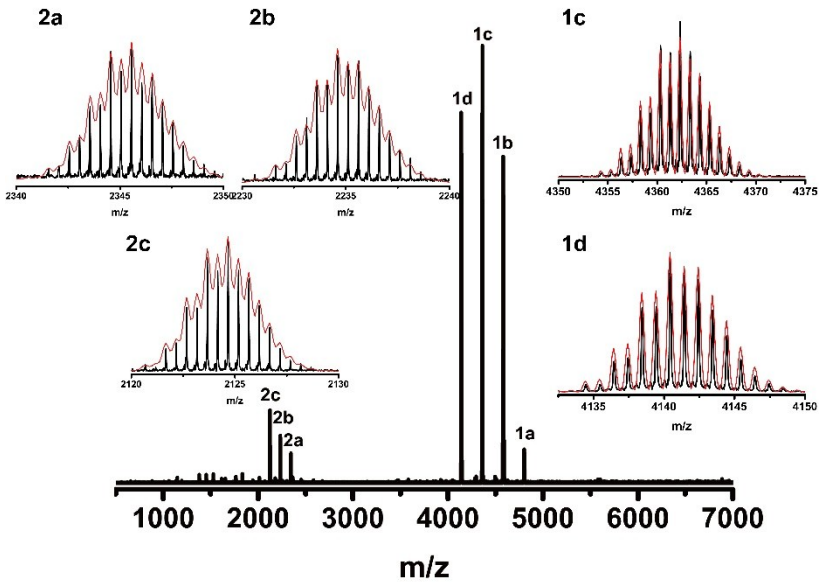

Fig. S2. Mass spectra of $[Au_7Ag_9(dppf)_3(CF_3CO_2)_7BF_4]_n$. Inset: The measure (black trace) and simulated (red trace) isotopic patterns of $[Au_7Ag_7(dppf)_3(CF_3CO_2)_5]^+$ (1c), $[Au_7Ag_6(dppf)_3(CF_3CO_2)_4]^+$ (1d), $[Au_7Ag_9(dppf)_3(CF_3CO_2)_6]^{2+}$ (2a), $[Au_7Ag_8(dppf)_3(CF_3CO_2)_5]^{2+}$ (2b) and $[Au_7Ag_7(dppf)_3(CF_3CO_2)_4]^{2+}$ (2c).

Table S1. Crystal data and structure refinement for $[Au_7Ag_9(dppf)_3(CF_3CO_2)_7BF_4]_n$.

Empirical formula	$C_{116}H_{84}Ag_9Au_7BF_{25}Fe_3O_{14}P_6$
Formula weight	4890.60
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	14.7746(3)
b/Å	17.3633(4)
c/Å	30.4935(6)
α/°	88.524(2)
β/°	86.188(2)
γ/°	65.006(2)
Volume/Å^3	7074.4(3)
Z	2
ρcalcg/cm^3	2.296
μ/mm-1	8.889
F(000)	4532
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	MoKα (*λ* = 0.71073)
2θ range for data collection/°	6.808 to 50
Index ranges	-15 ≤ h ≤ 17, -14 ≤ k ≤ 20, -36 ≤ l ≤ 36
Reflections collected	45544
Independent reflections	24649 [R_{int} = 0.0542, R_{sigma} = 0.0828]
Data/restraints/parameters	24649/10/884
Goodness-of-fit on F2	1.049
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.1468, wR_2 = 0.3586
Final *R* indexes [all data]	R_1 = 0.1638, wR_2 = 0.3669
Largest diff. peak/hole / e Å^{-3}	5.86/-6.11

III. Survey of the reaction conditions in purpose to obtain the monomer

Survey of the reaction conditions in purpose to obtain the monomer cluster of $[Au_7Ag_9]_n$ polymer. The procedure was similar to the synthesis of $[Au_7Ag_9]_n$, except for the types of reactants and/or the ratios of $CF_3CO_2^-$:Ag: Au were changed. The detail information was listed in Table S2. The condition in entry 1 was used for the synthesis of polymer **1**. It can be also obtained with lower yield by a little increase the amount of $AgCF_3CO_2$ (entry 4). The unidentified precipitates were obtained for all the other conditions (entries 2-3, 5-18).

Table S2. The types and amount of reactants in the synthesis process.

Entry	$AgCF_3CO_2$ (mmol)	$NaCF_3CO_2$ (mmol)	$AgBF_4$ (mmol)	$dppf(AuBF_4)_2$ (mmol)	$CF_3CO_2^-$:Ag:Au
1	0.10			0.02	2.5:2.5:1
2	0.04			0.02	1:1:1
3	0.06			0.02	1.5:1.5:1
4	0.08			0.02	2:2:1
5	0.12			0.02	3:3:1
6	0.14			0.02	3.5:3.5:1
7	0.16			0.02	4:4:1
8	0.18			0.02	4.5:4.5:1
9	0.2			0.02	5:5:1
10	0.1	0.02		0.02	3:2.5:1
11	0.1	0.04		0.02	3.5:2.5:1
12	0.1	0.06		0.02	4:2.5:1
13	0.1	0.08		0.02	4.5:2.5:1
14	0.1	0.1		0.02	5:2.5:1
15	0.1		0.02	0.02	2.5:3:1
16	0.1		0.04	0.02	2.5:3.5:1
17	0.1		0.06	0.02	2.5:4:1
18	0.1		0.08	0.02	2.5:4.5:1

The attempts to obtain monomers from $[Au_7Ag_9]_n$ polymers have also been tried. Chloride ions were introduced with the propose to breakdown the silver linkers in the polymer **1**. To 1 mL CH_2Cl_2 solution of $[Au_7Ag_9]_n$ (0.5 mg, 1.02×10^4 mmol), different amounts of NaCl (0.0001, 0.005, 0.01 mmol) or NH_4Cl (0.0001, 0.01 mmol) were added. The color of the mixture changed from dark red to yellow immediately. UV-vis spectra showed the newly formation species display greatly distinct absorption properties compared with that of **1**. Unfortunately, attempts to obtain the single-crystal structures all failed.

