Supporting Information

The positional isomerism in the bimetal nanocluster

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1. Experimental Details

1.1 Chemicals.

Silver nitrate ($AgNO_3$, 99.99%), Sodium borohydride ($NaBH_4$, 98.0%), Triphenylphosohine and 2-Ethylbenzenethiol (95%) were purchased from Aladdin. Tetrachloroauric(III) acid ($HAuCl_4$•$4H_2O$, 99.7%) was obtained from Shanghai chemical reagent co., ltd. Methanol (99.5%) and dichloromethane (AR) were purchased from Sinopharm chemical reagent co., ltd. All other chemicals were of analytical grade, and deionized water was used throughout the experiments, produced with a Milli-Q NANO pure water system (resistivity 18.2 MΩ cm).

1.2 Synthesis of $Au_{12}Ag_{32}$-1 nanocluster.

The synthesis of atomically precise $Au_{12}Ag_{32}$-1 nanocluster is called one-pot synthesis. In brief, to obtain the target nanocluster with precise structure, 80 mg Silver nitrate ($AgNO_3$) and 20 mg Tetrachloroauric (III) acid ($HAuCl_4$•$4H_2O$) were completely dissolved in 5mL of methanol and 5mL dichloromethane under vigorous stirring, after 15minutes, the mixed solution was cooled to 0 °C in an ice bath. Then, 200 mg Triphenylphosohine (PPh_3) and 70μL 2-Ethylbenzenethiol were added quickly for 20 minutes. Subsequently, 110 mg of solid $NaBH_4$ which dissolved in 2mL ice-cold pure water were added drop by drop using pipettor. The recitation was aged for 11h in an ice-bath under strring and the color of the total solution changed from light grey to dark immediately. The aqueous phase was discarded and the crude product was washed with CH_3OH four times to remove inorganic salt and excess thiolate utterly.

1.3 Synthesis of $Au_{12}Ag_{32}$-2 nanocluster.

(The nanoclusters were synthesized following literature report S1).

1.4 Single-crystal growth and analysis.

Black crystals were formed from a CH_2Cl_2/hexane solution of the nanoclusters at 4℃ after about three months. The diffraction data for $Au_{12}Ag_{32}$ nanoclusters were collected at 173K on a Bruker APEX DUO X-raydiffractometer using Cu Ka radiation (l¼1.54184 Å).

1.5 Characterization

Ultraviolet-visible-near-infrared absorption measurements were performed on a Shimadzu UV-

3600 spectrophotometer (DCM as solvent). The single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE AXS photon 100 diffractometer with helios mx multilayer monochromator Mo Kα radiation (λ = 0.71083 Å). Thermogravimetric analysis (TGA) (~ 6 mg sample used) was conducted in a N_2 atmosphere (flow rate ~ 50 mL/min) using a TG/DTA 6300 analyzer (Seiko Instruments, Inc.), and the heating rate was 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi XPS spectrometer (Thermo Scientific, America), using a monochromatized Al Kα source and equipped with an Ar^+ ion sputtering gun.

2. Supporting Figures

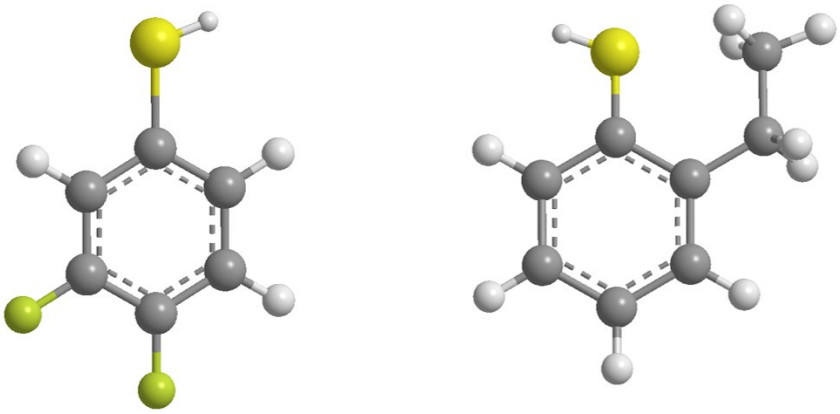

Figure S1. The total structures of 3, 4-difluorothiophenol (left) and 2-ethylbenzenethiol (right). Color labels: light green = F, yellow = S, white = H, gray = C.

