Supporting information

Reduction-Resistant and Reduction-Catalytic Double-Crown Nickel Nanoclusters

Min Zhu,[‡a,c] Shiming Zhou,[‡b] Chuanhao Yao,[‡a] Lingwen Liao,[a] Zhikun Wu[*a]

[a] Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031 (P.R. China)

[b] Hefei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, Hefei, 230026, China

[c] University of Science and Technology of China, Hefei, 230026, China

*To whom correspondence should be addressed

Email: zkwu@issp.ac.cn

Table of contents

EXPERIMENTAL SECTION

Chemicals. Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$, ≥99%, Shanghai Chemical Reagent Co., Ltd), tetraoctylammonium bromide (TOABr, 98%, Aladdin), 2-phenylethanethiol (PhC_2H_4SH, ≥99%, Aldrich), etha-nethiol (C_2H_5SH, ≥98%, Aladdin), 1-dodecanethiol ($C_{12}H_{25}SH$, ≥98%, Shanghai Chemical Reagent Co., Ltd), 4-(tert-Butyl) benzene-1-thiol ($C_{10}H_{12}SH$, TBBT, ≥99%, Aladdin), 4-nitrophenol ($C_6H_5NO_3$, AR, Tianjin Guangfu Fine Chemical Research Institute), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, ≥98.0%), cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, ≥99%), ferrous sulfate septihydrate ($FeSO_4·7H_2O$, ≥99%), palladium nitrate dehydrate ($Pd(NO_3)_2·2H_2O$, ≥99%) were purchased from Sinopharm Chemical Reagent Co. Ltd., 1-hexanethiol ($C_6H_{13}SH$, ≥98%), sodium borohydride ($NaBH_4$, ≥96%), sodium hydroxide (NaOH, ≥96%), tetrahydrofuran (C_4H_8O, ≥99.9%), dichloromethane (CH_2Cl_2, ≥99.5%), ethanol (EtOH, ≥99.7%), and methanol (CH_3OH, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd.

All chemicals were used as received except THF, through which N_2 (99.99% Nanjing Special Gas Corp.) was bubbled. The water used in all experiments was ultrapure (resistivity 18.2 MΩ cm), produced with a Milli-Q NANO pure water system.

Synthesis of $Ni_6(SC_2H_4Ph)_{12}$. The synthesis of Ni_6 follows a previous method used to synthesize Au_{25}.[1,2] In short, $Ni(NO_3)_2·6H_2O$ (0.1246 g, 0.42 mmol) was mixed with 2 equivalents of tetraoctylammonium bromide (TOABr (0.460 g, 0.84 mmol)) in THF (25 ml). Then, 6 equivalents of phenylethanethiol (0.340 ml, 2.54 mmol) were added to this solution and the solution was stirred for 3 hours. To this solution, 10 equivalents of $NaBH_4$ (0.160 g, 4.23 mmol) in cold water (5 ml) was added all at once under vigorous stirring (a dark-brown solution) and the reaction was allowed to proceed under constant stirring for 20 h (the progress of the reaction was monitored by UV-Vis spectroscopy). THF was removed via rotary evaporation at 25 °C to isolate the crude product. For purification, the crude product was washed with methanol three times and extracted with CH_2Cl_2 twice, during this procedure, traces of by-products, such as TOA^+ and NO_3^- were removed thoroughly. Then the as-obtained products were crystallized from the mixture of 2 ml CH_2Cl_2 and 2 ml ethanol. Crystals were separated and washed with ethanol for 3 times and dried under vacuum (yield: 30%). (All operations were performed under air atmosphere and at room temperature).

Control experiments.

Method I (without NaOH or $NaBH_4$): $Ni(NO_3)_2·6H_2O$ (0.1246 g, 0.42 mmol) and TOABr (0.460 g, 0.84 mmol) were first dissolved in THF (25 mL) to give a deep-blue solution, into which phenylethanethiol (0.340 mL, 2.54 mmol) was added, and the resulting mixture was stirred for an additional 3h. Then, THF was removed via rotary evaporation to isolate the crude product. The crude product was isolated and purified following the same procedure of Ni_6.

Method II (NaOH was used): The protocols are similar to the synthesis of Ni_6 except that $NaBH_4$ was replaced by NaOH.

General procedure for the synthesis of other Metal- phenylethanethiol complex: First, metal salts ($Co(NO_3)_2·6H_2O$, $Bi(NO_3)_3·5H_2O$, $FeSO_4·7H_2O$, $Pd(NO_3)_2·2H_2O$) (0.42 mmol) was mixed with 2 equivalents of TOABr (0.460 g, 0.84 mmol) in THF (25 ml) in a three-necked flask. After the resulting solution was cooled at ca. 0°C in an ice bath over a period of 30 min, phenylethane-thiol (340 uL, 6 equivalents per mole of metal) (for $Pd(NO_3)_2·2H_2O$, 1-dodecanethiol was used) was slowly added to the flask. Three hours later, an aqueous solution of $NaBH_4$ (160 mg, 10.0 equivalents per mole of metal, freshly dissolved in 5 mL ice-cold nanopure water) was rapidly added all at once under vigorous stirring. The reaction was allowed to proceed under constant stirring for additional 0.5-2 hours. The crude product was collected (rotary evaporation was used to remove THF) and thoroughly washed with water and methanol, then dissolve in small amount of CH_2Cl_2. After the removal of some insoluble solid, an adequate amount of MeOH was added until a large amount of precipitate were formed. The

precipitates were collected and dried for the subsequent reduction-resistance test.

