# **Supporting Information**

# Structure and Assembly of a Hexanuclear AuNi Bimetallic Nanocluster

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## Materials and characterizations

Tetrachloroauric(III) acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, > 99.9% metals basis), dichloromethane (DCM 99.0%), toluene (Tol, 99.0%), acetonitrile (MeCN, 99.0%), methanol (MeOH, 99.5%), ethyl acetate (EA, 99.0%), n-Hexane (99.0%), n-Pentane (99.0%), petroleum ether (PE, 99.0%) and tetrahydrofuran (THF, 99.0%) were purchased from Sinopharm chemical reagent Co. Ltd. Tetraoctylammonium bromide (TOAB) and nickel powder were purchased from Aladdin Co. Ltd. Sodium borohydride (NaBH<sub>4</sub>) was purchased from Shanghai Chemical Reagent Co. Ltd. Diphenylphosphine (HPPh<sub>2</sub>) and chlorodiphenylphosphine (CIPPh<sub>2</sub>) were purchased from Adamas. Resorcinol, 4-tertbutylthiophenol (TBBT), phenylmethanethiol (HSCH<sub>2</sub>Ph), 1-adamantanethiol (1-AdmSH), 2,4-dimethylbenzenethiol (2,4-DMBT), sulfoxide chloride (SOCl<sub>2</sub>), 2,6pyridinedimethanol and potassium thioglycolate (KSAc) were purchased from Shanghai Maclean Biochemical Technology Co Ltd. All the water used in experiments is ultrapure produced by AIC pure water system.

UV-vis absorption data were obtained on a SPECORD 210 PLUS spectrophotometer at room temperature. The single crystal X-ray diffraction (SC-XRD) data was measured at low temperature (T = 120 K), using a Stoe Stadivari diffractometer. A graphitemonochromatized Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) Radiation was used for the measurement. The structure was solved and refined using the SHELXT software. Fluorescence spectra were obtained by confocal fluorescence/Raman spectrometer, Confotect MR520, SOL. Matrix-assisted laser desorption ionization mass spectrometer (MALDI-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker). The electrochemical measurements were performed with a CHI770E electrochemistry workstation in a three-electrode system using an Ag/AgCl electrode as reference electrode, a glassy carbon electrode as working electrode and a platinum wire electrode as auxiliary electrode. Fourier Transform infrared (FT-IR) spectra were recorded on Nicolet 8700 with samples prepared as KBr pellets.

## Synthesis and characterizations of $Au_4Ni_2$ (3)

## 1. Synthesis of SNS (1)



2,6-Pyridinedimethanol (1.39 g, 10 mmol) was dissolved in 20 mL of DCM. SOCl<sub>2</sub> (3.57 g, 30 mmol) was added dropwise at 0 °C. After 4 hours, saturated aqueous sodium hydroxide was added to the system to adjust the pH to 13. After stirring for another ten minutes, DCM (20 mL) and H<sub>2</sub>O (30 mL) were added for extraction and the organic phase was dried by adding Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporator and then THF (30 mL) and KSAc (2.28 g, 20 mmol) were added. The mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation, and the resulting material was purified by flash column chromatography (PE/EA = 20/1) to yield the primary product as white solid. The obtained solid was dissolved in MeOH (20 mL) and 3 mL of concentrated HCl was added. The mixture was stirred at 80 °C overnight. The resulted residue was dried and concentrated to give the product (1.65 g, 80%) as white solid. The <sup>1</sup>H NMR data was consistent with that reported in the literature.<sup>1</sup>

#### 2. Synthesis of NiCl-PCP (2)



To a flask containing 4 mL of MeCN and resorcinol (832 mg, 7.56 mmol), nickel powder (438 mg, 7.56 mmol) was added. Under the atmosphere of nitrogen, ClPPh<sub>2</sub> (3.32 g, 15.1 mmol) was injected into the mixture and heated to 75 °C. Gas was produced at the beginning of the reaction and the mixture changed to orange and cloudy. After 18 h, the volatiles were evaporated and followed by flash chromatography of the solid residue on silica gel with DCM to obtain a yellow solid (1.51 g, 35%). The <sup>1</sup>H NMR data was consistent with that reported in the literature.<sup>2</sup>