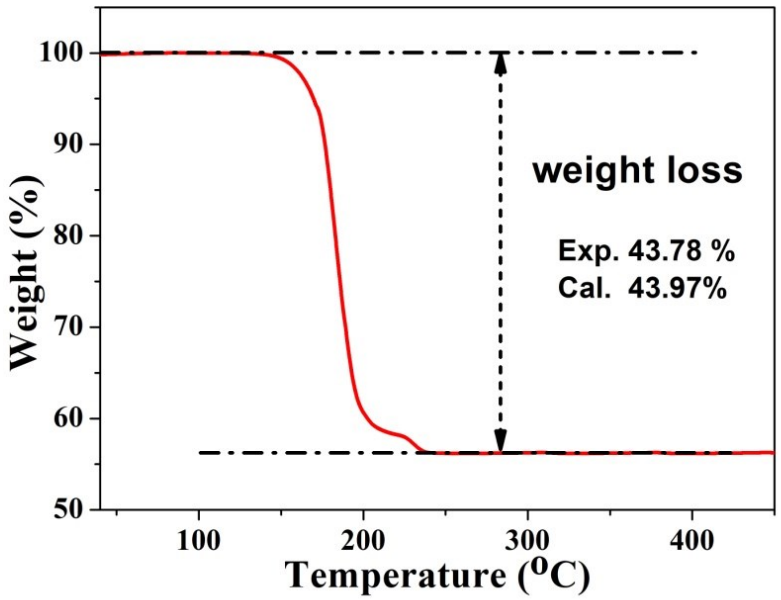

Figure S2. TGA of $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster.

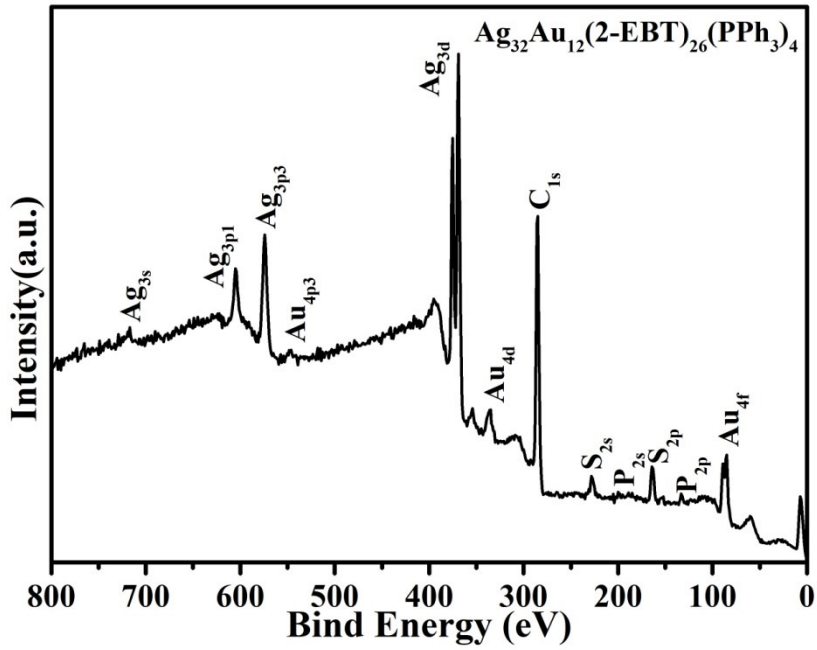

Figure S3. XPS spectrum of $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster.