General procedure for the synthesis of other thiolated Ni complexes: $Ni(NO_3)_2·6H_2O$ (0.1246 g, 0.42 mmol) was added into a THF solution (25 mL) of TOABr (460.0 mg,0.84 mmol). The resulting solution was cooled down to ca. 0 °C in an ice bath over a period of 30 min. Thiolates (4-(tert-butyl)benzene-1-thiol, tert-butyl thiol (TBBT), ethanethiol, 1-hexanethiol) (2.54 mmol, 6 equivalents per mole of nickel) was slowly added, and the solution was stirred for ca. 3h. A freshly made aqueous solution of $NaBH_4$ (160.0 mg, dissolved in 5 mL ice-cold H_2O) was then added rapidly into the reaction mixture under vigorous stirring. The reaction was stopped after constant stirring for 1-2 hours. Then THF was removed by rotary evaporation to get the crude product. After washing with water and methanol for several times, the crude product was dissolved in small amount of CH_2Cl_2, into which an adequate amount of MeOH was added until a large amount of precipitate was formed. The precipitates were collected and dried for the subsequent reduction-resistance test.

Reduction catalysis: In a typical catalytic reaction, 13.92 mg of nitrophenol was dissolved in 25 mL mixture of THF/water (20/5 by volume). Then, Ni_6 (5.005 × 10-3 mmol) were added, after stirring for several minutes, 40 equiv. of NaBH4 in ice cold water was added. Immediately after the addition of $NaBH_4$, UV/Vis/NIR spectra were recorded. The reaction was monitored by UV/Vis/NIR spectroscopy. Control experiments were carried out at the same conditions with or without $Au_{25}(SC_2H_4Ph)_{18}$ and no nitrophenol reduction was observed.

Reduction-resistance test: The reduction-resistance property (RRP) of Ni_6 and other complexes towards $NaBH_4$ was studied with UV/Vis/NIR spectroscopy. In a typical procedure; to a solution of Ni_6 or other complexes, 0.1 mmol $NaBH_4$ was added inportions and three minutes after every addition of $NaBH_4$, UV/Vis/NIR spectra were recorded.

Electrochemistry. A conventional three-electrode system was used for the experiment. A Pt disk electrode (0.5 mm diameter) was used as working electrode (WE). Before used, the WE was firstly polished on emery paper of decreasing grades then with Al_2O_3 powders with size down to 0.05μm and cleaned electrochemically by potential-cycling in 0.5 M H_2SO_4 solution, the electrode was then rinsed thoroughly with ultrapure water (18.2 MΩ cm). An SCE (with saturated KCl solution) electrode and carbon rods are used as a reference (RE) and counter electrode (CE), respectively. The electrode potentials were controlled by a potentiostat (Zahner, Germen). Ni clusters dissolved in 0.1 M Bu_4NPF_6 that was constantly purged by N_2 (99.99% Nanjing Special Gas Corp.) during the experiments. All electrochemical experiments were carried out at room temperature (ca. 25 °C).

Characterization. Transmission electron microscopy (TEM) images were taken by JEOL2010. The operating voltage on the microscope was 200 keV. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-pro-penylidene] malononitrile (DCTB) was used as the matrix, and the molar ratio of clusters to matrix was 1:500. All UV/Vis/NIR absorption spectra were recorded using a UV-2550 spectrophotometer (Shimadzu, Japan) at room temperature. TGA was conducted in a N_2 atmosphere (flow rate ~50 mL/min, ~ 3 mg sample used) on a TG/DAT 6300 analyzer (Seiko In struments, Inc)，and the heating rate was 10 °C /min. XPS measurements were performed on an ESCALAB 250Xi XPS spectrometer (Thermo Scientific, America), using a monochromatized Al Kasource and equipped with an Ar^+ ion sputtering gun. All binding energies were calibrated using the C (1s) carbon peak (284.8 eV). The diffraction data of single crystal (0.36 X 0.32 X 0.25 mm) were collected on an Agilent Gemini S Ultra diffractometer using Cu kα radiation and the crystal structure was solved by direct methods and refined by full-matrix least-squares methods with SHELXL-2013 program (Sheldrick, 2013).

1 M. Zhu, E. Lanni, N. Garg, M. E. Bier and R. Jin, J. Am. Chem. Soc., 2008, **130**, 1138.

2 Z. Wu, J. Chen and R. Jin, Adv. Fun. Mater., 2011, **21**, 177.

Table 1. Crystal data and structure refinement for $Ni_6(PET)_{12}$.

