Supporting Information

Sulphonate, Sulfide and Thiolate Ligands into Ultrasmall

Nanocluster: $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$

Sha Yang, Jinsong Chai, Hanbao Chong, Yongbo Song, Haizhu Yu and Manzhou Zhu,* Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui, 230601, China

1. Materials

All reagents and solvents were commercially available and were used as received without further purification, including AgNO₃ (99.85%), copper(II) chloride (\geq 98%) were received from ACROS Organic. Tert-Butyl mercaptan (\geq 98%) and Borane-tert-Butylamine complex were received from Sigma-Aldrich. All solvents in the experiment are chromatographically pure and were purchased from Sigma-Aldrich. Pure water was purchased from Wahaha Co. Ltd, and other chemicals were purchased from Aladdin (Shanghai, China). All glassware was thoroughly cleaned with aqua regia (HCl: HNO₃ = 3:1, v:v), rinsed with copious pure water, and then dried in an oven prior to use.

2. In Situ Two-phase Ligand Exchange Method for the Synthesis of NC-1 Alloy Nanoclusters.

First, 30 mg AgNO₃ (0.177 mmol) was dissolved in 20 mL water and poured in a 50 mL flask. After ~2 min stirring under 55 °C, 500 mg (1.63 mmol) GSH (glutathione) was added to the aqueous solution. The stirring was continued for about 15 min, and then 30 mg (0.223 mmol) copper (II) chloride was added. After ~20 min stirring, a solution of borane tert-butylamine complex (220 mg, 2.53 mmol) and 700 μ L tert-butyl mercaptan (6.21 mmol, dissolved in 10 mL toluene) was quickly added to the above solution to initiate the reaction. The aqueous solution immediately turned black. The two-phase mixture was allowed to react for a few hours (the aqueous solution turned colorless). After the reaction, the colorless aqueous solution was removed and the toluene organic phase (note: nanoclusters were dissolved in the organic phase) was evaporated with the aid of methanol. The crude product (with the yield of 3% based on silver atoms) was washed several times with CH₃OH to remove the excess thiol and the by-products.

3. Characterization.

All UV/vis/NIR absorption spectra were acquired in the range of 190-900 nm using a UV2600 spectrophotometer (Agilent). The solvent was used for recording UV-vis spectrum is CH_2Cl_2 and molar extinction coefficient of this nanocluster (410 nm) is $2.1*10^5$ mol·L⁻¹·cm⁻¹. The diffraction data of the single crystals were collected on an SMART (Bruker, 2008) diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and the crystal structure was determined by direct methods and refined by using the full-matrix least-squares methods within the SHELXL-2014/7 (Sheldrick, 2014). The placement of the heteroatoms and fractional site occupancy in these alloy nanoclusters were ascertained by the method of modifying the disorderly free variables. The solvents (presumably H₂O) have been remove from the unit cell and the squeeze result as blew: "loop

_platon_squeeze_void_nr

_platon_squeeze_void_average_x _platon_squeeze_void_average_y _platon_squeeze_void_average_z _platon_squeeze_void_volume _platon_squeeze_void_count_electrons _platon_squeeze_void_content

1 -0.005 -0.003 0.003 3880 37"

ESI-TOF-MS was recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 °C. The sample was directly infused into the chamber at 5 μ L/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer with monochromated Al K α radiation as the excitation source. All binding energies were calibrated using the C (1s) carbon peak (284.8 eV). Thermal gravimetric analysis (TGA) (~15 mg sample used) was conducted in a N₂ atmosphere (flow rate ~50 mL/min) on a TG/DTA 6300 analyzer (Seiko Instruments, Inc), and the heating rate was 10 °C /min. Nuclear magnetic resonance (NMR) analysis was performed on a Bruker AM spectrometer operating at 400 MHz for ¹H, CD₂Cl₂ was used as the solvent to dissolve ~30 mg clusters. Fourier transform infrared (FT-IR) spectroscopy on a Bruker VER-TEX80+HYPERION000, the KBr for the soild and CCl₄ for liquid.



Figure S1. Unit cell comprising two Ag_{54-x}Cu_x nanoclusters.



Figure S2. The bond lengths distribution in the $Ag_{54-x}Cu_x$ nanocluster. (a) M-L (M=Ag/Cu, L=S/O) (Color labels: light green/pink=Ag/Cu, black/red/purple=S, yellow=O). (b) M-M (M=Ag/Cu) (Color labels: green/red=Ag/Cu, light orange=S, yellow=O).



Figure S3. Positive mode ESI-MS of [Ag_{40.13}Cu_{13.87}S₁₉(*t*BuS)₂₀(*t*BuSO₃)₁₂] nanocluster in CH₂Cl₂.



Figure S4. Matching of isotope patterns between the experimental and simulated spectra of $[Ag_{40}Cu_{14}S_{18}(tBuS)_{20}(tBuSO_3)_{12}]^{2+}$ and $[Ag_{39}Cu_{15}S_{18}(tBuS)_{20}(tBuSO_3)_{12}]^{2+}$.



Figure S5. Negative mode ESI-MS of $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster in CH_2Cl_2 .



Figure S6. TGA of $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster.



Figure S7. IR spectrum of $[Ag_{40,13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster.