#### 3. Synthesis of Au<sub>4</sub>Ni<sub>2</sub>(3)

NiCl-PCP (28.5 mg, 0.05 mmol), TOAB (54.0 mg, 0.10 mmol) and SNS (20.0 mg, 0.10 mmol) were dissolved in the mixed solvent (10 mL DCM and 5 mL EA) at room temperature. After stirring for 10 min, HAuCl<sub>4</sub>·4H<sub>2</sub>O (17.0 mg, 0.05 mmol) was added and the color of the reaction solution turn turbid immediately. 15 min later, NaBH<sub>4</sub> (38.0 mg, 1.00 mmol) dissolved in 2 mL of ice-cold water was quickly added all at once. After 1 h of reaction, the solvent was removed under reduced pressure. The residue was dissolved in 25 ml of Toluene and heated at 70 °C for 3h. After evaporation of the solvent, the obtained solid was washed with MeOH for 2-3 times to give the crude product. Yellow square-shaped crystals (5 mg, yield: 18%, based on Au) suitable for MS, SC-XRD and the other characterizations were obtained in the mixed solvents of DCM and n-Pentane (50 mL) after 12 h. Notably, the purification of the nanoclusters were also achieved via column chromatography on silica gel (eluent: DCM).

#### 4. Control experiments by using the other sulfur source for cluster synthesis

We tried to replace SNS (1) by the other sulfur sources to synthesize  $Au_4Ni_2$  (3). However, the attempt was failed, and UV-vis spectra of the resulted product suggest that the similar compounds were formed by using these thiols (Fig. S1).



Fig. S1 The UV-vis spectra of the products obtained by replacing SNS (1) with the other sulfur sources.

Taking TBBT as an example, NiCl-PCP (28.5 mg, 0.05 mmol), TOAB (54.0 mg, 0.10 mmol) and TBBT (33.0 mg, 0.20 mmol) were dissolved in 10 mL DCM at room temperature. After stirring for 10 min, HAuCl<sub>4</sub>·4H<sub>2</sub>O (17.0 mg, 0.05 mmol) was added and the color of the reaction solution turn turbid immediately. 15 min later, NaBH<sub>4</sub> (19.0 mg, 0.50 mmol) dissolved in 2 mL of ice-cold water was quickly added all at once. After 12 h of reaction, the product was isolated by preparative thin-layer chromatography (PTLC, DCM/PE = 1/1). Orange-red diamond crystals suitable for SC-XRD analysis were obtained by slow evaporation of the purified product solution in DCM/n-Pentane. The UV-vis spectrum and the resolved SC-XRD structure were shown below.



**Fig. S2** (a) UV-vis spectrum of the product; (b) The total structure of the product, which was determined to be NiTBBT-PCP. Green: Ni; purple: P; pink: O; yellow: S; gray: C; white: H.

### 5. Characterizations of Au<sub>4</sub>Ni<sub>2</sub> (3)

#### (1) UV-vis and FT-IR

UV-vis spectrum of  $Au_4Ni_2$  (**3**) was obtained by dissolving the crystal nanocluster sample in DCM at room temperature. FT-IR spectra of  $Au_4Ni_2$  (**3**) and NiCl-PCP were obtained by KBr compression method.

For the FT-IR spectra, the peaks at 3054 cm<sup>-1</sup> are C–H stretching vibrations on the aromatic ring. The peaks at 1441-1568 cm<sup>-1</sup> are stretching vibrations on the aromatic

ring. The peaks at 1100-1303 cm<sup>-1</sup> are C-O stretching vibrations and the peaks at 713-843 cm<sup>-1</sup> are C-H out-of-plane bending vibrations on the aromatic ring.



Fig. S3 (a) UV-vis spectrum of  $Au_4Ni_2$  (3); (b) FT-IR spectra of  $Au_4Ni_2$  (3) and NiCl-PCP.

