Supporting Information

Supporting Information for the paper entitled "Nonresonant Chemical Mechanism in Surface-Enhanced Raman Scattering of Pyridine on M@Au_{12} Clusters" by Lei Chen, Yang Gao, Y. K. Cheng, Haichao Li, Zhigang Wang, Zhengqiang Li, and Rui-Qin Zhang.

1. Part 1: The calculations of the HOMO-LUMO gap for neutral metal clusters (Cr@Au_{12}, Mo@Au_{12} and W@Au_{12}), metal clusters carrying one unit of positive charge (Mn@Au+ 12, Tc@Au+ 12 and Re@Au+ 12), and metal clusters carrying one unit of negative charge (V@Au- 12, Nb@Au- 12 and Ta@Au- 12).
2. Part 2: The DOS spectra for neutral metal clusters (Cr@Au_{12}, Mo@Au_{12} and W@Au_{12}), metal clusters carrying one unit of positive charge (Mn@Au+ 12, Tc@Au+ 12 and Re@Au+ 12), and metal clusters carrying one unit of negative charge (V@Au- 12, Nb@Au- 12 and Ta@Au- 12).
3. Part 3: The Au-N vibrational frequencies of pyridine on different charged metal clusters without scale factor at the BP86/6-311+G(d, p) (C, N, H) /ECP-Lanl2DZ (metal atoms) level
4. Part 4: Cartesian coordinates (in Å) of pyridine on metal clusters (Cr@Au_{12}, Mo@Au_{12}, W@Au_{12}, Mn@Au+ 12, Tc@Au+ 12, Re@Au+ 12, V@Au- 12, Nb@Au- 12 and Ta@Au- 12) obtained using BP86.

Part 1

Gold and doped gold clusters have attracted increasing research interest, primarily prompted by the discovery of their unique properties in terms of surface analysis, biological and chemical sensors, biomedical detection, and so on. The chemistry of gold is dominated by its strong relativistic effects and the so-called aurophilic attraction, which can lead to highly unusual structures for gold clusters and compounds compared to those for copper and silver. Despite the fact that the bare 13-atom gold cluster anion has been shown not to possess a high-symmetry icosahedral structure, a series of M@Au 12 (Ta^-, W, Re^+) clusters have been reported theoretically to form highly stable gold clusters containing an icosahedral Au 12 cage and a central heteroatom. Shortly afterward, Wang and colleagues successfully produced some of these M@Au 12 (W, Mo, V^-, Nb^-, Ta^-) clusters experimentally, revealing a the closed-shell electronic structure through the observation of a large energy gap in the PES spectra. However, the positively charged $M@Au_{12}$ ($M = Mn^+$, Tc^+, Re^+) means that it cannot be characterized experimentally using ultraviolet PES due to its very high electron binding energy. We adopted nine metal clusters with different core atoms, including neutral metal clusters ($Cr@Au_{12}$, $Mo@Au_{12}$ and $W@Au_{12}$), metal clusters carrying one unit of positive charge (Mn@Au+ 12, Tc@Au+ 12 and Re@Au+ 12), and metal clusters carrying one unit of negative charge (V@Au- 12, Nb@Au- 12 and Ta@Au- 12). The cluster model was a series of icosahedral Au_{12} gold nanocages containing a central heteroatom. All calculations were performed using DFT methods implemented with the Gaussian09 package. The geometric optimizations and vibrational analysis of all the clusters was carried out using the Becke-Perdew (BP86) functional, which has been shown to provide an adequate description of the interaction of transition metal-organic molecule complexes and yielded harmonic frequencies close to the experimental results without the need for scaling factors. All the metal atoms were described by the basis function LANL2DZ for the valence electrons and internal shells. Vibrational frequency analysis was performed on the basis of the optimized geometries and showed that all the electronic ground states were stable.

Table S1. The HOMO-LUMO gaps for the $M@Au_{12}$ ($M=V^-$, Nb^-, Ta^-, Cr, Mo, W, Mn^+, Tc^+, Re^+) bare metal clusters.

