Supporting Information
Surface Functionalization: An Efficient Alternative for Promoting the Catalytic Activity of Closed Shell Gold Clusters

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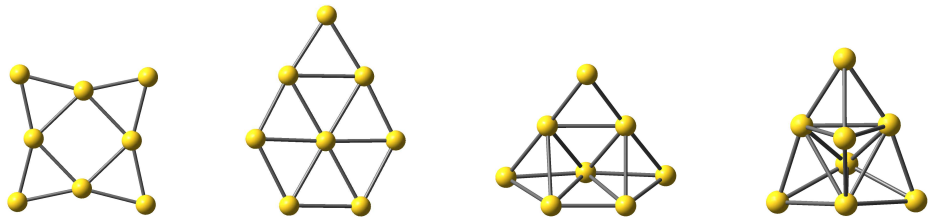

1	2	3	4
0.00 eV (0.00 eV)	**0.21 eV (0.06 eV)**	**0.86 eV (0.14 eV)**	**0.89 eV (0.31 eV)**
0.00 eV (0.00 eV)	**0.39 eV (0.35 eV)**	**0.46 eV (0.55 eV)**	**0.53 eV (0.57 eV)**

Figure S1

Low laying conformations of $Au_8^{-/0}$ cluster. The energy values given below the images represents: red for anion, blue for neutral. The values in parenthesis are from previous combined experimental and theoretical studies (*Z. Phys. Chem.*, 2014; **228**, 337–350, *J. Am. Chem. Soc.*, 2009, **131**, 10605–10609, *J. Phys. Chem. A*, 2003, **107**, 6168–6175).

Table S1: Au-Au bond distance, vertical ionization potential (VIP) and vertical electron affinity (VEA) of Au_2 cluster with respect to earlier theoretical and experimental studies.

Method	**(Au-Au) Å**	**VIP (eV)**	**VEA (eV)**
PBE/LANL2DZ	2.55	9.58	1.99
R-CCSD(T)[a]	2.51	9.15	1.83
Expt.[b]	2.47	9.50	1.94

(a). R. Wesendrup, T. Hunt, and P. Schwerdfeger, J. Chem. Phys. 2000, **112**, *9356*

(b), K. P. Huber and G. Herzberg, Constants of Diatomic Molecules Van Nostrand Reinhold, New York, 1979. R. N. Barnett, C. I. Cleveland, H. Häkkinen, W. D. Luedtke, C. Yamouleas, and U. Landsman, Eur. Phys. J. D, 1999, **9**, *95–104.*

