Supporting Information for

Mode of Adsorption of $(CH_3)_2Au(acac)$ onto Partially-Dehydroxylated Silica

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Table of contents

Additional XAS experimental details

Data acquisition. XAS experiments at the Au L_{III}-edge were performed at the Stanford Synchrotron Radiation Lightsource on beamline 2-3 (Bend), operating at 3.0 GeV with a current of 75-100 mA. X-rays were monochromatized via reflection from a double crystal monochromator with either Si(220) crystals for XANES, or Si(111) crystals for EXAFS, through a 1 x 10 mm entrance slit. The monochromator was detuned by 30% to suppress harmonics. Samples were mounted at a 45° angle to the beam in order to collect transmission and fluorescence spectra simultaneously. The intensity of the incident beam was measured with a N_2-filled ionization chamber installed in front of the sample. Transmitted X-rays were detected in a second, N_2-filled ionization chamber, then passed through a Au calibration foil (11.915 keV) into a third, N_2-filled ionization chamber. Fluorescence from the sample was recorded at right angles to the beam, using an Ar-filled Lytle detector installed without Soller slits.

The spectrum of $(CH_3)_2Au(acac)$/silica (0.7 wt% Au) was recorded without sample dilution. Polycrystalline $(CH_3)_2Au(acac)$ and $AuCl_3$ were diluted with BN to ca. 1.0 wt% Au, in order to reduce the absorption length to 2.8 μm and prevent distortion of the fluoresence spectra due to self-absorption. The samples were loaded as powders into slotted aluminum sample plates (window size 35 x 5 x 2 mm), between windows of 12.0 μm polypropylene film (Chemplex #475) affixed with double-sided tape to each side of the plate. The sample plates containing the air-sensitive organogold complexes were packed under N_2 in a glovebox to prevent exposure to air. Five data sets (total acquisition time ca. 100 mins) were obtained at room temperature. Consecutive data sweeps showed no changes due to sample decomposition, although if the sample was exposed to the monochromatic X-ray beam for a much longer period of time, it became discolored (turning pink), indicating formation of Au(0). Fluorescence data generally showed better signal-to-noise ratios than transmission data and were used in subsequent data analysis.

Data analysis. Spectra were analyzed using WinXAS v.3.1.[1] Spectra were background-corrected by subtracting a linear fit to the pre-edge region extrapolated the entire length of the spectrum, then normalized by a 3rd-degree polynomial fitted to the post-edge region. The $\chi(k)$ EXAFS data was k^3-weighted and fitted with a polynomial spline with 8 knots between 2.0 and 13.2 $Å^{-1}$ (for the polycrystalline organogold complex) and between 2.0 and 11.5 $Å^{-1}$ (for the organogold complex supported on silica). The k^3-weighting was chosen because it generates a uniform χ amplitude across the range of usable data.[2] Subtraction of the spline minimizes contributions from low frequency atomic X-ray absorption fine structure (AXAFS).[3] Nevertheless, truncation of the data in early *k*-space, at 2.0 $Å^{-1}$, was necessary in order to avoid interference from the AXAFS; without this truncation, a prominent shoulder apparent at low *R* values in the Fourier-transformed spectrum affects the curve-fitting. A Kaiser-Bessel window function (α = 4) was applied to the data range prior to Fourier transformation, to minimize ringing in the spectrum. Paths in the EXAFS equation, eq 1, were fitted to the *R*-space spectra, with least-squares refinement:[4]

$$\chi(k) = S_0^2 \sum_i \frac{N_i F_i(k)}{kR_i^2} \exp(-2k^2\sigma_i^2) \exp\left(\frac{-2R_i}{\lambda(k)}\right) \sin(2kR_i + \phi_i(k)) \qquad (1)$$

N_i is the number of scatterers in the ith shell at a distance *R* from the absorber. The Debye-Waller factor, σ_i^2, is the root-mean-squared relative displacement of the scatterer, $\lambda(k)$ is the mean-free path of the photoelectron and $\phi(k)$ and $F(k)$ are its phase shift and backscattering amplitude, respectively. The phase-shift and backscattering amplitude functions were calculated using FEFF 8.20,[5] eliminating the need to estimate them from the spectra of model compounds.

The EXAFS equation has a large number of degrees of freedom, and several of its parameters are strongly correlated. Bond distances from the crystal structure of $(CH_3)_2Au(acac)$,[6] and from the DFT models described below, were used as initial values. To minimize the number of variables, the coordination numbers, *N*, were kept fixed at integer values while the phase shift, ΔE_0, was constrained to be the same for all paths. After refinement of *R* and σ^2, ΔE_0 was allowed to vary. The global amplitude reduction factor, S_0^2, was fixed at the value predicted by FEFF, 0.93, for an isolated molecule of $(CH_3)_2Au(acac)$ molecule. The residual is defined as $\Sigma(y_{obs} - y_{fit})/\Sigma y_{obs}$ where y_{obs} and y_{fit} are the observed and calculated values of each data point. However, goodness-of-fit was judged primarily by the appropriateness of the fit parameters (bond lengths, Debye-Waller factors). The total number of independent fitted parameters was not allowed to exceed N_{idp}, calculated by eq 2:[7]

$$N_{idp} = \frac{2\Delta k \Delta R}{\pi} \qquad (2)$$

where Δk and ΔR are the data ranges over which the model was refined in *k*-space and *R*-space, respectively.

References

(1) Ressler, T. *J. Synchrotron Rad.* **1998**, *5*, 118.
(2) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A. L.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* **1995**, *52*, 2995.
(3) Wang, W. C.; Chen, Y. *Phys. Status Solidi A* **1998**, *168*, 351.
(4) Sayers, D. E.; Stern, E. A.; Lytle, F. W. *Phys. Rev. Lett.* **1971**, *27*, 1204.
(5) Ankudinov, A. L.; Bouldin, C.; Rehr, J. J.; Sims, J.; Hung, H. *Phys. Rev. B* **2002**, *65*, 104107.
(6) Hisamoto, M.; Chattopadhyay, S.; Eckert, J.; Wu, G.; Scott, S. L. *J. Chem. Crystallogr.* **2009**, *39*, 173.
(7) Weckhuysen, B. M.; Wachs, I. E.; Schoonheydt, R. A. *Chem. Rev.* **1996**, *96*, 3327.

Table S1. Calculated distances (Å) for an isolated molecule of $(CH_3)_2Au(acac)$, [a] and for its H-bonded adducts with various octasilsesquioxane silanol cubes [b]

distances	$(CH_3)_2Au(acac)$	octasilsesquioxane silanol adducts			
		IIIb	**IVa**	**IVb**	**Vb**
Au-C1	2.047	2.045	2.043	2.044	2.043
Au-C2		2.051	2.049	2.047	2.050
Au-O1	2.146	2.157	2.166	2.180	2.162
Au-O2		2.180	2.181	2.180	2.176
O1-C3	1.277	1.272	1.267	1.284	1.272
O2-C4		1.290	1.286	1.284	1.289
O1…O3	-	2.727	2.769	2.788	2.731
O2…O4			3.210 [c]	2.794	

[a] The atom-labeling scheme corresponds to that shown in **Chart 2**. [b] See main text (**Charts 3** and **4**) for model pictures. For models with only one hydrogen-bond to an acetylacetonate oxygen, the hydrogen-bonded oxygen is designated O2. The silanol oxygens of the octasilsesquioxane cubes are labelled O3 and O4. [c] Refers to the O4...C3 (hydrogen-bond) distance.

Figure S1. Transmission IR spectra of (a) S952 silica, partially dehydroxylated at 400 °C; and (b) after deposition of $(CH_3)_2Au(acac)$ and elimination of volatiles. The former spectrum is vertically offset. The difference spectrum (b – a) in shown in (c) the O-H and C-H stretching regions; and (d) the C-O and C-C stretching regions.