		HOMO	LUMO	Ban gap	Exp
Anion	V@Au- 12	-2.114	-0.866	1.25	1.29[1]
	Nb@Au- 12	-2.193	-0.298	1.89	1.26[1]
	Ta@Au- 12	-2.193	-0.323	1.87	1.29[1]
Neutral	Cr@Au 12	-5.553	-4.456	1.10	
	Mo@Au 12	-5.607	-4.028	1.58	1.48[2]
	W@Au 12	-5.610	-3.811	1.80	1.68[2]
Cation	Mn@Au+ 12	-9.106	-8.026	1.08	
	Tc@Au+ 12	-9.164	-7.689	1.48	
	Re@Au+ 12	-9.160	-7.538	1.62	

From Table S1, the band gap analysis shows that all the metal clusters exhibited a large gap from 1.10 eV to 1.90 eV, and the theoretical prediction of the band gaps of V@Au- 12, Mo@Au 12, and W@Au 12 agree well with experimental observations [1, 2]. Although our calculation of the Nb@Au- 12 and Ta@Au- 12 clusters are about 0.6 eV higher than found by PES observation, these results are consistent with previous DFT predictions at the PW91/TZ2P/ZORA level from Wang and colleagues [1].

Part 2

The DOS spectra of the bare metal clusters $M@Au_{12}$($M=V^-$, Nb^-, Ta^-, Cr, Mo, W, Mn^+, Tc^+, Re^+) clearly show that the occupied molecular orbitals of the neutral clusters are distributed in the range -10 eV to -7 eV. However, in comparison, the occupied molecular orbitals of the positively charged clusters shift to a lower energy region due to the loss of an electron in the center of the cluster, making the electron density more compact than that of the neutral clusters. This effect is combined with the shift in the occupied molecular orbitals to a lower energy region, from -14 eV to -8 eV. For the negatively charged clusters, the electron density is looser than that of the neutral adsorption systems due to the reception of an electron in the center of the cluster, which results in the occupied molecular orbitals shifting to a higher energy region (from -6 eV to -2 eV).

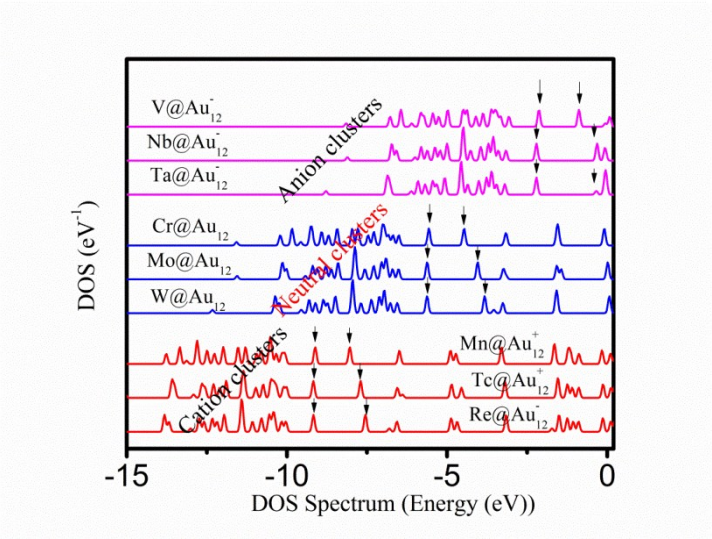

Figure S1. The DOS graphs of $M@Au_{12}$($M=V^-$, Nb^-, Ta^-, Cr, Mo, W, Mn^+, Tc^+, Re^+). The arrows represent the positions of the HOMO and LUMO.