Identification code	$Ni_6(PET)_{12}$
Empirical formula	$C_{96}H_{108}Ni_6S_{12}$
Formula weight	1998.80
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3662(2)
b/Å	12.5415(3)
c/Å	32.7762(8)
α/°	90
β/°	91.676(2)
γ/°	90
Volume/$Å^3$	4670.22(18)
Z	2
ρcalcg/cm^3	1.421
μ/mm^{-1}	4.150
F(000)	2088.0
Crystal size/mm^3	0.36 × 0.32 × 0.25
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.548 to 130.162
Index ranges	$-13 \leq h \leq 8$, $-13 \leq k \leq 14$, $-38 \leq l \leq 38$
Reflections collected	18303
Independent reflections	7239 [Rint= 0.0559, Rsigma= 0.0587]
Data/restraints/parameters	7239/31/514
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R1= 0.0922, wR2= 0.2378
Final R indexes [all data]	R1= 0.1052, wR2= 0.2468
Largest diff. peak/hole / e $Å^{-3}$	1.23/-0.68

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ni_6(PET)_{12}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ni2	-443.6(11)	2114.6(11)	52.7(4)	42.6(4)
Ni1	1620.1(11)	1611.2(10)	-267.2(4)	40.6(4)
Ni3	-2090.3(11)	593.2(10)	325.0(4)	40.9(4)
S4	1567.5(17)	2367.6(16)	313.9(6)	42.6(5)
S3	-67.0(17)	2537.1(16)	-517.5(6)	43.9(5)
S2	3349.6(16)	704.5(15)	-44.3(6)	41.3(5)
S1	1420.2(17)	605.5(16)	-809.5(6)	41.8(5)
S5	-2368.3(17)	1604.2(16)	-216.1(6)	44.1(5)
S6	-908.7(18)	1928.2(16)	625.6(6)	45.2(5)
C40	-6173(8)	4019(7)	-377(3)	72(3)
C11	5286(7)	1736(7)	1111(3)	49(2)
C39	-6801(10)	4923(8)	-487(4)	85(4)
C16	6544(8)	1751(8)	1308(3)	59(2)
C38	-6682(10)	5590(9)	-806(4)	94(4)
C43	1070(8)	1160(8)	1820(3)	54(2)
C37	-5813(12)	5207(10)	-1028(4)	123(6)
C36	-5180(12)	4312(10)	-908(4)	108(5)
C48	1191(10)	1626(10)	2191(3)	75(3)
C35	-5265(7)	3635(7)	-585(3)	57(2)
C42	41(8)	1480(8)	1447(3)	54(2)
C18	-2241(7)	2717(7)	-1155(3)	57(2)
C2	2347(8)	1961(8)	-1282(3)	72(3)
C27	1433(7)	4355(7)	942(3)	61(3)
C4	1107(10)	1111(11)	-1933(3)	87(4)
C14	6176(11)	1886(12)	1959(3)	92(4)
C6	-689(14)	1828(15)	-2311(5)	195(11)
C15	6989(10)	1815(11)	1726(3)	78(3)
C3	1333(7)	1946(9)	-1619(3)	71(3)
C7	-542(14)	2618(17)	-2019(5)	191(10)
C34	-4581(7)	2649(7)	-464(3)	60(2)
C26	1052(9)	4478(7)	481(3)	61(3)
C12	4479(9)	1803(9)	1350(3)	67(3)
C28	387(10)	4490(9)	1120(4)	84(4)
C44	1952(9)	334(9)	1832(3)	75(3)
C13	4930(10)	1883(11)	1763(3)	84(4)
C45	2734(9)	46(10)	2150(3)	77(3)
C5	216(12)	1103(14)	-2236(4)	133(6)

C46	2867(11)	483(11)	2528(4)	83(3)
C29	706(16)	4455(12)	1536(5)	107(5)
C30	1767(16)	4258(12)	1771(5)	118(6)
C32	2500(9)	4194(9)	1177(3)	78(3)
C47	2068(12)	1313(12)	2541(3)	92(4)
C8	374(10)	2586(13)	-1728(4)	126(6)
C31	2847(14)	4157(11)	1604(5)	104(5)
C1	2676(8)	952(8)	-1020(3)	56(2)
C41	411(7)	1530(7)	1053(2)	50(2)
C25	1761(9)	3820(7)	264(3)	59(2)
C9	3968(7)	674(7)	503(3)	48(2)
C33	-3298(7)	2794(7)	-200(3)	53(2)
C10	4790(8)	1652(7)	653(3)	52(2)
C17	-1201(6)	1963(7)	-977(2)	48(2)
C19	-3326(6)	2334(6)	-1463(2)	56(2)
C20	-3875(8)	2759(10)	-1820(2)	76(3)
C21	-4833(9)	2492(10)	-2084(3)	97(4)
C22	-5460(9)	1557(10)	-2013(3)	100(4)
C23	-4941(8)	1088(10)	-1664(3)	79(3)
C24	-3970(7)	1398(7)	-1411(3)	64(3)

