Supporting Information

Metal Synergistic Effect on Cluster Optical Properties: Based on Ag_{25} Series Nanoclusters

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Experimental Details:

1. Chemicals: Silver nitrate ($AgNO_3$, 99.85%, metal basis), tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, 99.99%, metal basis), hexachloroplatinic(IV) acid ($H_2PtCl_6 \cdot 6H_2O$, 99.99%, metal basis), 2,4-dimethylbenzenethiol ($HSPhMe_2$, 95%), triphenylphosphine (PPh_3, 99%), tetraphenylphosphonium bromide (PPh_4Br, 98%), 1-adamantanethiol ($C_{10}H_{16}S$, 99%), sodium borohydride ($NaBH_4$, > 98%). Methylene chloride (CH_2Cl_2, HPLC grade, Aldrich), methanol (CH_3OH, HPLC, Aldrich), *n*-hexane (Hex, HPLC grade, Aldrich), 2-methyltetrahydrofuran ($C_5H_{10}O$, 99%). Pure water was purchased from Wahaha Co. Ltd. All reagents were used as received without further purification.

2. Synthesis of $Ag_{25}(SPhMe_2)_{18}PPh_4$ nanoclusters

Silver nitrate (37 mg, 0.22 mmol) was dissolved in 2 mL methanol, 90 µL 2, 4-dimethylbenzenethiol was added to above solution, and then 17 mL CH_2Cl_2 was added to the reaction bottle. The reaction mixtures was vigorously stirred for 20 min under ice-bath. Subsequently, a freshly prepared PPh_4Br (7 mg in 0.5 mL methanol) was added, after then, fresh ice-cold aqueous $NaBH_4$ (17 mg in 0.5 ml DI water) was added; during this procedure, the color of the reaction mixture changed from colorless to light yellow and then to dark. The reaction was carried out overnight. The reaction liquid was centrifuged and the supernatant liquid was left. The obtained supernatant was concentrated by evaporating solvents. And then the crude product was washed with methanol for 3 times to remove excess ligands.

3. Synthesis of $Au_1Ag_{24}(SPhMe_2)_{18}PPh_4$ nanoclusters

$Ag_{25}(SPhMe_2)_{18}PPh_4$ as a precursor to synthesize $Au_1Ag_{24}(SPhMe_2)_{18}PPh_4$. About 20 mg $Ag_{25}(SR)_{18}$ was dissolved in 5 mL CH_2Cl_2, following, 8 µL $AuClPPh_3$(~1 mg/200 µL DCM) was added under vigorously stirred for 4h at room temperate. The color of the reaction solution changed from reddish brown to green. After the reaction, the purification process of the crude product was similar to $Ag_{25}(SR)_{18}$. The precipitate of the clusters was then dissolved in CH_2Cl_2 and crystallized in CH_2Cl_2/hexane at room temperate.

4. Synthesis of $Pt_1Ag_{24}(SPhMe_2)_{18}PPh_4$ nanoclusters

30 mg $AgNO_3$ was dissolved in 2 mL methanol, 20 mL $CH_3COOC_2H_5$ was added and subsequently 50 µL H_2PtCl_6 (0.2 g/mL water) solution, at this moment, the color of the solution was yellowish.

Next, 100 μL 2,4-dimethylbenzenethiol was added to above reaction solution under vigorously magnetic stirred for 20 min. Afterward, 2 ml $NaBH_4$ ice cold aqueous solution (20 mg/ 2 mL) was added quickly with the reaction color changed immediately from yellow to black. The reaction mixtures was continue stirred overnight. Ultimately, an emerald green rude product was obtained. The rude product was centrifuged, and the resulting supernatant was rota-evaporated under vacuum to remove the solvents of organic-phrase mixture. Then, 20 mL methane was used to extract the product, subsequently, excess PPh_4Br dissolved in methanol was added into above CH_3OH solution to precipitate, and then centrifuged to obtain the solid. The synthesized clusters was washed by methanol for twice.