Part 3

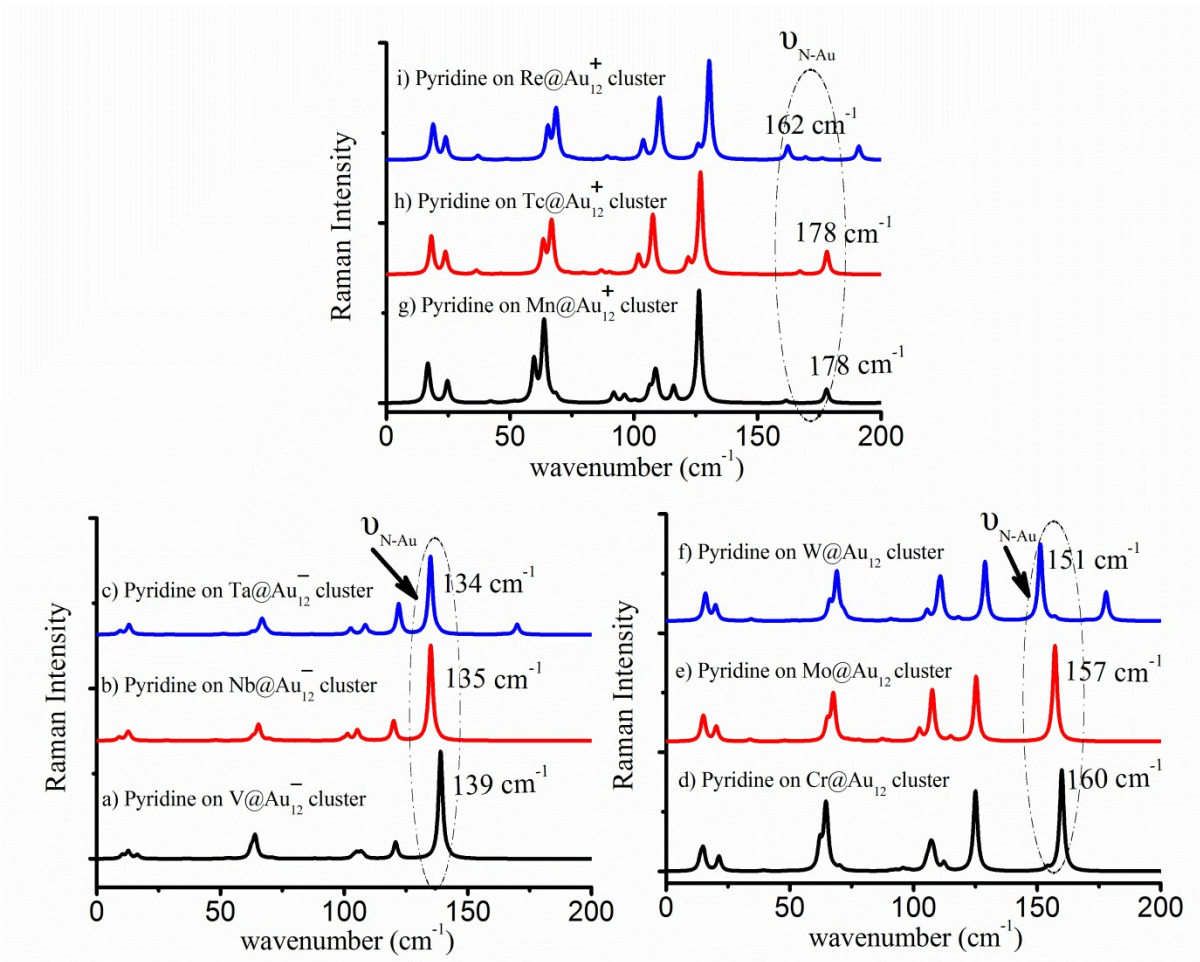

Figure S2. The Au-N vibrational frequencies of pyridine on different charged metal clusters without scale factor at the BP86/6-311+G(d, p) (C, N, H) /ECP-Lanl2DZ (metal atoms) level

Our calculation indicates that the N-Au vibrational frequencies distribute from 134 to 178 cm^{-1} when pyridine molecules interact with different charged metal clusters, and the Raman spectra of pyridine on cation clusters, neutral clusters and anion clusters are listed in Figure S3 in the range of 0-200 cm^{-1}. It is obvious that the our calculated values are smaller than the experimental value 260 cm^{-1} of pyridine adsorbed on gold surface (J. Chem. Soc., Faraday Trans. 2 1979, 75, 790), but these results are in agreement with the frequencies of pyridine on Au_2 cluster with the value of 137 cm^{-1} (J. Chem. Phys., 2003, 118, 4073-4085). This is due to the DFT method can give more accurate prediction of high frequencies of vibrational modes compared to the low frequencies. We note that the N-Au vibrational frequencies of pyridine on cation clusters vary in 162-178 cm^{-1}, which are obviously larger than that of pyridine on neutral and anion metal clusters. This phenomenon can be ascribed to the strong Au-H bonding interaction in complexes of pyridine on cation clusters.