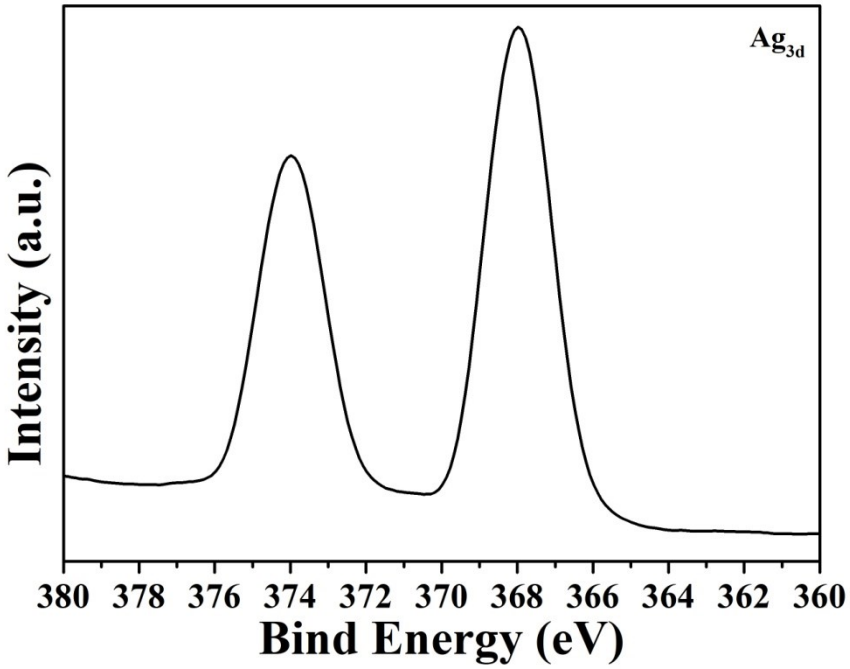

Figure S4. XPS spectrum of Ag3d in the $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster.

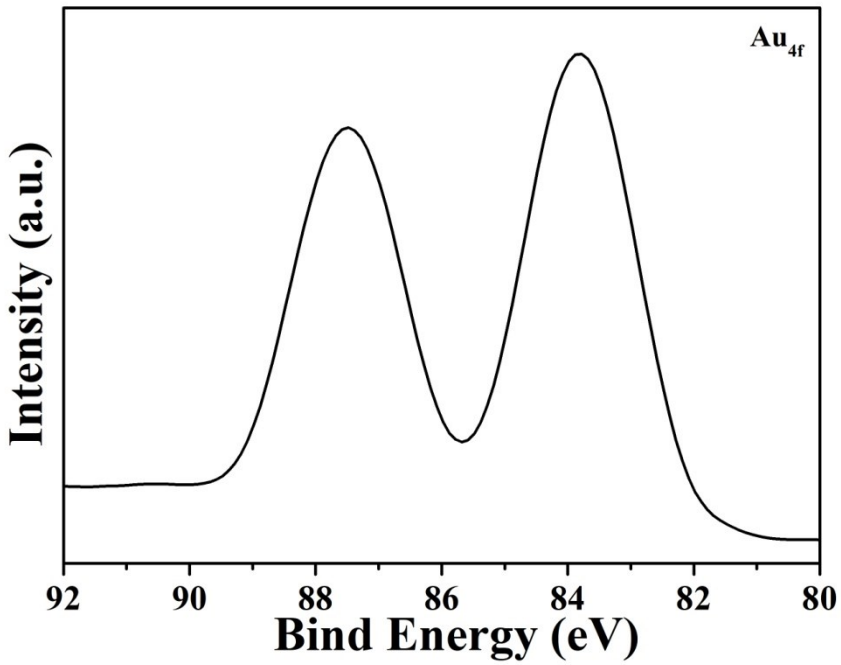

Figure S5. XPS spectrum of Au4f in the $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster.