5. Synthesis of $M_1Ag_{24-x}Au_x(SPhMe_2)_{18}PPh_4$ (M = Au, Pt)

$M_1Ag_{24}(SR)_{18}$ (M = Au, Pt) was dissolved in CH_2Cl_2, and then Me_2PhSAu was added into the solution under stirred. The reaction was continued about 1 h, afterward, the obtained clusters was washed similar to $Ag_{25}(SR)_{18}$.

6. Synthesis of $Pt_1Ag_{28}(S\text{-}Adm)_{18}(TPP)_4$

10 mg of $Pt_1Ag_{24}(SPhMe_2)_{18}$ was dissolved in 10 mL of CH_2Cl_2. Then, 5 mg of PPh_3 and 10 mg of AdmSH (1-adamantanethiol) were added to the solution simultaneously. The reaction continue to stirred for 30 min at room temperature. The colour of solvent transformed from bright green to orange. The organic layer was separated from the precipitate and evaporated to dryness. The $Pt_1Ag_{28}(S\text{-}Adm)_{18}(PPh_3)_4$ nanocluster was obtained afterwards. The dried nanocluster was washed with methanol about 3 times and collected by centrifugation. The precipitate of the clusters was then dissolved in CH_2Cl_2 and crystallized in CH_2Cl_2/hexane at 4 °C for 2-3 days.

7. Characterization

All UV-Vis spectrum of nanoclusters was recorded using Agilent 8453 instrument with a test range of 190 nm to 1100 nm, the samples was dissolved in CH_2Cl_2 and whose background correction was made using a CH_2Cl_2 blank. The temperature-dependent absorption spectrum of nanoclusters was dissolved into 2-methyltetrahydrofuran, and whose background correction was made using a 2-methyltetrahydrofuran blank.

Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) measurement was performed by HClass XEVO G2 XS QTof (Waters. Crop), all samples were recorded in negative ion mode, the clusters was dissolved in CH_2Cl_2 and diluted with an equal volume of methanol and then centrifuged for 3-5 min (12000 rpm) to remove any undissolved impurities. Instrumental parameters were maintained at the following values unless otherwise indicated: capillary voltage, 1.8-2.5 kV; sampling cone, 20V; source offset, 80 V; cone gas flow rate, 50 L/h; transfer collision energy, 1.0 eV; source temperature, 60 °C; and desolvation temperature, 400 °C. External calibration was performed in positive ionization mode in the range 1000m/z ~8000 m/z using a solution of sodium iodide. Mass spectra were processed using Masslynx 4.1 software (Waters Corp.).

Photoluminescence spectra were measured on a FL-7000 spectrofluorometer with the same optical density (OD) ~0.1. In these experiments, the nanoclusters solution were prepared in CH_2Cl_2 at a concentration of less than 1 mg mL^{-1}. The low temperature Photoluminescence spectra of all samples were dissolved into 2-methyltetrahydrofuran and other parameter was same with room temperature.

X-ray photoelectron spectroscopy (XPS) was measured on a Thermo ESCALAB 250, equipped with a monochromated AlKα (1486.8 eV) 150W X-ray source and a chamber at a base pressure of ~$1x10^{-9}$ mbar, data were collected with FAT=20 eV.

