Supplementary Information

Heteroatom Number-Dependent Cluster Frameworks in Structurally Comparable Pd-Au Nanoclusters

Ziwei Fu,[#a] Chen Li,[#a] Ye Tian,[a] Fakhari Alam,[a] Daqiao Hu,[a] Honglei Shen,*[a] Xi Kang,*[a] Manzhou Zhu[a]

[a]Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, P. R. China.

This Supplementary Information file includes:

Experimental Methods

Materials and Reagents

All reagents were purchased from Sigma-Aldrich and used without further purification, including $HAuCl_4 \cdot 3H_2O$ (99% metal basis), H_2PdCl_4 (99% metal basis), 6-(dibutylamino)-1,3,5-triazine-2, 4-dithiol (TDT, 97%), triphenylphosphine (TPP, 99%), dichloromethane (DCM, HPLC), methanol (MeOH, HPLC), n-hexane (Hex, HPLC) and sodium borohydride ($NaBH_4$, 99.9%).

Synthesis of the Pd_1Au_{12} and Pd_2Au_{12} nanoclusters

The **Pd_1Au_{12}** was synthesized using a one-pot synthetic method at 60 °C. Specifically, 0.1 mmol of $HAuCl_4 \cdot 3H_2O$ and 0.016 mmol of H_2PdCl_4 were dissolved in a mixed organic solvent (10 mL of MeOH and 10 mL of DCM). Then, 0.184 mmol of TDT and 0.382 mmol of TPP were added into the solution with vigorous stirring. The color of the solution turned to light yellow. After 30 minutes, 30 mg of $NaBH_4$ (dissolved in 1 mL of ice water) was added to the solution, and the color of the solution turned red immediately. The reaction lasted for 10 hours. Then, the crude products were collected by centrifugation and then washed three times with hexane. The precipitate was then dissolved in CH_2Cl_2 and diffused by hexane at room temperature. After five days, cubical crystals were obtained. The yield was ~65% based on the Au element (calculated from the $HAuCl_4 \cdot 3H_2O$) for synthesizing the **Pd_1Au_{12}** nanocluster. The synthesis method of **Pd_2Au_{12}** was almost the same as that of **Pd_1Au_{12}**. The only difference was that the **Pd_2Au_{12}** nanocluster was synthesized at room temperature (about 25 °C). Needle-shaped crystals of **Pd_2Au_{12}** were obtained. The yield was ~34% based on the Au element (calculated from the $HAuCl_4 \cdot 3H_2O$) for synthesizing the **Pd_2Au_{12}** nanocluster.

Measurements

UV-vis absorption spectroscopy

All UV-vis optical absorption spectra of PdAu-bimetallic nanoclusters dissolved in DCM were recorded using an Agilent 8453 diode array spectrometer, whose background correction was made using a DCM blank.

ESI-MS spectrometry

ESI-MS measurements were performed by Waters XEVO G2-XS QT of the mass spectrometer. The sample was directly infused into the chamber at 5 μL/min. For preparing the ESI samples, nanoclusters were dissolved in DCM (1 mg/mL) and diluted (v/v = 1:1) by CH_3OH.

XPS spectroscopy

XPS measurements were performed on a Thermo ESCALAB 250 configured with a monochromatized Al Kα (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, flood gun to counter charging effects, and analysis chamber base pressure lower than 1×10^{-9} mbar.

X-Ray Crystallography

The data collection for SC-XRD of crystal samples was carried out on a Stoe Stadivari diffractometer under nitrogen flow, using graphite-monochromatized Cu Kα radiation (λ = 1.54186 Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structure was solved by direct methods and refined with full-matrix least squares on F^2 using the SHELXTL software package. The CCDC number of **Pd_1Au_{12}** is 2401398. The CCDC number of **Pd_2Au_{12}** is 2401397.