Part 4

Cartesian coordinates (in Å) of pyridine on metal clusters ($Cr@Au_{12}$, $Mo@Au_{12}$, $W@Au_{12}$, Mn@Au+ 12, Tc@Au+ 12, Re@Au+ 12, V@Au- 12, Nb@Au- 12 and Ta@Au- 12) obtained using BP86.

V@Au- 12 -Py

1 Au	1.50037	1.096155	2.199894
2 Au	-0.96585	2.201274	1.135348
3 Au	-2.48869	0.008588	-0.0054
4 Au	-0.9791	-2.44523	0.364778
5 Au	1.49422	-1.75611	1.72516
6 Au	-0.97379	-0.40285	2.436034
7 Au	3.035836	-0.00867	0.006006
8 Au	1.500861	-2.1842	-1.1289
9 Au	-0.96762	-1.10365	-2.21271
10 Au	-0.96031	1.769049	-1.73593
11 Au	1.514476	2.425363	-0.36256
12 Au	1.506321	0.400237	-2.4217
13 V	0.226537	0.000123	-0.00017
14 C	-5.44659	-1.15858	-0.00802
15 C	-5.45441	1.163368	0.006391
16 C	-6.85151	1.201393	0.008558
17 C	-7.56364	-0.00461	0.001807
18 C	-6.84341	-1.20579	-0.00661
19 H	-4.83533	-2.06492	-0.01423
20 H	-4.84991	2.074133	0.01157
21 H	-7.36622	2.16515	0.015597
22 H	-8.65686	-0.0083	0.003204
23 H	-7.35174	-2.17293	-0.01195
24 N	-4.75909	0.004761	-0.00223

Nb@Au- 12 -Py

1 Au	1.516717	1.115264	2.234828
2 Au	-0.98562	2.233271	1.151764
3 Au	-2.52842	0.008118	-0.0035
4 Au	-0.99885	-2.48009	0.372503
5 Au	1.508083	-1.78411	1.755009
6 Au	-0.99188	-0.40617	2.473358
7 Au	3.080014	-0.00879	0.00465
8 Au	1.512821	-2.22127	-1.1472
9 Au	-0.9886	-1.11923	-2.24488
10 Au	-0.98055	1.792275	-1.76324
11 Au	1.526284	2.465778	-0.37088
12 Au	1.521321	0.404902	-2.4623
13 Nb	0.246342	-2.2E-05	0.000019
14 C	-5.51492	-1.15738	-0.01109
15 C	-5.52281	1.162396	0.010058
16 C	-6.92042	1.201529	0.011246
17 C	-7.6322	-0.00459	0.000431
18 C	-6.91222	-1.20584	-0.01088
19 H	-4.90423	-2.06436	-0.01985
20 H	-4.91891	2.073833	0.018149
21 H	-7.43542	2.165157	0.020511
22 H	-8.72547	-0.00831	0.000944
23 H	-7.42076	-2.17289	-0.01956
24 N	-4.82774	0.004874	-0.00117

Ta@Au- 12 -Py

1 Au	1.504295	-1.11441	-2.2302
2 Au	-0.98836	-2.22859	-1.1486
3 Au	-2.52473	-0.00792	0.002874
4 Au	-1.00131	2.474597	-0.37309
5 Au	1.495886	1.780296	-1.75244
6 Au	-0.99498	0.40439	-2.46748
7 Au	3.062884	0.008501	-0.00409
8 Au	1.499445	2.218169	1.144813
9 Au	-0.99247	1.117523	2.238568
10 Au	-0.98446	-1.78708	1.75957
11 Au	1.5125	-2.46209	0.371779
12 Au	1.508193	-0.40335	2.45828
13 Ta	0.242604	0.000075	-6.4E-05
14 C	-5.5186	1.157157	0.011119
15 C	-5.52627	-1.16224	-0.01089
16 C	-6.92394	-1.20171	-0.01153
17 C	-7.63575	0.004354	0.000043
18 C	-6.91596	1.205685	0.011484
19 H	-4.90795	2.064206	0.019954
20 H	-4.92226	-2.07364	-0.01958
21 H	-7.43894	-2.16534	-0.02096
22 H	-8.72904	0.007968	0.000005
23 H	-7.42468	2.172638	0.020723
24 N	-4.83125	-0.00485	0.000552