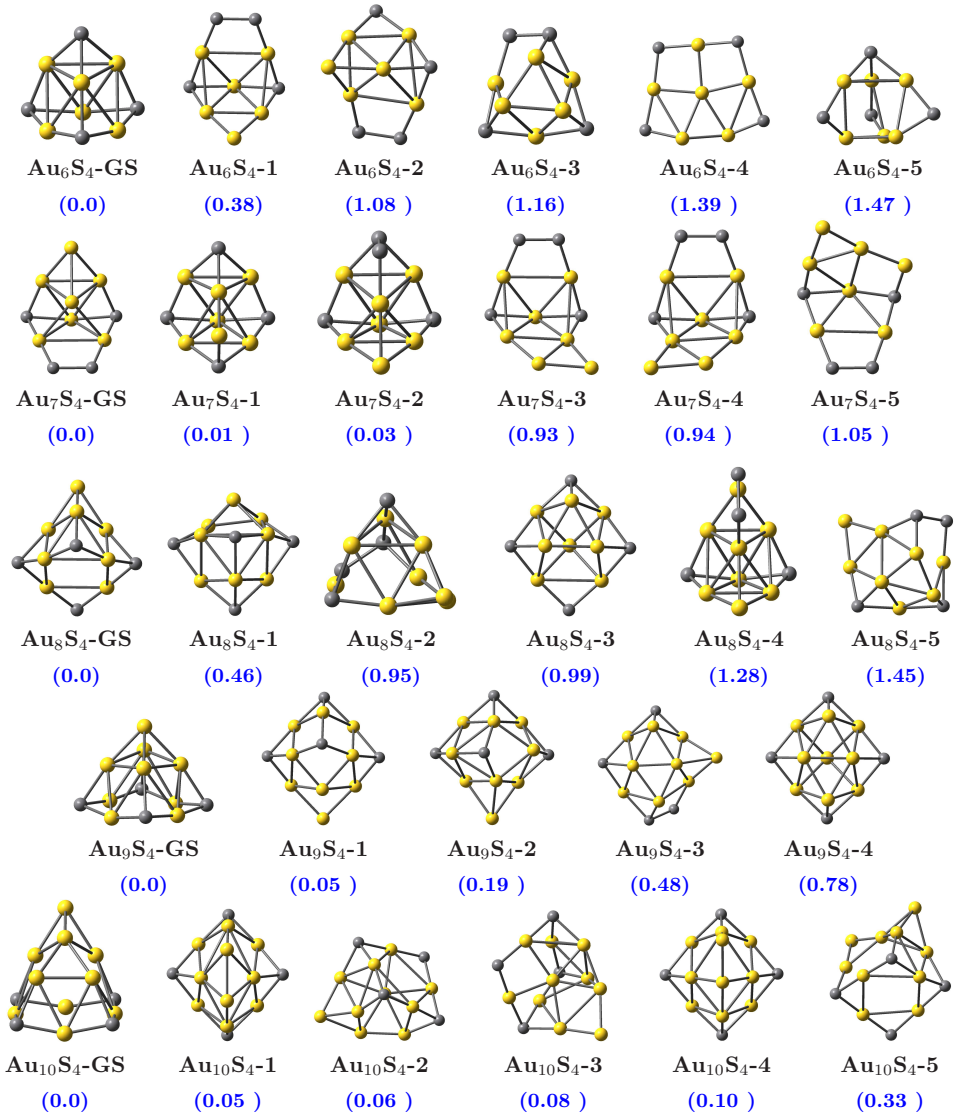

Figure S2
Low laying configurations of $Au_mS_4^-$ (m = 6 - 10) clusters. The values below the images in blue colour represents reative energy in eV.

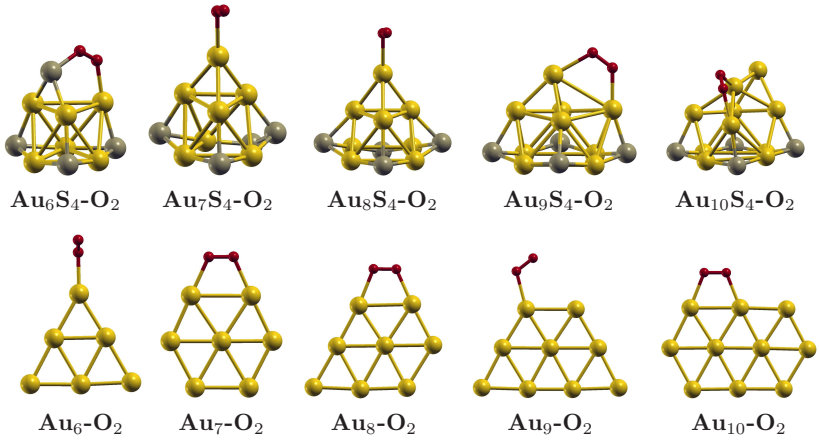

Figure S3
Lowest energy configurations of O_2 adsorbed $Au_mS_4^-$ (m = 6 - 10) and Au_n^- (n = 6 - 10) clusters.

Table S2: Oxygen binding energies (BE (O_2)), O-O bond distances (BL (O-O)) and O-O bond stretching frequencies (ν (O-O)) for $Au_mS_4^-$ (m = 6 - 10) and Au_n^- (n = 6 - 10) clusters

$Au_mS_4^-$	BE (O_2) (eV)	BL (O-O) Å	ν (O-O) cm^{-1}	Au_n^-	BE (O_2) (eV)	BL (O-O) Å	ν (O-O) cm^{-1}
$Au_6S_4^-$	-0.34	1.36	860	Au_6^-	-0.95	1.30	1145
$Au_7S_4^-$	-0.25	1.26	1301	Au_7^-	-0.81	1.32	1068
$Au_8S_4^-$	-0.17	1.25	1308	Au_8^-	-0.71	1.33	1073
$Au_9S_4^-$	-0.19	1.31	1087	Au_9^-	-0.30	1.27	1265
$Au_{10}S_4^-$	-0.27	1.33	1037	Au_{10}^-	-0.76	1.32	1081