Electrochemical measurement

All electrochemical tests were carried out in an H-type electrolytic cell, and the two chambers were separated by Nafion 117 proton exchange membrane. Carbon paper loaded with ink reagent was used as working electrode for CO_2 reduction. The Ag / AgCl electrode was used as the reference electrode and the platinum electrode was used as the auxiliary electrode. The prepared **Pd_1Au_{12}** and **Pd_2Au_{12}** clusters were dissolved in a mixed solution of DMF and Nafion and dropped onto carbon paper to prepare a working electrode. The electrolyte was 0.5 M $KHCO_3$ solution. The PANNA A91 PLUS gas phase detector with FID detector was used to quantify the reactants. The CO_2RR reaction was carried out for 10 min. During the reaction, the electrolyte in the cathode chamber was stirred at a speed of 600 rpm. Electrochemical impedance spectroscopy (EIS) was used to determine the uncompensated resistance at each potential before the electrochemical test, and 90 % iR correction was performed.

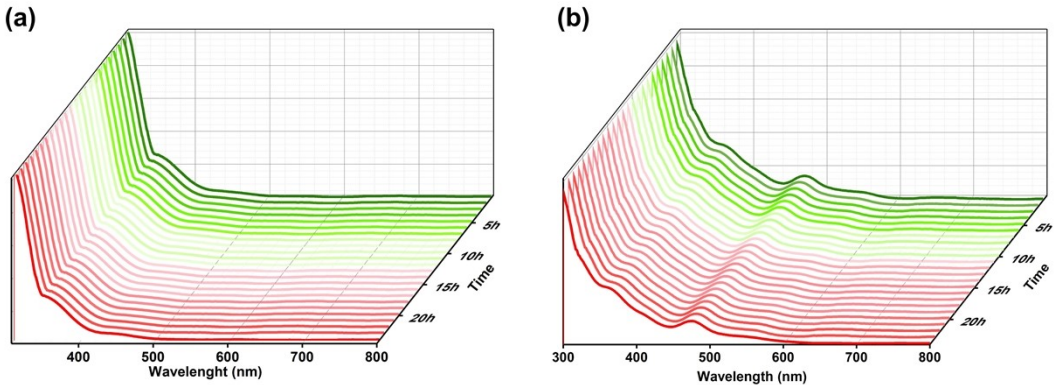

Figure S1. Time-dependent UV-vis spectra of (a) Pd_1Au_{12} and (b) Pd_2Au_{12} under ambient conditions in solution.