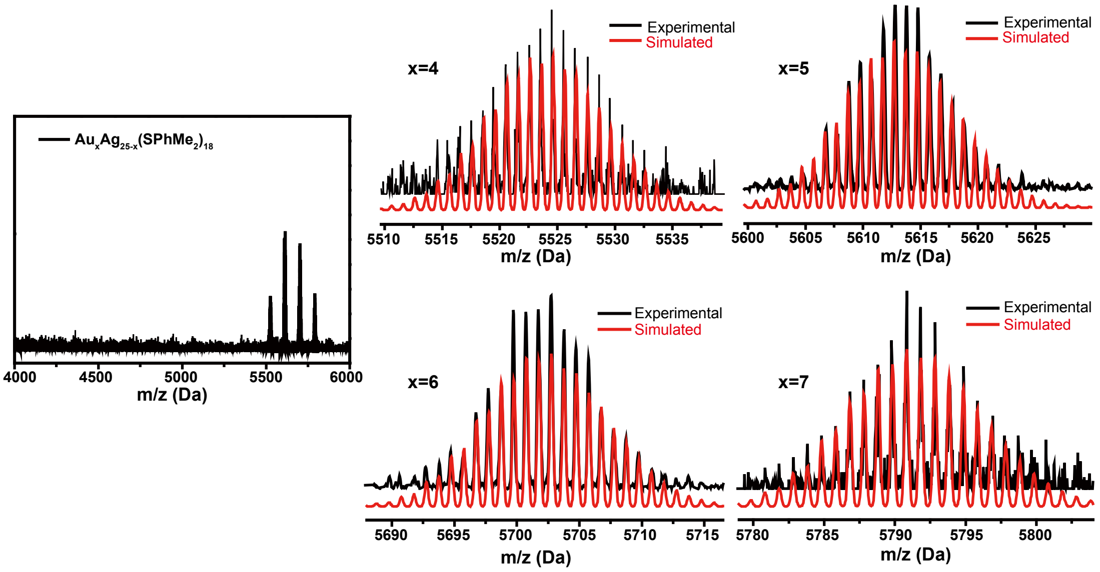

Fig. S1 Experimental mass spectrum matched with the theoretical simulation mass spectrum of $Au_xAg_{25-x}(SPhMe_2)_{18}$.

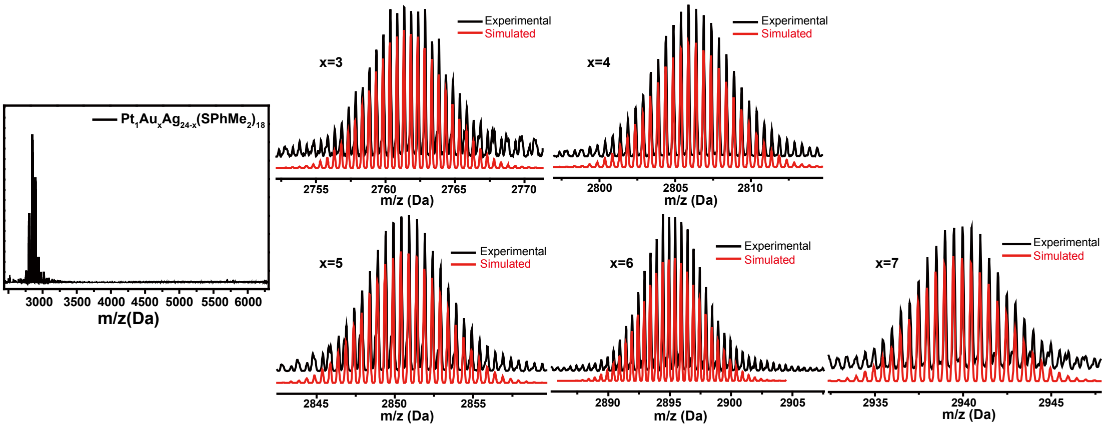

Fig. S2 Experimental mass spectrum matched with the theoretical simulation mass spectrum of $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$.