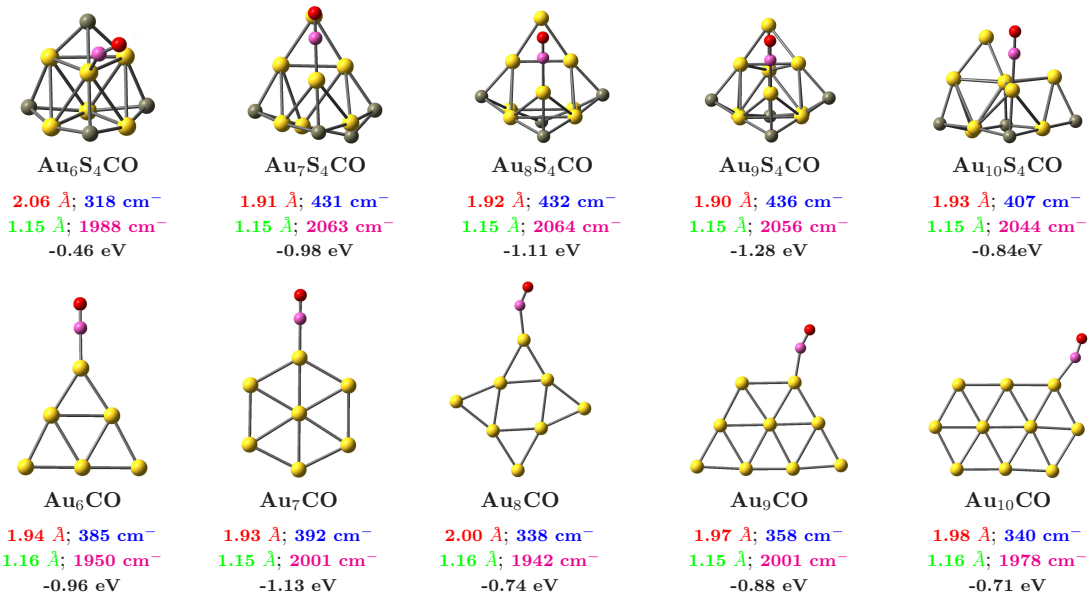

Figure S4

Lowest energy configurations of CO adsorbed $Au_mS_4^-$ (m = 6 - 10) and Au_n^- (n = 6 - 10) clusters. The values presented below the images represent; Au-C and C-O bond distances (red, green), Au-C and C-O bond stretching frequencies (blue, magenta) and CO binding energy (black).

Table S3: First [E_{a1}] and second [E_{a2}] CO activation barriers for $Au_mS_4^-$ (m = 6 - 10) and Au_n^- (n = 6 - 10) clusters calculated using TPSS functional.

$Au_mS_4^-$	$Au_6S_4^-$	$Au_7S_4^-$	$Au_8S_4^-$	$Au_9S_4^-$	$Au_{10}S_4^-$
E_{a1} (eV)	0.70	0.04	0.40	0.33	0.12
E_{a2} (eV)	0.22	0.24	0.30	0.26	0.48
Au_n^-	Au_6^-	Au_7^-	Au_8^-	Au_9^-	Au_{10}^-
E_{a1} (eV)	0.58	0.31	0.02	0.29	0.11
E_{a2} (eV)	0.25	0.21	0.50	0.32	0.44

Cartesian coordinates of transition states [TS(1)] and [TS(2)] of $Au_mS_4^-$ clusters:

$Au_6S_4^-$: [TS(1)]

S -1.14297400 -0.66330100 2.68914600
Au 0.31081800 1.00971900 1.92011300
Au -0.74353000 -1.12675000 -1.76207000
S 1.12078600 -2.51850000 -1.09098900
Au 0.15557600 -1.91131700 1.05098800
Au -2.28665200 -0.04795900 0.63496300
S -2.60295800 0.44328100 -1.72489300
Au -0.80462300 1.91674500 -1.14304500
S 1.12894800 3.12288100 -0.76167700
O 1.66520500 2.46385800 0.86799500
O 3.00239900 2.28236900 0.98866600
Au 2.41510700 -0.57528400 -0.64268700
C 3.79142900 0.80235600 -0.31847100
O 4.89508400 1.13988300 -0.41631300