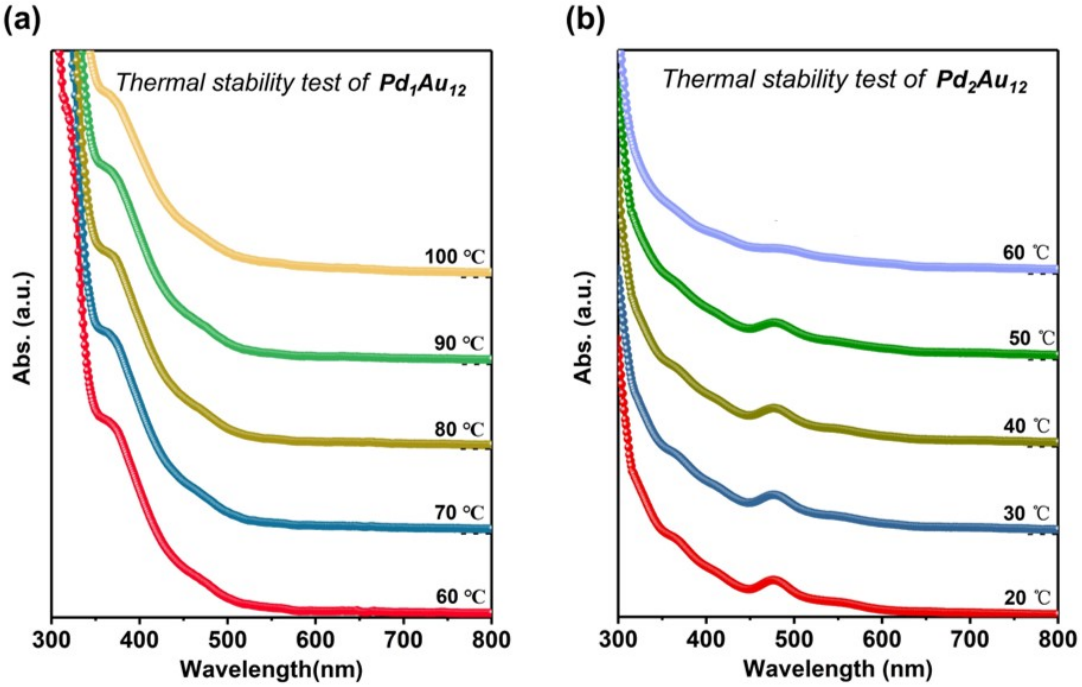

Figure S2. Thermal stability of (a) Pd_1Au_{12} and (b) Pd_2Au_{12} nanoclusters.

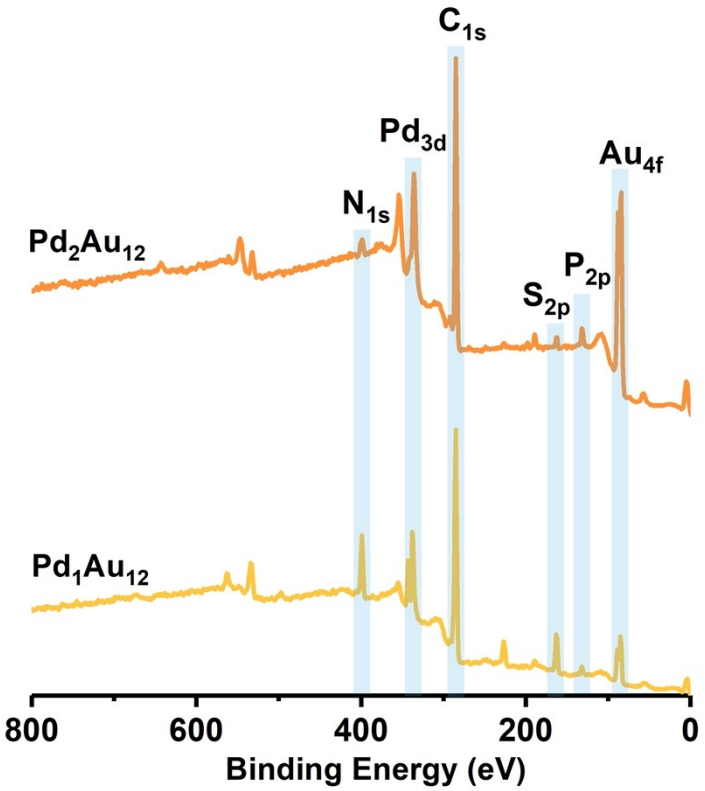

Figure S3. Full scan XPS spectra of **Pd_1Au_{12}** and **Pd_2Au_{12}**.

