A novel geometric structure of nanocluster with irregular kernel: $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$

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Supporting Information

1. Materials

Acquisition of commercial experimental drugs including AgNO3 (99.85%), copper (II) chloride (≥ 98%) were from ACROS Organic. 3-methylbenzenethiol (≥ 98%), triphenylphosphine (≥ 98%) and sodium borohydride were purchased 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). Before the experiment, all the glass bottles were washed by aqua regia (HCl: HNO_3 = 3: 1, v/v), and then rinsed with copious pure water, and dried in an oven prior to use.

2. Synthesis of the $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ nanocluster.

Firstly, $AgNO_3$ (30 mg, 0.18mmol) and TPP (60 mg, 0.23mmol) were dissolved in 6 mL of ethanol to form a colorless solution. After stirring for 5 min, 3-methylbenzenethiol (50 μL, 0.42mmol) and $CuCl_2$ (34 mg, 0.25mmol) were added to the above system, leading to the formation of a white cloudy solution. After further reaction for 10 min, the solution was centrifuged at 10000 rpm for 3 min to obtain the white precipitation while the supernatant containing excess ligands (phosphine and thiophenol) was discarded. The white precipitation was then dispersed in a mix solution consist of ethanol and dichloromethane (16 mL, v/v = 1:1), following by the addition of ethanol solution of $NaBH_4$ (2 mL, 0.40M) drop by drop. The color of the mixture turned from white to grey and finally dark brown. After further stirring for six hours, the reaction mixture was centrifuged at 10000 rpm for 3 min to collect the precipitation of $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$, which can be dissolved in dichloromethane. Dark black crystals can be obtained by diffusion of n-hexane into a dichloromethane solution of $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ over a period of one week. The yield is 59.13% based on silver atoms.

3. Characterization.

Ultraviolet−visible (UV−vis) absorption spectra were recorded on an Agilent 8453 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a thermal ESCALAB 250, equipped with a monochromated Al Kα (1486.8 eV) 150 WX-ray source, 0.5 mm circular spot size, and a flood gun (to counter charging effects). The analysis chamber base pressure was lower than 1×10^{-9} mbar, and data were collected with FAT = 20 eV. Thermal gravimetric analysis (TGA) was conducted on samples of about 3 mg, under an atmosphere of anhydrous N_2 (flow rate ~50 mL/min), using a TG/DTA 6300 analyzer (Seiko Instruments, Inc), with a heating rate of 10 ℃/min. Single crystal X-ray diffraction (SCXRD) was carried out on a Stoe Stadivari diffractometer at 296 K, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Data reductions were performed using SAINT (Bruker), and absorption corrections using SHELXTL (Bruker, 2008). The structure was solved by direct methods and refined with full-matrix least-squares on F_2 using the SHELXL-2014/7 (Sheldrick, 2014) suite of programs. The placement of the heteroatoms was ascertained by the method of modifying the disorderly free variables.

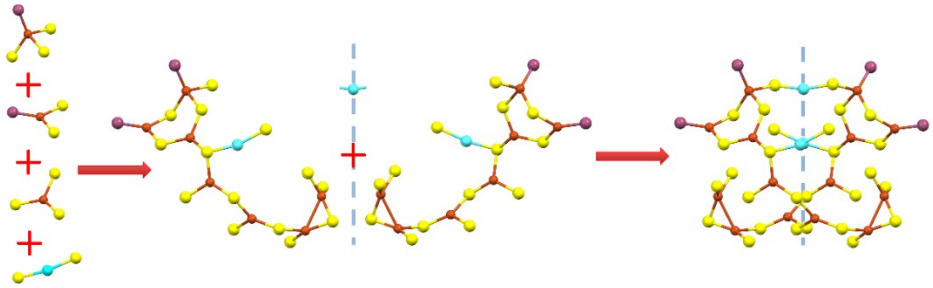


Figure S1. Illustration of the structure of the shell made up of CuS_3P, CuS_2P, CuS_3 and AgS_2 motifs. The C_2 axis of symmetry was shown as grey dash line (Color labels: aquamarine = Ag, red = Cu, purple = P, yellow = S).

