Supporting Information

Structures and magnetism ofmono-palladium and mono-platinum doped $Au_{25}(PET)_{18}$ nanoclusters

Shubo Tian,[a] Lingwen Liao,[a] Jinyun Yuan,[b] Chuanhao Yao,[a] Jishi Chen, [a] Jinlong Yang, [b] Zhikun Wu[a]

[1]Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China. Email: zkwu@issp.ac.cn.
[2]Hefei National Laboratory for Physical Sciences at the Microscale and Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

1. Experimental section

Reagents. All chemicals and reagents are commercially available and were used as received. The water used in all experiments was ultrapure (resistivity 18.2 MΩ cm), produced with a Milli-Q NANO pure water system. Toluene (99.5%), methanol (AR), dichloromethane (AR), petroleum ether (AR) and Sodium borohydride ($NaBH_4$, 99.0%), were purchased from Sinopharm chemical reagent co., ltd. Tetraoctylammonium bromide (TOAB, 98.0%), Sodium tetrachloropalladate ($NaPdCl_4$, 98%) and Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}4H_2O$) was obtained from Aladdin. 2-Phenylethanethiol (PhC_2H_4SH, 99.0%) and 1-hexanethiol ($CH_3(CH_2)_5SH$, 99.0%) were purchased from Sigma-Aldrich. Tetrachloroauric(III) acid ($HAuCl_4{\cdot}4H_2O$, 99.7%) were purchased from Shanghai chemical reagent co., ltd.

Synthesis of the anion and neutral $Au_{25}(SR)_{18}$. $[Au_{25}(PET)_{18}]^-TOA^+$ was prepared via the previous method reported.[1] $[Au_{25}(PET)_{18}]^0$ was synthesized through the controlled oxidation of $[Au_{25}(PET)_{18}]^-TOA^+$ by O_2 in air.[2] $[Au_{25}(SC_6H_{13})_{18}]^0$ was synthesized referring to the above methods.

Synthesis of $[Au_{24}Pd(PET)_{18}]^0$ and $[Au_{24}Pt(PET)_{18}]^0$. Both $[Au_{24}Pd(PET)_{18}]^0$ and $[Au_{24}Pt(PET)_{18}]^0$ nanoclusters were synthesized according to a reported method[3,4,5] with some modifications.

The first step: $H_2PtCl_6{\cdot}4H_2O$ (0.1036 g, 0.20 mmol), $HAuCl_4{\cdot}4H_2O$ (0.329g, 0.80 mmol) and TOAB (0.634 g, 1.16 mmol) were dissolved in 30 mL THF in a 125 mL tri-neck round bottom flask. After vigorously stirred for 60 min, the solution color changed from yellow to red. Then, phenylethanethiol (0.345 mL) was added to the flask at room temperature without changing the stirring speed. Stirring was continued for 10 min until the solution color changed from dark red to orange. After that, $NaBH_4$ (0.380 g, 10.0 mmol) dissolved in 5 mL cold water was added all at once. After stirred for additional 5 h, the aqueous phase was removed and the remaining

organic phase was washed with abundant water to remove water soluble impurities. Then the products in organic phase were precipitated out by the addition of CH_3OH.

The second step: the crude products were dissolved in a small amount of CH_2Cl_2 then separated by preparative thin-layer chromatography (dichloromethane: petroleum ether=2:3). The isolated mixture products of $Au_{25}(PET)_{18}$ and $[Au_{24}Pt(PET)_{18}]^0$ were dissolved in 10 ml toluene and into the resulting solution 15 mL H_2O_2 (30 wt%) solution was added to selectively decompose the $Au_{25}(PET)_{18}$ nanoclusters. When the homo-gold nanoclusters was completely decomposed after about 10 hours, the alloy nanoclusters were further purified using PTLC.

The third step: high qualified single crystals of $[Au_{24}Pt(PET)_{18}]^0$ were obtained by slowly diffusing methanol into the toluene solution of the purified product at 4 °C for 5 days**.**

The first step of $[Au_{24}Pd(PET)_{18}]^0$ synthesis is similar to that of $[Au_{24}Pt(PET)_{18}]^0$ except using Na_2PdCl_4 (0.0589 g, 0.20 mmol) instead of $H_2PtCl_6{\cdot}4H_2O$ (0.1036 g, 0.20 mmol) as the second metal source; and the remaining protocols are also similar to those of $[Au_{24}Pt(PET)_{18}]^0$ synthesis except that the etching time by H_2O_2 was adjusted to ~3 hours.

