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Supporting Information

Cu^{2+} Induced Formation of $Au_{44}(SC_2H_4Ph)_{32}$ and Its High Catalytic Activity for the Reduction of 4-Nitrophenol at Low Temperature

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General information

All the chemicals and reagents were commercially available. UV-Vis measurements were conducted on a Shimadzu UV-2550 spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were acquired on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The sample was dissolved in toluene (~1 mg/ml) and diluted 1:1 in dry ethanol (5 mM CsOAc). The sample was directly infused at 5 μL/min. The source temperature was fixed at 70 °C. The spray voltage was set at 2.20 kV and the cone voltage at 60V. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MOLDI-TOF-MS) was performed on a Bruker Autoflex Speed MALDI-TOF/TOF instrument using DCTB (*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile) as the matrix. Thermal gravimetric analysis (TGA) was conducted in a N_2 atmosphere (flow rate ~ 50 mL/min) on a TG/DAT 6300 analyzer (Seiko Instruments, Inc), and the heating rate was 10 °C/min. X-ray Photoelectron Spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi XPS spectrometer (Thermo Scientific, America) using a monochromatized Al K_a source and equipped with an Ar^+ ion sputtering gun. All binding energies were calibrated using the C (1s) carbon peak (284.8 eV). Transmission electron microscopy (TEM) images for $Au_{44}(SCH_2CH_2Ph)_{32}$ were taken by JEOL2010. The operating voltage on the microscope was 200 kV. Elemental analysis (EA) was performed on Elementar vario EL cube (Elementar, Germany). Atomic absorption spectroscopy (AAS) was performed on Perkin Elmer AA800 atomic absorption spectrometer. ^1H NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, m = multiplet. Chemical shifts (δ) were expressed in ppm. $Au_{25}(SCH_2CH_2Ph)_{18}$,[s1] $Au_{38}(SCH_2CH_2Ph)_{24}$,[s2] $Au_{44}(TBBT)_{28}$,[s3] $Au_{144}(SCH_2CH_2Ph)_{60}$,[s4] $Ni_6(SC_2H_4Ph)_{12}$,[s5] $Ag_{152}(SC_2H_4Ph)_{60}$,[s6] Co nanoparticle[s5] and Cu nanoparticle[s5] were synthesized following the previous methods.

Synthesis of $Au_{44}(SCH_2CH_2Ph)_{32}$

2.0 equivalent of $Cu(NO_3)_2{\cdot}3H_2O$ (2.41 mg, 0.010 mmol) dissolved in CH_3CN (0.5 mL) was added to a solution of $Au_{25}(SC_2H_4Ph)_{18}^{-}TOA^+$ (39.3 mg, 0.005 mmol) in 5.0 mL of CH_2Cl_2

dropwise over a period of 10 minutes at room temperature. The reaction process was monitored by UV-vis. After being stirred at room temperature for 12 h, the reaction mixture was stopped by the addition of a large amount of CH_3OH. The separated solids were washed by excess CH_3OH for at least three times. Tiny brown pellets were collected after crystallization from CH_2Cl_2/CH_3OH = 1/1 solution (29.0 mg, ~ 75% yield).

Three control experiments to probe the role of Cu^{2+}

First, other oxidant (*eg:* H_2O_2) instead of Cu(II) was employed to oxidate Au_{25}^-, and it was found that Au_{25}^+ can't be converted to Au_{44} in the presence of H_2O_2 after 12 h. (Figure S 6A). Secondly, isolated Au_{25}^+ (from Au_{25}-Cu^{2+} system) was dissolved in DCM and the resulting solution was stirred at room temperature for 12 h, but no Au_{44} clusters was detected (Figure S 6B). Thirdly, isolated Au_{25}^+ (from Au_{25}-Cu^{2+} system) and 0.5 equivalent of Cu (II) were mixed in DCM and stirred at room temperature for 12 h. Obviously the UV/Vis/NIR spectrum indicated the formation of Au_{44} clusters (Figure S 6C). Taken together, these experimental results unambiguously demonstrate that Cu (II) ion not only acts as an oxidant, but also plays important roles in the subsequent decomposition and recombination steps.

General procedure for the fractional isolation of reaction mixture and re-exposure to reaction conditions:

2.0 equivalent of $Cu(NO_3)_2{\cdot}3H_2O$ (2.41 mg, 0.010 mmol) dissolved in CH_3CN (0.5 mL) was added to a solution of $Au_{25}(SC_2H_4Ph)_{18}^-TOA^+$ (39.3 mg, 0.005 mmol) in 5.0 mL of CH_2Cl_2 over a period of 10 minutes at room temperature. The mixture was stirred at room temperature for 3 h. A large amount of petroleum ether was added to the mixture and the resulting precipitates were separated from the supernatant by centrifugation. The obtained precipitates were dissolved with DCM (1.0 mL) and three fractions were isolated after stepwise precipitation by the use of methanol. After that, these three fractions were dissoved in DCM (5.0 mL) respectively and 0.5 equivalent of $Cu(NO_3)_2{\cdot}3H_2O$ (0.60 mg, 0.0025 mmol) was added into every fraction. These mixtures were stirred at room temperature for 12 h.

General procedure for the reduction of 4-nitrophenol catalyzed by nanoclusters

The clusters used were as a homogeneous solution, and they were not adsorbed on support or calcinated. The catalytic reactions were performed under atmospheric conditions. 4-nitrophenol (69.5 mg, 0.5 mmol) and the nanocluster catalyst (0.1 mol% or 1 mol%) were dissolved in 5 mL THF at 0 or 25 ^oC. The solution was stirred for 5 min. $NaBH_4$ (189 mg, 5.0 mmol) dissolved in 1.0 mL H_2O was added slowly to the reaction solution. The mixture was stirred at 0 or 25 ^oC for 30 min or 5 min. After that, a large amount of water was added to quench the reaction. The mixture was extracted with ethyl acetate (2 × 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate, then concentrated. The residue was purified by preparative thin layer chromatography, developing with ethyl acetate/petroleum ether = 1/5 to afford the reduction product.

Analytical Data for the product (4-aminophenol)

White solid, m.p. 185-186℃; ^{1}H NMR (400 MHZ, acetone-d6) δ 7.44 (s, 1H), 6.62-6.50 (m, 4H), 4.06 (s, 2H); HRMS (ESI) calcd for C_6H_8NO $(M+H)^+$ 110.0606, found 110.0594.

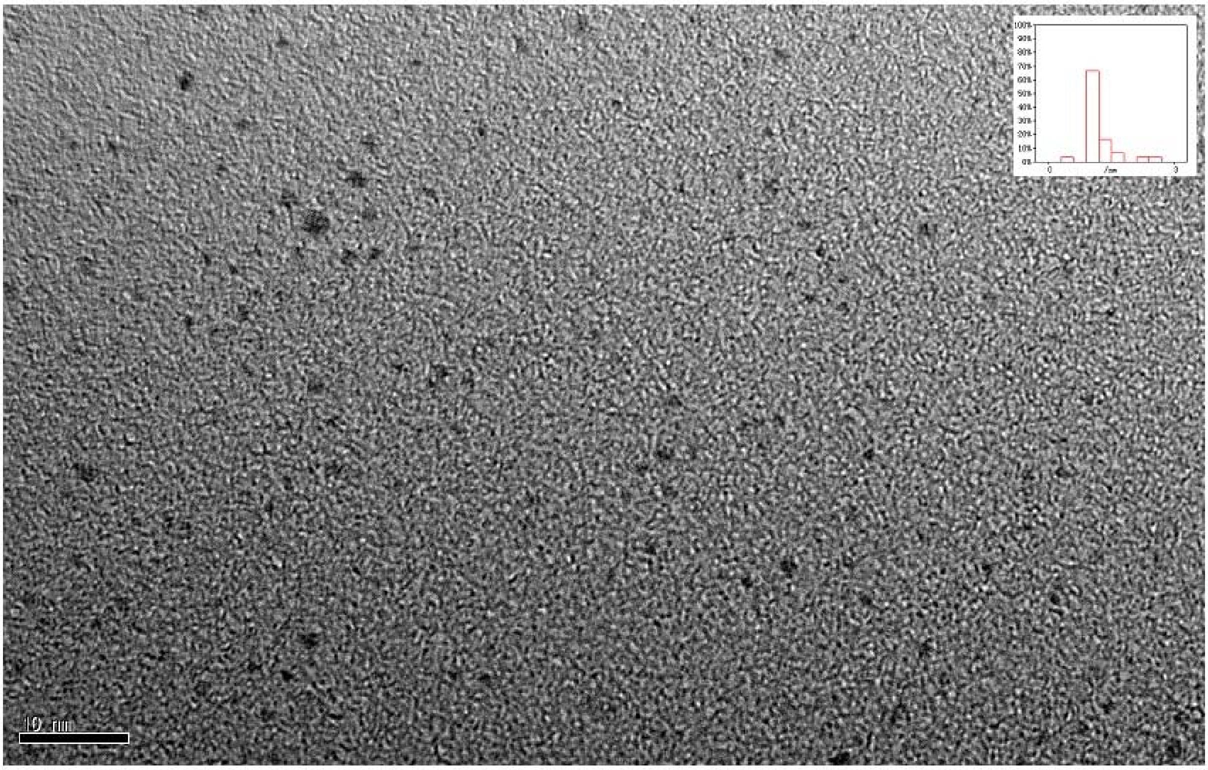


Figure S1. TEM imaging of $Au_{44}(SC_2H_4Ph)_{32}$ (Inset is the size distribution histogram. Scale bar: 10 nm)