Table 3. Bond lengths for $Ni_6(PET)_{12}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni2	Ni1	2.6727(16)	C36	C35	1.363(8)
Ni2	Ni3	2.8352(17)	C48	C47	1.548(17)
Ni2	S4	2.438(2)	C35	C34	1.508(12)
Ni2	S3	2.001(2)	C42	C41	1.370(11)
Ni2	S5	2.421(3)	C18	C17	1.610(8)
Ni2	S6	1.979(2)	C18	C19	1.643(8)
Ni1	Ni3[1]	2.8233(18)	C2	C3	1.572(9)
Ni1	S4	2.130(2)	C2	C1	1.567(13)
Ni1	S3	2.368(2)	C27	C26	1.570(14)
Ni1	S2	2.368(2)	C27	C28	1.350(8)
Ni1	S1	2.186(2)	C27	C32	1.431(9)
Ni3	Ni1[1]	2.8232(18)	C4	C3	1.486(17)
Ni3	S2[1]	2.338(2)	C4	C5	1.398(5)
Ni3	S1[1]	2.300(2)	C14	C15	1.219(15)
Ni3	S5	2.196(2)	C14	C13	1.539(17)
Ni3	S6	2.345(2)	C6	C7	1.386(5)
S4	C25	1.842(9)	C6	C5	1.390(5)
S3	C17	2.081(9)	C3	C8	1.393(5)
S2	Ni3[1]	2.338(2)	C7	C8	1.391(5)
S2	C9	1.908(9)	C34	C33	1.683(11)
S1	Ni3[1]	2.300(2)	C26	C25	1.368(11)
S1	C1	1.662(8)	C12	C13	1.436(15)
S5	C33	1.830(8)	C28	C29	1.402(19)
S6	C41	2.083(9)	C44	C45	1.396(5)
C40	C39	1.382(8)	C45	C46	1.359(16)
C40	C35	1.342(6)	C46	C47	1.383(18)
C11	C16	1.553(13)	C29	C30	1.43(2)
C11	C12	1.225(12)	C30	C31	1.364(9)
C11	C10	1.591(12)	C32	C31	1.445(17)
C39	C38	1.350(9)	C9	C10	1.610(12)
C16	C15	1.449(14)	C19	C20	1.413(5)
C38	C37	1.333(9)	C19	C24	1.397(5)
C43	C48	1.353(13)	C20	C21	1.410(5)
C43	C42	1.715(13)	C21	C22	1.395(5)
C43	C44	1.441(13)	C22	C23	1.403(5)
C37	C36	1.384(9)	C23	C24	1.415(5)

[1]-X,-Y,-Z

Table 4. Bond angles for $Ni_6(PET)_{12}$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Ni1	Ni2	Ni3	124.03(6)	C41	S6	Ni3	120.2(3)
S4	Ni2	Ni1	49.00(6)	C35	C40	C39	124.1(9)
S4	Ni2	Ni3	126.71(7)	C16	C11	C10	133.7(7)
S3	Ni2	Ni1	58.80(7)	C12	C11	C16	115.5(9)
S3	Ni2	Ni3	129.31(9)	C12	C11	C10	110.9(9)
S3	Ni2	S4	93.99(9)	C38	C39	C40	130.4(9)
S3	Ni2	S5	86.89(9)	C15	C16	C11	133.4(8)
S5	Ni2	Ni1	126.08(7)	C37	C38	C39	106.9(9)
S5	Ni2	Ni3	48.60(6)	C48	C43	C42	126.1(9)
S5	Ni2	S4	172.02(9)	C48	C43	C44	103.4(9)
S6	Ni2	Ni1	127.30(9)	C44	C43	C42	130.5(8)
S6	Ni2	Ni3	54.88(7)	C38	C37	C36	121.7(10)
S6	Ni2	S4	87.48(9)	C35	C36	C37	132.6(10)
S6	Ni2	S3	171.00(11)	C43	C48	C47	127.1(11)
S6	Ni2	S5	92.89(9)	C40	C35	C36	104.2(8)
Ni2	Ni1	$Ni3^1$	115.32(6)	C40	C35	C34	123.9(8)
S4	Ni1	Ni2	59.75(7)	C36	C35	C34	131.9(7)
S4	Ni1	$Ni3^1$	120.43(8)	C41	C42	C43	117.4(7)
S4	Ni1	S3	92.74(8)	C17	C18	C19	125.6(7)
S4	Ni1	S2	89.01(9)	C1	C2	C3	122.2(8)
S4	Ni1	S1	168.25(10)	C28	C27	C26	100.4(9)
S3	Ni1	Ni2	46.29(6)	C28	C27	C32	122.0(11)
S3	Ni1	$Ni3^1$	127.59(8)	C32	C27	C26	137.6(8)
S3	Ni1	S2	177.43(8)	C5	C4	C3	127.2(13)
S2	Ni1	Ni2	136.27(7)	C15	C14	C13	116.2(11)
S2	Ni1	$Ni3^1$	52.65(6)	C7	C6	C5	105.7(17)
S1	Ni1	Ni2	112.56(8)	C14	C15	C16	110.3(11)
S1	Ni1	$Ni3^1$	52.82(6)	C4	C3	C2	127.1(9)
S1	Ni1	S3	86.41(9)	C8	C3	C2	136.5(13)
S1	Ni1	S2	92.26(8)	C8	C3	C4	96.3(11)
$Ni1^1$	Ni3	Ni2	120.65(5)	C6	C7	C8	121.8(18)
$S2^1$	Ni3	Ni2	138.30(7)	C35	C34	C33	118.7(7)
$S2^1$	Ni3	$Ni1^1$	53.62(6)	C25	C26	C27	107.0(8)
$S2^1$	Ni3	S6	177.06(9)	C11	C12	C13	110.7(10)
$S1^1$	Ni3	Ni2	116.67(8)	C27	C28	C29	102.1(12)
$S1^1$	Ni3	$Ni1^1$	49.22(6)	C45	C44	C43	129.4(10)
$S1^1$	Ni3	$S2^1$	90.19(8)	C12	C13	C14	133.9(9)
$S1^1$	Ni3	S6	90.15(9)	C46	C45	C44	128.8(11)