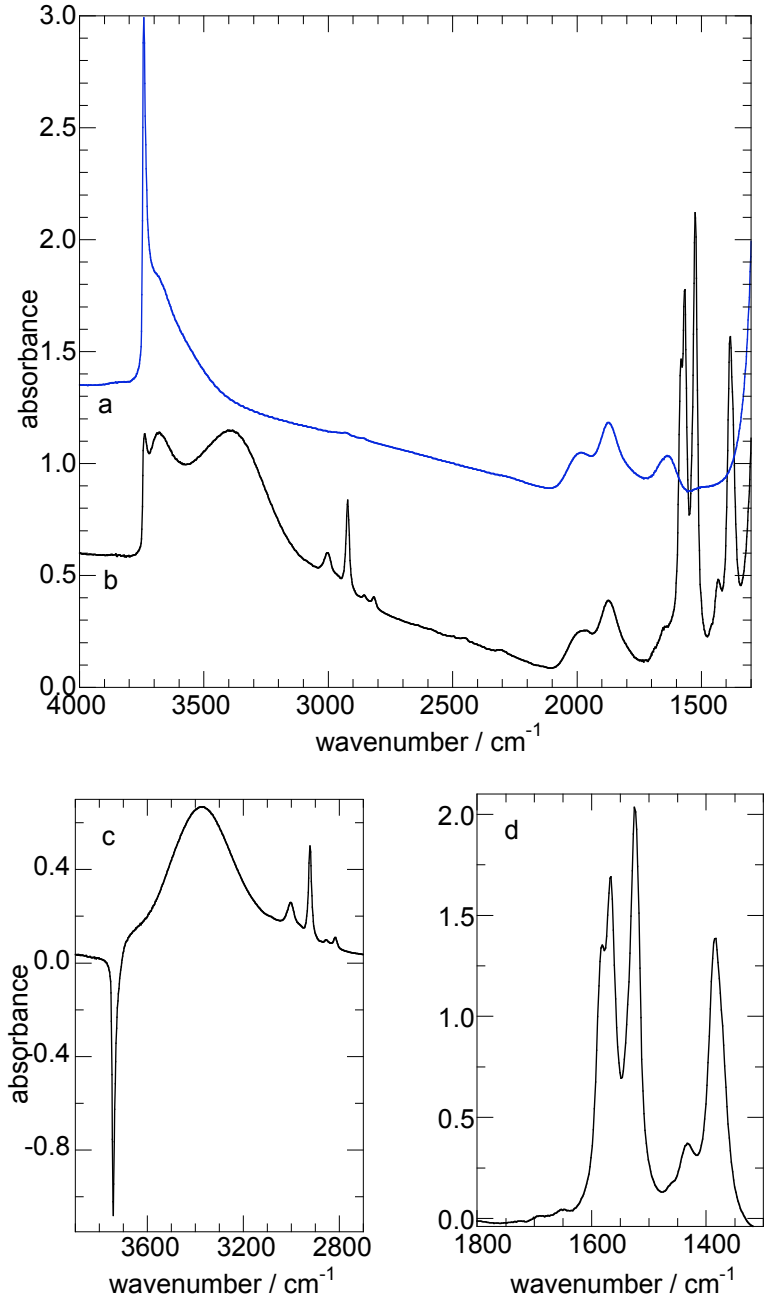


Figure S2. Comparison of calculated IR spectra for $(CH_3)_2Au(acac)$ and $(CH_3)_2Au(acac)/SiO_2$: (a) model **IIIb** (green); (b) model **IVa** (blue); (c) model **IVb** (red). The positions of the overtones 2γ(CH), predicted from the calculated frequencies of the fundamentals γ(CH), are indicated by the solid lines. Vibrations of the isolated molecule $(CH_3)_2Au(acac)$ are shown as black dashed lines.

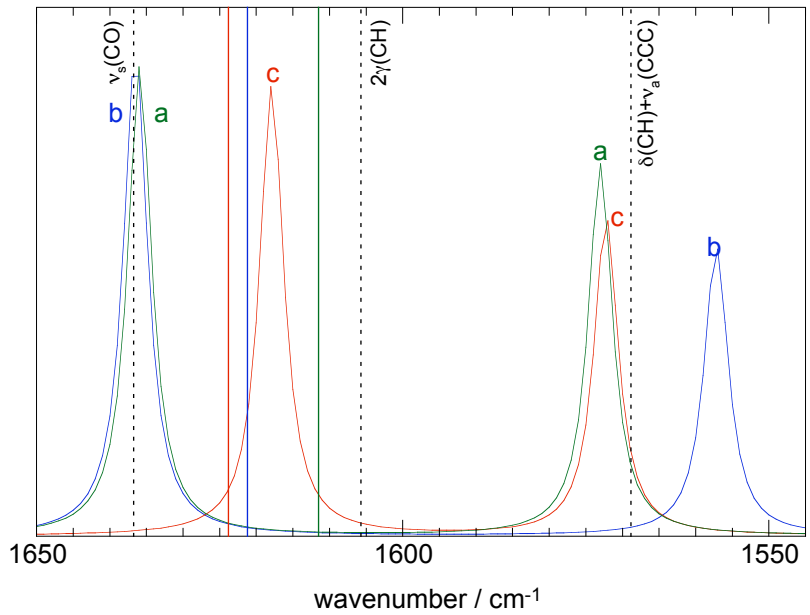


Table S2. Selected calculated IR frequencies (cm^{-1}) for an isolated molecule of $(CH_3)_2Au(acac)$ and its H-bonded adducts with various octasilsesquioxane silanol cubes

vibration	$(CH_3)_2Au(acac)$	**IIIb**	**IVa**	**IVb**
ν_s(CO)	1637	1636	1636	1618
2γ(CH) [a]	1608	1614	1624	1626
δ(CH) + ν_a(CCC)	1568	1573	1557	1572
ν_a(CO) + ν_a(CCC)	1460	1457	1461	1444

[a] Reported as twice the calculated fundamental frequency.

Figure S3. Comparison of calculated IR spectra for (a) $(CH_3)_2Au(acac)/SiO_2$ (model **IVb**, red); and (b) an isolated molecule of $(CH_3)_2Au(acac)$ (blue), in the C-H stretching region (i), and in the C-O and C-C stretching regions (ii).