Table S1. Mass calculation of $Au_x(SC_2H_4Ph)_y$ with candidate x and y values (exp. MW=13057.94, based on ESI-MS).

x (Au)	y (SR)	MW(cal.)	Deviation	x (Au)	y (SR)	MW(cal.)	Deviation
38	40	12973.61	-84.33	38	41	13110.83	52.89
39	39	13033.36	-24.58	39	40	13170.58	112.64
40	37	12955.88	-102.06	40	38	13093.10	35.16
41	36	13015.62	-42.32	41	37	13152.84	94.9
42	34	12938.15	-119.79	42	35	13075.37	17.43
43	33	12997.89	-60.05	43	34	13135.11	77.17
44	32	13057.90	-0.04	44	33	13194.86	136.92
45	30	12980.16	-77.78	45	31	13117.38	59.44
46	29	13039.90	-18.04	46	30	13177.12	119.18
47	27	12962.42	-95.52	47	28	13099.65	41.71

48	26	13022.17	-35.77	48	27	13159.39	101.45

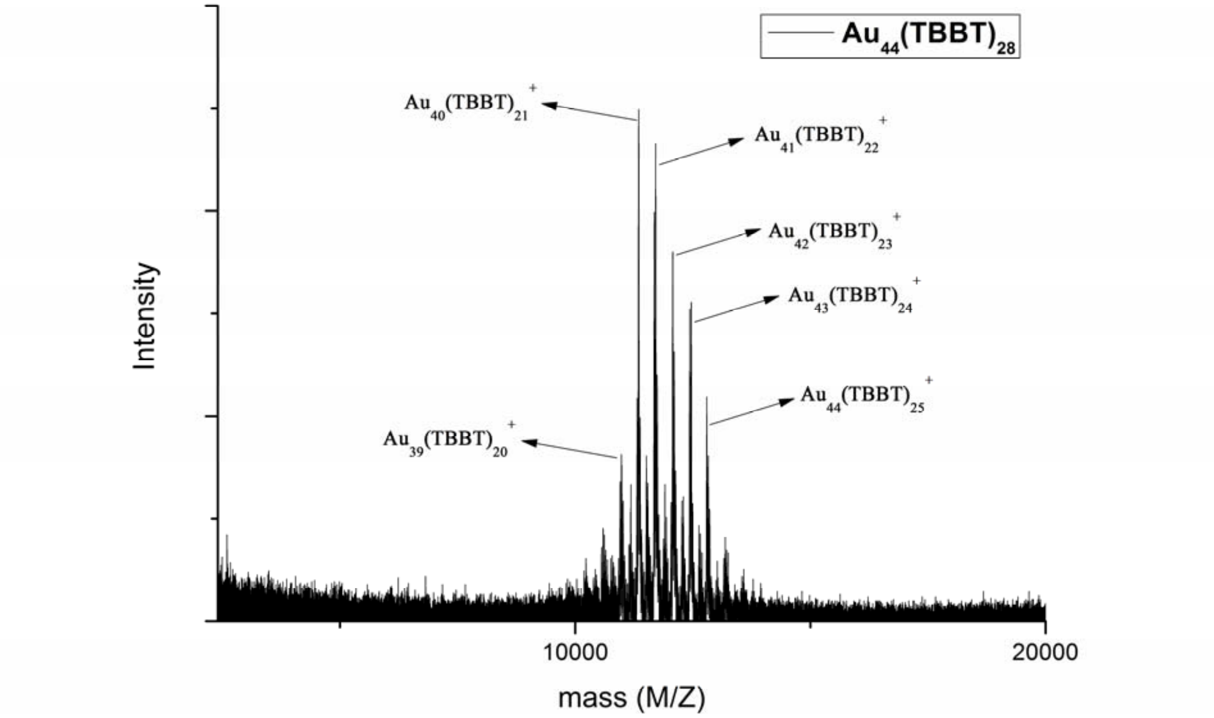


Figure S2. MALDI-TOF-MS spectrum of $Au_{44}(TBBT)_{28}$

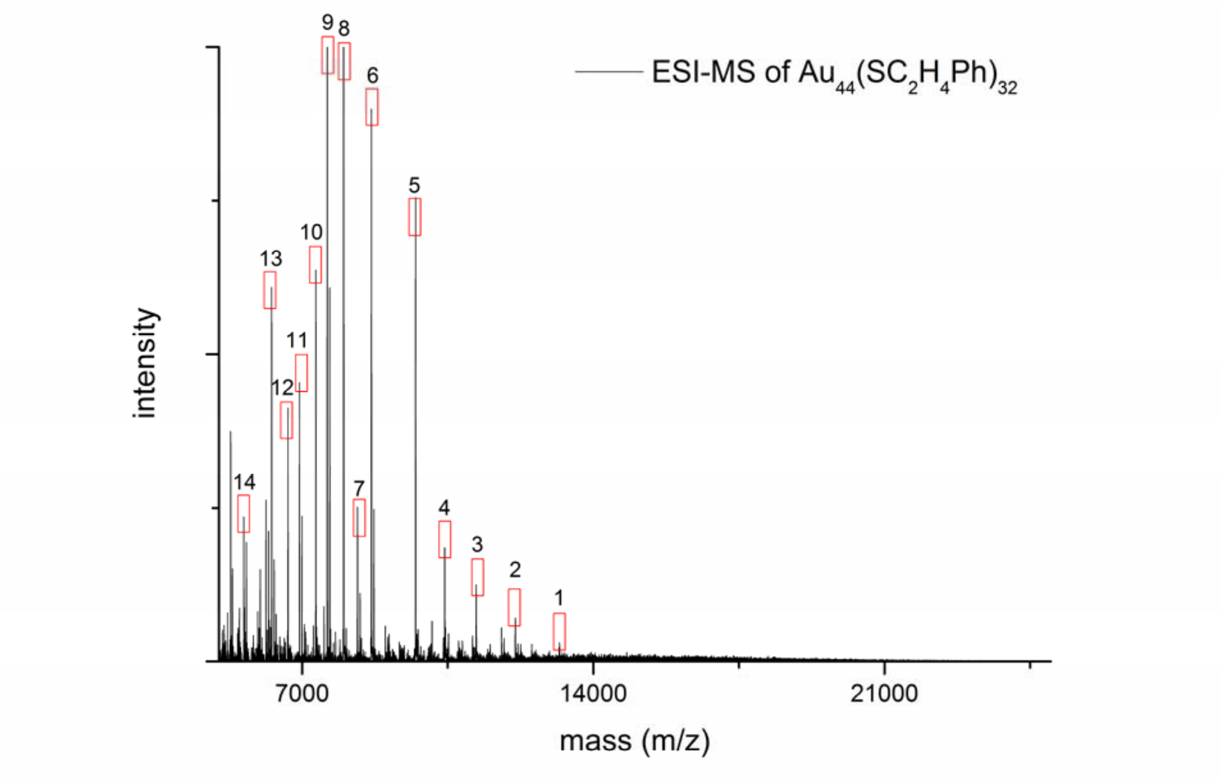


Figure S3. Full scale mass spectrum of $Au_{44}(SC_2H_4Ph)_{32}$

Table S2. Assignments of peaks in ESI-MS spectrum (see Figure S3).

Entry	Assignment	Experimental value	Calculated value	Deviation
1	[Au44(SC2H4Ph)32Cs]$^+$	13190.85	13190.81	-0.04
2	[Au40(SC2H4Ph)30Cs]$^+$	12129.17	12128.86	-0.31
3	[Au38(SC2H4Ph)26Cs]$^+$	11184.91	11185.75	0.84
4	[Au34(SC2H4Ph)26Cs]$^+$	10398.30	10397.89	-0.41
5	[Au32(SC2H4Ph)24Cs]$^+$	9729.12	9729.86	0.74
6	[Au28(SC2H4Ph)22Cs]$^+$	8667.11	8666.92	-0.19
7	[Au27(SC2H4Ph)21Cs]$^+$	8332.14	8332.90	0.76
8	[Au26(SC2H4Ph)20Cs]$^+$	7998.10	7998.89	0.79
9	[Au24(SC2H4Ph)20Cs]$^+$	7604.15	7604.96	0.81
10	[Au24(SC2H4Ph)18Cs]$^+$	7329.11	7329.88	0.77
11	[Au22(SC2H4Ph)18Cs]$^+$	6935.12	6935.94	0.82
12	[Au22(SC2H4Ph)16Cs]$^+$	6661.07	6661.86	0.79
13	[Au20(SC2H4Ph)16Cs]$^+$	6267.08	6267.92	0.84
14	[Au18(SC2H4Ph)14Cs]$^+$	5599.06	5599.91	0.85