S5	Ni3	Ni2	55.79(7)	C6	C5	C4	129.7(16)
S5	Ni3	Ni1[1]	122.30(8)	C45	C46	C47	106.0(11)
S5	Ni3	S2[1]	90.69(9)	C28	C29	C30	135.8(12)
S5	Ni3	S1[1]	166.42(9)	C31	C30	C29	123.6(14)
S5	Ni3	S6	89.66(9)	C27	C32	C31	136.8(11)
S6	Ni3	Ni2	43.66(6)	C46	C47	C48	125.3(10)
S6	Ni3	Ni1[1]	128.33(8)	C7	C8	C3	139.2(16)
Ni1	S4	Ni2	71.25(8)	C30	C31	C32	99.3(12)
C25	S4	Ni2	102.2(4)	C2	C1	S1	104.2(6)
C25	S4	Ni1	110.7(3)	C42	C41	S6	114.2(6)
Ni2	S3	Ni1	74.91(8)	C26	C25	S4	118.4(7)
Ni2	S3	C17	116.0(2)	C10	C9	S2	117.7(6)
C17	S3	Ni1	124.0(2)	C34	C33	S5	112.9(6)
Ni3[1]	S2	Ni1	73.72(8)	C11	C10	C9	121.6(7)
C9	S2	Ni1	125.4(3)	C18	C17	S3	119.5(6)
C9	S2	Ni3[1]	124.1(3)	C20	C19	C18	134.7(8)
Ni1	S1	Ni3[1]	77.96(8)	C24	C19	C18	123.8(7)
C1	S1	Ni1	96.7(4)	C24	C19	C20	101.5(8)
C1	S1	Ni3[1]	100.8(3)	C21	C20	C19	137.0(11)
Ni3	S5	Ni2	75.61(8)	C22	C21	C20	119.1(11)
C33	S5	Ni2	106.9(3)	C21	C22	C23	106.4(10)
C33	S5	Ni3	121.1(3)	C22	C23	C24	131.7(11)
Ni2	S6	Ni3	81.46(9)	C19	C24	C23	124.1(9)
Ni2	S6	C41	117.3(2)				