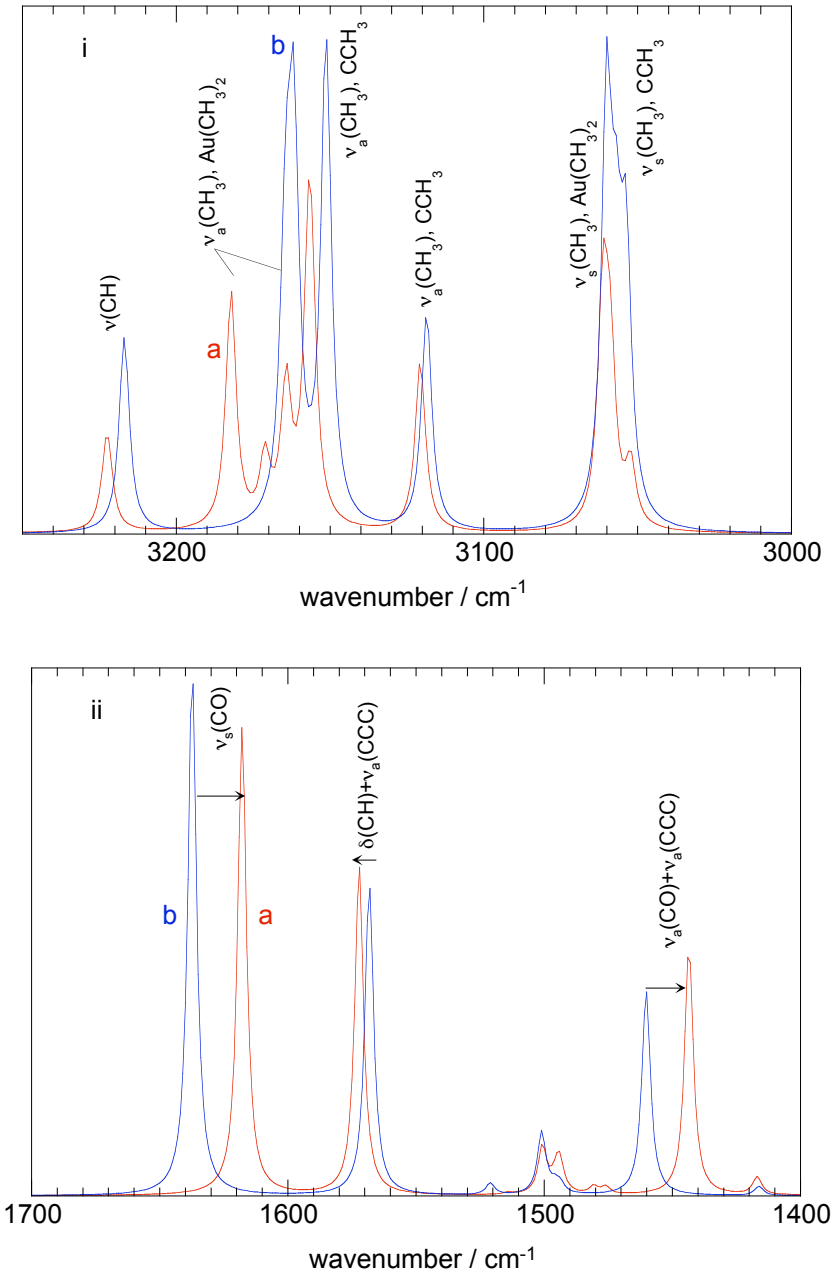
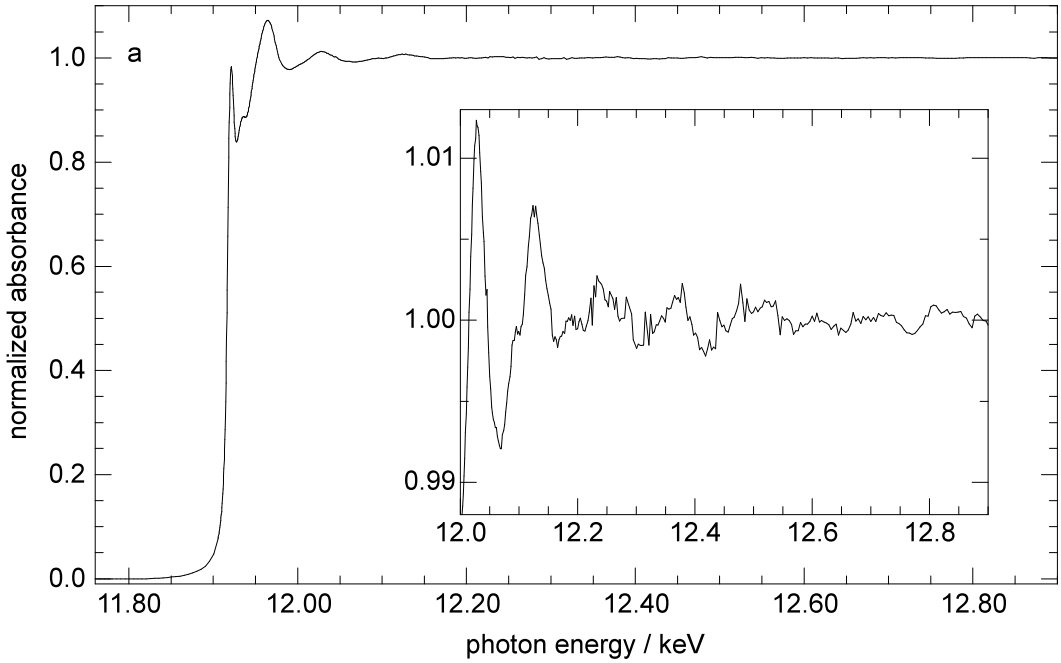


Figure S4. Complete X-ray absorption spectra for (a) polycrystalline $(CH_3)_2Au(acac)$, diluted in BN; and (b) $(CH_3)_2Au(acac)$ grafted onto S952 silica partially dehydroxylated at 400 °C (S952-400). Both spectra are background-corrected, deglitched and normalized.



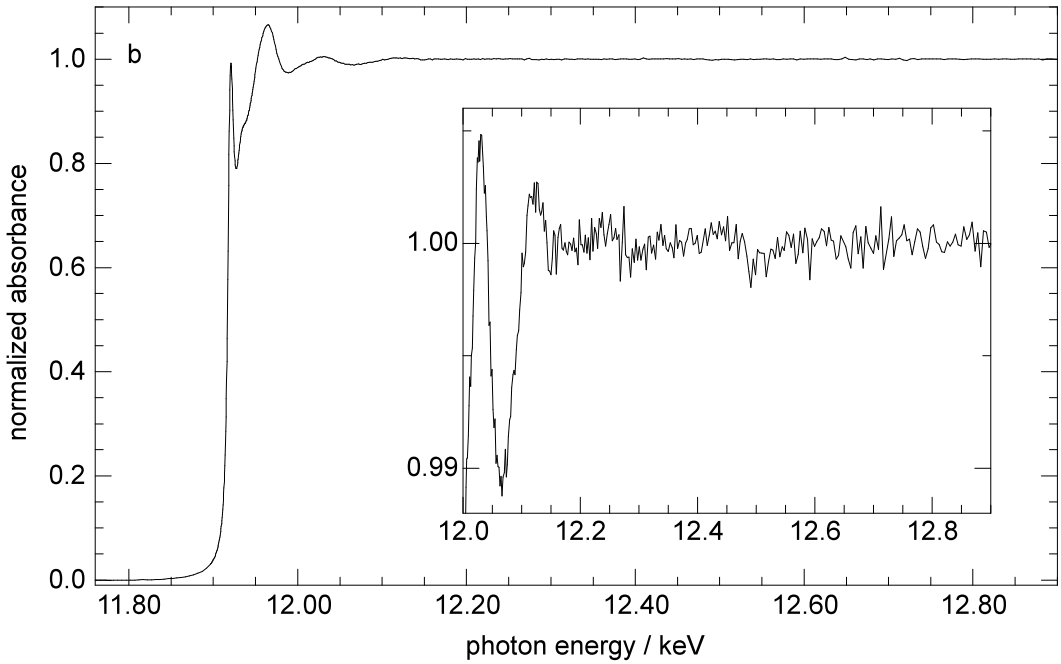


Figure S5. Fourier-filtered (1.13 – 2.05 Å) EXAFS of polycrystalline $(CH_3)_2Au(acac)$ in (a) k^3-weighted *k*-space (red); and (b) non-phase-corrected *R*-space (FT magnitude, red points; imaginary FT, black points). Parameters for the curve-fit (solid blue lines in frames a and c) to a two-shell single-scattering model of an isolated molecule of $(CH_3)_2Au(acac)$ are given in **Table 4**. Frames (b) and (d) show the contributions of the individual paths to the *k*-space and *R*-space curvefits, respectively.