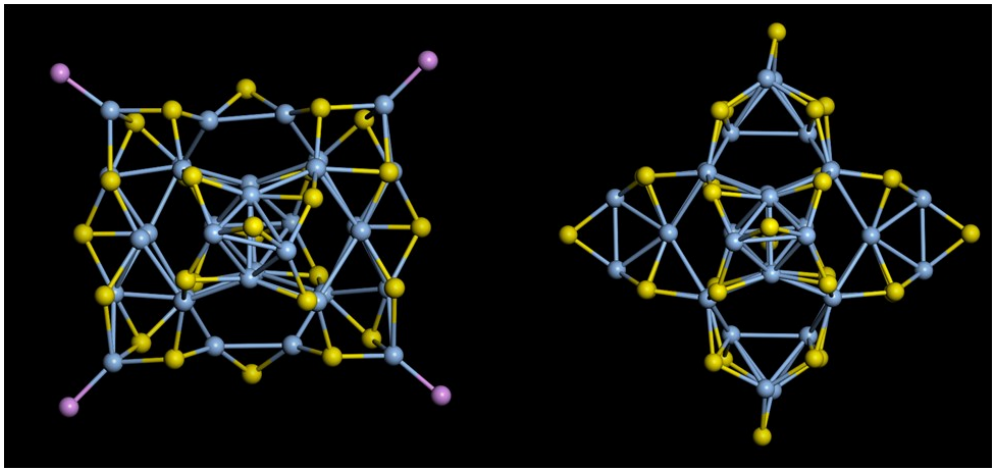

Figure S6. The totally surface staple structure of $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster (left) and $Ag_{32}Ag_{12}(3,4\text{-DFT})_{30}$ nanocluster (right). Color labels: Ag, light blue; S, yellow; P, pink.

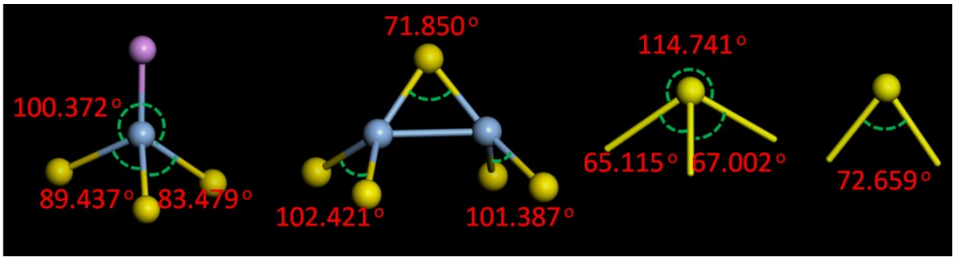

Figure S7. The detailed structure of four types of surface staples in the $Au_{12}Ag_{32}$(2-EBT)$_{26}$(PPh_3)$_4$ nanocluster. Color labels: Ag, light blue; S, yellow; P, pink.