$Cr@Au_{12}$-Py

1 Au	1.50004	-1.08874	-2.1839
2 Au	-0.96727	-2.18273	-1.13077
3 Au	-2.50922	-0.00363	0.002445
4 Au	-0.97107	2.429883	-0.36313
5 Au	1.499831	1.740052	-1.71143
6 Au	-0.97254	0.403556	-2.42215
7 Au	3.038456	0.002931	-0.00234
8 Au	1.503547	2.164439	1.123532
9 Au	-0.96965	1.097809	2.198102
10 Au	-0.9661	-1.75482	1.723255
11 Au	1.508729	-2.4092	0.360706
12 Au	1.501427	-0.4001	2.406247
13 Cr	0.216539	-0.0001	0.000229
14 C	-5.41013	1.163868	0.003637
15 C	-5.41368	-1.16378	-0.0062
16 C	-6.80956	-1.20159	-0.00648
17 C	-7.52206	0.003155	-0.00119
18 C	-6.8059	1.205739	0.003885
19 H	-4.8065	2.073885	0.007444
20 H	-4.81316	-2.07581	-0.01019
21 H	-7.32224	-2.16555	-0.01089
22 H	-8.61465	0.004828	-0.00113
23 H	-7.31576	2.171196	0.007931
24 N	-4.72216	-0.00103	-0.00074

Mo@Au_{12}-Py				W@Au_{12}-Py			
1 Au	1.513823	1.104365	2.209872	1 Au	1.502701	1.104315	2.206808
2 Au	-0.98485	2.213511	1.150287	2 Au	-0.98851	2.210346	1.148685
3 Au	-2.54371	-0.00051	0.002848	3 Au	-2.53853	-0.0012	0.003609
4 Au	-0.98359	-2.46797	0.371942	4 Au	-0.98608	-2.46511	0.372711
5 Au	1.515723	-1.76025	1.732343	5 Au	1.504956	-1.7577	1.730719
6 Au	-0.98384	-0.41034	2.460631	6 Au	-0.98692	-0.40942	2.457318
7 Au	3.072516	0.00135	-0.00317	7 Au	3.057373	0.002201	-0.00406
8 Au	1.514183	-2.19111	-1.14025	8 Au	1.502427	-2.18909	-1.139
9 Au	-0.98851	-1.11522	-2.2288	9 Au	-0.99263	-1.11456	-2.22458
10 Au	-0.98777	1.778058	-1.74786	10 Au	-0.99245	1.774525	-1.74558
11 Au	1.513988	2.442321	-0.36838	11 Au	1.500762	2.440631	-0.36922
12 Au	1.508104	0.406093	-2.4398	12 Au	1.495879	0.40542	-2.43777
13 Mo	0.223499	-0.00021	0.000109	13 W	0.219349	-0.00026	0.000132
14 C	-5.45505	-1.16351	-0.00597	14 C	-5.45469	-1.1633	-0.00664
15 C	-5.45498	1.162644	0.010238	15 C	-5.4538	1.162262	0.011619
16 C	-6.85096	1.203368	0.007686	16 C	-6.84976	1.20372	0.008222
17 C	-7.56529	-0.00029	-0.0024	17 C	-7.5646	0.000389	-0.00342
18 C	-6.85104	-1.20402	-0.00926	18 C	-6.8507	-1.20353	-0.01083
19 H	-4.85296	-2.0747	-0.01146	19 H	-4.85305	-2.0748	-0.01252
20 H	-4.85311	2.073943	0.017702	20 H	-4.85171	2.073433	0.020298
21 H	-7.36244	2.167981	0.013466	21 H	-7.36087	2.168519	0.014548
22 H	-8.65792	-0.00024	-0.00479	22 H	-8.65722	0.000842	-0.00654
23 H	-7.36266	-2.16854	-0.01723	23 H	-7.36264	-2.16786	-0.01996
24 N	-4.76476	-0.00048	0.003338	24 N	-4.76352	-0.00081	0.004053