2. Characterization.

The ultraviolet–visible–near-infrared absorption spectra were measured on a UV-2600 spectrophotometer (Shimadzu, Japan) at room temperature. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker) using Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. The diffraction data for $PdAu_{24}(PET)_{18}$ and $PtAu_{24}(PET)_{18}$ were collected at 130K on a Bruker APEX DUO X-ray diffractometer using Mo Ka radiation (λ = 0.71073). NMR spectra were recorded on an agilent spectrometer (VNMRS600) using tetramethylsilane as an internal reference. The Pt and Au L_3-edge XAFS spectra were measured at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF), China.

3. Theoretical method.

In order to confirm the relative stability of the three isomers of Pt locating at core, inner-shell and out-shell for $Au_{24}Pt(PET)_{18}$, their single point energies were calculated using Density Functional Theory (DFT) with the hybrid functional B3LYP[6-9] and all electron basis set 6-31g (d, p) for H, C, and S, pseudopotential basis set LANL2DZ for Au and Pt, as implemented in the Gaussian 09 program package.[10] These three isomers were constructed by placing the Pt atom in the core, inner-shell, and outer-shell of $Au_{24}Pt$ crystallized in this work, respectively.

4. REFERENCES

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thiol-functionalized Au_{25} nanoclusters. *J. Mater. Chem.* **2009,** *19*, 622-626.
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10. Frisch, M. J. et al. Gaussian 09, Revision B.01 (Gaussian, Inc., **2010**).