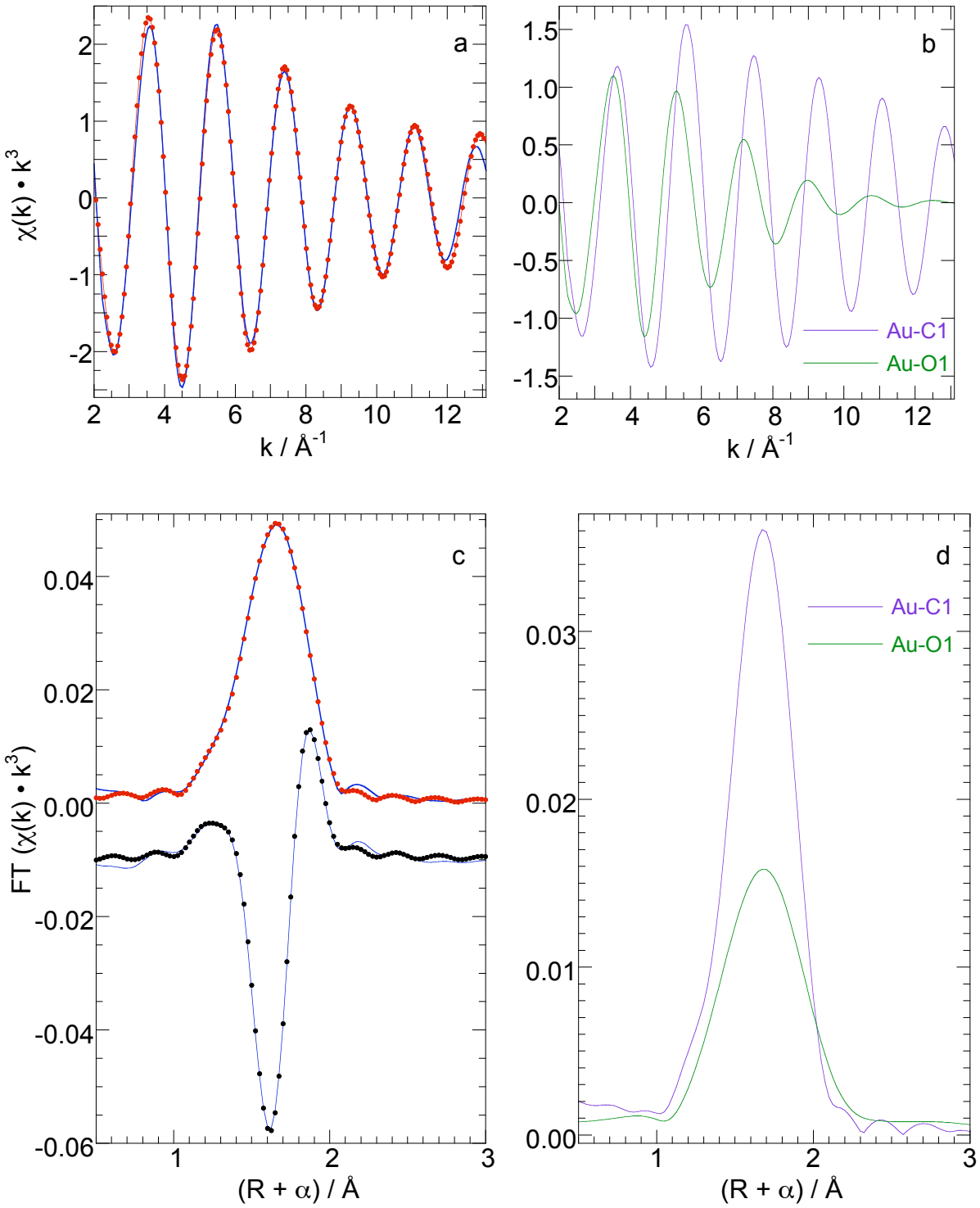


Figure S6. Fourier-filtered (1.15 – 2.35 Å) EXAFS spectrum of $(CH_3)_2Au(acac)/S952\text{-}400$ (0.7 wt% Au), in (a) k^3-weighted *k*-space (red); and (b) non-phase-corrected *R*-space (FT magnitude, red points; imaginary FT, black points). Parameters for the curve-fit (solid blue lines in frames a and c) to a three-shell single-scattering model for $(CH_3)_2Au(acac)/SiO_2$ are given in **Table 4**. Frames b and d show the contributions of the individual paths to the *k*-space and *R*-space curvefits, respectively.

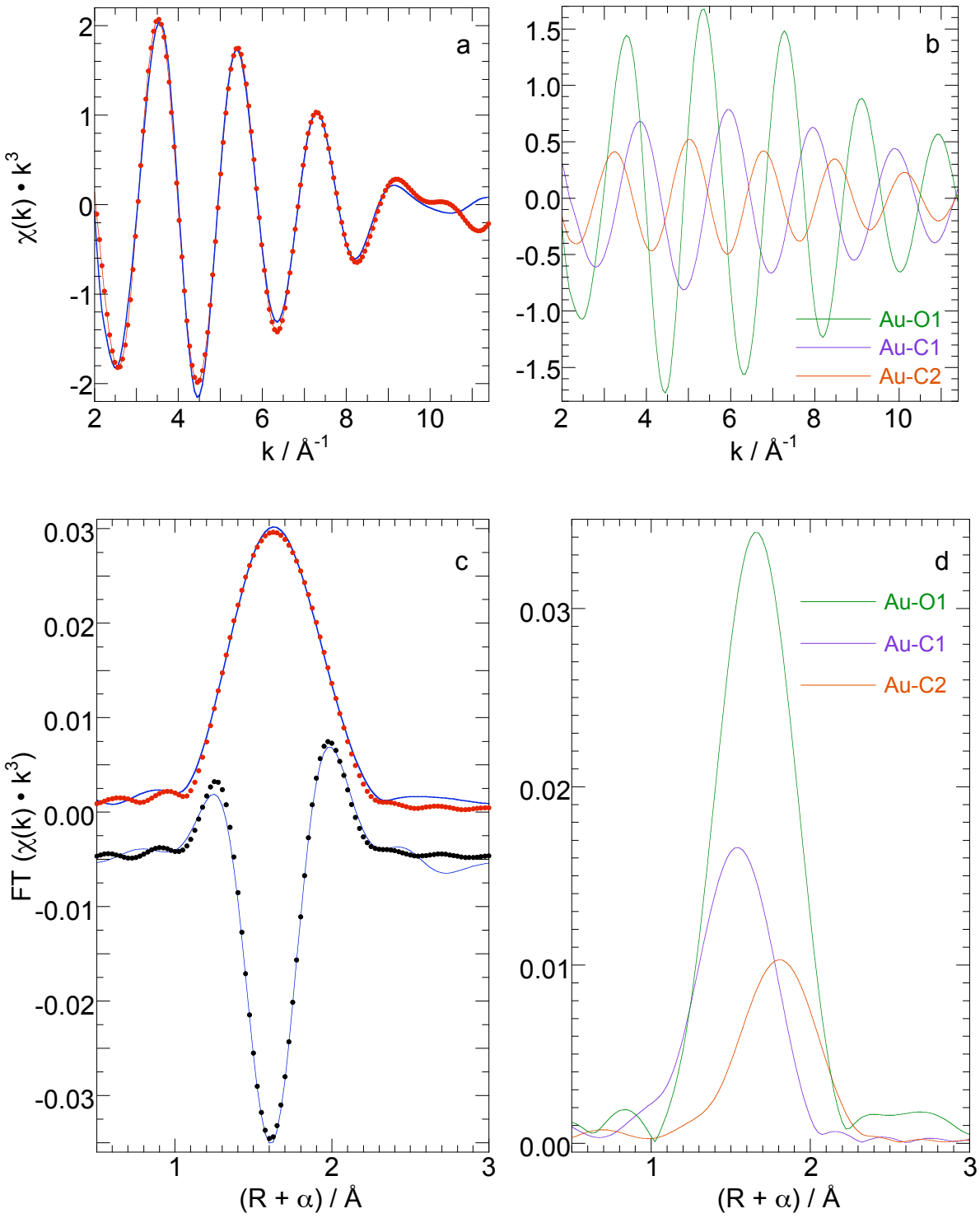


Figure S7. EXAFS of $(CH_3)_2Au(acac)$/S952-400 (0.7 wt% Au), in (a) k^3-weighted *k*-space (red); and (b) non-phase-corrected *R*-space (FT magnitude, red points; imaginary FT, black points). Parameters for the curve-fit (solid blue lines) to model **II** (a dimethylgold fragment coordinated to two oxygen atoms of silica) are given in **Table S2**.