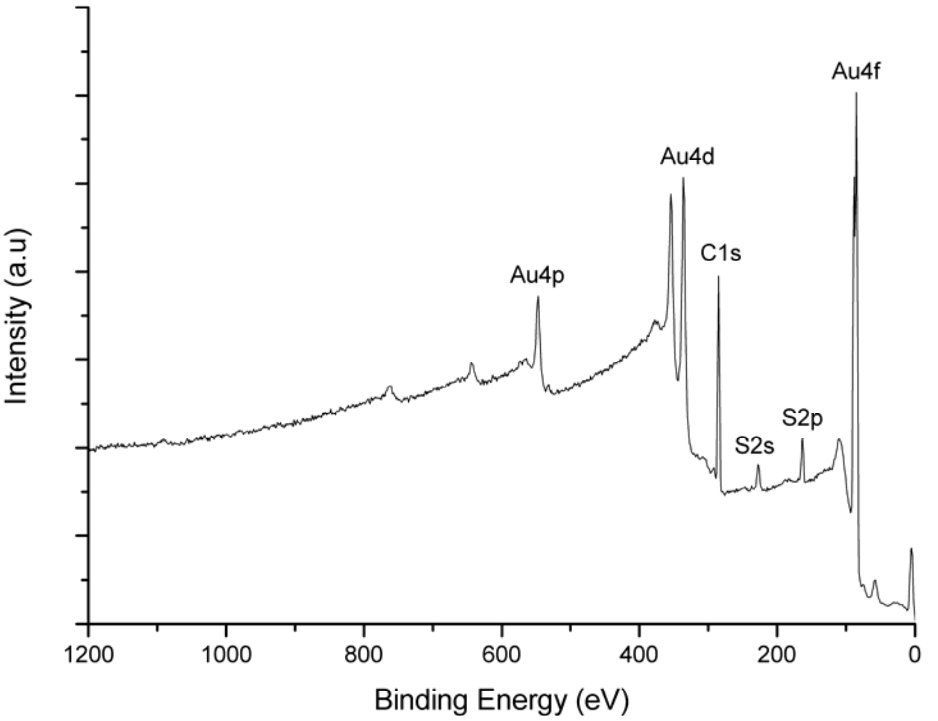


Figure S4. XPS survey spectrum of $Au_{44}(SC_2H_4Ph)_{32}$

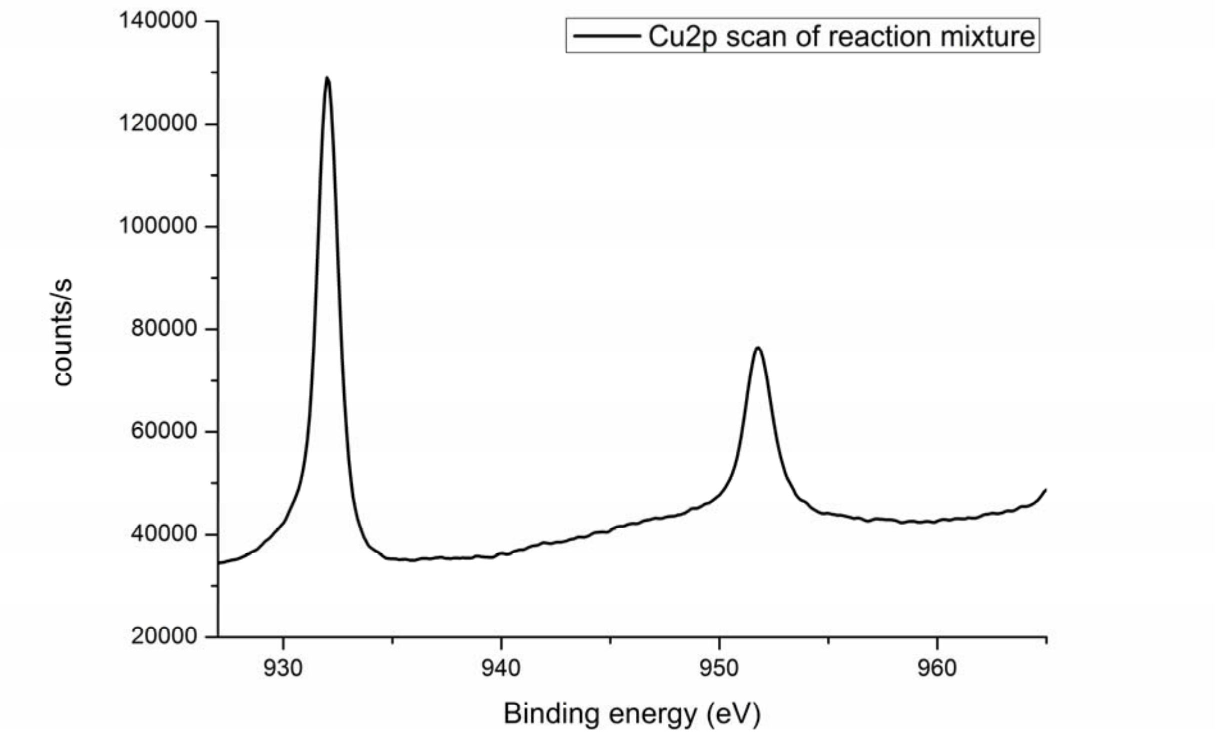
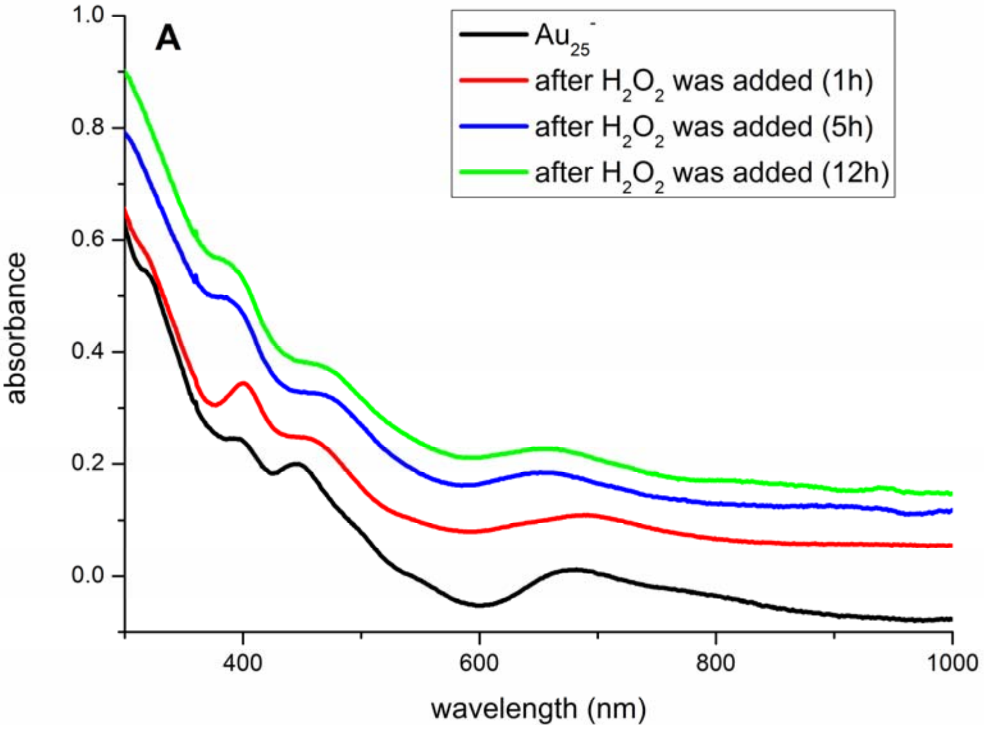
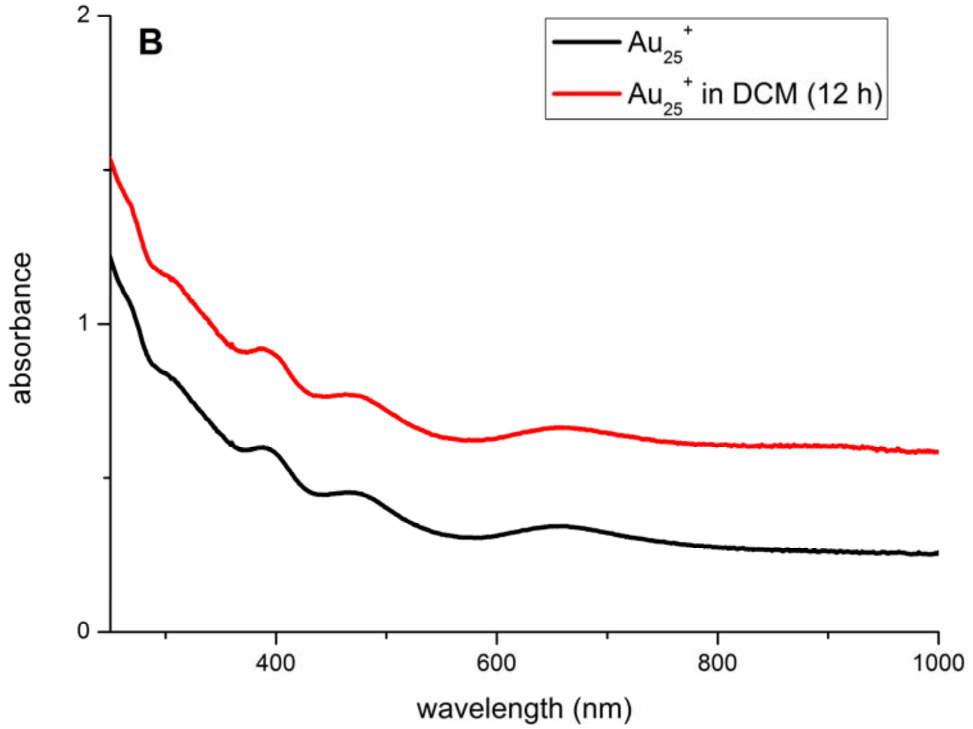


Figure S5. XPS spectrum of the reaction mixture.