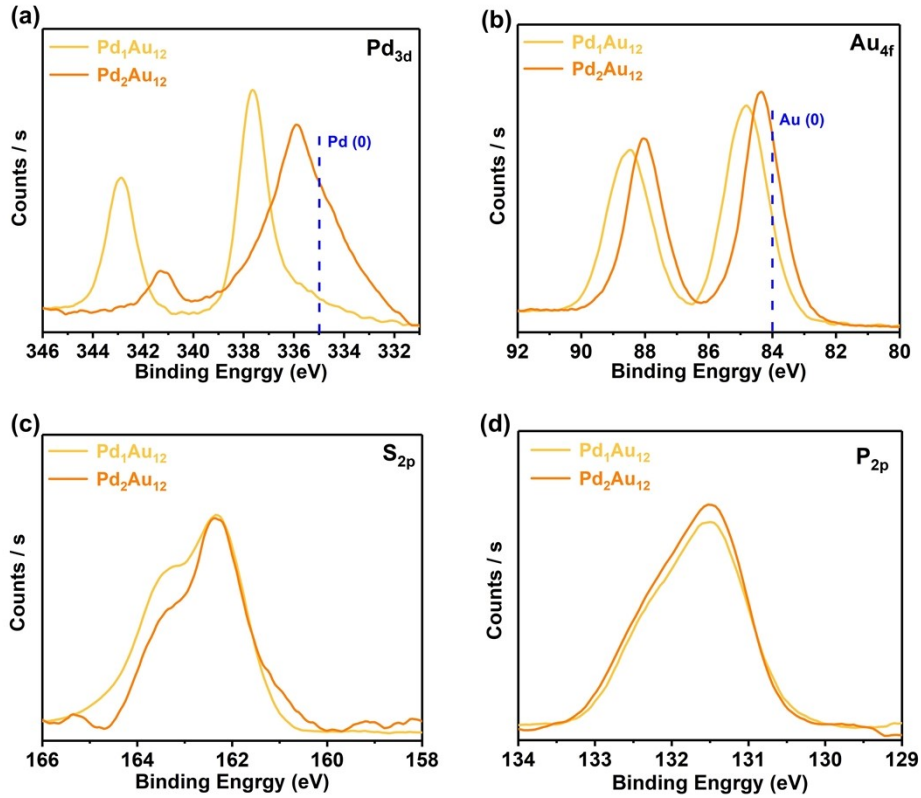

Figure S4. XPS spectra of (a) Pd_{3d}, (b) Au_{4f}, (c) S_{2p} and (d) P_{2p} of **Pd_1Au_{12}** and **Pd_2Au_{12}**.

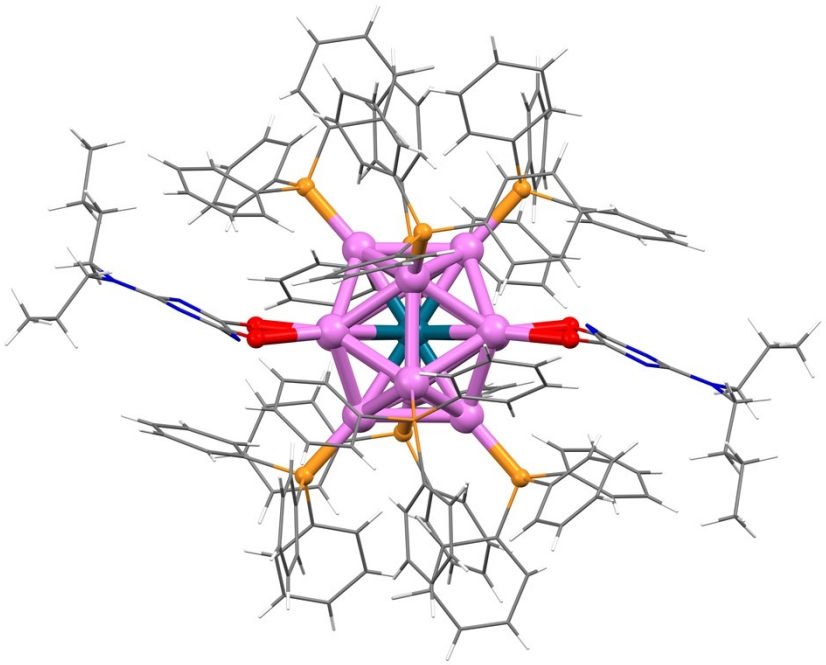

Figure S5. Total structure of the $Pd_1Au_{12}(TDT)_2(TPP)_8$ nanocluster. Color codes: cyan = Pd, pink = Au, red = S, orange = P. The H, C and N atoms are shown in stick mode.