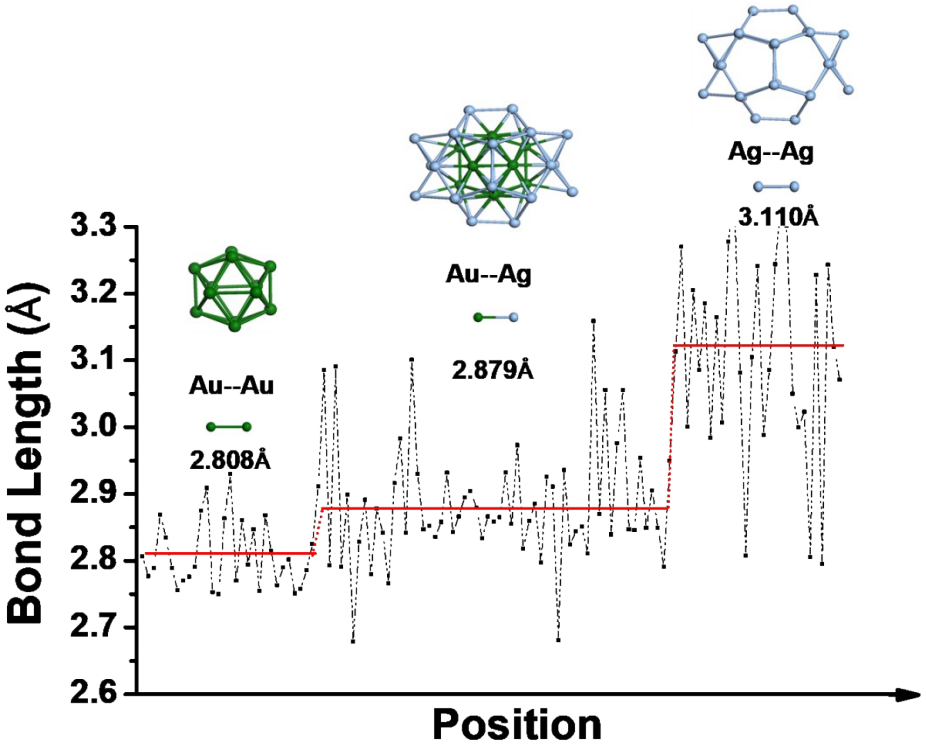

Figure S8. Bond lengths of $Au_{12}Ag_{32}$(2-EBT)$_{26}$(PPh_3)$_4$ nanocluster. Color labels: Au, green; Ag, light blue.

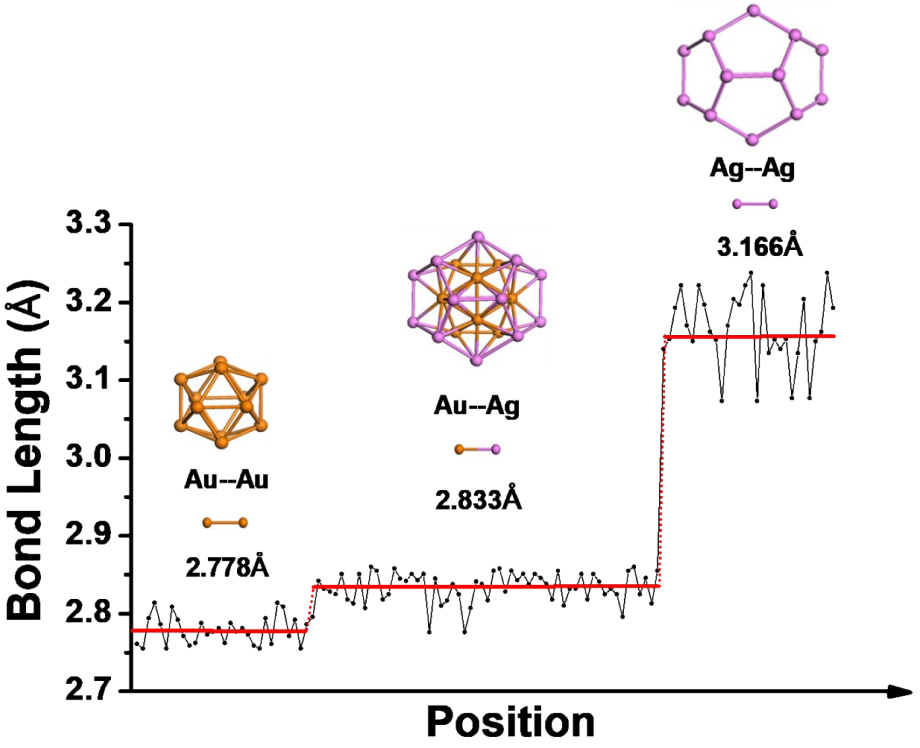

Figure S9. Bond lengths of $Au_{12}Ag_{32}(3,4\text{-DFT})_{30}$ nanocluster. Color labels: Au, brown; Ag, pink.