A
Au_{25}^-
after H_2O_2 was added (1h)
after H_2O_2 was added (5h)
after H_2O_2 was added (12h)
absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
wavelength (nm)


B
Au_{25}^+
Au_{25}^+ in DCM (12 h)
absorbance
0
1
2
400
600
800
1000
wavelength (nm)

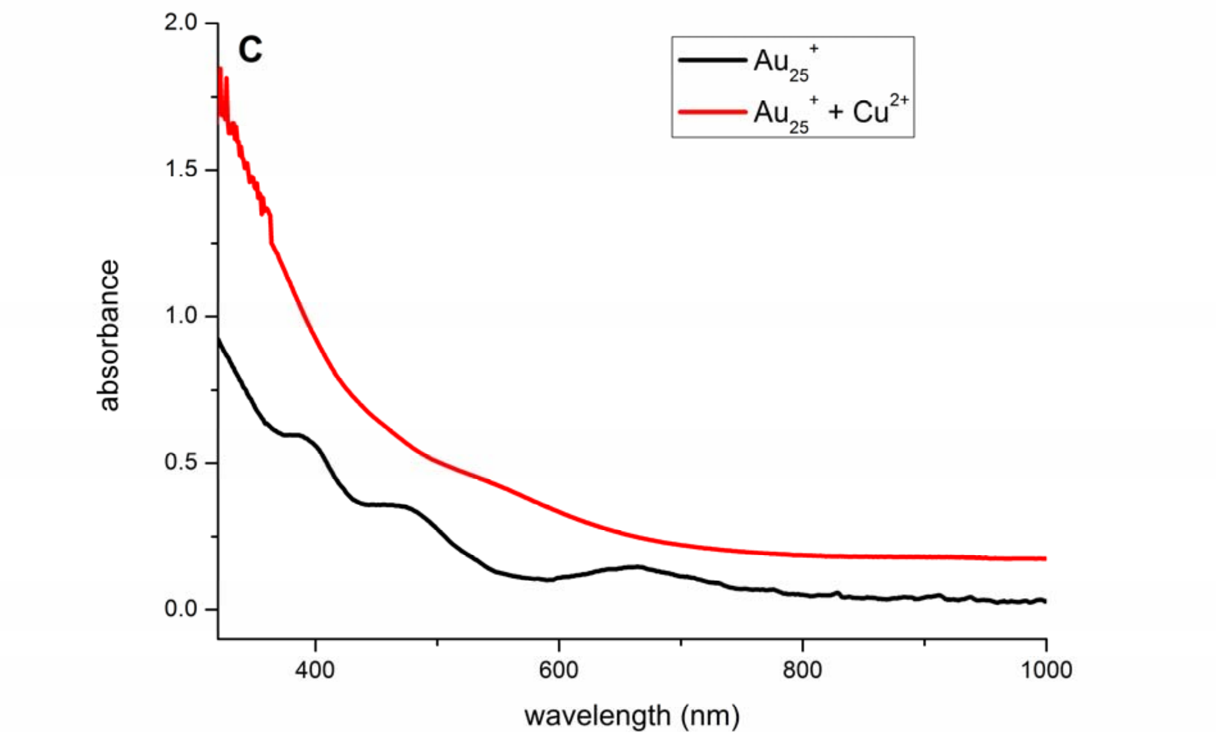


Figure S6. (A) Reaction of Au_{25}^{-} with H_2O_2; (B) isolated Au_{25}^{+} (from Au_{25}-Cu^{2+} system) was stirred in DCM at room temperature for 12 h; (C) isolated Au_{25}^{+} and Cu(II) was stirred in DCM at room temperature for 12 h.

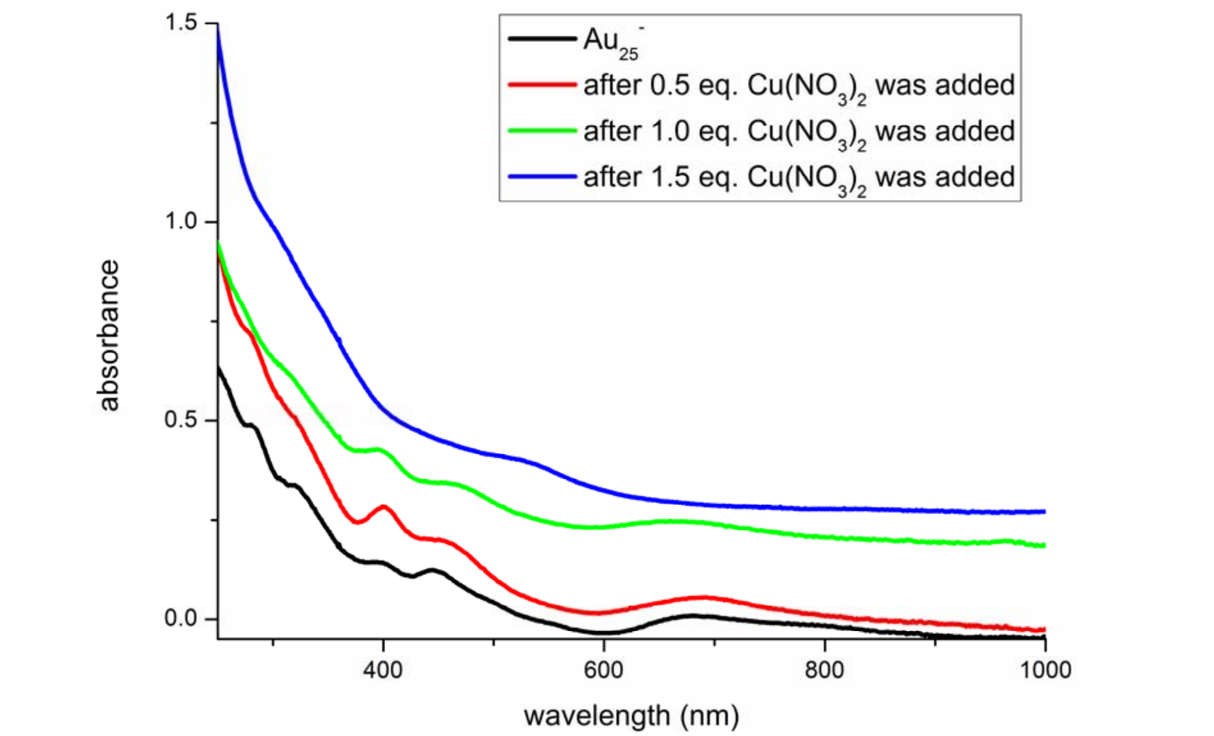


Figure S7. The spectral changes of Au_{25}^- with gradual addition of anhydrous cupric nitrate.

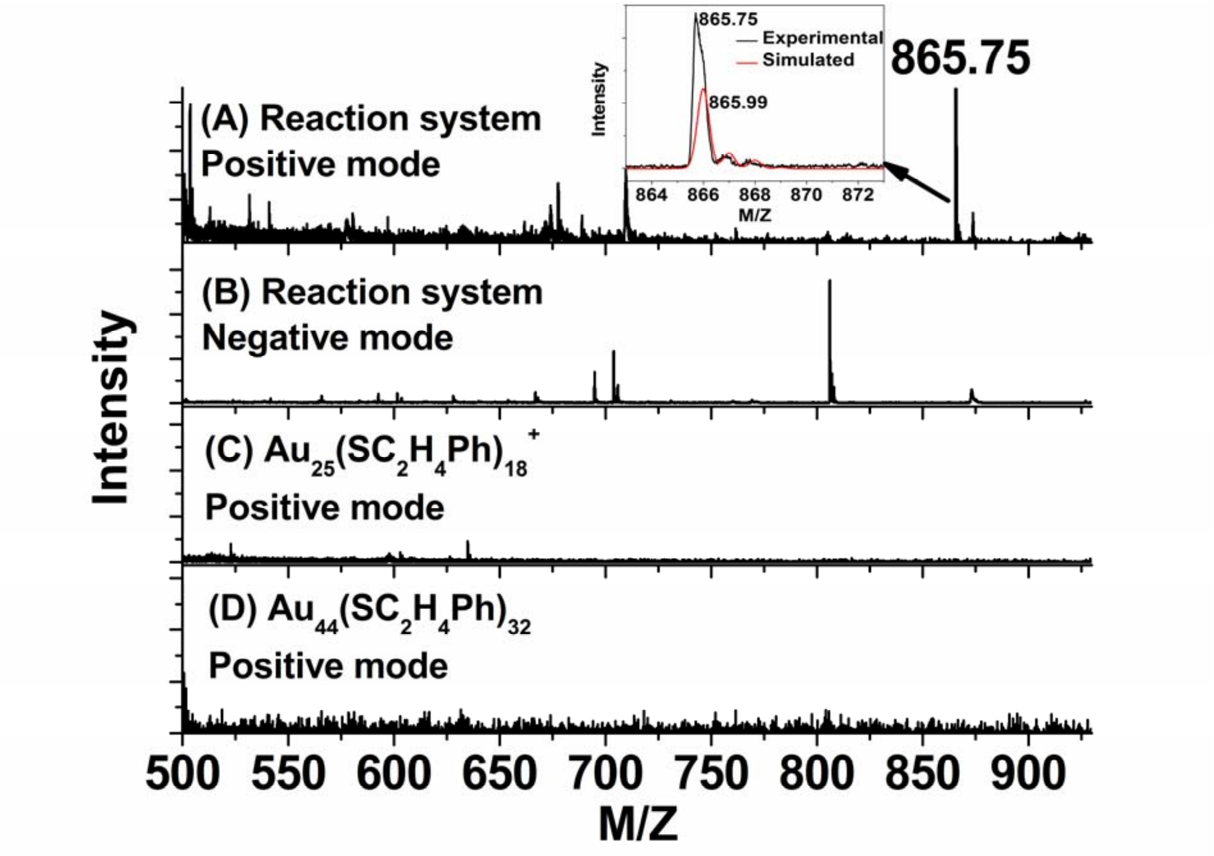


Figure S8. MALDI-TOF-MS spectra of the reaction system in positive ionization mode (A) or negative ionization mode (B), $[Au_{25}(SC_2H_4Ph)_{18}]^+$ in positive ionization mode (C), and purified $Au_{44}(SC_2H_4Ph)_{32}$ in positive ionization mode (D). (Inset) Comparison of simulated and experimental isotope patterns.