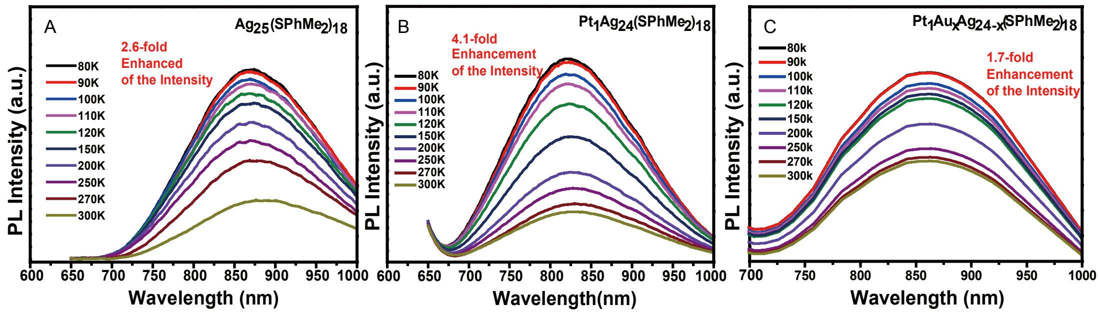

Fig. S3 Temperature-dependent photoluminescence spectra of A) $Ag_{25}(SPhMe_2)_{18}$, B) $Pt_1Ag_{24}(SPhMe_2)_{18}$ and C) $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$. The PL spectra of all samples was excited at 405 nm with the OD = 0.1.

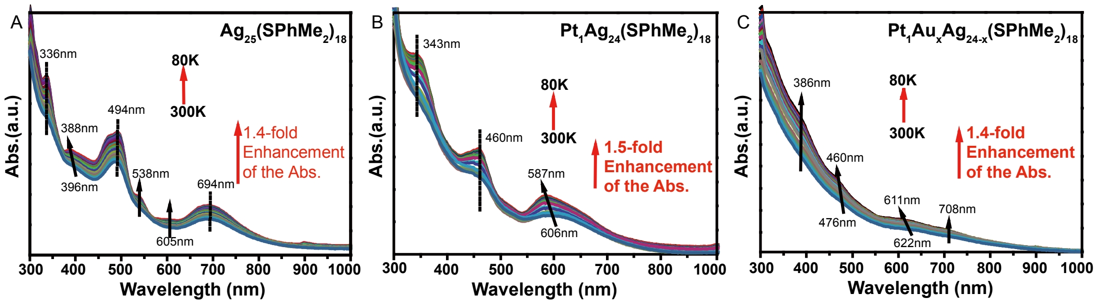

Fig. S4 Temperature-dependent absorption spectra of A) $Ag_{25}(SPhMe_2)_{18}$, B) $Pt_1Ag_{24}(SPhMe_2)_{18}$ and C) $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$.

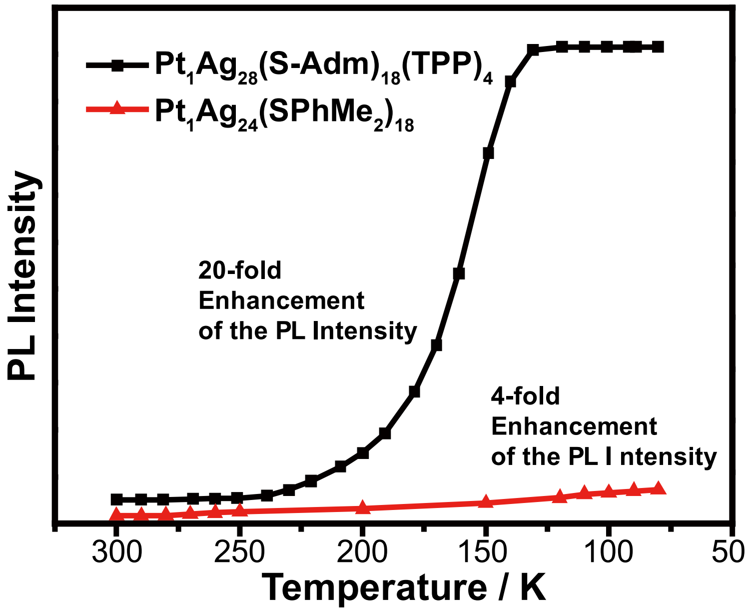

Fig. S5 PL intensity variation with temperature decreasing. Black: $Pt_1Ag_{28}(S\text{-}Adm)_{18}(TPP)_4$

(monitored at 672 nm); red: $Pt_1Ag_{24}(2,4\text{-DMBT})_{18}$ (monitored at 822 nm).