5. Supporting Figures

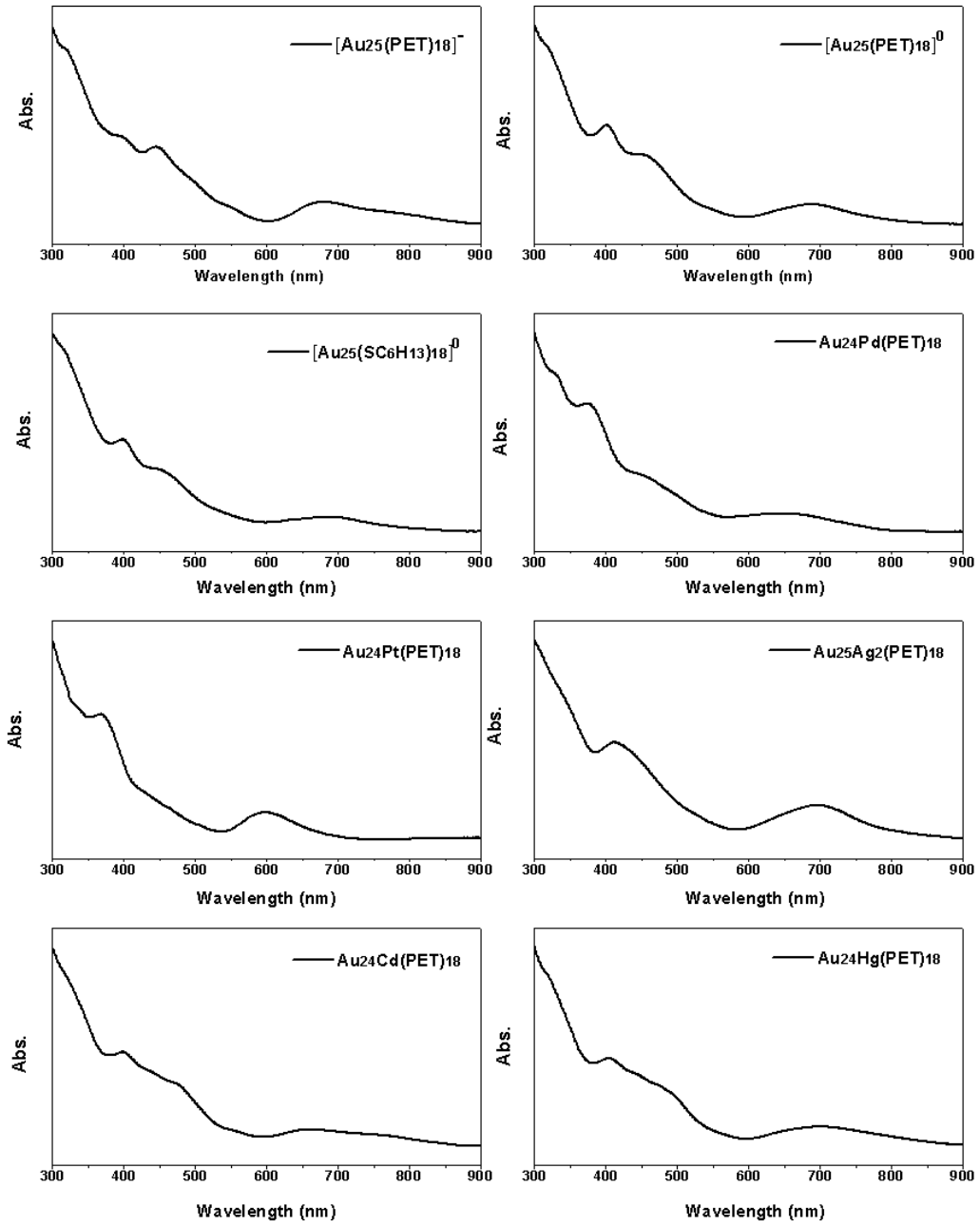

Figure S1 The ultraviolet–visible–near-infrared spectra of $[Au_{25}(PET)_{18}]^-$, $[Au_{25}(PET)_{18}]^0$, $[Au_{25}(SC_6H_{13})_{18}]^0$, $Au_{24}Pd(PET)_{18}$, $Au_{24}Pt(PET)_{18}$, $Au_{25}Ag_2(PET)_{18}$, $Au_{24}Cd(PET)_{18}$ and $Au_{24}Hg(PET)_{18}$。

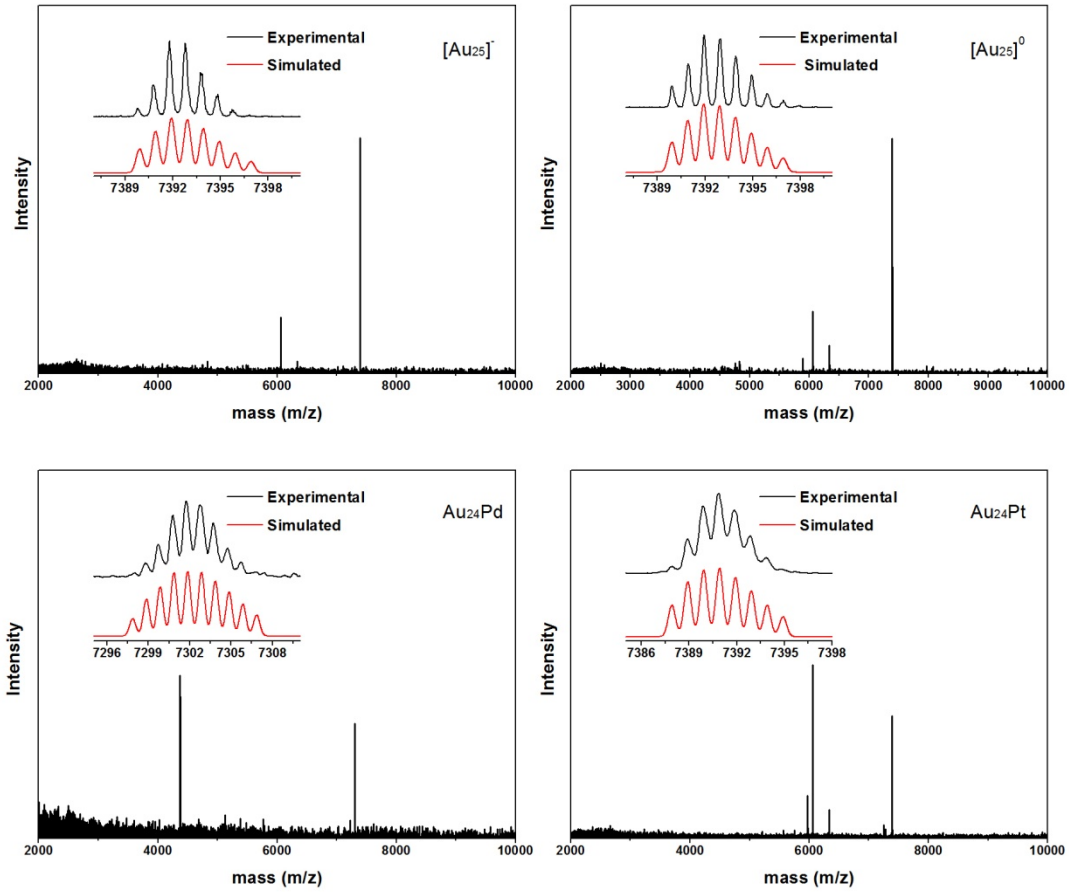

Figure S2 The matrix-assisted laser desorption ionization mass spectra of $[Au_{25}(PET)_{18}]^-$, $[Au_{25}(PET)_{18}]^0$, $Au_{24}Pd(PET)_{18}$ and $Au_{24}Pt(PET)_{18}$.