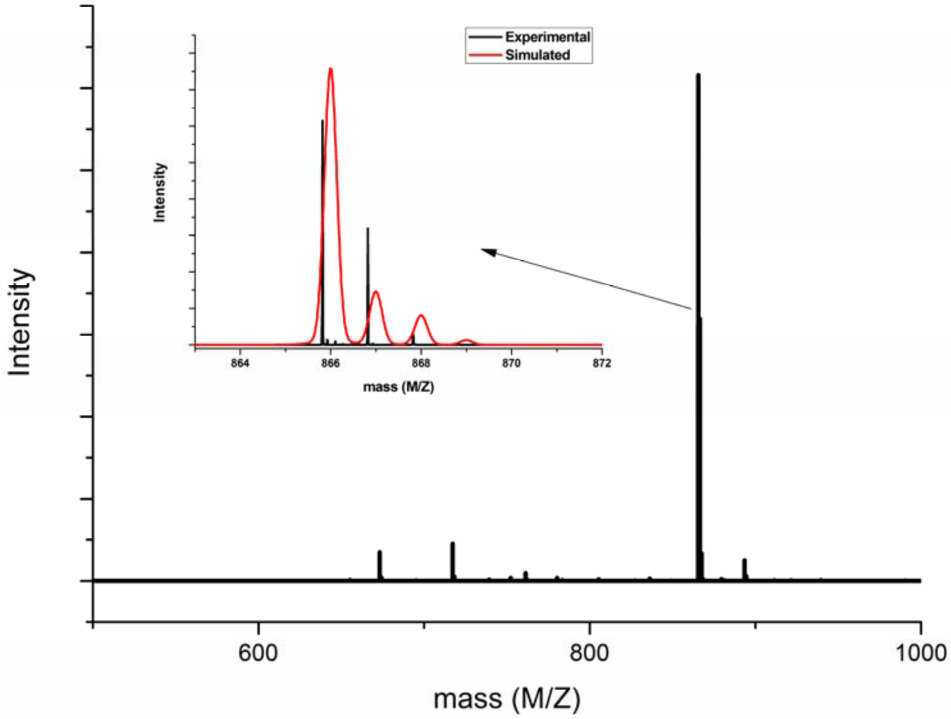
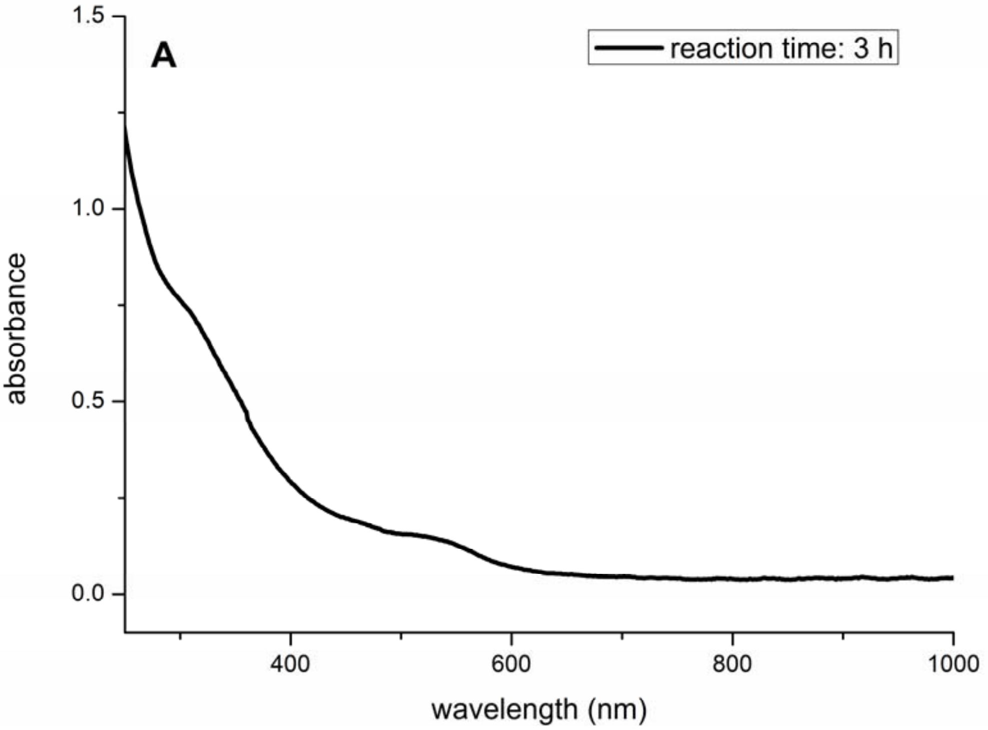
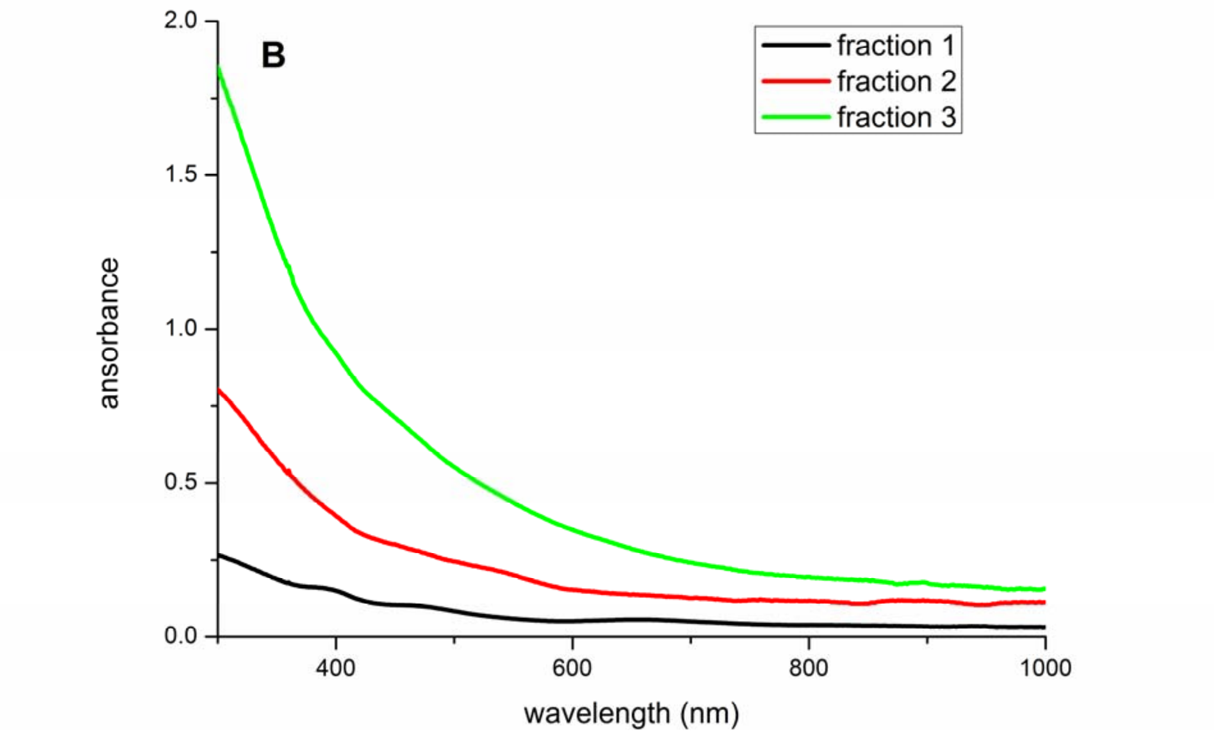


Figure S9. ESI-MS spectra of the reaction system. (Inset) Comparison of simulated and experimental isotope patterns.