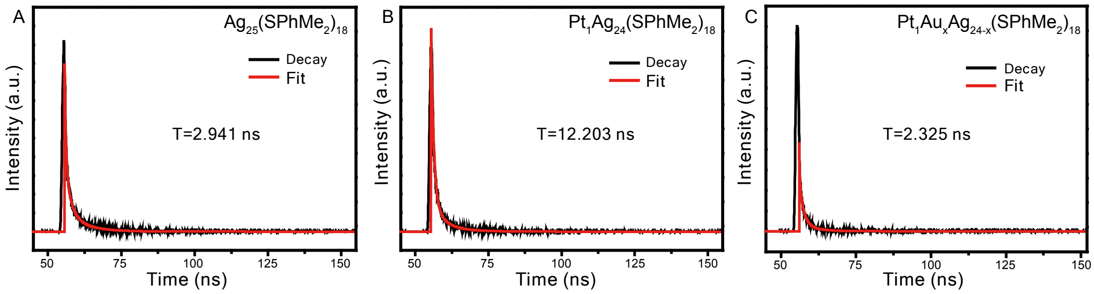

Fig. S6 Photoluminescence lifetime spectra of A) $Ag_{25}(SPhMe_2)_{18}$, B) $Pt_1Ag_{24}(SPhMe_2)_{18}$ and C) $Pt_1Au_xAg_{24\text{-}x}(SPhMe_2)_{18}$.

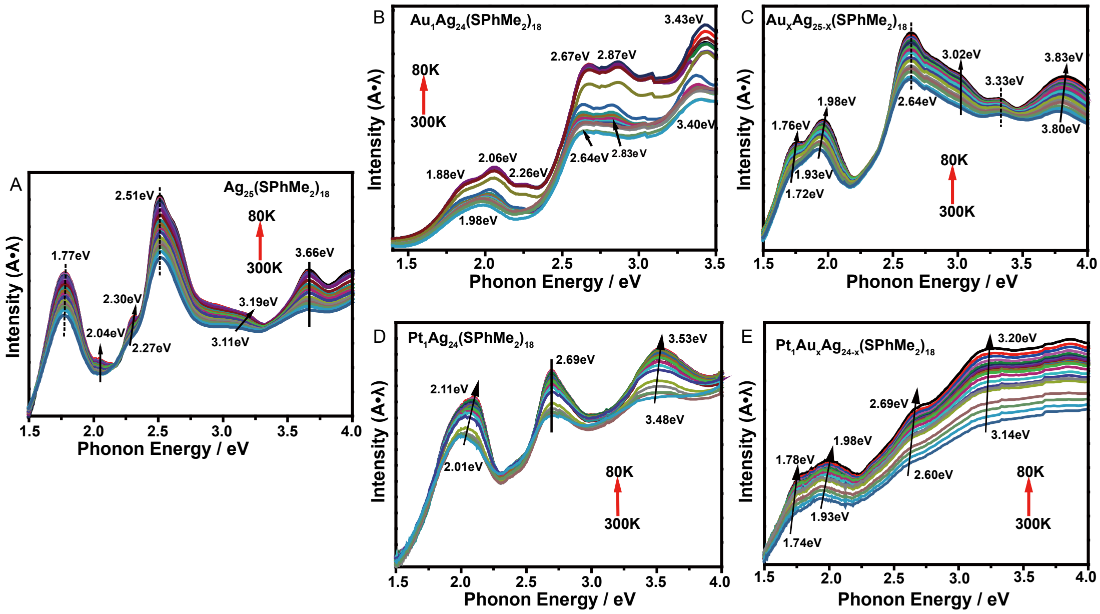

Fig. S7 Intensity spectra at different temperatures of A) $Ag_{25}(SPhMe_2)_{18}$, B) $Au_1Ag_{24}(SPhMe_2)_{18}$, C) $Au_xAg_{25\text{-}x}(SPhMe_2)_{18}$, D) $Pt_1Ag_{24}(SPhMe_2)_{18}$ and E) $Pt_1Au_xAg_{24\text{-}x}(SPhMe_2)_{18}$.