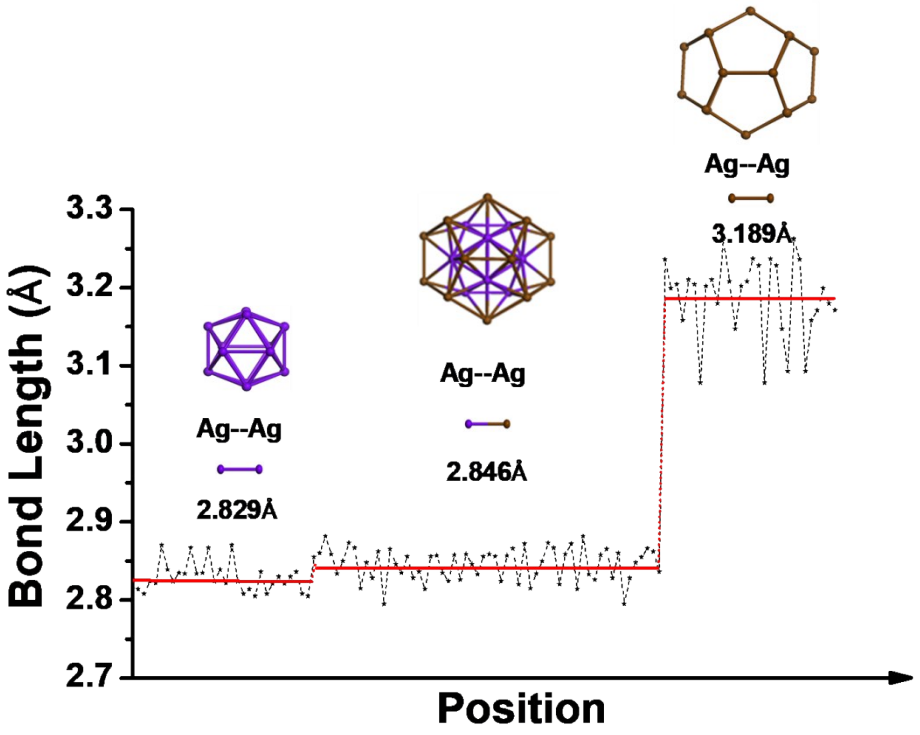

Figure S10. Bond lengths of $Ag_{44}(3,4\text{-DFT})_{30}$ nanocluster. Color labels: Ag, brown and purple.

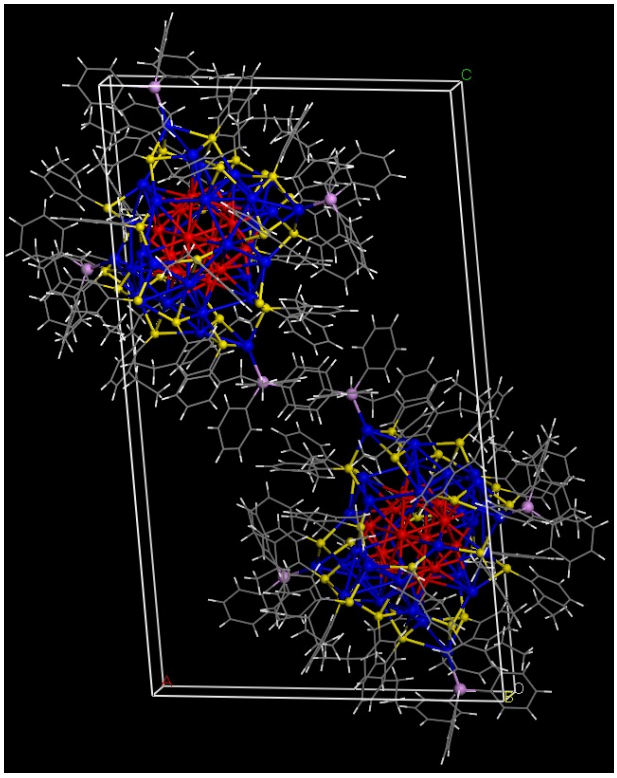

Figure S11. Unit cell of $Ag_{32}Ag_{12}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster. Color labels: Au, red; Ag, blue; S, yellow; P, pink; C, gray; H, white.