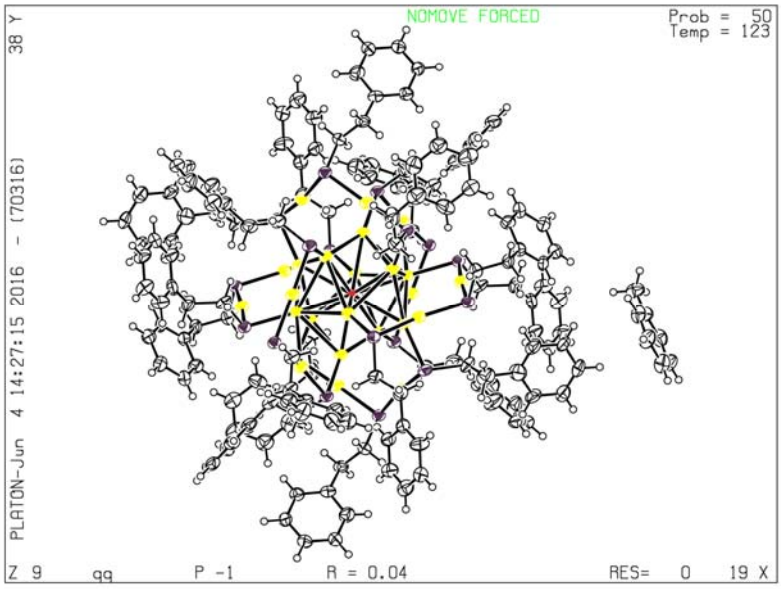

Figure S3 The total structure of $[Au_{24}Pd(PET)_{18}]^0$.

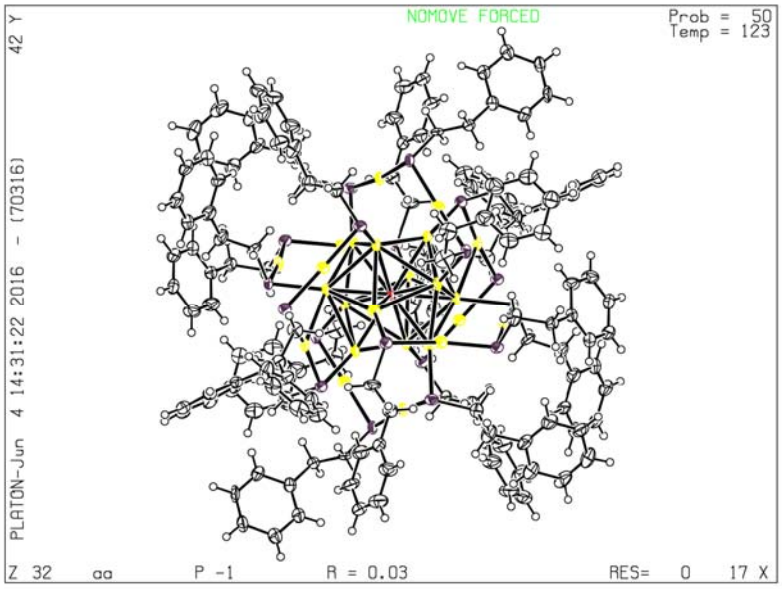

Figure S4 The total structure of $[Au_{24}Pt(PET)_{18}]^0$.

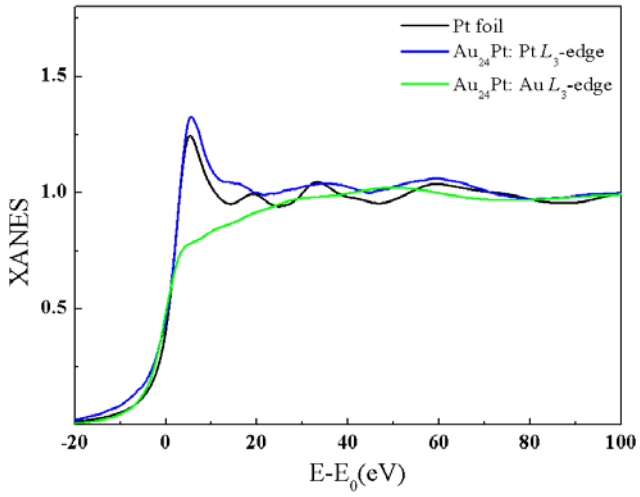

Figure S5 XANES of Pt foil and $Au_{24}Pt(PET)_{18}$ nanoclusters.