[1] -X,-Y,-Z

Table 5. Anisotropic displacement parameters ($Å^2×10^3$) for $Ni_6(PET)_{12}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni2	40.3(7)	40.6(7)	48.1(8)	1.7(6)	24.7(6)	0.0(6)
Ni1	39.6(7)	39.0(7)	44.5(7)	0.3(6)	21.7(6)	4.6(6)
Ni3	39.6(7)	37.9(7)	46.5(8)	1.4(6)	22.3(6)	1.1(6)
S4	39.9(10)	42.2(11)	46.8(11)	-1.7(8)	18.8(8)	1.3(8)
S3	42.0(11)	41.0(11)	49.8(11)	1.9(8)	18.6(9)	5.9(9)
S2	37.1(10)	38.6(10)	49.0(11)	1.8(8)	15.2(8)	0.6(8)
S1	40.8(10)	40.6(10)	44.7(10)	0.7(8)	15.6(8)	1.7(8)
S5	44.4(11)	41.8(11)	47.1(11)	2.5(8)	17.0(9)	0.3(9)
S6	43.9(11)	43.7(11)	49.2(11)	-1.9(9)	21.2(9)	-5.1(9)
C40	70(6)	59(6)	90(7)	14(5)	52(6)	9(5)
C11	50(5)	38(4)	59(5)	-4(4)	21(4)	-1(4)
C39	81(7)	55(6)	122(10)	9(6)	54(7)	23(6)
C16	51(5)	71(6)	56(5)	-12(5)	15(4)	0(5)
C38	78(8)	64(7)	143(12)	22(7)	55(8)	27(6)
C43	55(5)	57(5)	50(5)	-3(4)	25(4)	-7(4)
C37	133(12)	98(10)	144(13)	64(10)	93(11)	44(9)
C36	104(10)	102(10)	120(11)	49(8)	70(8)	56(8)
C48	85(7)	80(8)	62(6)	-16(5)	27(6)	5(6)
C35	43(5)	57(6)	74(6)	5(5)	26(4)	3(4)
C42	58(5)	52(5)	54(5)	-6(4)	28(4)	-4(4)
C18	60(6)	47(5)	64(6)	10(4)	23(5)	10(4)
C2	84(7)	57(6)	78(7)	11(5)	53(6)	0(5)
C27	75(7)	36(5)	72(6)	-8(4)	25(5)	0(5)
C4	88(8)	98(10)	75(8)	27(7)	25(7)	-11(7)
C14	94(9)	129(12)	54(6)	-18(7)	18(6)	-6(8)
C6	79(10)	360(30)	148(15)	188(15)	-19(11)	-66(13)
C15	63(6)	107(10)	65(7)	-12(6)	12(5)	0(6)
C3	59(6)	82(8)	74(7)	37(6)	33(5)	3(6)
C7	91(12)	270(20)	220(20)	168(16)	65(10)	67(16)
C34	53(5)	44(5)	84(7)	4(5)	28(5)	-1(4)
C26	70(6)	33(4)	82(7)	-7(4)	28(5)	6(4)
C12	58(6)	84(8)	61(6)	-11(5)	24(5)	10(5)
C28	87(8)	74(8)	92(9)	-5(6)	46(7)	0(6)
C44	90(8)	77(7)	60(6)	-3(5)	38(6)	10(6)
C13	80(8)	109(10)	66(7)	-20(6)	37(6)	1(7)
C45	79(7)	94(9)	60(6)	12(6)	28(6)	17(6)
C5	153(14)	169(17)	77(9)	51(10)	-1(10)	-75(12)

C46	74(7)	103(10)	74(8)	12(7)	8(6)	5(7)
C29	138(13)	100(11)	88(10)	-1(8)	62(9)	4(10)
C30	197(19)	83(10)	78(9)	1(7)	52(11)	12(11)
C32	89(8)	66(7)	80(8)	-8(6)	19(6)	16(6)
C47	112(10)	109(10)	55(6)	-22(7)	25(7)	-8(9)
C8	117(11)	136(13)	129(11)	64(9)	81(8)	45(10)
C31	128(12)	85(10)	99(10)	-12(8)	0(9)	26(9)
C1	50(5)	66(6)	53(5)	4(4)	25(4)	5(4)
C41	47(5)	55(5)	49(5)	-3(4)	26(4)	-7(4)
C25	72(6)	39(5)	69(6)	-6(4)	36(5)	-7(4)
C9	46(5)	37(4)	61(5)	4(4)	17(4)	-1(4)
C33	56(5)	40(5)	63(5)	3(4)	31(4)	7(4)
C10	53(5)	46(5)	57(5)	3(4)	19(4)	-6(4)
C17	43(4)	47(5)	55(5)	-1(4)	21(4)	4(4)
C19	50(5)	67(6)	54(5)	2(4)	24(4)	15(5)
C20	64(6)	113(10)	51(6)	15(6)	14(5)	25(6)
C21	92(9)	140(11)	60(7)	25(8)	25(7)	38(7)
C22	55(7)	157(12)	88(9)	-38(9)	10(6)	9(7)
C23	58(6)	110(10)	70(7)	-9(7)	18(6)	1(6)
C24	57(6)	75(7)	61(6)	2(5)	24(5)	12(5)

Table 6. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $Ni_6(PET)_{12}$.

Atom	*x*	*y*	*z*	U(eq)
H40	-6392	3653	-145	87
H39	-7402	5100	-313	102
H16	7136	1711	1119	71
H38	-7123	6201	-861	113
H37	-5628	5550	-1269	148
H36	-4577	4139	-1083	129
H48	692	2196	2241	90
H42A	-589	960	1456	65
H42B	-293	2167	1514	65
H18A	-1856	3299	-1293	68
H18B	-2608	3027	-920	68
H2A	3058	2180	-1416	86
H2B	2159	2524	-1092	86
H4	1614	529	-1927	104
H14	6301	1940	2240	110
H6	-1273	1791	-2516	234
H15	7781	1803	1806	94
H7	-1069	3184	-2016	229
H34A	-4420	2258	-712	72
H34B	-5089	2205	-303	72
H26A	233	4276	439	73
H26B	1145	5211	393	73
H12	3684	1803	1274	81
H28	-355	4581	997	100
H44	2010	-65	1595	90
H13	4341	1946	1952	101
H45	3231	-522	2096	93
H5	231	526	-2414	160
H46	3389	268	2736	100
H29	71	4595	1701	129
H30	1717	4195	2053	142
H32	3137	4084	1011	93
H47	2056	1716	2779	110
H8	333	3169	-1553	151
H31	3588	4085	1729	125
H1A	3272	1122	-813	67
H1B	2965	384	-1191	67