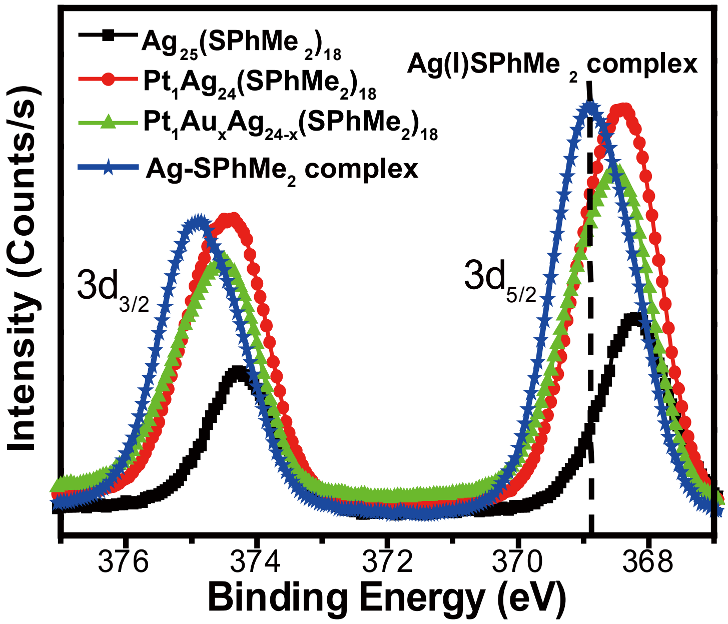

Fig. S8 X-ray photoelectron spectroscopy: Ag 3d spectral region of $Ag_{25}(SPhMe_2)_{18}$, $Pt_1Ag_{24}(SPhMe_2)_{18}$ and $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$.

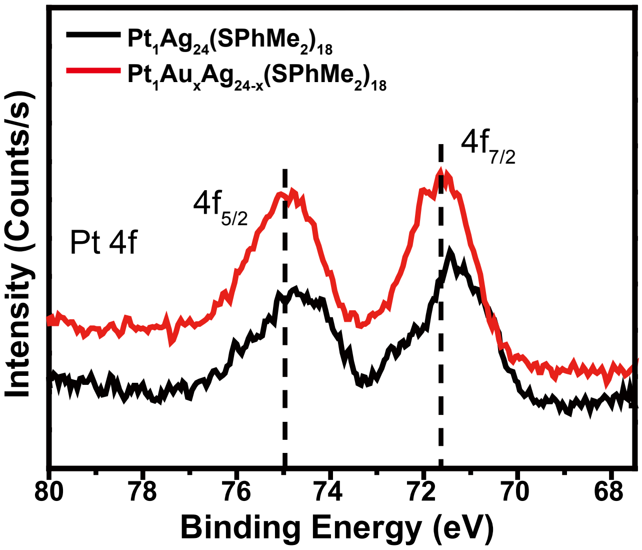

Fig. S9 X-ray photoelectron spectroscopy: Pt 4f region of $Pt_1Ag_{24}(SPhMe_2)_{18}$ and $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$.