## (2) MALDI-TOF-MS



Fig. S4 MALDI-TOF-MS spectrum of Au<sub>4</sub>Ni<sub>2</sub> (3) nanocluster.

(3) SC-XRD



Fig. S5 The SC-XRD structure of  $Au_4Ni_2$  (3). (a) The nanocluster in a cubic unit cell; (b) Arrangement of the nanocluster molecules.

## Intra- and inter-cluster interactions of $Au_4Ni_2$ (3)



## 1. Intra-cluster interactions

**Fig. S6** Intra-cluster C $-H\cdots\pi$  (cyan) and  $H\cdots H$  (red) interactions of Au<sub>4</sub>Ni<sub>2</sub> (**3**).

Intra-cluster	Distance / Å	Average distance / Å
$C-H\cdots\pi$	3.909; 3.183	
	3.851; 3.521 2.974; 3.225	3.487
	3.488; 3.460	
	3.849; 3.408	
Н…Н	2.595	2 714
	2.838	2.714
	2.805	

**Table S1**. Intra-cluster  $C = H \cdots \pi$  and  $H \cdots H$  interactions of  $Au_4Ni_2$  (3) nanocluster.

## 2. Inter-cluster interactions



Fig. S7 Inter-cluster (x axis)  $C - H \cdots \pi$  (cyan) and  $H \cdots H$  (red) interactions of Au<sub>4</sub>Ni<sub>2</sub> (3).

**Table S2.** Inter-cluster (x axis)  $C-H\cdots\pi$  and  $H\cdots H$  interactions of Au<sub>4</sub>Ni<sub>2</sub> (3) nanocluster.

Inter-cluster (x axis)	Distance / Å	Average distance / Å
$C-H\cdots\pi$	3.049	
	3.635	3.409
	3.542	
Н…Н	2.708	
	2.584	2.714
	2.850	



**Fig. S8** Inter-cluster (y axis)  $C = H \cdots \pi$  (cyan) and  $H \cdots H$  (red) interactions of Au<sub>4</sub>Ni<sub>2</sub> (3).

Inter-cluster (y axis)	Distance / Å	Average distance / Å
$C - H \cdots \pi$	3.497	
	3.994	
	3.211	3.490
	3.531	
	3.217	
Н…Н	2.715	
	2.971	2.833
	2.812	

**Table S3.** Inter-cluster (y axis)  $C-H\cdots\pi$  and  $H\cdots H$  interactions of Au<sub>4</sub>Ni<sub>2</sub> (3) nanocluster.



Fig. S9 Inter-cluster (z axis)  $C = H \cdots \pi$  (cyan) and  $H \cdots H$  (red) interactions of Au<sub>4</sub>Ni<sub>2</sub> (3).

**Table S4.** Inter-cluster (z axis)  $C-H\cdots\pi$  and  $H\cdots H$  interactions of Au<sub>4</sub>Ni<sub>2</sub> (3) nanocluster.

Inter-cluster (z axis)	Distance / Å	Average distance / Å
$C-H\cdots\pi$	3.147	3.570
	3.992	
$\mathbf{H}\cdots\mathbf{H}$	2.984	2.984



Fig. S10 The channels along the y and z axes.

## Solubility experiments

## **1.** Determination of extinction coefficient (ε)

The concentrations of the nanocluster (Au<sub>4</sub>Ni<sub>2</sub> (**3**) or Au<sub>4</sub>Ni<sub>2</sub> (octahedral)) solution were gradually increased, and the corresponding UV-vis absorptions were measured. The absorbance (A<sub>380 nm</sub> for Au<sub>4</sub>Ni<sub>2</sub> (**3**) and A<sub>457 nm</sub> for Au<sub>4</sub>Ni<sub>2</sub> (octahedral)) of different concentrations were taken and plotted against bc (optical range and concentration), and linearly fitted to obtain the slope of 3762 L/(mol·cm) and 33934 L/(mol·cm). The values are the extinction coefficients of Au<sub>4</sub>Ni<sub>2</sub> (**3**) and Au<sub>4</sub>Ni<sub>2</sub> (octahedral) at 380 nm and 457 nm, respectively. A quartz cuvette with an optical range (b) of 1 cm is used in the experiments.

$$_{\varepsilon} = \frac{A}{b \cdot c}$$



Fig. S11 (a) UV-vis spectra of  $Au_4Ni_2$  (3) under different concentrations; (b) The linear fit for the determination of extinction coefficient.