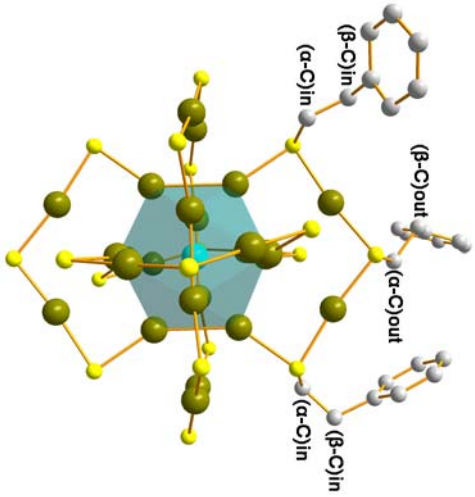

Figure S6 The illustration of (α- CH_2)$_{in}$, (α- CH_2)$_{out}$, (β-CH_2)$_{in}$, and (β- CH_2)$_{out}$ in Au_{25} family nanoclusters.

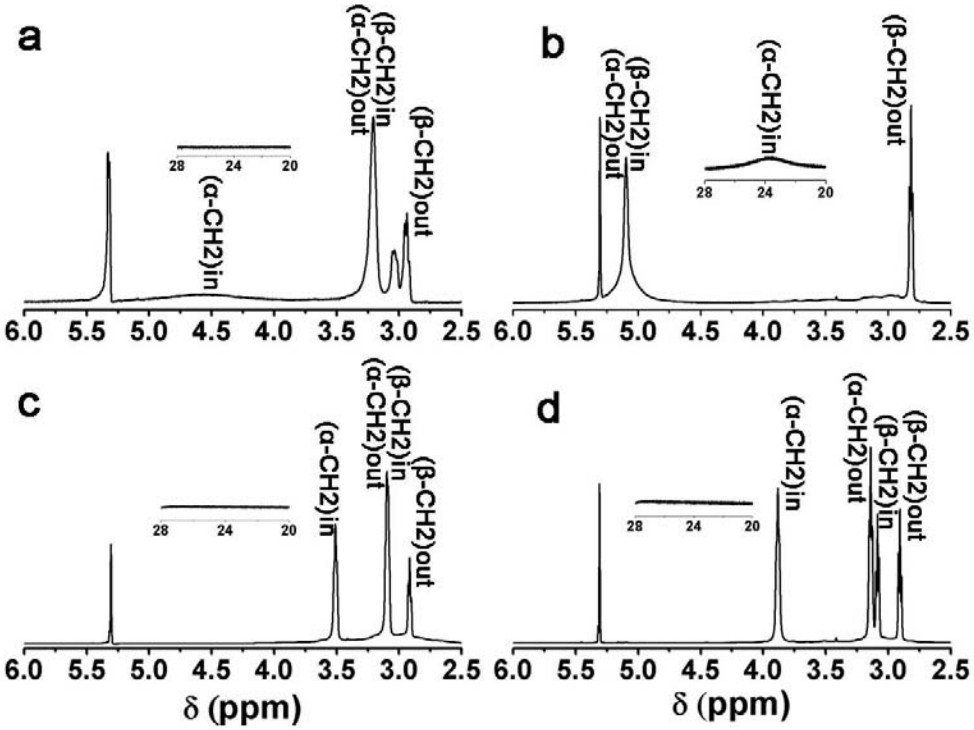

Figure S7 The ^{1}H NMR spectra of $[Au_{25}(PET)_{18}]^-$ (a), $[Au_{25}(PET)_{18}]^0$ (b), $[Au_{24}Pd(PET)_{18}]^0$ (c) and $[Au_{24}Pt(PET)_{18}]^0$ (d). (2.5ppm-6.0ppm)