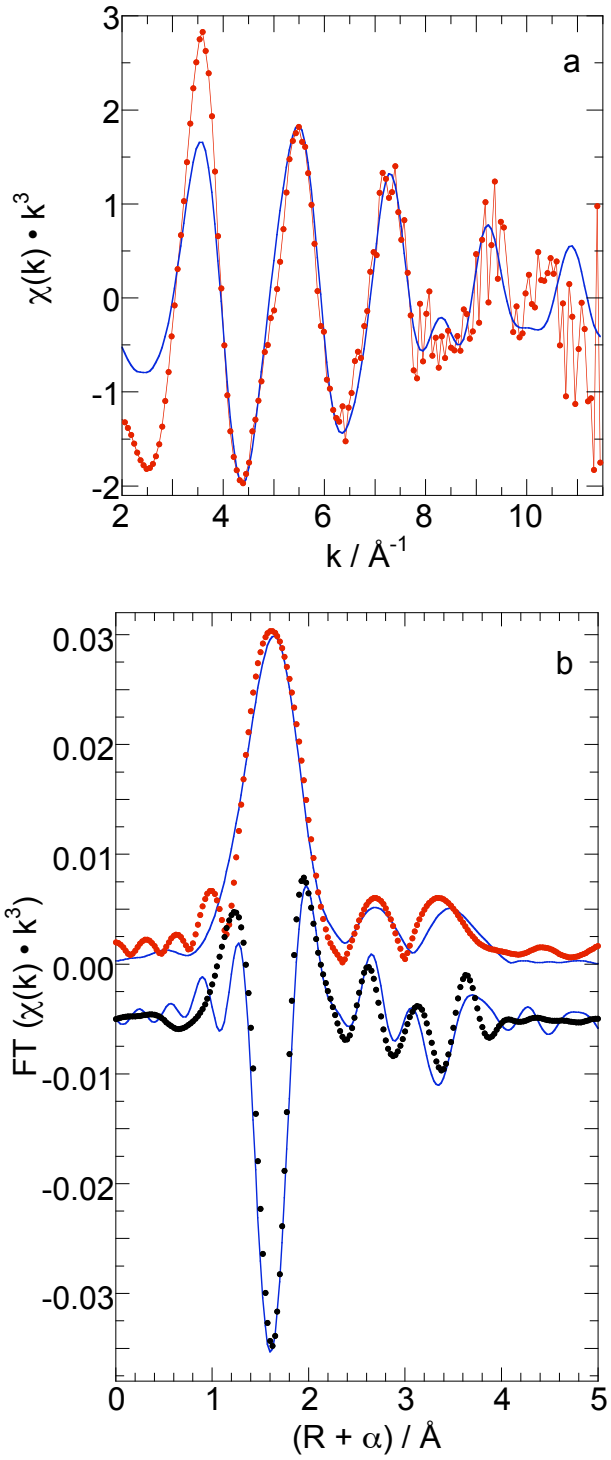


Figure S8. EXAFS of $(CH_3)_2Au(acac)$/S952-400 (0.7 wt% Au), in (a) k^3-weighted *k*-space (red); and (b) non-phase-corrected *R*-space (FT magnitude, red points; imaginary FT, black points). Parameters for the curve-fit (solid blue lines) to model **IIIb**, involving one hydrogen bond between a hydroxyl group of the silica surface and an oxygen atom of the intact organogold complex, are given in **Table S3**.

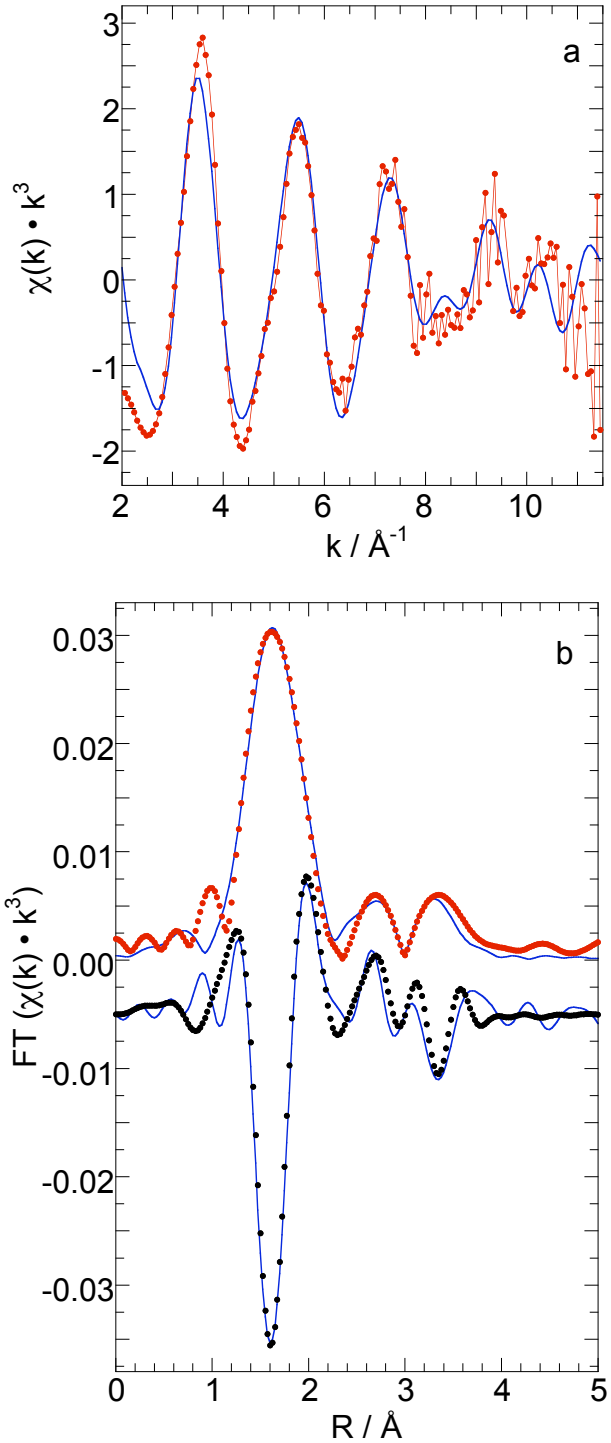


Table S3. Comparison of DFT-calculated bond distances and EXAFS curve-fit parameters [a] for $(CH_3)_2Au(acac)$/silica, for a model (**II**) involving direct coordination of the dimethylgold(III) fragment to the silica surface

path	DFT *d* / Å	EXAFS *R* / Å	σ^2 / Å^2	*N*
Au-C1	2.040 2.051	1.99	0.0034	2
Au-O1	2.151	2.09	0.0001	1
Au-O2	2.437	2.58	0.0086	1
Au-Si1	2.927	3.18	0.0115	1
Au-Si2	3.778	3.95	0.0049	1

[a] The values of *N* were not refined, in order to give physical meaning to the Debye-Waller factors. S_o^2 was fixed at its FEFF-predicted value, 0.93. A single phase shift, ΔE_0, was refined at -3.7 eV for all paths; the residual is 14.2 using 13 of 18 possible free parameters.

Table S4. Comparison of DFT-calculated bond distances and EXAFS curve-fit parameters [a] for $(CH_3)_2Au(acac)$/S952-400, for a model (**IIIb**) involving one hydrogen bond between a hydroxyl group of the silica surface and an oxygen atom of the intact organogold complex

path	DFT *d* / Å	EXAFS *R* / Å	σ^2 / Å^2	*N*
Au-C1 Au-C2	2.045 2.051	2.02	0.0013	2
Au-O1 Au-O2	2.157 2.180	2.13	0.0029	2
Au-C3 Au-C4	3.078 3.103	3.09	0.0056	2
Au-C5	3.438	[b]	[b]	1
Au-C3-O1 Au-C4-O2	3.254 3.286	3.33	-0.0011	4
Au-C5-C1 Au-C5-C2	3.463	3.56	0.0118	2
Au-O3	4.165	3.72	-0.0001	1

[a] The values of *N* were not refined, in order to give physical meaning to the Debye-Waller factors. S_o^2 was fixed at its FEFF-predicted value, 0.93. A single phase shift, ΔE_0, was refined at 5.2 eV for all paths; the residual is 10.4 using 13 of 18 possible free parameters. [b] Not included in the fit.