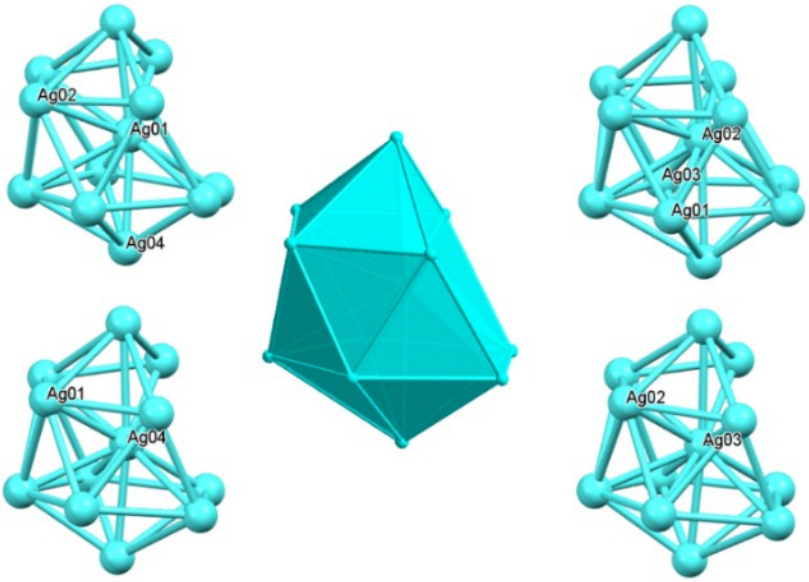


Figure S2. Four units and the polyhedron at the same orientation.

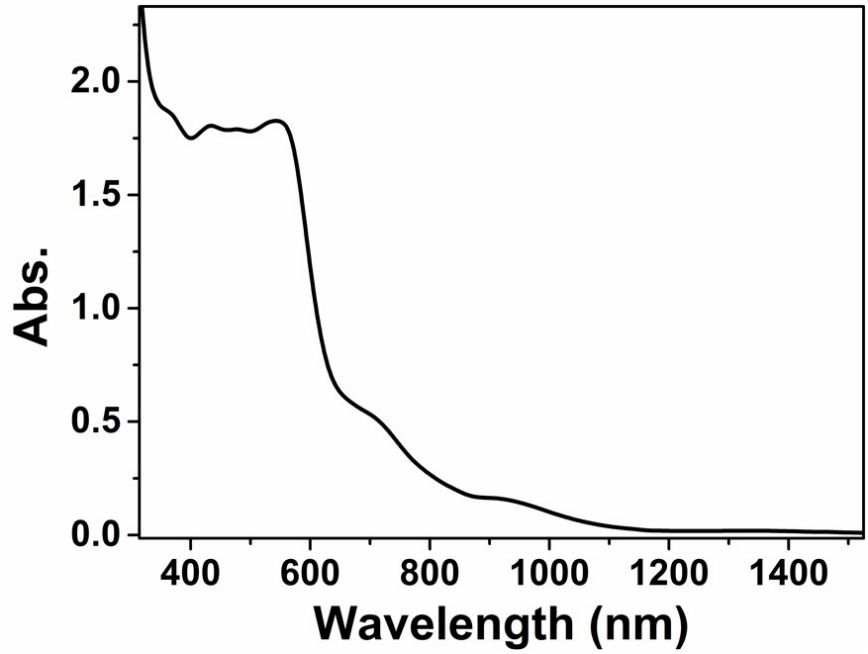


Figure S3. UV−vis absorption spectrum of $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$.