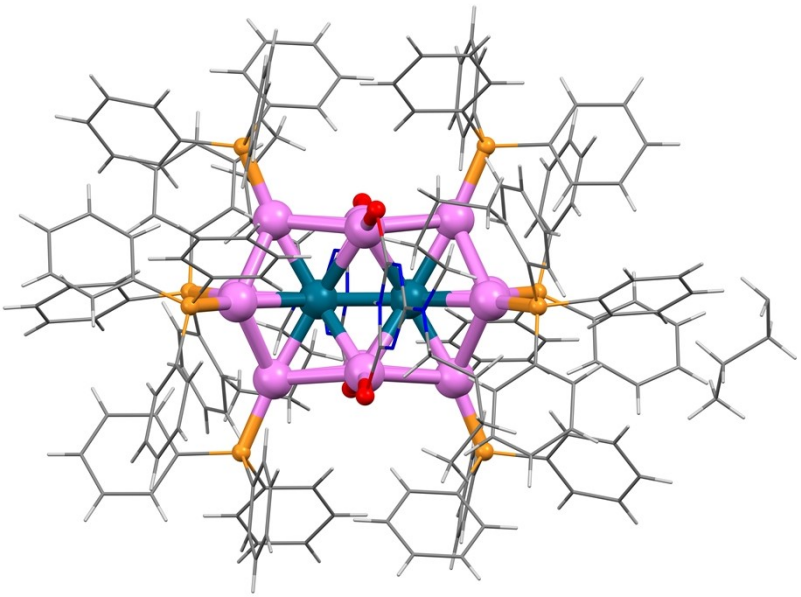

Figure S6. Total structure of the $Pd_2Au_{12}(TDT)_2(TPP)_8$ nanocluster. Color codes: cyan = Pd, pink = Au, red = S, orange = P. The H, C and N atoms are shown in stick mode.

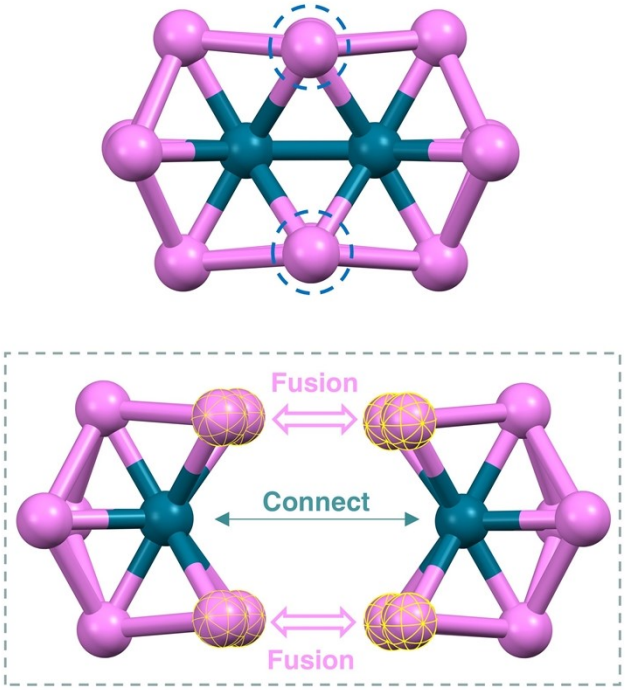

Figure S7. The fused mode of two Pd_1Au_8 sub-framework to form the Pd_2Au_{12} structure. Color codes: cyan = Pd, pink = Au, red = S, orange = P.