Table S5. Cartesian coordinates for optimized structure of $(CH_3)_2Au(acac)$
Absolute E = -560.491508791 Hartrees

C	2.855726	-2.505294	0.000006
C	1.986471	-1.262475	-0.000039
C	2.610197	-0.000016	-0.000046
C	1.986524	1.262470	0.000055
C	2.855833	2.505253	0.000065
O	0.732670	-1.503885	0.000043
O	0.732734	1.503933	0.000120
Au	-0.798732	0.000057	0.000095
C	-2.263350	-1.429571	0.000102
C	-2.263289	1.429746	0.000076
H	2.618427	-3.112979	0.882367
H	3.924968	-2.273676	-0.000475
H	2.617712	-3.113543	-0.881765
H	3.695050	-0.000039	-0.000106
H	2.618417	3.113063	0.882305
H	2.617986	3.113396	-0.881826
H	3.925065	2.273589	-0.000227
H	-2.885756	-1.333634	0.895437
H	-1.741045	-2.392092	-0.000304
H	-2.886307	-1.333158	-0.894798
H	-2.886470	1.333195	0.894802
H	-2.885480	1.334002	-0.895432
H	-1.740944	2.392245	0.000779

Table S6. Cartesian coordinates for optimized structure **Ia**
Absolute E = -3299.87934695 Hartrees

H	-1.438661	4.018667	-0.004308
H	4.764371	0.496486	-0.000289
H	-1.617937	-1.909900	-3.445655
H	1.136008	-3.998412	0.004243
H	-4.362866	0.159001	-0.000342
H	1.304876	1.927783	-3.439179
H	-1.618202	-1.902708	3.449482
O	4.195622	-0.280383	0.000473
O	-2.378886	-0.699910	1.340739
O	-0.072246	2.344537	1.337309
O	1.912624	-1.571915	0.001620
O	-0.138130	-0.006604	-2.626547
O	2.081432	0.745126	-1.328606
O	2.081163	0.747859	1.327111
O	-0.138421	-0.001008	2.626633
O	-2.276558	1.615843	-0.001733
O	-2.378813	-0.702672	-1.339523
O	-0.264303	-2.348436	1.342877
O	-0.072097	2.341554	-1.342066
O	-0.264304	-2.351391	-1.338003
Si	0.650644	-2.617861	0.002737
Si	-1.116696	-1.265479	-2.230415
Si	0.810310	1.277200	2.224021
Si	-2.900193	0.095126	-0.000223
Si	2.575229	-0.084445	0.000160
Si	-1.116856	-1.260765	2.232975
Si	0.810525	1.272493	-2.226608
Si	-0.982176	2.627539	-0.002751
H	1.304709	1.934959	3.435235

Table S7. Cartesian coordinates for optimized structure **Ib**
Absolute E = -3375.14769062 Hartrees

H	3.690636	2.408208	0.159262
H	0.126735	2.409829	3.456395
H	3.677490	-2.427997	0.145462
H	-3.909468	-2.626967	0.482389
H	0.356048	2.449538	-3.408863
H	0.115631	-2.428838	3.443883
O	-3.262757	2.570845	-0.226654
O	1.519003	1.909588	1.386445
O	0.401302	0.007287	-2.693828
O	1.508295	-1.924680	1.375045
O	-3.274568	-2.555103	-0.237595
O	-1.017819	-1.819874	-1.356425
O	-1.162927	1.903300	1.327513
O	1.660860	1.912275	-1.291046
O	-1.008281	1.834397	-1.346790
O	-2.440907	0.005996	-0.018917
O	-1.173572	-1.905394	1.319086
O	1.650688	-1.912686	-1.302236
O	2.890288	-0.007614	0.117904
O	0.153456	-0.007525	2.665220
Si	0.350275	1.583434	-2.229471
Si	2.473939	-1.596715	0.084734
Si	0.159519	1.582582	2.248584
Si	2.482496	1.583952	0.094008
Si	-1.984291	-1.568799	-0.070410
Si	-1.976522	1.578811	-0.063019
Si	0.151581	-1.595289	2.240467
Si	0.341693	-1.571076	-2.238352
H	0.342176	-2.430469	-3.422662
H	-3.925425	2.603586	0.470779

Table S8. Cartesian coordinates for optimized structure **Ic**
Absolute E = -3450.41669888 Hartrees

H	-3.687148	-1.756575	1.504142
H	-0.555809	-4.243214	-1.269070
H	0.016195	-0.190208	4.259532
H	-0.072177	-0.365229	-4.147322
O	0.489629	3.798024	1.545705
O	-2.645793	0.075394	0.080826
O	1.226056	-1.175789	2.248166
O	-0.248400	-1.857175	-2.097121
O	2.592127	-0.613311	0.012233
O	-1.021858	2.198540	-0.024520
O	-1.433092	-0.866569	2.279376
O	0.162953	1.276337	2.182527
O	1.602406	1.876420	0.009734
O	1.338361	0.300411	-2.138745
O	0.993930	-2.758235	0.096419
O	-1.667385	-2.415160	0.106429
O	-1.323725	0.597647	-2.156089
Si	-0.005676	-0.232838	2.797081
Si	-0.376424	-2.866172	-0.804790
Si	-2.074580	1.286676	-0.866890
Si	-2.402958	-1.254447	1.011509
Si	2.320326	0.726683	-0.894202
Si	0.310138	2.301661	0.924163
Si	-0.075387	-0.331147	-2.683197
Si	2.027850	-1.823002	0.969103
H	3.146071	-2.639716	1.444964
H	0.645551	4.539439	0.951226
O	-3.276835	2.276540	-1.356881
H	-3.997265	1.914947	-1.883355
O	3.720026	1.364232	-1.441681
H	4.311328	0.818350	-1.970041

Table S9. Cartesian coordinates for optimized structure **Id**
Absolute E = -3301.01484742 Hartrees

H	2.046852	1.002064	3.547083
H	-2.062388	-1.119637	3.411176
H	-1.763283	-1.229791	-3.509091
H	2.438239	0.758351	-3.417037
H	-4.951360	0.747621	0.111882
H	3.862461	-2.083220	0.275690
H	-0.480784	-4.266437	0.087158
H	3.001951	3.562578	0.055218
H	-2.090805	3.116230	0.364838
H	0.612432	4.007140	-0.143641
O	-1.829566	2.374691	-0.191505
O	0.217383	-0.017347	-2.474555
O	-4.305128	1.388130	-0.204811
O	-2.462990	0.148096	1.260295
O	2.358616	-0.400125	1.448551
O	-2.235609	0.080505	-1.392160
O	-0.064911	0.131904	2.454084
O	1.385490	2.092678	1.348497
O	2.526052	-0.520411	-1.220168
O	-0.845088	-2.198891	-1.347557
O	1.365007	-2.521846	0.143313
O	-1.005862	-2.107140	1.323885
O	1.605650	1.986050	-1.354703
Si	1.648801	2.963150	-0.029909
Si	2.570018	-1.403282	0.163812
Si	-0.247899	-2.820951	0.050933
Si	-2.713607	0.995054	-0.129406
Si	1.449899	0.721307	2.237323
Si	-1.172537	-0.844651	-2.224898
Si	1.715284	0.566241	-2.156299
Si	-1.413220	-0.747244	2.150687

Table S10. Cartesian coordinates for optimized structure **Id´**
Absolute E = -3301.018219 Hartrees