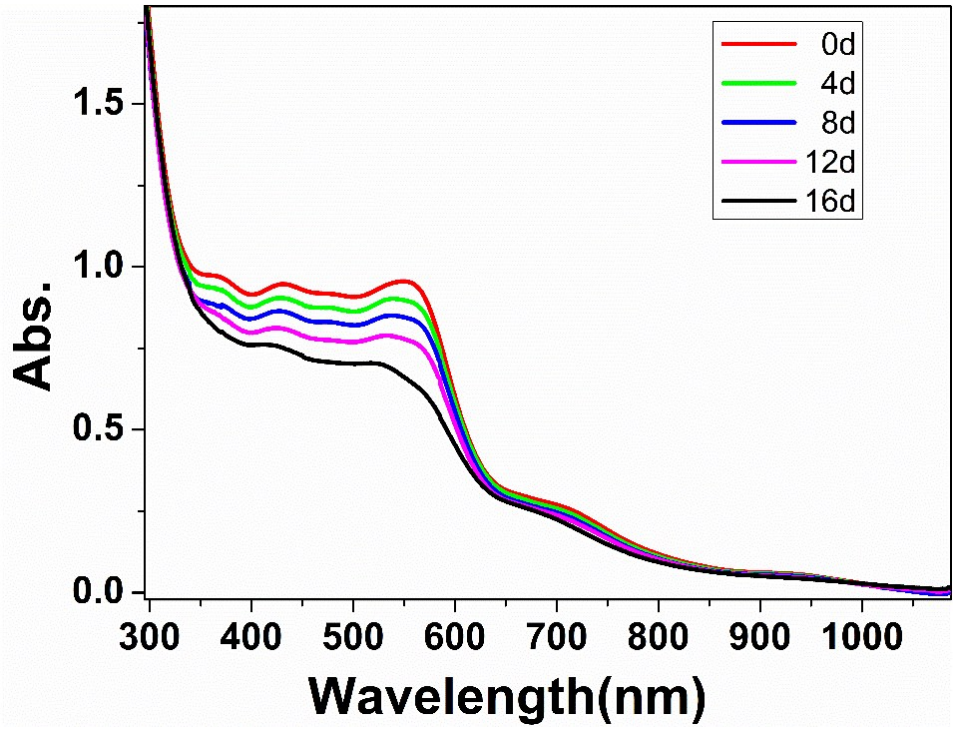


Figure S4. Time tracking UV–vis spectra of $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ in DCM (sealed to prevent volatilization) at room temperature.

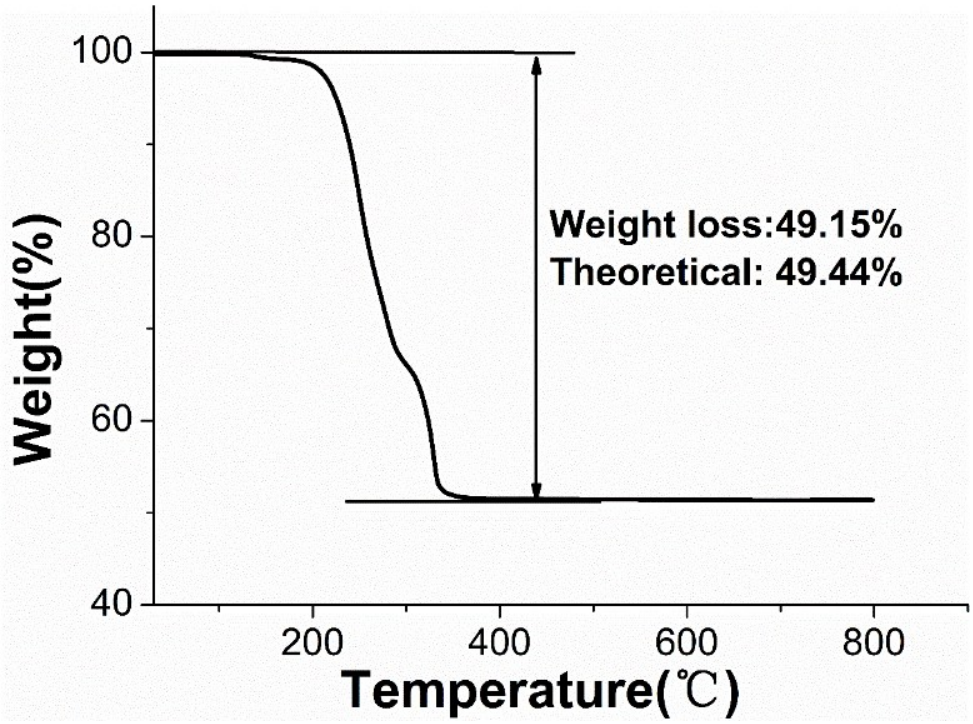


Figure S5. Thermogravimetric Analysis (TGA) curve of the $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ nanocluster.