$Au_6S_4^-$:[TS(2)]

S 1.12672500 0.65240100 2.56110700
S 1.42821500 -1.92352500 -1.52178200
Au 0.61509900 0.42704600 -1.86774900
S -0.59697000 2.51914200 -1.45895300
Au 0.32455300 2.07623800 0.75771400
Au -0.97514500 -0.44313900 1.94760300
S -2.76548800 -1.26723800 0.49103400
Au -0.80560000 -2.05857200 -0.67018200
Au -2.08968000 0.76036300 -0.68949400
O 2.56326700 1.17909600 -1.58255100
O 3.91003100 0.35028000 -0.90489700
Au 1.69373500 -0.78759900 0.66642000
C 3.74017000 -0.38776500 0.12607300
O 4.55235800 -0.94668300 0.82499000

$Au_7S_4^-$: [TS(1)]

Au -0.66549400 -0.60303900 1.55658800
S 1.41177100 2.33206100 -2.64908600
S 0.37483600 3.35802900 -1.18029300
S 0.91498400 0.78473300 2.77760300
Au 0.53629600 2.10665800 0.80881600
Au 2.15673700 0.29946500 -1.75693200
S 2.90386900 -1.72635300 -0.73785000
Au 2.28721400 -0.47109700 1.22269600
Au 0.47784500 -2.09652300 -0.66955800
Au -2.14121600 -1.73142200 -0.38714100
O -4.34510300 -0.98937300 -0.72357400
O -4.66076600 0.11378500 -1.38534500
Au -2.12881600 1.25767400 0.01613200
O -4.46393200 2.45776700 -1.39422300
C -3.86861300 1.53192900 -0.96636300

$Au_7S_4^-$: [TS(2)]

Au -0.24350800 -1.33582800 1.44730400
S -3.62490300 -0.32843300 1.78504600

S -1.80241000 -0.04707900 2.84690500
S 0.57273700 2.95719300 -0.03459600
Au -0.60189900 1.60221000 1.54295600
Au -2.90560600 -0.22872700 -0.44544700
S -1.85907800 -0.28486600 -2.59782700
Au -0.59555200 1.49097700 -1.53783000
Au -0.18346700 -1.49564700 -1.35098300
Au 2.01796300 -1.94787900 0.14987900
O 3.56829900 -0.63684300 -0.74841000
O 4.73212100 -0.03945900 0.23785100
Au 2.22727100 1.23303700 -0.32869600
C 4.23848300 1.12457200 0.56216400
O 4.76040200 1.97257800 1.25270000

$Au_8S_4^-$: [TS(1)]

S -1.14858400 -2.96753000 0.32318100
Au -3.02684800 -1.52824300 0.07931600
S -4.60901900 0.12595000 -0.29216100
Au -2.84339500 1.64864400 -0.14944300
S -0.92282600 3.00132800 -0.19167800
Au 0.35900700 1.42209800 -1.50633700
Au 2.05137300 -0.69075700 -1.73283300
O 4.18245100 -1.03029400 -1.91976100
O 5.03096000 -0.17167900 -1.28383400
Au 0.20608200 1.71443300 1.48801700
S 1.32577300 0.15745900 2.90113500
Au 2.86047200 0.01641800 0.98912700
Au -0.52310900 -1.11988300 -1.18651200
Au 0.14835500 -1.53132500 1.72344800
C 4.67943200 0.34198200 0.10076600
O 5.57095200 0.98864500 0.56233100

$Au_8S_4^-$: [TS(2)]

S -2.50838400 -2.51987500 0.48919000
Au -3.06728500 -0.45361700 -0.54605600
S -3.61595000 1.64121200 -1.37448300
Au -1.59078200 2.54177900 -0.67650700
S 0.47915400 3.49162800 -0.02623200
Au 1.93471000 1.83882900 -0.86208300
Au 1.75172200 -1.36680800 -1.85033500
O 3.20886800 0.41615200 -1.58191400
O 4.25723600 -0.11750600 -0.18163500
Au 0.48376400 1.76900900 1.68105100
S 0.79017900 -0.19721300 2.99374800
Au 1.58564500 -1.01682300 0.79735500
Au -0.55701400 -2.28160700 -0.94390000
Au -1.03091500 -1.33772200 1.93768900
C 3.74105300 -0.84708800 0.72857200
O 4.27839300 -1.46360700 1.62269400