A
reaction time: 3 h
absorbance
1.5
1.0
0.5
0.0
400
600
800
1000
wavelength (nm)


B
fraction 1
fraction 2
fraction 3
ansorbance
0.0
0.5
1.0
1.5
2.0
400
600
800
1000
wavelength (nm)

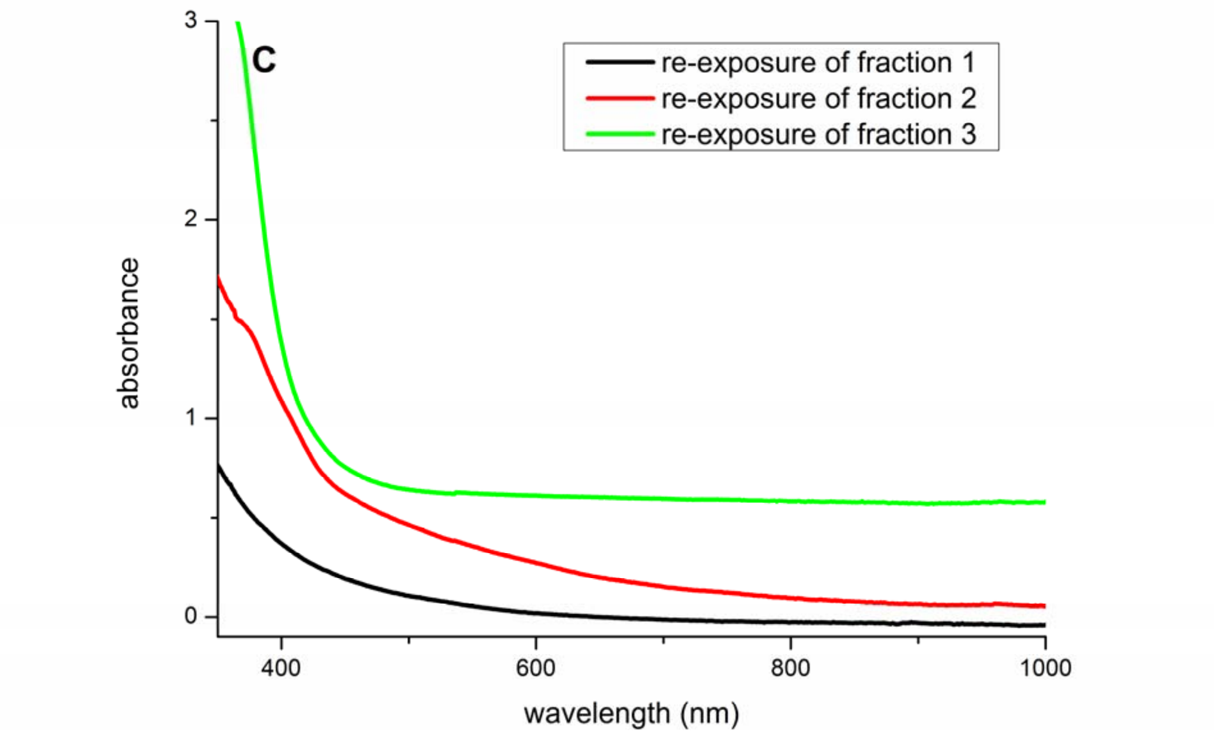


Figure S10. (A) UV-Vis spectrum of the reaction mixture after 3h. (B) UV-Vis spectrum of three fractions isolated by fractional precipitation. (c) UV-Vis spectrum of the three isolated fractions after re-exposure to the reaction conditions.

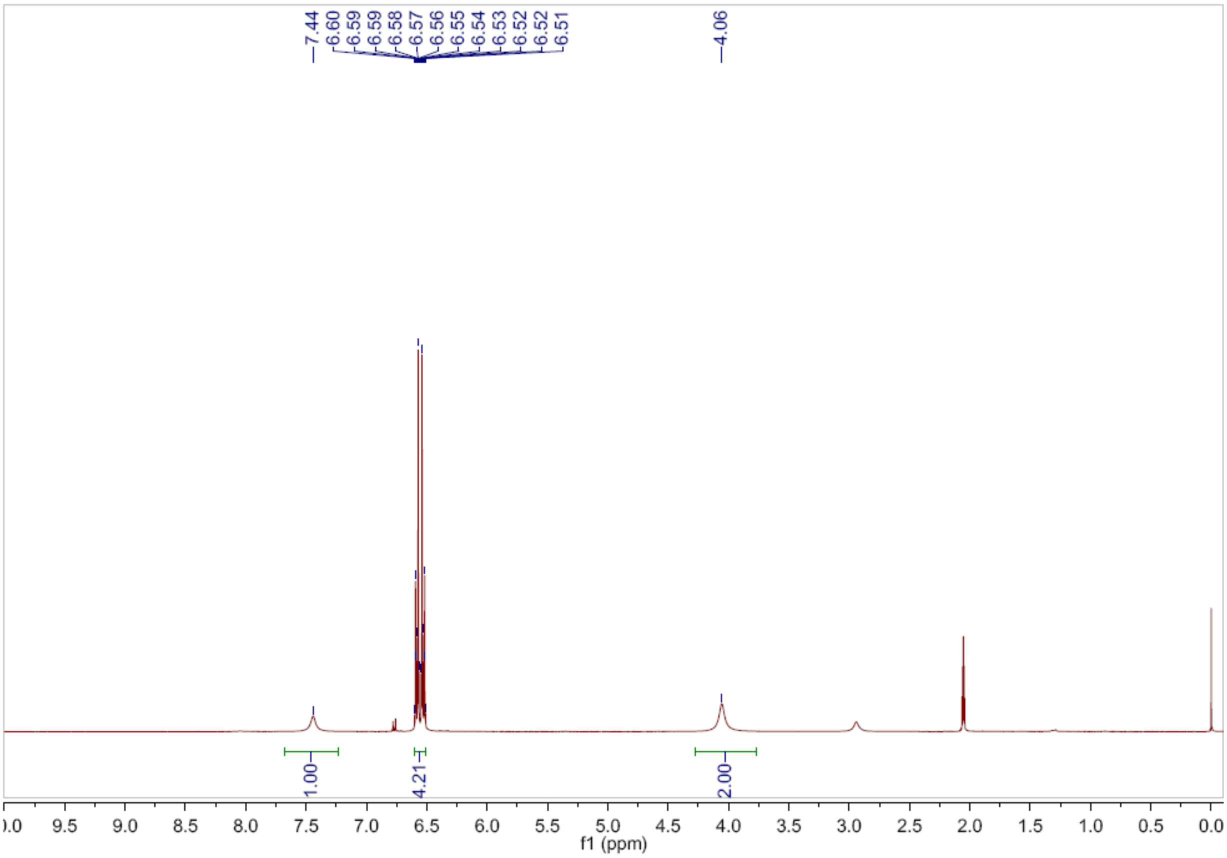
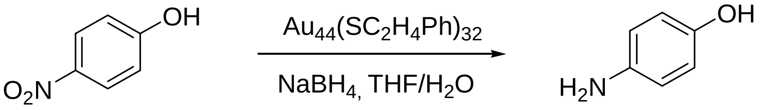


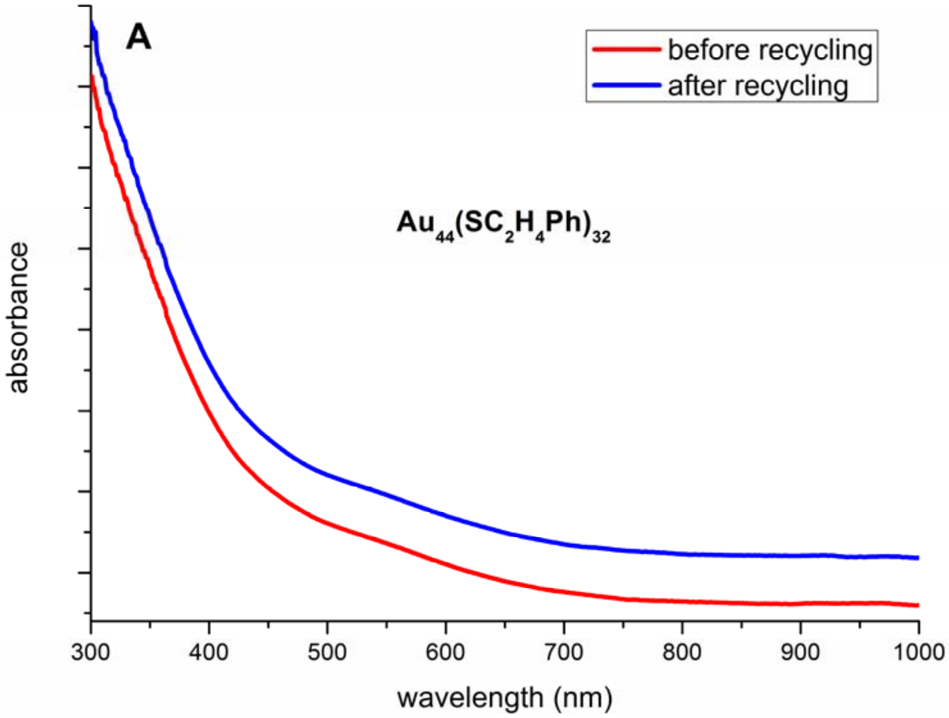
Figure S11. ^{1}H NMR spectrum of 4-aminophenol.