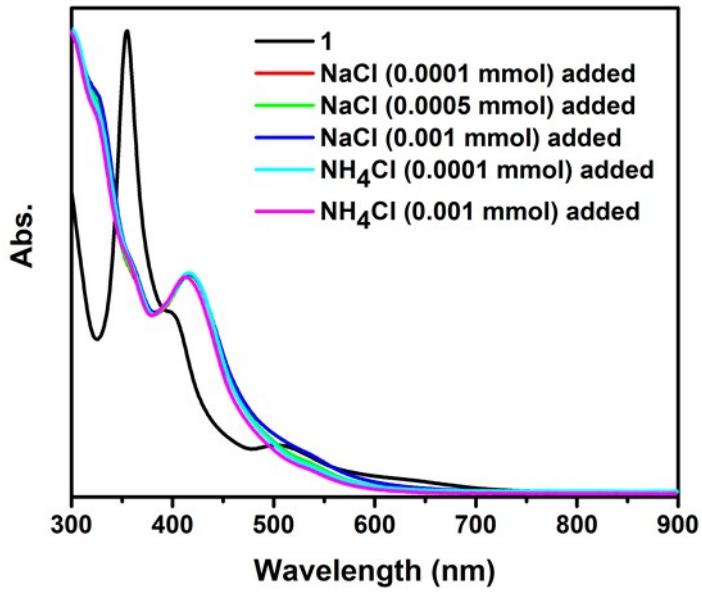

Fig. S3. Absorption spectra of **1** and the solutions after addition of the different amounts of NaCl or NH_4Cl.

IV. The stability of 1 in solution state.

The solubility and stability of **1** in several common solvents have been tested. Polymer **1** is nearly insoluble in toluene, and has very poor solubility in ether. It can be dissolved in acetone, acetonitrile and methanol. As monitored by UV-Vis spectra, the degradation can be observed in all these solvents (Fig. S4-S6).

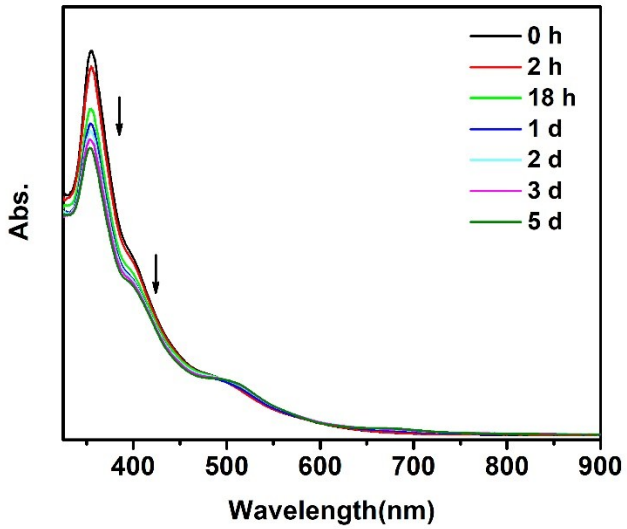

Fig. S4. Time dependences of absorption spectra of **1** in CH_3COCH_3.

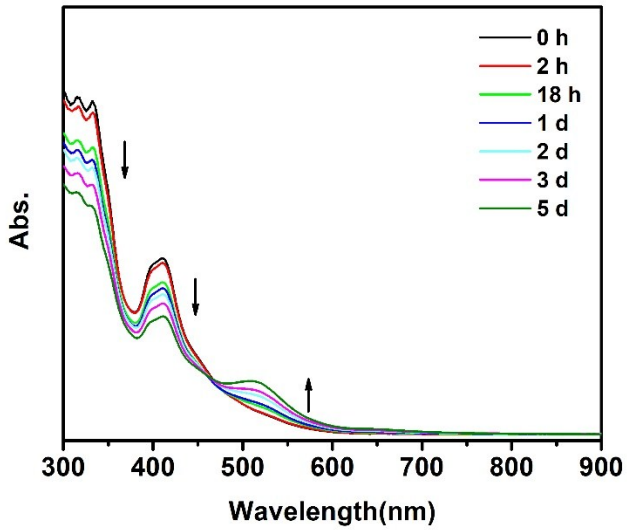

Fig. S5. Time dependences of absorption spectra of **1** in CH_3OH.

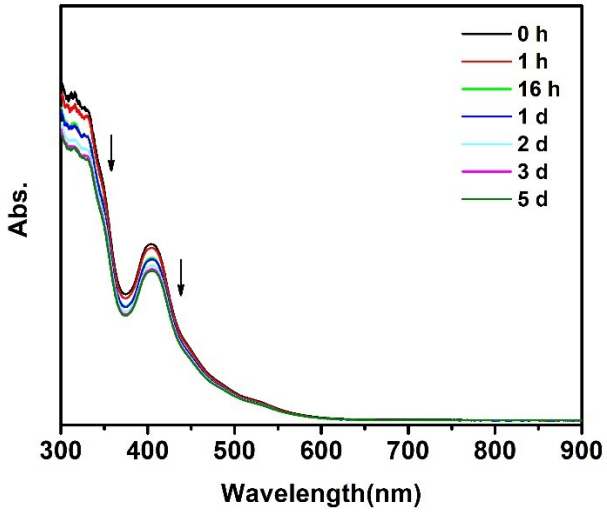

Fig. S6. Time dependences of absorption spectra of **1** in CH_3CN.