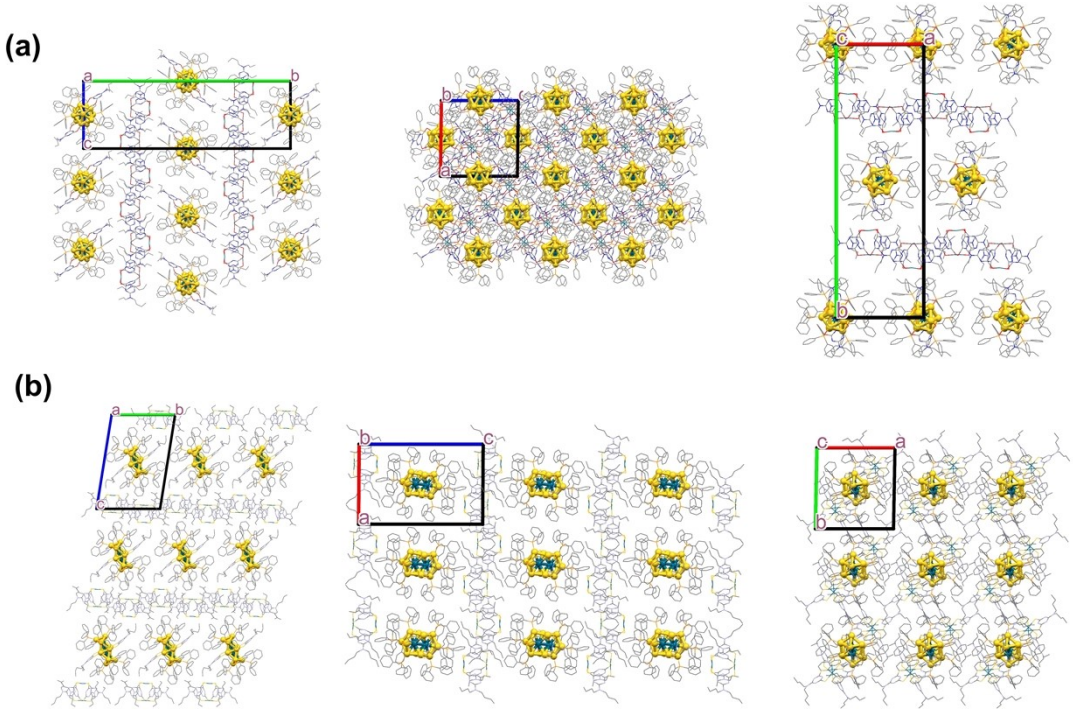

Figure S8. Packing models of (a) **Pd_1Au_{12}** and (b) **Pd_2Au_{12}** nanoclusters, viewed from different angles.

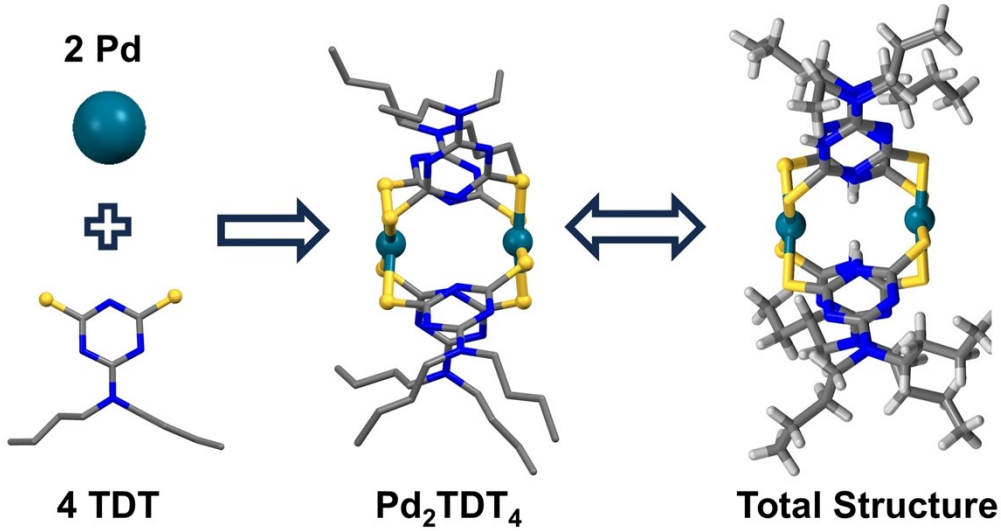

Figure S9. Structural analysis of the Pd_2TDT_4 complex in **Pd_1Au_{12}** and **Pd_2Au_{12}**. Taken that the $Pd_2(TDT)_4$ complexes in two cluster systems displayed the same structure, we proposed that differences in catalysis originated from the differences of clusters themselves.