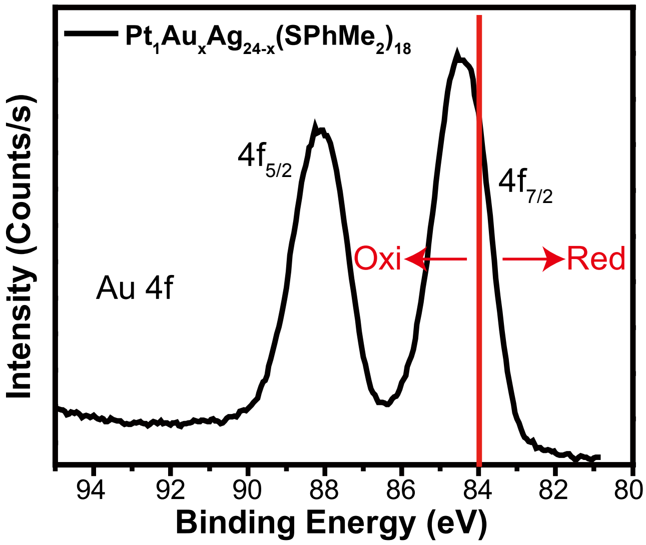

Fig. S10 X-ray photoelectron spectroscopy: Au 4f region of $Pt_1Au_xAg_{24-x}(SPhMe_2)_{18}$.

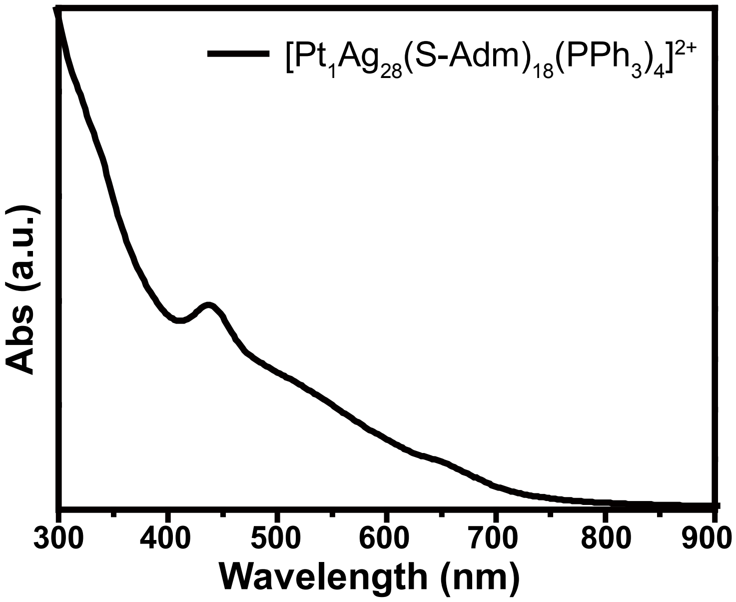

Fig. S11 UV-Vis spectrum of the $Pt_1Ag_{28}(S\text{-}Adm)_{18}(PPh_3)_4$ nanocluster crystal.

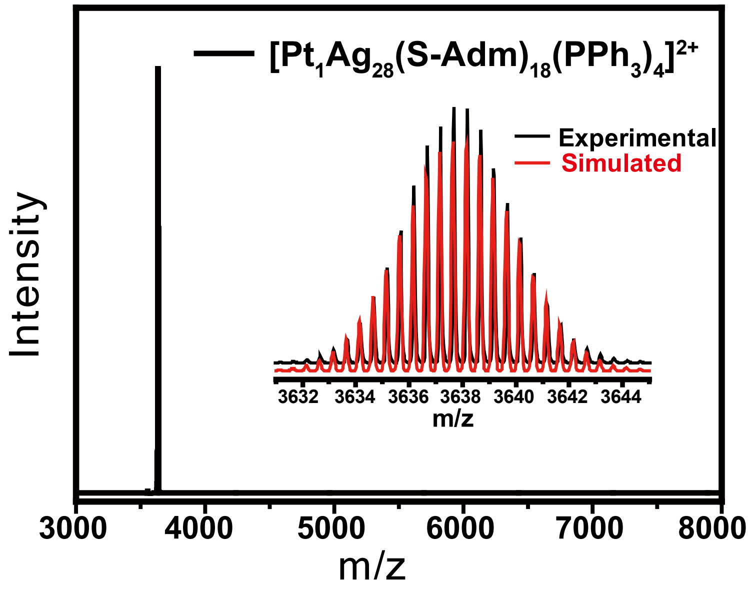

Fig. S12 ESI-MS spectrum of the Pt$_1$Ag$_{28}$(S-Adm)$_{18}$(PPh$_3$)$_4$ nanocluster crystal.