H41A	737	843	980	60
H41B	1037	2053	1039	60
H25A	2571	3986	341	71
H25B	1654	3999	-23	71
H9A	3310	631	684	57
H9B	4419	22	538	57
H33A	-3462	2956	82	63
H33B	-2872	3393	-311	63
H10A	5465	1661	478	62
H10B	4352	2301	596	62
H17A	-723	1756	-1204	57
H17B	-1562	1319	-875	57
H20	-3507	3381	-1903	91
H21	-5043	2933	-2302	116
H22	-6097	1296	-2167	120
H23	-5300	459	-1583	95
H24	-3747	950	-1196	77

Supporting figures

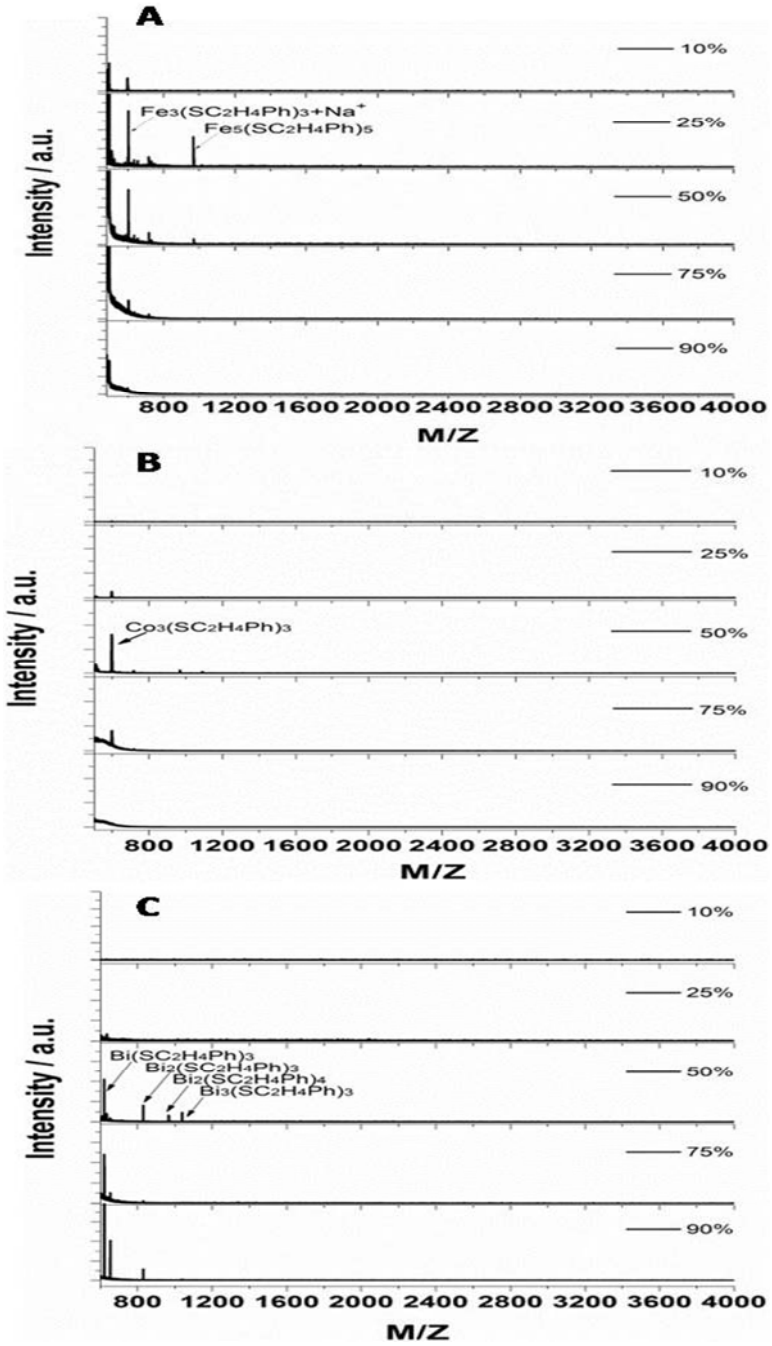

Figure.S1 MALDI-TOF-MS of M-SCH_2CH_2Ph complex (acquired in various laser intensity). (A) M:Fe; (B) M:Co; (C) M:Bi.