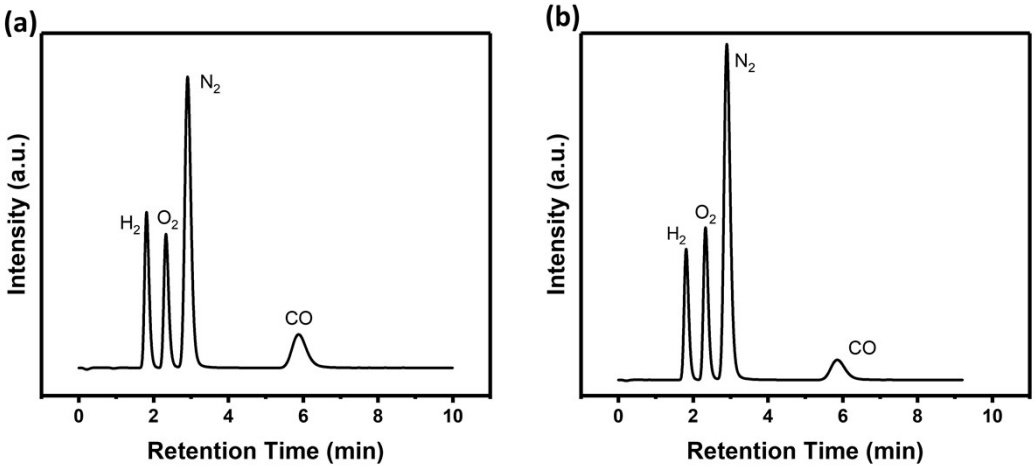

Figure S10. GC plots of (a) **Pd_1Au_{12}** and (b) **Pd_2Au_{12}** tested at -0.7 V vs RHE.

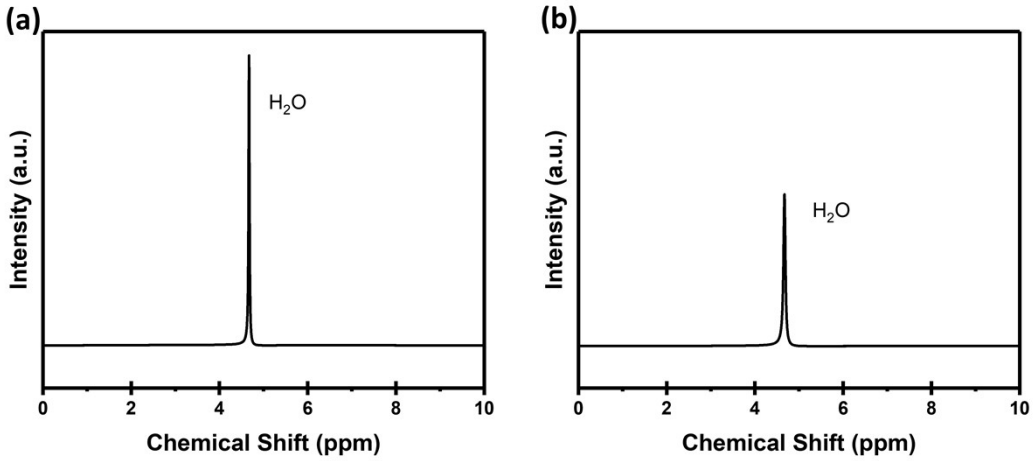

Figure S11. ^{1}H NMR spectrum of the electrolyte after CO_2RR electrolysis by using (a) **Pd_1Au_{12}** and (b) **Pd_2Au_{12}**.