H	-3.187299	-0.551929	4.002235
H	-1.124985	3.265825	2.043551
H	-2.800836	0.418667	-3.920492
H	-5.829605	-2.778020	-1.976602
H	1.823667	0.244183	-1.286839
H	-7.181462	0.420474	1.484326
H	-4.831593	3.815560	-1.097724
H	-3.873591	-3.741092	2.114560
O	-3.003642	2.854495	0.385733
O	-1.652909	0.004634	-1.668404
O	-0.089105	-1.069996	0.269510
O	-4.063523	-0.971939	-2.217743
O	0.956998	0.436934	-1.659906
O	-0.642233	1.568787	0.208439
O	-4.757905	-0.113147	2.053437
O	-3.967212	-2.792754	-0.247354
O	-2.315791	1.019442	2.209450
O	-2.541103	-1.583610	1.732552
O	-5.872375	-0.920352	-0.235837
O	-3.731266	1.666075	-1.909566
O	-5.407733	1.694270	0.180838
Si	-0.350900	0.220683	-0.703832
Si	-3.208778	-0.300219	2.557571
Si	-3.038553	0.286301	-2.481334
Si	-4.957457	-1.893325	-1.200958
Si	-1.742867	2.218643	1.227350
Si	-3.056197	-3.043791	1.094836
Si	-5.853497	0.281066	0.883750
Si	-4.259401	2.551045	-0.632116
H	-0.763954	-1.276018	0.937493
H	-1.842457	-3.796916	0.731622

Table S11. Cartesian coordinates for optimized structure **IIa**
Absolute E = -4010.89749388 Hartrees

Au	-4.229072	-0.901578	-0.253528	O	6.462831	-0.058589	-0.247495
C	5.381472	-0.059914	-2.386927	O	4.890888	-3.261358	0.790373
C	7.215581	-2.795501	1.054236	O	-3.508694	0.781728	-1.382387
C	-6.092581	-0.956057	-1.082705	O	-1.692090	2.341399	-0.023964
C	5.971374	-0.702443	-1.149550	O	0.517081	-1.435931	0.512853
C	-4.779955	-2.510709	0.893406	O	2.017543	1.334831	2.415702
C	5.916453	-2.819649	0.292716	O	-0.370443	0.132539	2.463234
H	4.474033	1.260299	1.779233	O	-1.936786	-0.320458	0.335496
H	-5.661335	-2.275995	1.499260	O	-0.799475	0.693980	-1.876273
H	8.000619	-3.322869	0.495493	O	0.605309	3.707654	-0.218218
H	7.531115	-1.748020	1.149544	O	2.900307	2.360771	0.101904
H	5.747429	-0.550558	-3.298588	O	1.544851	-0.584332	-1.789095
H	5.627239	1.005373	-2.405110	Si	0.454523	1.488723	2.895929
H	-3.916162	-2.709631	1.538467	Si	1.936886	3.131103	-0.986190
H	-6.828542	-0.737663	-0.305139	Si	1.905741	-1.279371	-0.348112
H	-4.987866	-3.380278	0.260767	Si	3.128713	1.171553	1.213575
H	2.674709	4.239088	-1.597382	Si	-2.030691	0.945341	-0.820224
H	-6.054947	-0.168614	-1.840158	Si	-0.806531	-0.976233	1.343890
H	0.396300	1.654366	4.349694	Si	0.710894	0.649808	-2.490471
H	0.682216	0.449873	-3.941211	Si	-0.716886	3.421070	0.719406
O	-1.531179	-2.272708	2.035547	H	-1.426267	4.679462	0.958442
H	-6.265064	-1.940510	-1.523503	H	-0.974899	-2.996954	2.342139
H	7.087703	-3.248698	2.040616	O	2.614016	-2.710575	-0.622270
H	4.289702	-0.182007	-2.372451	H	3.362718	-3.001996	-0.055546
O	2.922886	-0.288058	0.483610	C	5.912939	-2.245794	-1.119173
O	-0.221912	2.790370	2.159602	H	6.797401	-2.599659	-1.671075
O	1.485997	2.064274	-2.153836	H	5.022755	-2.592200	-1.654318

Table S12. Cartesian coordinates for optimized structure **IIb**
Absolute E = -4010.90051634 Hartrees

Au	-4.116111	-1.472488	-0.181114	O	5.353254	-2.198322	0.156836
C	9.380482	-2.202549	-1.341594	O	-3.453410	-0.207844	-1.788185
C	5.862400	-0.901401	2.099814	O	-2.094790	2.030246	-0.941732
C	-5.804066	-2.154323	-1.101864	O	0.450963	-0.853164	1.246771
C	7.979890	-2.196913	-0.812070	O	1.235666	2.680031	2.062742
C	-4.624704	-2.633376	1.432463	O	-0.950116	1.158601	2.293004
C	6.246497	-1.598136	0.815580	O	-2.046219	-0.328726	0.365165
H	3.753595	2.809094	1.750620	O	-0.712346	0.022164	-1.945623
H	-5.643601	-2.418436	1.770485	O	-0.007932	3.646037	-1.407880
H	5.403459	-1.627587	2.782517	O	2.348698	2.920689	-0.364296
H	6.717456	-0.430365	2.593572	O	1.720964	-0.653600	-1.090693
H	10.063042	-1.655459	-0.685890	Si	-0.394675	2.705157	2.276134
H	9.399088	-1.751677	-2.342108	Si	1.491461	3.076948	-1.761270
H	-3.901736	-2.371721	2.213948	Si	1.924921	-0.752656	0.534923
H	-6.672883	-1.760432	-0.568566	Si	2.532553	2.279313	1.135468
H	-4.537646	-3.695327	1.177472	Si	-2.115073	0.405824	-1.186468
H	2.177381	4.013941	-2.654173	Si	-1.036144	-0.350634	1.674648
H	-5.726819	-1.741029	-2.111053	Si	0.878542	0.045542	-2.315712
H	-0.714768	3.360569	3.545848	Si	-1.419768	3.472600	-0.579900
H	1.134237	-0.676689	-3.563920	H	-2.324473	4.571028	-0.925228
O	-1.681885	-1.393670	2.761602	H	-1.085177	-2.038448	3.157923
H	-5.805377	-3.246601	-1.103843	O	2.774177	-2.049682	0.987010
H	5.098310	-0.142955	1.887676	H	3.698259	-2.172389	0.668515
H	9.731334	-3.236923	-1.449330	C	7.605930	-1.570982	0.359900
O	2.650089	0.645591	1.033359	H	8.356979	-1.049475	0.941935
O	-1.098147	3.520369	1.037132	O	7.121675	-2.851608	-1.574285
O	1.374367	1.608560	-2.487238	H	6.227989	-2.781180	-1.130816

Table S13. Cartesian coordinates for optimized structure **IIIa**
Absolute E = -3860.38035868 Hartrees

Au	-3.379756	-0.938286	0.042654	H	-0.378702	-1.638982	-2.721500
C	-3.610137	2.467545	0.282335	H	5.207963	1.618822	2.639713
C	-2.749442	2.611284	2.647077	O	-0.700578	2.940174	-0.823087
C	-4.544637	2.816293	-2.033553	O	4.706767	-0.480783	1.295923
C	-2.775450	-2.459988	1.268007	O	-2.948231	0.538213	1.558047
C	-3.130307	1.791748	1.430450	O	-4.045503	0.660683	-1.243948
C	-3.793051	-2.337059	-1.391516	O	1.012069	-1.011730	1.997531
C	-4.043881	1.895048	-0.938704	O	1.877848	2.432896	-0.983492
H	0.766729	-3.517758	1.627173	O	2.076869	-1.031113	-2.497281
H	-1.599763	2.801591	-0.476560	O	0.155511	0.422406	-1.326422
H	4.338212	-0.976473	-3.661083	O	0.489694	1.463781	1.091437
H	-2.863576	-2.805559	-1.729954	O	2.758116	0.973546	2.422812
H	-4.670700	3.848513	-1.693878	O	2.965013	-2.477145	0.892533
H	-1.660001	2.567991	2.772557	O	4.357357	-1.475640	-1.166964
H	-3.200471	2.165578	3.541014	O	4.147231	1.963474	0.352924
H	-4.265950	-1.789335	-2.213514	O	0.683731	-2.053142	-0.450013
H	-3.650000	-3.034655	1.590963	O	3.816918	0.972968	-2.112787
H	-5.497783	2.436739	-2.419197	Si	3.499764	2.253984	-1.130905
H	-3.055070	3.658505	2.564563	Si	3.669740	-0.637455	-2.403155
H	-3.828459	2.803091	-2.865626	Si	1.161353	0.595044	2.309129
H	-2.069553	-3.114995	0.749849	Si	4.412405	-1.847879	0.432315
H	-3.732307	3.542280	0.376270	Si	0.437136	1.821734	-0.513666
H	4.088814	3.467699	-1.698969	Si	4.237277	1.040356	1.708413
H	-4.470803	-3.100211	-0.996696	Si	0.597918	-1.087814	-1.780417
H	5.474890	-2.825186	0.677575	Si	1.336615	-2.305015	1.037202
H	-2.297697	-1.979914	2.128614	H	0.493019	0.917586	3.571878