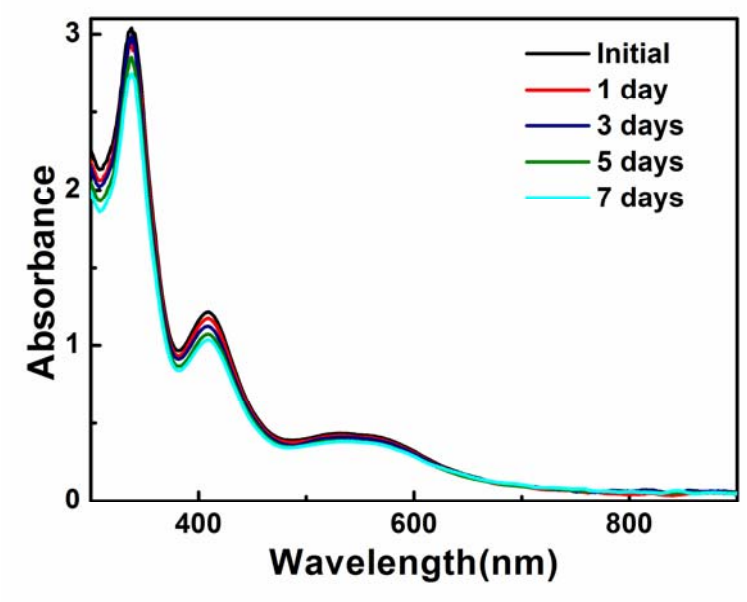

Figure.S2. UV-Vis spectra of $Ni_6(PET)_{12}$ in CH_2Cl_2 recorded at RT over seven days.

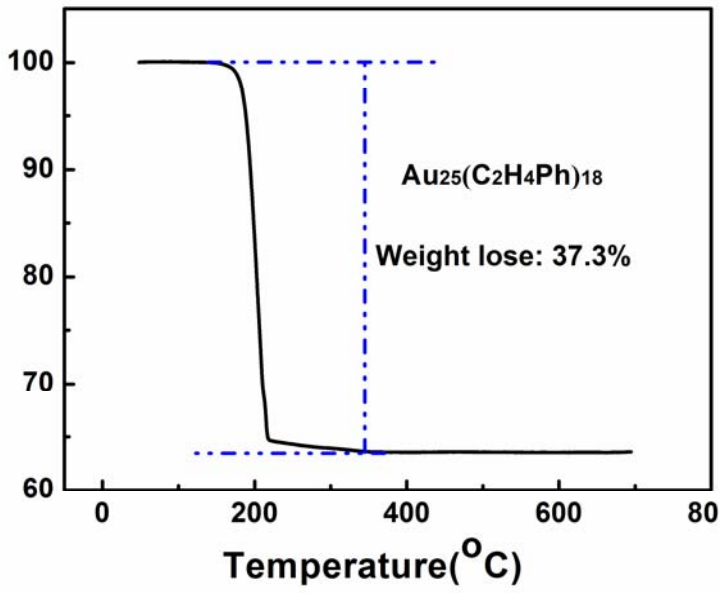

Figure.S3 Thermogravimetric analysis (N_2 atmosphere, 10 ^oC min^{-1}) of $Au_{25}(SCH_2CH_2Ph)_{18}$.

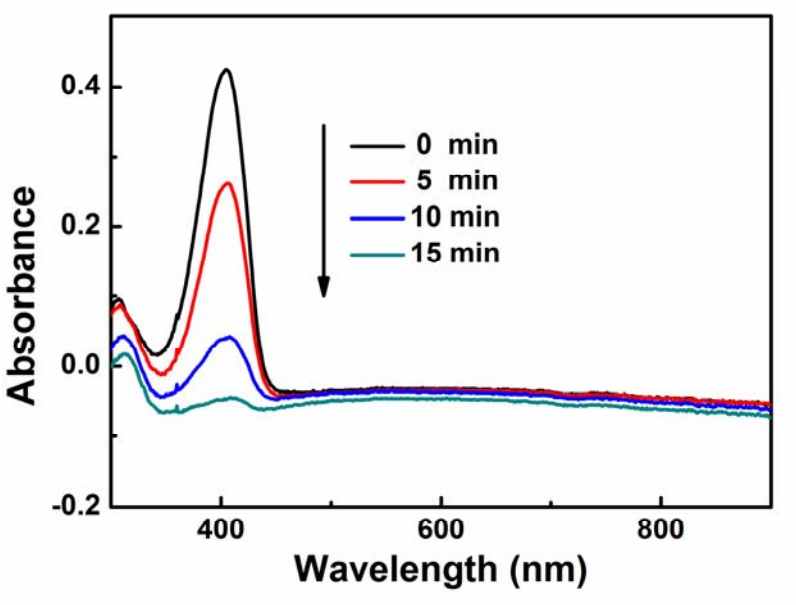

Figure.S4 UV/Vis/NIR spectra monitoring the reduction of 4-nitrophenol to 4-aminophenol catalyzed by $Ni_6(PET)_{12}$ at room temperature.