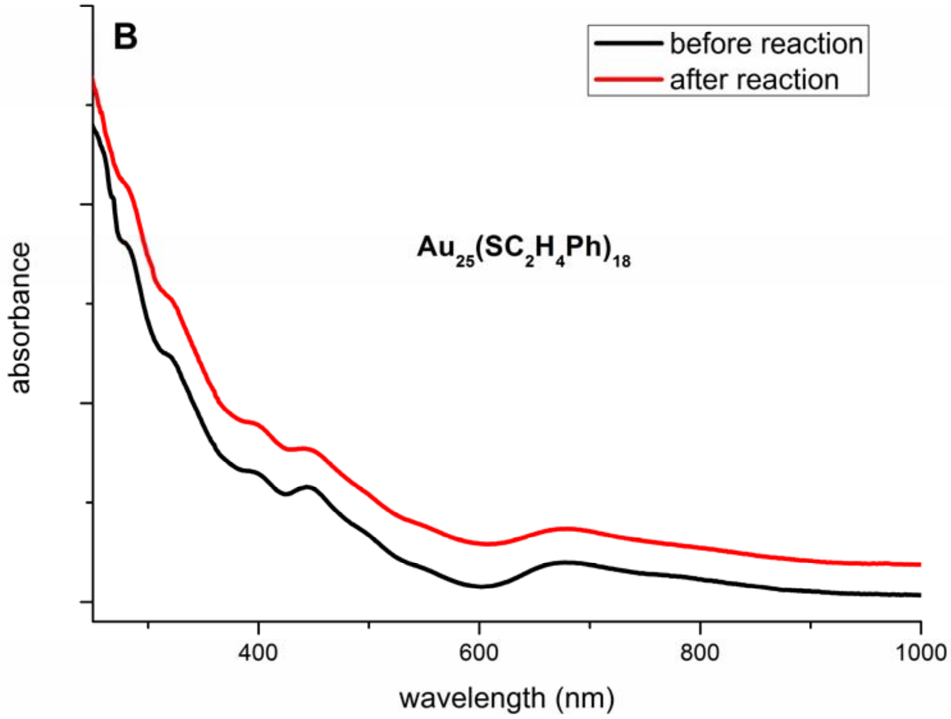
Table S3. Recyclability of $Au_{44}(SC_2H_4Ph)_{32}$

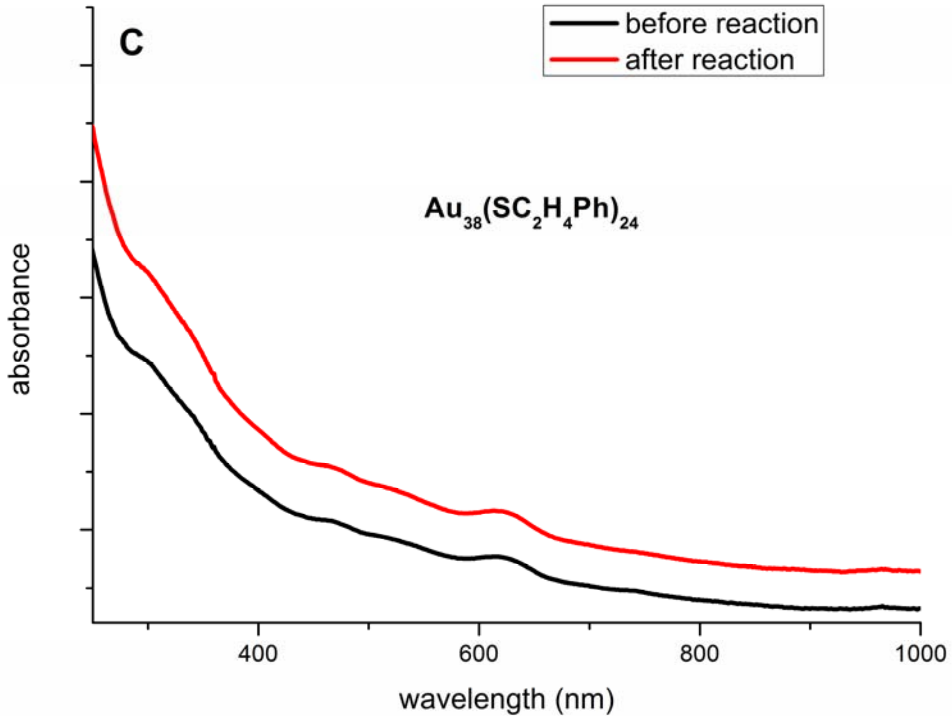


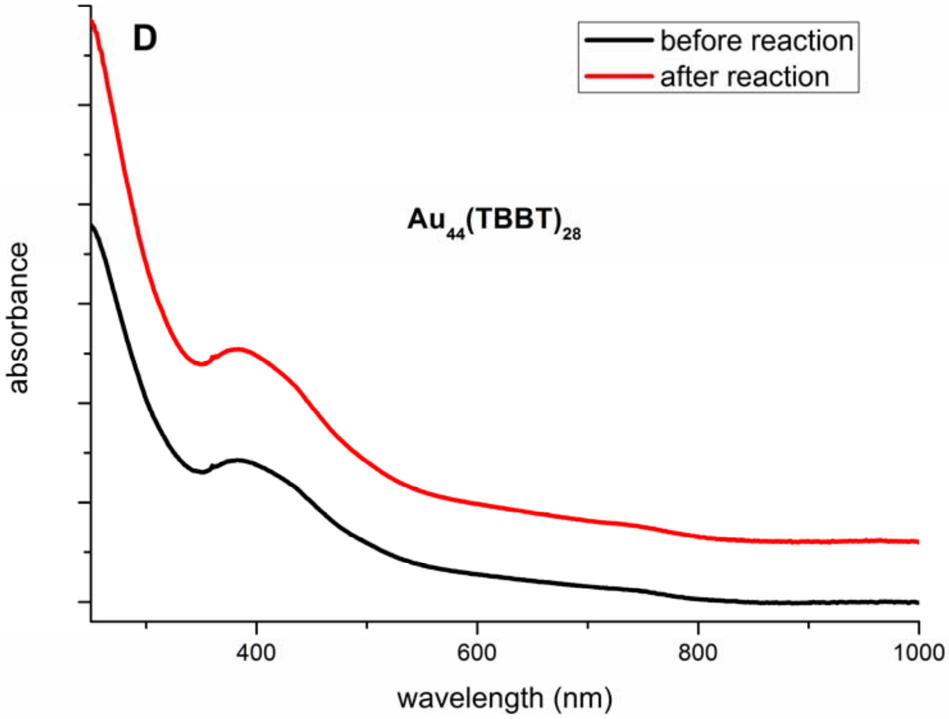
Entry	Number of cycles	Yield[b] (%)
1	1	96
2	2	92
3	3	88
4	4	88
5	5	87
6	6	86

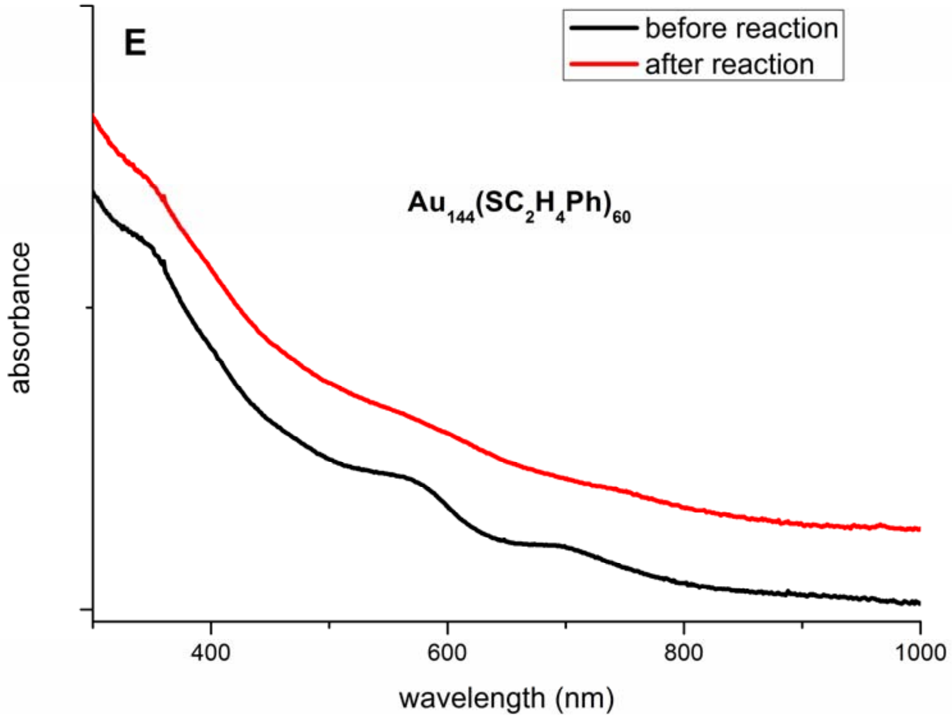
[a] Reaction conditions: 4-nitrophenol (69.5 mg, 0.5 mmol), $Au_{44}(SC_2H_4Ph)_{32}$ (1 mol%), $NaBH_4$ (190 mg, 10 equivalents), THF (5.0 mL), H_2O (1.0 mL), 25℃. [b] Isolated yield.