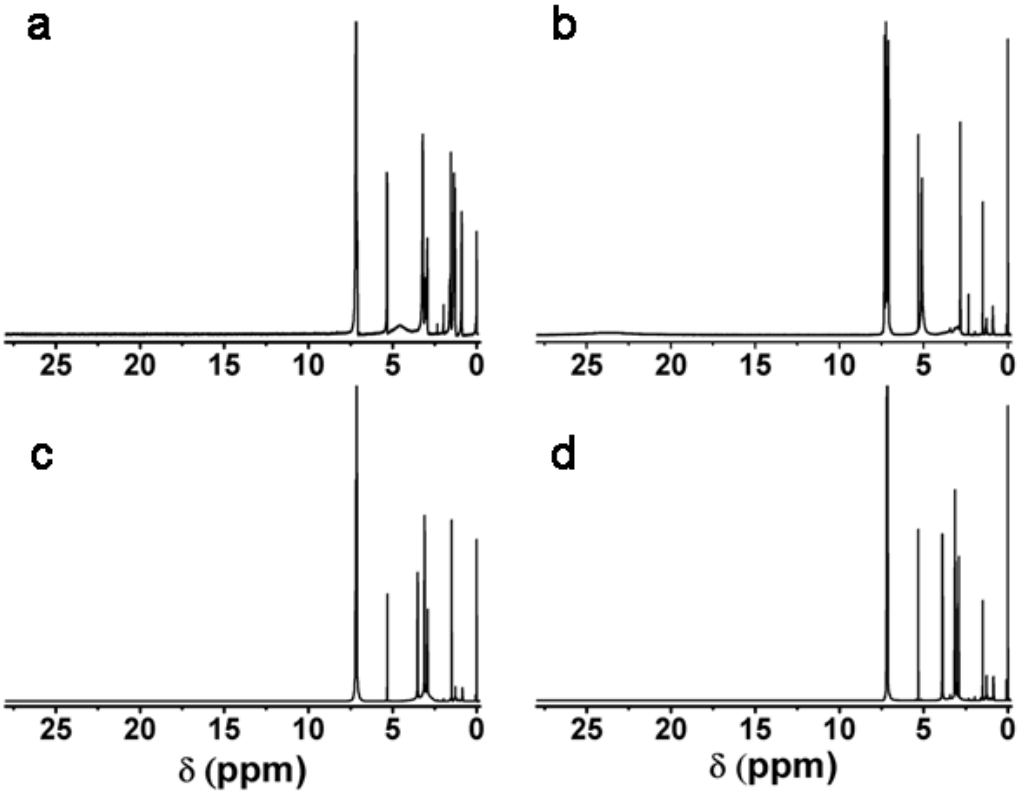

Figure S8 The ^{1}H NMR spectra of $[Au_{25}(PET)_{18}]^{-}$ (a), $[Au_{25}(PET)_{18}]^{0}$ (b), $[Au_{24}Pd(PET)_{18}]^{0}$ (c) and $[Au_{24}Pt(PET)_{18}]^{0}$ (d).

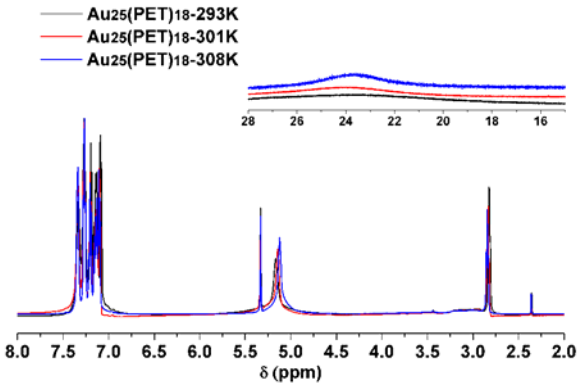

Figure S9 The temperature-dependent ^{1}H NMR spectra of neutral $[Au_{25}(PET)_{18}]^{0}$.

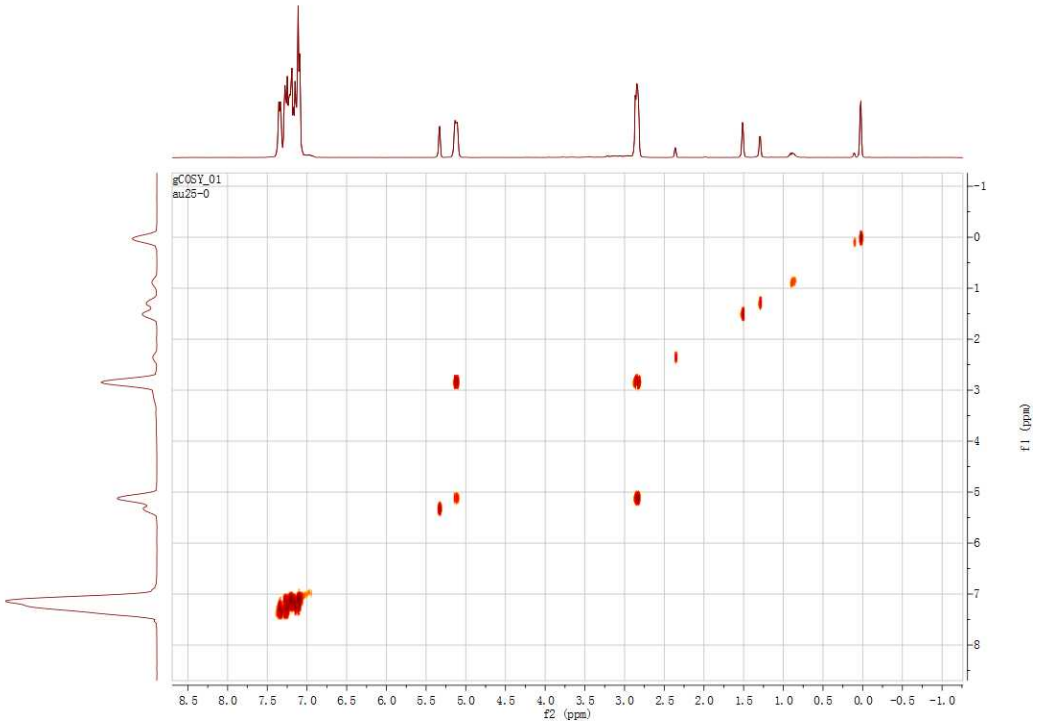

Figure S10 The 2D H-H COSY NMR spectrum of $[Au_{25}(PET)_{18}]^0$.