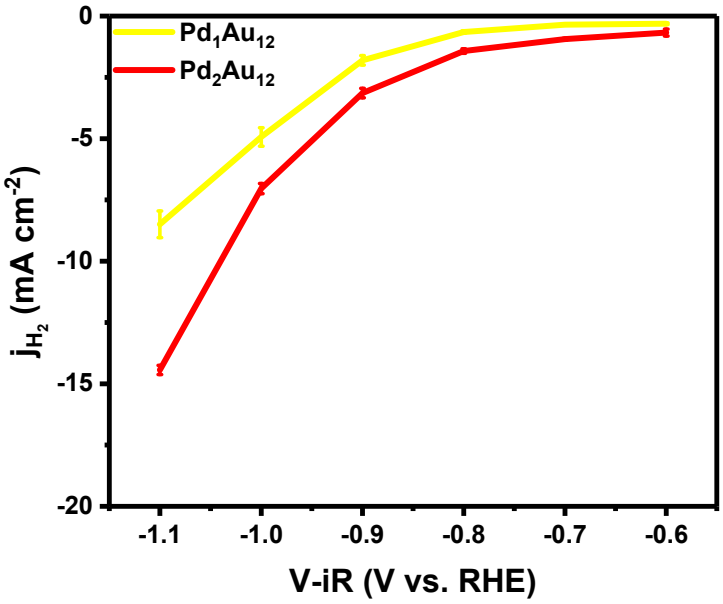

Figure S12. H_2 partial current density (j_{H2}) of **Pd_1Au_{12}** and **Pd_2Au_{12}**.

Table S1. Crystal data and structure refinement of **Pd_1Au_{12}**.

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.130
b/Å	53.449
c/Å	17.415
α/°	90
β/°	90.68
γ/°	90
Volume/$Å^3$	15943.8
Z	2
ρcalcg/cm^3	1.574
μ/mm^{-1}	14.290
F(000)	7504.0
Radiation	Cu Ka (λ = 1.54186)
Index ranges	-14≤h≤19, -61≤k≤54, -19≤l≤19
Final R indexes [I>=2σ (I)]	R_1 = 0.0692 wR_2 = 0.1886
Final R indexes [all data]	R_1 = 0.0818, wR_2 = 0.1983

Table S2. Crystal data and structure refinement of **Pd_2Au_{12}**.

Crystal system	triclinic
Space group	P-1
a/Å	16.7465(5)
b/Å	17.5624(5)
c/Å	26.3391(7)
α/°	99.096(2)
β/°	90.215(2)
γ/°	91.009(2)
Volume/$Å^3$	7647.8(4)
Z	2
ρcalcg/cm^3	1.678
μ/mm^{-1}	15.349
F(000)	3730.0
Radiation	Cu Ka (λ= 1.54186)
Index ranges	-14≤h≤19, -62 ≤k≤ 54, -20 ≤1≤ 20
Final R indexes [I>=2σ (I)]	R_1= 0.0651, wR_2= 0.1811
Final R indexes [all data]	R_1= 0.0766, wR_2= 0.1908

Table S3. Comparison of the bond lengths between **Pd_1Au_{12}** and **Pd_2Au_{12}** nanoclusters.

Cluster	$D_{Pd\text{-}Pd}$	$D_{Pd\text{-}Au}$	$D_{Au\text{-}Au}$
Pd_1Au_{12}	-	2.72 Å - 2.80Å Ave: 2.77 Å	2.81 Å - 3.07 Å Ave: 2.91 Å
Pd_2Au_{12}	2.61 Å	2.59 Å - 2.79 Å Ave: 2.71 Å	2.65 Å - 2.93 Å Ave: 2.84 Å