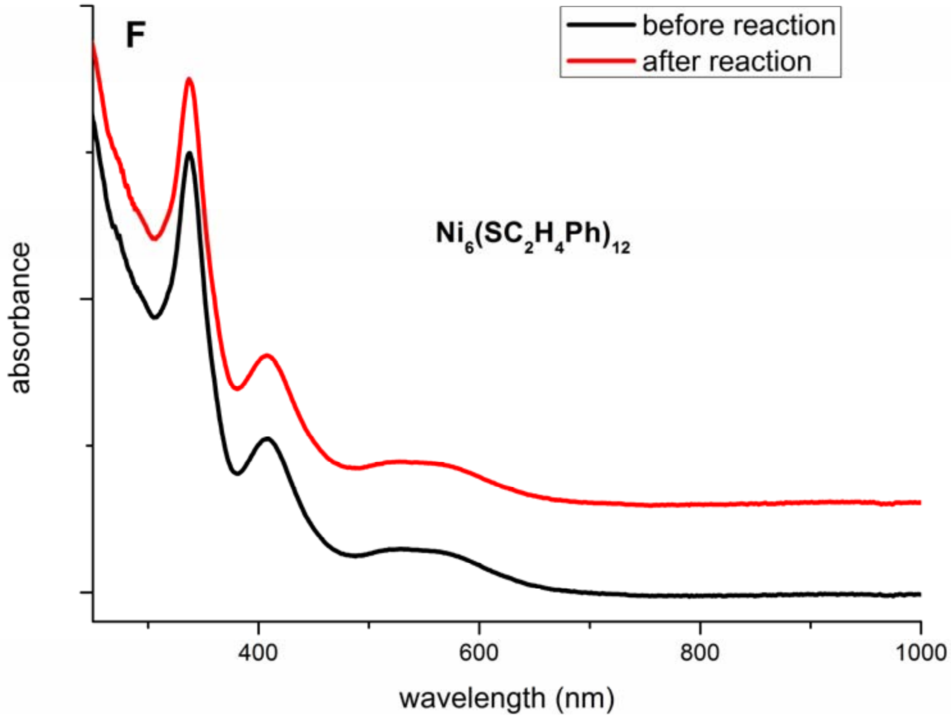

A
before recycling
after recycling
$Au_{44}(SC_2H_4Ph)_{32}$
absorbance
300
400
500
600
700
800
900
1000
wavelength (nm)

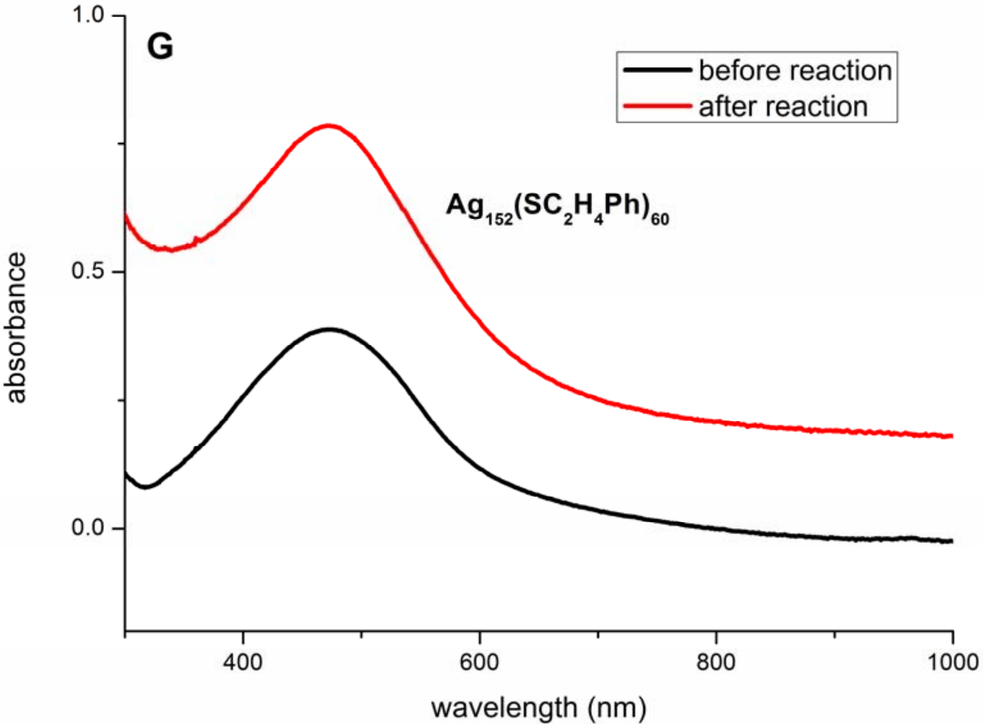

B
before reaction
after reaction
$Au_{25}(SC_2H_4Ph)_{18}$
absorbance
400
600
800
1000
wavelength (nm)

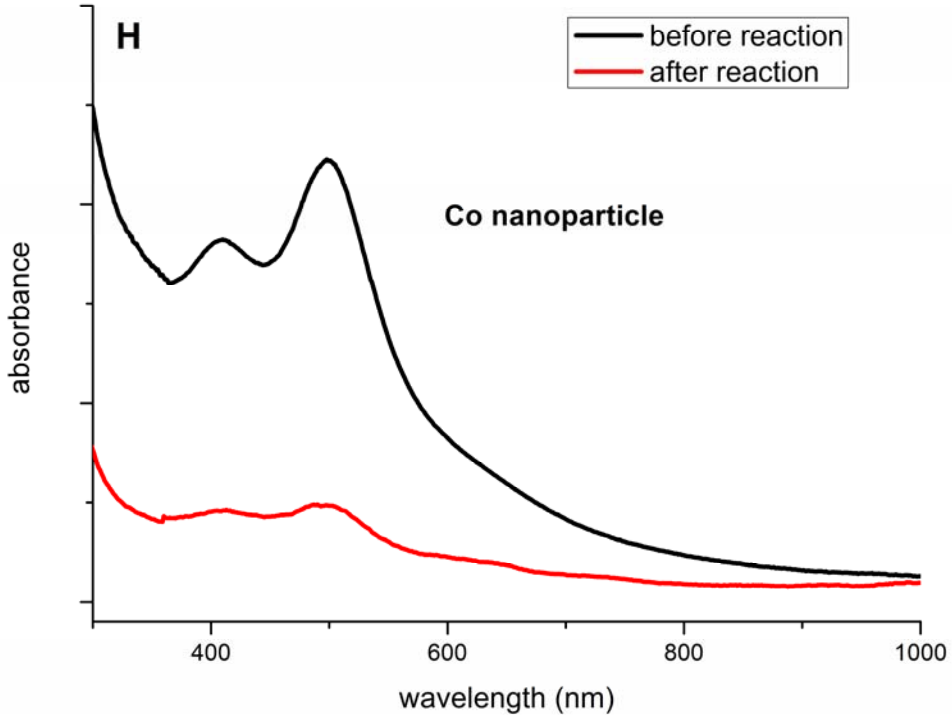

C
before reaction
after reaction
$Au_{38}(SC_2H_4Ph)_{24}$
absorbance
400
600
800
1000
wavelength (nm)


D
before reaction
after reaction
Au44(TBBT)28
absorbance
wavelength (nm)
400
600
800
1000


E
before reaction
after reaction
$Au_{144}(SC_2H_4Ph)_{60}$
absorbance
400
600
800
1000
wavelength (nm)


F
before reaction
after reaction
$Ni_6(SC_2H_4Ph)_{12}$
absorbance
400
600
800
1000
wavelength (nm)


G
before reaction
after reaction
$Ag_{152}(SC_2H_4Ph)_{60}$
absorbance
1.0
0.5
0.0
400
600
800
1000
wavelength (nm)


H
before reaction
after reaction
Co nanoparticle
absorbance
400
600
800
1000
wavelength (nm)

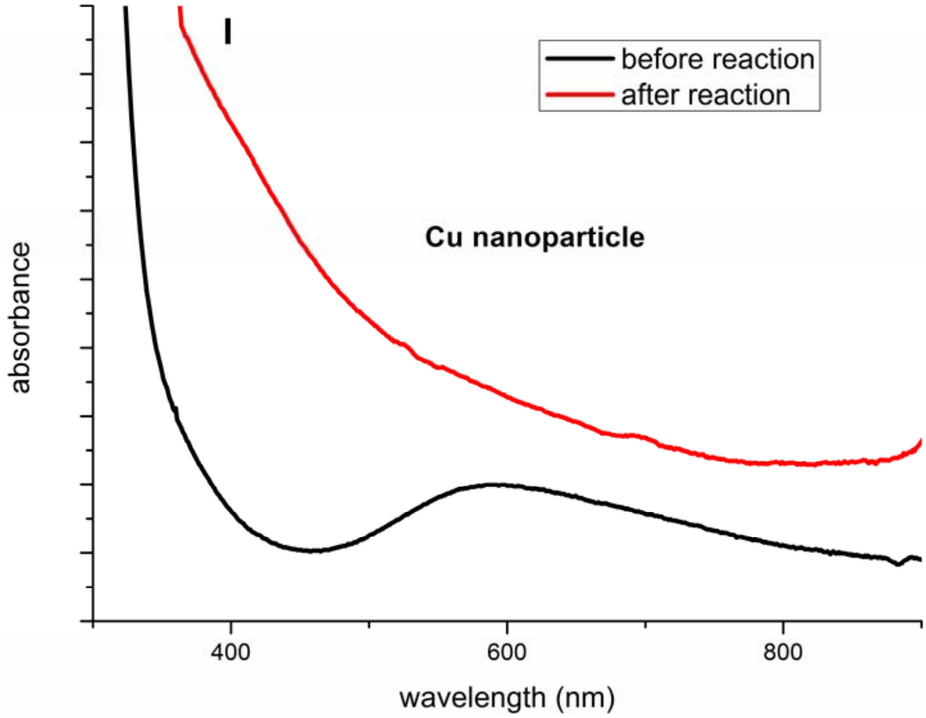


Figure S12. UV/Vis/NIR spectra of nanocatalysts before and after reaction. (A) $Au_{44}(SC_2H_4Ph)_{32}$; (B) $Au_{25}(SCH_2CH_2Ph)_{18}$; (C) $Au_{38}(SCH_2CH_2Ph)_{24}$; (D) $Au_{44}(TBBT)_{28}$; (E) $Au_{144}(SCH_2CH_2Ph)_{60}$; (F) $Ni_6(SC_2H_4Ph)_{12}$; (G) $Ag_{152}(SC_2H_4Ph)_{60}$; (H) Co nanoparticles; (I) Cu nanoparticles.

References

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s4 H. Qian, R. Jin, *Chem. Mater*., 2011, **23**, 2209.
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