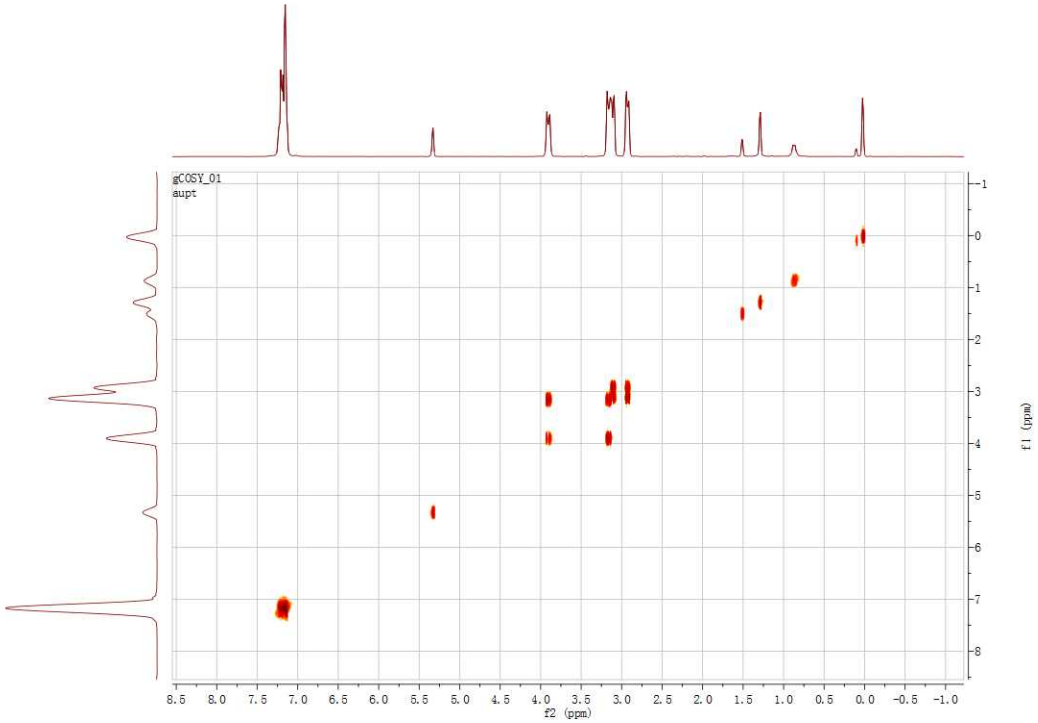

Figure S11 The 2D H-H COSY NMR spectrum of $[Au_{24}Pt(PET)_{18}]^0$.