Fig. S12 (a) UV-vis spectra of  $Au_4Ni_2$  (octahedral) under different concentrations; (b) The linear fit for the determination of extinction coefficient.

### 2. Determination of solubility (c)

 $Au_4Ni_2$  (3) were dissolved in different solvents to form the saturated solutions. The corresponding absorbance (A) were obtained based on their UV-vis spectra (Fig. S13a). The concentrations of  $Au_4Ni_2$  (3) in these solvents (i.e. solubility, c) were determined based on the equation shown below.

 $Au_4Ni_2$  (octahedral) were dissolved in different solvents to form the saturated solutions. After that, these solutions were diluted (1000 times) until they gave proper absorbance. The corresponding absorbance (A) were obtained based on their UV-vis spectra (Fig. S13b). The concentrations of these diluted  $Au_4Ni_2$  (**3**) solutions were determined based on the equation shown below. The solubilities (c) of  $Au_4Ni_2$  (**3**) in these solvents were 1000 times of the concentrations.

$$=\frac{A}{b\cdot\varepsilon}$$



Fig. S13 (a) UV-vis spectra of the saturated Au<sub>4</sub>Ni<sub>2</sub> (3) solutions in different solvents.
(b) UV-vis spectra of the diluted Au<sub>4</sub>Ni<sub>2</sub> (octahedral) solutions in different solvents.

## Photoluminescence experiments

The solution samples were prepared by using the saturated  $Au_4Ni_2$  (**3**) or dissolving 1.0 mg of  $Au_4Ni_2$  (octahedral) in 10 mL of different solvents at room temperature. The crystalline samples were prepared by spreading 1.0 mg of  $Au_4Ni_2$  (**3**) or  $Au_4Ni_2$  (octahedral) crystals in the center of the slide. The excitation wavelength was set to 375, 405, or 532 nm, and the corresponding emission spectra were measured by confocal fluorescence/Raman spectrometer (All data were obtained by using the same parameters).



Fig. S14 Emission spectra of  $Au_4Ni_2$  (3) (a-c) and  $Au_4Ni_2$  (octahedral) (d) in crystalline and solution states.

## Stability experiments

#### 1. Time-dependent UV-vis

(1) Stability tests at different temperatures.

1.0 mg of  $Au_4Ni_2$  (3) were dissolved in 10 mL of DCM or toluene. The timedependent UV-vis absorption spectra were recorded at room temperature or 80 °C.



Fig. S15 Time-dependent UV-vis spectra of  $Au_4Ni_2$  (3) at room temperature (a) and high temperature (b).

(2) Stability tests under oxidative and reduction conditions.

1.0 mg of Au<sub>4</sub>Ni<sub>2</sub> (**3**) were dissolved in 10 mL of DCM, and then 150  $\mu$ L of H<sub>2</sub>O<sub>2</sub> (30%) or 0.5 mg of NaBH<sub>4</sub> (dissolved in 100  $\mu$ L of EtOH) were added. The timedependent UV-vis absorption spectra were recorded based on the samples.



Fig. S16 Time-dependent UV-vis spectra of  $Au_4Ni_2$  (3) under oxidative (a) and reductive (b) conditions.

## 2. Differential pulse voltammetry (DPV)

1.0 mg of Au<sub>4</sub>Ni<sub>2</sub> (**3**) were dissolved in 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub>-DCM solution and the electrochemical properties were measured using an electrochemical workstation. The Ag/AgCl, glassy carbon and platinum wire electrodes were used as the reference, working and auxiliary electrodes, respectively. Before experiment, the working electrode was polished with a mixture of  $Al_2O_3$  and water, and then cleaned sequentially with water and MeOH. The experiment was performed at an amplitude of 0.05 V, a pulse width of 0.05 s, a sampling width of 0.02 s and a pulse period of 0.1 s. The sample was always in a nitrogen atmosphere.