Figure S8. IR spectrum of [Ag_{40.13}Cu_{13.87}S₁₉(*t*BuS)₂₀(*t*BuSO₃)₁₂] nanocluster dissolved in CCl₄.



Figure S9. XPS spectrum of $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster.



Result quality : See result quality report

Figure S10. Zeta potential of $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster in EtOH.



Figure S11. ¹H NMR spectrum of $[Ag_{40,13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster in CD_2Cl_2 .



Figure S12. UV-vis of $[Ag_{40.13}Cu_{13.87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}]$ nanocluster in CH_2Cl_2 .

4. The details including the occupancy data, coordination number and structure for metal

atoms in these alloy nanocluster



Figure S13. The framework of Core and Shell for NC-1 nanocluster.

Table S	I. The	occupa	ancies	or meta	al sites	1-341	In INC	/-1							
Site	1	2	3	4	5	6	7	8	;	9	10	11	12	13	14
Ag(%)	100	100	0	0	0	0	0	0)	0	0	0	0	52.1	100
Cu(%)	0	0	100	100	100	100	100	10	0	100	100) 100	100	47.9	0
								·							
Site	15	16	17	18	19	20	21	2	2	23	24	25	26	27	28
Ag(%)	100	100	100	100	100	100	100	10)0	100	10	0 100) 100	100	100
Cu(%)	0	0	0	0	0	0	0	()	0	0	0	0	0	0
Site	29	30	30	32	33	34	4	35	3	6	37	38	39	40	41
Ag(%)	100	100	100	100	52.	6 52	.6	100	10	00	100	100	100	100	100
Cu(%)	0	0	0	0	47.	4 47	.4	0	(0	0	0	0	0	0
<u>.</u>				·	·	·	•					•			
Site	42	43	44	45	46	4	7	48	4	9	50	51	52	53	54
Ag(%)	100	100	100	100	10) 10	0 1	00	10)0	100	100	100	100	47.9
Cu(%)	0	0	0	0	0	0		0	()	0	0	0	0	52.1
L.	•					•		·					•	•	

Table S1. The occupancies of metal sites 1-54 in NC-1

 Table S2. The coordination number and structure of each core metal atom of 1-12 in NC-1

Site	1	2	3	4	5
coordination	8	8	7	6	8
number					
Structure	$\mathbf{\mathbf{x}}$	*		4	\mathbf{A}

Site	6	7	8	9	10
coordination	6	6	6	6	8
number					
Structure	626	←			
				•	
					V
	🧉 🎽				

site	11	12
coordination	6	7
number		
Structure		

Table S3. The coordination number and structure of each shell metal atom of 13-54 in NC-1

Site	13-Ag	13-Cu	14	15	16
coordination	3	2	5	5	5
number					
Structure		••••	4.	- 12	\sim

Site	17	18	19	20	21
coordination	5	6	6	6	7
number					
Structure	\sim	*			×

site	22	23	24	25	26
coordination	5	5	5	5	5
number					
Structure	X	X		~	\mathbf{Y}

site	27	28	29	30	31
coordination	5	5	6	2	6
number				_	
Structure	Y	X	K		~

site	32	33-Ag	33-Cu	34-Ag	34-Cu
coordination	6	4	2	4	2
number					
Structure		•	I	•	

site	35	36	37	38	39
coordination	6	6	2	6	6
number					
Structure		\rightarrow	••		*

site	40	41	42	43	44
coordination	5	5	5	5	5
number					
	\succ	\checkmark	K	×	X

site	45	46	47	48	49
coordination	5	7	6	6	6
number					
Structure	×.	*	+	+	\$ -

site	50	51	52	53	54-Ag	54-Cu
coordination	5	5	5	5	3	2
number						_
Structure	×	~	*	>>>		1

5. X-ray Crystallographic Determination

Tuble 5 II erystal Data and Straet	
Identification code	$Ag_{40,13}Cu_{13,87}S_{19}(tBuS)_{20}(tBuSO_3)_{12}$
Empirical formula	$C_{128}H_{288}Ag_{40.13}Cu_{13.87}S_{51}O_{36}$
Formula weight	18497.50 g/mol
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a=21.0609(18) Å α =79.041(2)°
	b=22.3168(12) Å β=78.4307(15)°
	c=34.112(2) Å γ=71.641(2)°
Volume	14768.1(18) Å ³
Ζ	1
Density (calculated)	2.080Mg/m ³
Absorption coefficient	3.966 mm ⁻¹
F(000)	8897
Crystal size	0.25 x 0.20 x 0.18 mm ³
Theta range for data collection	2.64 to 22.61°
Index ranges	-26<=h<=26
	-27<=k<=28
	-31<=1<=43
Reflections collected	121300
Independent reflections	63566 [R(int) = 0.127]
Completeness to theta = 25.24°	99.1%
Absorption correction	Multi scan
Data / restraints / parameters	63566 / 1 / 2520
Goodness-of-fit on F ²	1.006
Final R indices [I>2sigma(I)]	R1=0.0390, wR2=0.0711
R indices (all data)	R1=0.0843, wR2=0.0800
Largest diff. peak and hole	3.743 and -1.896 e.Å ⁻³

Table S4. Crystal Data and Structure Refinement for the $Ag_{54-x}Cu_xS_{19}(tBuS)_{20}(tBuSO_3)_{12}$ nanocluster.