$Au_9S_4^-$: [TS(1)]

Au -0.85812600 -1.91883000 1.94250300
Au -0.98169200 -2.43210900 -1.36111100
Au 2.33070300 -0.92869400 -1.71905000
Au 2.52692200 -0.56219200 1.62297500

Au -0.32947200 0.36133700 -1.35818700
Au -0.13101400 0.85454300 1.50223000
Au 1.83865100 1.76238700 -0.29332000
Au -3.00004900 -0.35393100 -0.10178300
S 3.81651300 0.18695200 -0.23650200
S 0.42504300 -1.47337400 -3.01170200
S -2.54122400 -2.63125700 0.43246400
S 0.76030600 -0.72860000 3.21247700
O -3.39830600 1.61431000 -0.84973500
O -3.69381800 2.58639200 0.02959800
Au -0.68126800 2.93146200 -0.25229900
O -2.99837100 4.96487200 0.23770800
C -2.51733400 3.93534600 -0.04385900

$Au_9S_4^-$: [TS(2)]

Au -1.08126200 -1.96178400 1.84219400
Au -0.71304400 -2.41883400 -1.39643200
Au 2.65275900 -0.90776300 -1.28316900
Au 2.25094500 -0.33965600 1.96495700
Au 0.01236900 0.34020300 -1.71490600
Au -0.38344400 0.74899400 1.30938200
Au 1.75188100 1.91421500 -0.17539800
Au -2.91482100 -0.27587800 -0.25091600
S 3.75544900 0.46815300 0.31294400
S 1.02674800 -1.67836600 -2.84499800
S -2.55288900 -2.61753400 0.09791200
S 0.29877000 -0.65987500 3.28623900
O -3.30193600 1.66172700 -0.85105700
O -3.67616700 2.74691800 0.43321100
Au -0.93011400 2.63651100 -0.57689300
O -2.45377200 4.54034800 1.11513800
C -2.66174900 3.51089000 0.50024000

$Au_{10}S_4^-$: [TS(1)]

Au 2.61892200 0.42897300 -1.43215200
Au 0.51984900 -2.38969300 -1.47714500
Au -2.09708800 -0.34282600 -1.95486800
Au -0.05756400 2.47976000 -1.40819800
Au -1.96297100 -1.89952100 0.74018700
Au 1.81053300 1.70939000 1.22665000
Au -2.70610600 1.37024900 0.51029700
Au 2.24178500 -1.34456800 0.97212600
S -2.36925400 2.04172300 -1.81948200
S -1.86229300 -2.70275800 -1.49593100
S 2.87205700 -1.96881200 -1.29317000
S 2.27129000 2.76780600 -0.92489600
Au -0.06278000 0.04379500 -0.00010300
Au 0.64192100 -0.17081400 2.83658700
O -1.78325300 -1.12330200 2.77752200
O -2.71730000 -0.28611400 3.29201000
C -3.35338100 0.98905200 2.39234900
O -4.15472100 1.52985800 3.07102200

$Au_{10}S_4^-$: [TS(2)]

Au -1.33853800 -2.58073000 0.65113200

Au 0.71794400 -1.99912700 -1.96763300
Au 3.15114500 -0.79824600 0.12929100
Au 0.84076100 -0.81538500 2.61416200
Au 1.99057200 1.01074200 -1.95441100
Au -1.83741900 0.26127800 1.44566200
Au 1.43464700 1.59873300 1.16650700
Au -2.15987800 -0.53252900 -1.38620700
S 3.03554300 0.06336400 2.34523200
S 2.91916500 -1.13851600 -2.23818600
S -1.49597700 -2.81827200 -1.73276500
S -1.36328900 -1.65897800 2.87005200
Au -0.71039500 1.91257900 -0.58332100
Au -3.40013100 1.68232100 -0.33025700
O 0.97372600 2.80997000 -1.63913500
O 1.86556600 3.91620200 -0.64700200
C 1.97310100 3.56934200 0.59559600
O 2.43900200 4.27270700 1.47463300

MD Trajectory Movies:

In addition to above mentioned informations, MD trajectory movie files (.avi) of $Au_7S_4^-$ and $Au_{10}S_4^-$ at 300 K temperature are also provided.