Mn@Au+ 12-Py				Tc@Au+ 12-Py			
1 Au	1.500338	-1.07386	-2.17803	1 Au	1.513783	1.092291	2.203609
2 Au	-0.96713	-2.16323	-1.13465	2 Au	-0.98416	2.201387	1.151277
3 Au	-2.53851	-0.0021	0.002117	3 Au	-2.57149	-0.00062	0.001461
4 Au	-0.96771	2.41703	-0.35109	4 Au	-0.98174	-2.45865	0.363179
5 Au	1.50193	1.737171	-1.69561	5 Au	1.517018	-1.75536	1.720211
6 Au	-0.97099	0.412511	-2.40735	6 Au	-0.98677	-0.41572	2.449714
7 Au	3.049594	0.001115	-0.00191	7 Au	3.079936	0.001519	-0.00182
8 Au	1.504821	2.147307	1.12821	8 Au	1.517012	-2.17654	-1.14039
9 Au	-0.96848	1.081765	2.190794	9 Au	-0.98824	-1.10481	-2.22434
10 Au	-0.96668	-1.75037	1.706312	10 Au	-0.98721	1.775681	-1.73684
11 Au	1.507208	-2.399	0.348949	11 Au	1.516792	2.430558	-0.3595
12 Au	1.501623	-0.40911	2.392997	12 Au	1.510287	0.410629	-2.42688
13 Mn	0.22212	-0.00012	0.000201	13 Tc	0.216863	-0.00012	0.000017
14 C	-5.40036	1.168058	0.005715	14 C	-5.4337	-1.16726	-0.00624
15 C	-5.40283	-1.16653	-0.00868	15 C	-5.43347	1.165914	0.009088
16 C	-6.79746	-1.20202	-0.0093	16 C	-6.82811	1.203628	0.007966
17 C	-7.50944	0.00293	-0.00173	17 C	-7.54162	-0.0004	-0.00086
18 C	-6.79491	1.206381	0.00578	18 C	-6.82836	-1.20459	-0.00804
19 H	-4.80274	2.081077	0.011738	19 H	-4.83717	-2.08106	-0.01209
20 H	-4.80735	-2.08094	-0.01416	20 H	-4.83694	2.079715	0.015499
21 H	-7.30977	-2.16578	-0.01557	21 H	-7.33943	2.167888	0.013896
22 H	-8.60171	0.004098	-0.00182	22 H	-8.63389	-0.00029	-0.00207
23 H	-7.30527	2.171172	0.011757	23 H	-7.33994	-2.16869	-0.0151
24 N	-4.71302	0.000048	-0.00101	24 N	-4.74408	-0.00077	0.001969

Re@Au+ 12-Py

1 Au	1.506379	1.098468	2.199416
2 Au	-0.99063	2.203645	1.147356
3 Au	-2.57105	-0.00223	0.003256
4 Au	-0.98542	-2.45925	0.370448
5 Au	1.510838	-1.74998	1.723385
6 Au	-0.99075	-0.41044	2.451741
7 Au	3.070604	0.0036	-0.00407
8 Au	1.508812	-2.17824	-1.1358
9 Au	-0.9952	-1.11136	-2.22073
10 Au	-0.99544	1.770624	-1.74081
11 Au	1.505331	2.43043	-0.36642
12 Au	1.499687	0.405326	-2.42829
13 Re	0.210616	-0.00027	0.000123
14 C	-5.43422	-1.16746	-0.00481
15 C	-5.4326	1.165145	0.009118
16 C	-6.82719	1.203871	0.006844
17 C	-7.54158	0.000379	-0.00183
18 C	-6.82888	-1.20413	-0.00768
19 H	-4.83834	-2.08169	-0.00962
20 H	-4.83561	2.078646	0.015459
21 H	-7.33792	2.168453	0.01177
22 H	-8.63385	0.001155	-0.00393
23 H	-7.34102	-2.16795	-0.01452
24 N	-4.74322	-0.00168	0.00323

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