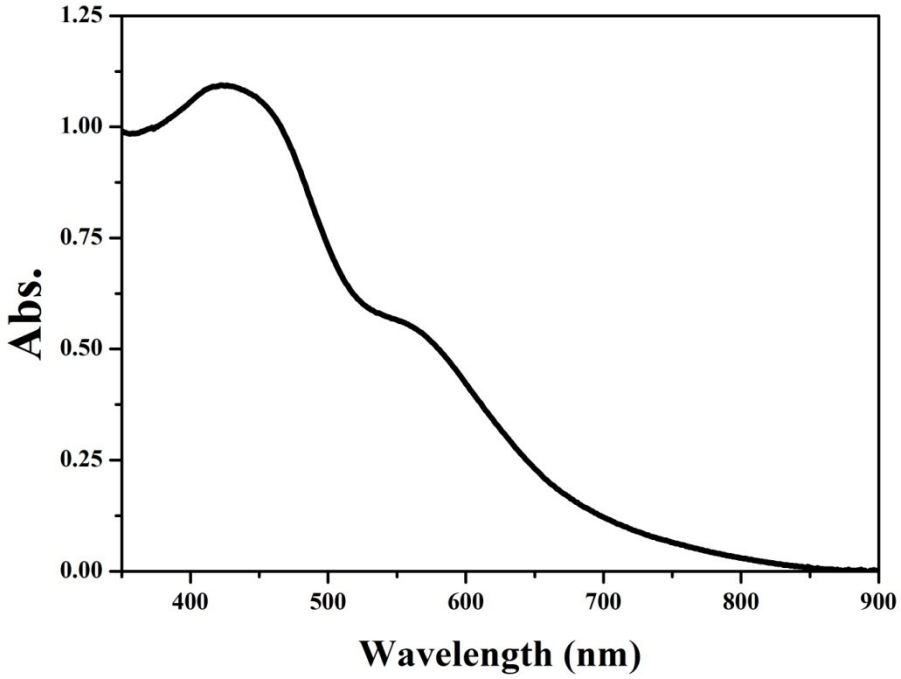

Figure S12. UV/Vis spectrum of $Au_{12}Ag_{32}(2\text{-EBT})_{26}(PPh_3)_4$ nanocluster.

3 Single crystal data

3.1 Single crystal data for $Ag_{32}Au_{12}$ nanocluster

Table 1. Crystal data and structure refinement for $Ag_{32}Au_{12}$.

Empirical formula	$C_{280}\ H_{294}\ Ag_{32}\ Au_{12}\ P_4\ S_{26}$
Formula weight	10432.01
Temperature/ K	173
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a=21.071(3) Å α= 80.137(4)° b=21.271(3) Å β= 82.278(4)° c=36.786(5) Å γ = 78.032(4)°
Volume/ $Å^3$	15807(4) $Å^3$
Z	2
$\rho_{calc}g/cm^3$	2.192
μ/mm^{-1}	7.708
F(000)	9804.0
Index ranges	-27<=h<=21, -27<=k<=27, -48<=l<=43
Reflections collected	140783
Independent reflections	73291 [R(int) = 0.0861]
Theta range for data collection	1.976 to 27.762°
Completeness to theta = 25.242°	99.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	73291 / 1733 / 3163
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R_1 = 0.0963, wR_2 = 0.2516
R indices (all data)	R_1 = 0.1697, wR_2 = 0.3022
Extinction coefficient	n/a

Largest diff. peak and hole/ e $Å^{-3}$	4.748 and -7.871

4. References:

(S1) Yang, H.; Wang, Y.; Huang, H.; Gell, L.; Lehtovaara, L.; Malola, S.; Hakkinen, H.; Zheng, N. All-thiol-stabilized Ag_{44} and $Au_{12}Ag_{32}$ nanoparticles with single-crystal structures. *Nat. Commun.* **2013**, *4*, 2422.