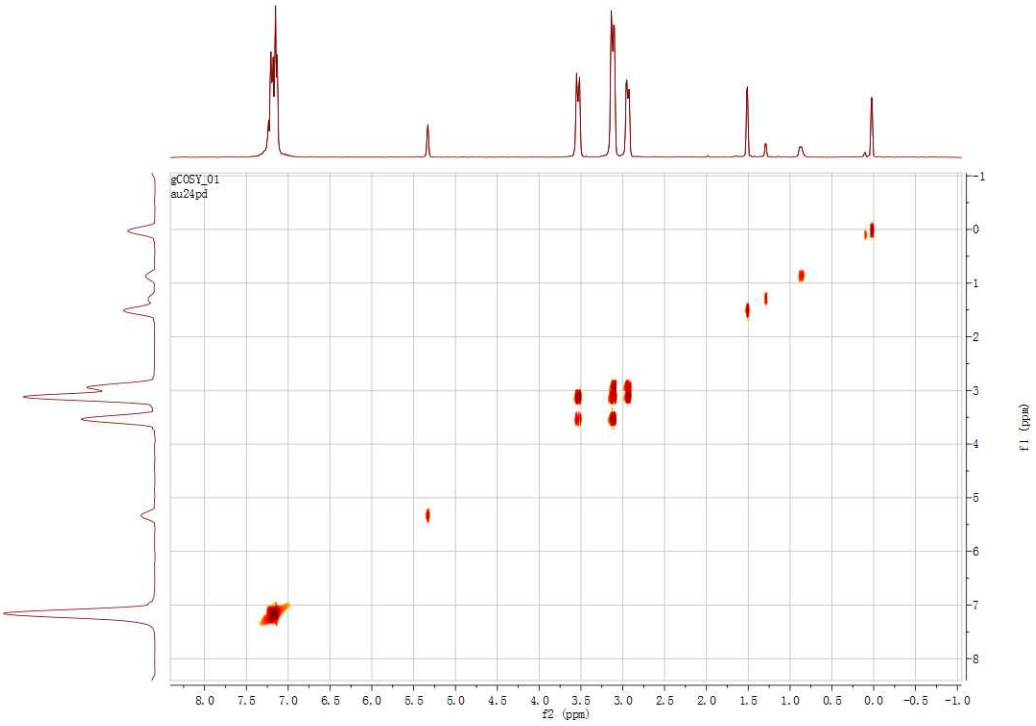

Figure S12 The 2D H-H COSY NMR spectrum of $[Au_{24}Pd(PET)_{18}]^0$.

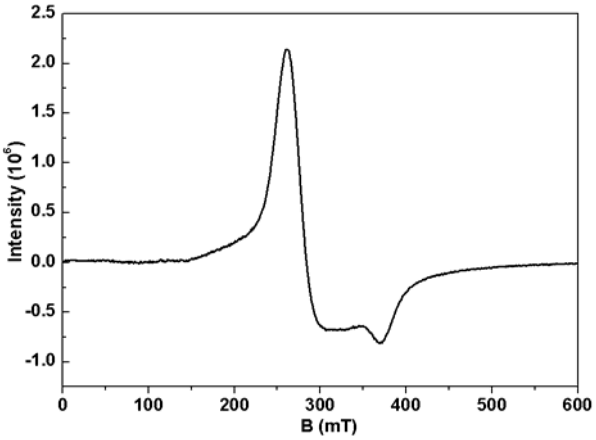

Figure S13 EPR signals of the $[Au_{25}(SC_6H_{13})_{18}]^0$.

Table S1 Crystal data and structure refinement for $Au_{24}Pd(PET)_{18}$.

Bond precision:	C-C = 0.0191 A	Wavelength=0.71073	
Cell:	a=16.1244(15)	b=17.6398(17)	c=17.7651(19)
	alpha=65.152(2)	beta=64.342(2)	gamma=81.391(4)
Temperature:	123 K		
	Calculated	Reported	
Volume	4129.8(7)	4129.8(7)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C_{144} H_{162} Au_{24} Pd S_{18}, 2(C_7 H_8)	C_{144} H_{162} Au_{24} Pd S_{18}, 2(C_7 H_8)	
Sum formula	C_{158} H_{178} Au_{24} Pd S_{18}	C_{158} H_{178} Au_{24} Pd S_{18}	
Mr	7487.78	7487.67	
Dx,g cm^{-3}	3.011	3.011	
Z	1	1	
Mu (mm^{-1})	21.596	21.596	
F000	3356.0	3356.0	
h,k,l_{max}	20,22,22	20,22,22	
Nref	18047	18037	
T_{min},T_{max}	0.037,0.075	0.100,0.180	

Correction method= # Reported T Limits: T_{min}=0.100 T_{max}=0.180

AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 27.000

R(reflections)= 0.0394(12898) wR_2(reflections)= 0.0810(18037)

S = 1.049 Npar= 908

Table S2 Crystal data and structure refinement for $Au_{24}Pt(PET)_{18}$.

Bond precision:	C-C = 0.0172 A	Wavelength=0.71073	
Cell:	a=16.1900(18)	b=17.7140(12)	c=17.8666(11)
	alpha=65.106(2)	beta=64.289(2)	gamma=81.343(2)
Temperature:	123 K		
	Calculated	Reported	
Volume	4184.5(6)	4184.5(6)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C_{144} H_{162} Au_{24} Pt S_{18}, 2(C_7 H_8)	C_{144} H_{162} Au_{24} Pt S_{18}, 2(C_7 H_8)	
Sum formula	C_{158} H_{178} Au_{24} Pt S_{18}	C_{158} H_{178} Au_{24} Pt S_{18}	
Mr	7576.46	7576.36	
Dx,g cm^{-3}	3.007	3.007	
Z	1	1	
Mu (mm^{-1})	22.041	22.041	
F000	3388.0	3388.0	
h,k,l_{max}	20,22,22	20,22,22	
Nref	18279	17659	
T_{min},T_{max}	0.006,0.010	0.070,0.090	

Correction method= # Reported T Limits: T_{min}=0.070 T_{max}=0.090

AbsCorr = MULTI-SCAN

Data completeness= 0.966 Theta(max)= 27.000

R(reflections)= 0.0298(14915) wR_2(reflections)= 0.0752(17659)

S = 1.082 Npar= 896