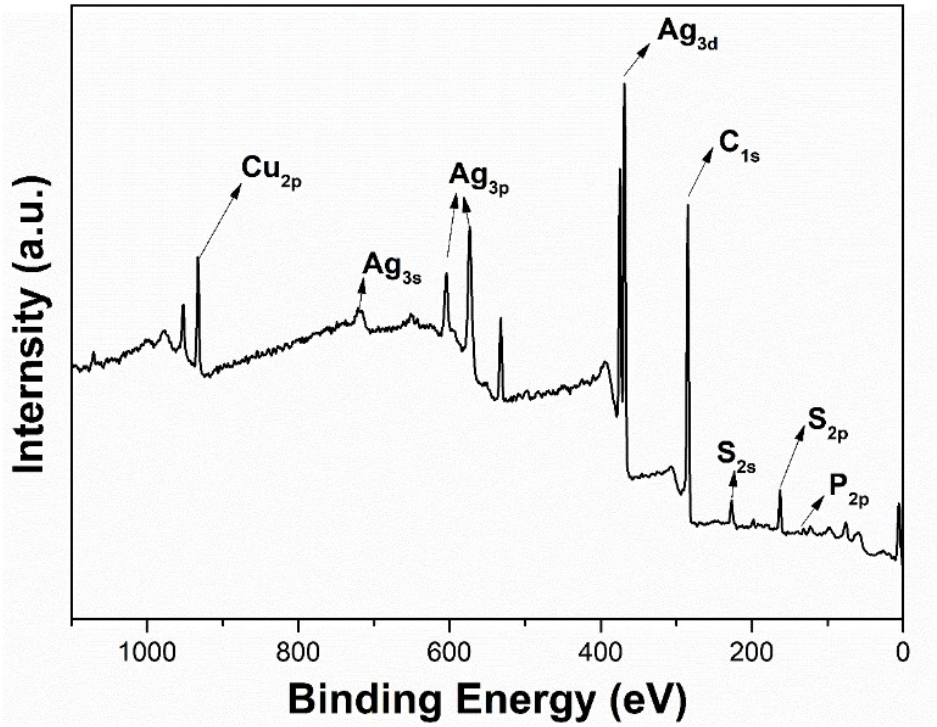


Figure S6. X-ray photoelectron spectroscopy (XPS) curve of the $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ nanocluster.

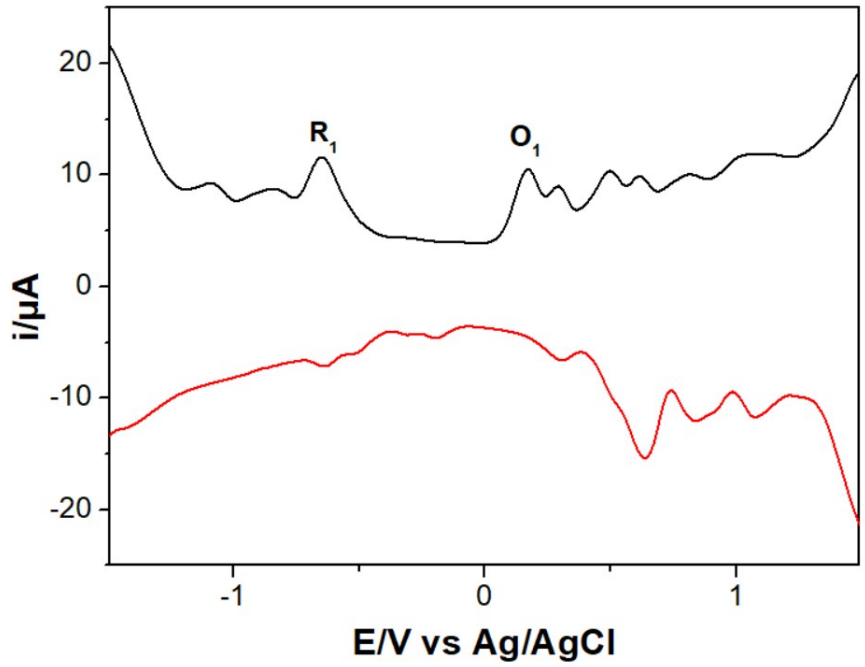


Figure S7. Differential pulse voltammogram (DPV) of $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$ in CH_2Cl_2 in the existence of Bu_4NPF_6. The black curve represents the scan from positive to negative potential ranged from 1.6 to -1.6 V, and the red curve is the opposite from -1.6 to 1.6 V. The first oxidation step (O_1) is at 0.17 V (V *vs.* Ag/AgCl), and the reduction step (R_1) is -0.64 V (V *vs.* Ag/AgCl).

Table S1. The average distance of four units.

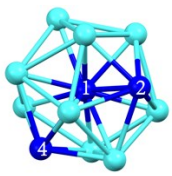
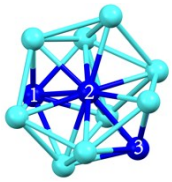
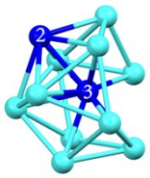
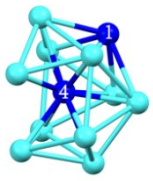
Site	1	2	3	4
Average distance（Å）	2.85	2.85	2.84	2.84
Structure				

Table S2. Crystal data for $Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$.

Empirical formula	$C_{268}H_{256}Ag_{30}Cu_{14}P_4S_{28}$
Formula weight	8623.93
Temperature	296/K
Wavelength	0.71073Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a=21.347(9)
	b=22.304(9)
	c=34.107(14)
	α=96.042(5) °
	β=91.353(5) °
	γ=112.889(5) °
Volume	14840(11)
Z	2
Density(calculated)	1.930 g/cm^3
Absorption coefficient	3.168
F(000)	8376.0
Crystal size	0.08 × 0.06 × 0.05 mm^3