Fig. S16 DPV spectrum of  $Au_4Ni_2$  (3).

### 3. Cyclic voltammetry (CV)

1.0 mg of  $Au_4Ni_2$  (**3**) were dissolved in 0.1 mol/L  $Bu_4NPF_6$ -DCM solution and the electrochemical properties were measured using an electrochemical workstation (CHI700E). The Ag/AgCl, glassy carbon and platinum wire electrodes were used as the reference, working and auxiliary electrodes, respectively. The stability test of  $Au_4Ni_2$ 

(3) under oxidative and reductive conditions were conducted by 50 CV scans in a voltage range from 0.5 to 1.5 V (-0.7 to -1.3 V) vs. Ag/AgCl at a scan rate of 100 mV/s.



Fig. S17 CV spectra of  $Au_4Ni_2$  (3) nanocluster under the reductive (left) and oxidative (right) conditions.

## Crystal data of Au<sub>4</sub>Ni<sub>2</sub> (3)

Empirical formula	$C_{84}H_{66}Au_4Ni_2O_4P_6S_2\\$	
Formula weight	2294.59	
Temperature/K	296.15	
Crystal system	triclinic	
Space group	P-1	
a/Å	12.3838(12)	
b/Å	13.8890(14)	
c/Å	14.7679(14)	
$\alpha/^{\circ}$	64.065(2)	
β/°	80.669(3)	
$\gamma/^{\circ}$	83.914(3)	
Volume/Å <sup>3</sup>	2252.3(4)	
Z	1	
pcalcg/cm <sup>3</sup>	1.692	
μ/mm <sup>-1</sup>	7.095	
F(000)	1096.0	
Radiation	MoKa ( $\lambda = 0.71073$ )	
$2\Theta$ range for data collection/° 4.24 to 56.68		
Index ranges	$-14 \le h \le 16, -17 \le k \le 18, -19 \le l \le 18$	
Reflections collected	19187	
Independent reflections	11117 [Rint = 0.0453, Rsigma = 0.0862]	
Data/restraints/parameters	11117/433/376	
Goodness-of-fit on F2	1.047	
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0667, wR_2 = 0.1857$	
Final R indexes [all data]	$R_1 = 0.1105, wR_2 = 0.2134$	
Largest diff. peak/hole / e Å-3 5.42/-2.11		

Table S5. Crystal data and structure refinement for  $Au_4Ni_2$  (3).

## Crystal data of NiTBBT-PCP

Identification code	NiTBBT-PCP
Empirical formula	$C_{40}H_{36}NiO_2P_2S$
Formula weight	701.40
Temperature/K	296.15
Crystal system	monoclinic
Space group	P21/c
a/Å	39.250(5)
b/Å	9.8991(14)
c/Å	17.585(2)
α/°	90
β/°	92.559(4)
γ/°	90
Volume/Å <sup>3</sup>	6825.7(15)
Z	8
pcalcg/cm <sup>3</sup>	1.365
$\mu/\text{mm}^{-1}$	0.758
F(000)	2928.0
Crystal size/mm <sup>3</sup>	0.1 imes 0.1 imes 0.08
Radiation	MoKa ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/ <sup>c</sup>	<sup>2</sup> 4.244 to 56.7
Index ranges	$-52 \le h \le 37, -13 \le k \le 12, -23 \le l \le 23$
Reflections collected	52201
Independent reflections	16962 [Rint = 0.0641, Rsigma = 0.0752]
Data/restraints/parameters	16962/30/795
Goodness-of-fit on F2	1.049
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0801, wR_2 = 0.1758$
Final R indexes [all data]	$R_1 = 0.1212, wR_2 = 0.1947$
Largest diff. peak/hole / e Å-3	1.01/-0.60

 Table S6. Crystal data and structure refinement for NiTBBT-PCP.

## References

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