Table S14. Cartesian coordinates for optimized structure **IIIb**
Absolute E = -3860.38615141 Hartrees

Au	-4.531817	-0.809626	-0.007390	Si	2.894131	-2.379246	-1.258482
C	-3.325879	-2.388517	-0.514999	Si	5.653005	0.129784	1.221524
C	-5.583925	2.048578	0.438300	Si	3.436100	2.380052	1.411265
C	-3.261730	1.967986	-0.557487	Si	0.653643	-0.138433	-1.066286
C	-6.692886	2.967625	0.911784	Si	5.080757	-0.174531	-1.876176
C	-4.400534	2.624767	-0.076147	H	6.102838	-0.261587	-2.921147
C	-5.924362	-2.183202	0.588374	H	2.684479	3.172663	-2.626920
C	-2.090201	2.797719	-1.039150	H	0.234066	0.266074	3.079874
O	0.503530	0.055775	0.563104	H	3.625709	-3.180407	2.787644
O	1.527575	-1.487174	-1.375793	H	-1.605160	0.099645	-1.344336
O	2.187864	-1.146445	2.271238	H	6.979589	0.192705	1.838468
O	-0.797331	-0.266842	-1.769882	H	3.576049	3.649827	2.127758
O	1.490195	1.155710	-1.642605	H	-2.320238	3.866394	-1.064497
O	5.805422	-0.025849	-0.406967	H	-2.501270	-1.987086	-1.111349
O	3.201176	-2.691311	0.328688	H	-6.905858	2.761531	1.968227
O	4.126777	1.137063	-2.139918	H	-4.367283	3.708606	-0.095595
O	4.155331	-1.531171	-1.888085	H	-3.885948	-3.131112	-1.090138
O	4.825536	-1.160082	1.814551	H	-6.445598	4.026631	0.794366
O	2.184962	1.523170	2.045552	H	-1.783984	2.468017	-2.039126
O	4.821362	1.507556	1.559532	H	-6.715761	-1.602314	1.073135
O	3.140985	2.672435	-0.178493	H	-7.609279	2.746158	0.350592
O	-5.841271	0.808820	0.558715	H	-1.232728	2.638288	-0.371686
O	-3.081556	0.693161	-0.631937	H	-5.483905	-2.899308	1.287834
Si	1.242831	0.174628	2.021491	H	-6.316631	-2.708923	-0.287694
Si	3.465033	-2.083007	1.831453	H	-2.940134	-2.845525	0.402562
Si	2.850010	2.065992	-1.681619	H	2.740089	-3.641397	-1.984224

Table S15. Cartesian coordinates for optimized structure **IVa**
Absolute E = -3935.65892262 Hartrees

Au	-3.576685	-0.878751	-0.116714	H	3.935583	0.371681	3.864971
C	-3.457643	2.524175	0.363240	H	-1.681129	-0.226308	2.461412
C	-2.809259	2.430495	2.792549	O	-0.519479	2.993580	-0.842497
C	-4.023440	3.134305	-2.012536	O	4.229168	-1.026876	1.761706
C	-3.297612	-2.540618	1.049136	O	-3.081621	0.457545	1.534274
C	-3.137087	1.741392	1.485842	O	-3.894214	0.881354	-1.338643
C	-4.035223	-2.103760	-1.686239	O	-0.786555	-0.486897	2.761983
C	-3.797952	2.082442	-0.945416	O	0.591934	-1.687741	0.770058
H	0.810871	-3.859428	-0.532700	O	2.050267	2.598666	-0.215417
H	-1.365394	2.872185	-0.380513	O	3.217450	-0.051139	-2.654956
H	5.717607	0.403891	-2.768055	O	0.843119	0.917106	-1.881520
H	-3.159362	-2.702057	-1.955045	O	0.164717	0.935146	0.703250
H	-4.410753	4.069777	-1.595615	O	1.830225	-0.110894	2.522138
H	-1.824959	2.097634	3.143855	O	2.979577	-2.664812	0.045675
H	-3.541184	2.126224	3.551942	O	4.915743	-1.033404	-0.829820
H	-4.309501	-1.432051	-2.506388	O	3.696404	1.596417	1.647305
H	-4.121126	-2.565206	1.771971	O	1.295810	-1.721009	-1.815014
H	-4.707886	2.749611	-2.774123	O	4.431128	1.600035	-0.927740
H	-2.814313	3.520705	2.707245	Si	3.619582	2.433343	0.234428
H	-3.060553	3.351997	-2.496259	Si	4.607847	0.236782	-1.827388
H	-3.284357	-3.462633	0.463664	Si	0.434699	-0.342959	1.701148
H	-3.489430	3.597796	0.523894	Si	4.417953	-1.968268	0.428106
H	4.225845	3.754676	0.407946	Si	0.627928	1.867037	-0.563714
H	-4.871528	-2.759153	-1.424707	Si	3.437100	0.212809	2.497599
H	5.415955	-3.006357	0.693952	Si	1.596815	-0.327620	-2.636329
H	-2.342746	-2.405988	1.567598	Si	1.399020	-2.526176	-0.383923
H	1.103175	-0.452177	-4.009364				

Table S16. Cartesian coordinates for optimized structure **IVb**
Absolute E = -3935.66338556 Hartrees

Au	-3.739685	-0.616046	-0.039596	H	-2.426806	3.762129	2.580813
C	-2.477336	2.676668	2.705091	O	3.584406	1.588320	-1.726041
C	-2.813525	2.683485	0.211650	O	2.859784	-2.690548	-0.286643
C	-2.617347	3.093919	-2.262843	O	3.602839	1.203736	2.008590
C	-4.239771	-2.081609	1.299499	O	-3.072717	0.708241	1.558588
C	-2.827345	1.960825	1.418978	O	-3.160220	0.960014	-1.429068
C	-4.373213	-1.836085	-1.551686	O	-1.001815	-0.930095	2.452940
C	-2.900473	2.173583	-1.096164	O	1.416919	-1.742829	1.762989
H	5.880040	0.710526	-2.387428	O	0.918628	1.281484	-1.775770
H	-3.748546	-2.733439	-1.586610	O	4.067230	-1.033026	-2.010461
H	-2.553417	4.143904	-1.963396	O	1.411669	-1.331755	-2.084083
H	-1.662454	2.799864	-2.720205	O	-0.074981	-0.460260	-0.042296
H	-1.499994	2.316882	3.055521	O	0.938506	0.881904	2.007444
H	-3.213497	2.427341	3.478135	O	4.071273	-1.421867	1.737686
H	-4.257554	-1.253354	-2.471825	O	5.167916	0.324899	0.022988
H	-4.668603	-2.963380	0.818825	O	2.089104	2.570504	0.268214
H	-2.599758	3.743535	0.295317	Si	2.831856	-2.105228	-1.822710
H	2.006222	3.554393	-2.070379	Si	4.724168	0.078022	1.586760
H	-5.421702	-2.110013	-1.400721	Si	2.145241	2.284857	-1.351558
H	5.896923	0.196792	2.455638	Si	4.713956	0.406850	-1.555331
H	-1.793532	-0.369494	2.343818	Si	0.300705	-0.569467	1.549409
H	-3.314215	-2.341973	1.824268	Si	0.288940	-0.236872	-1.625537
H	2.989263	-3.205190	-2.775738	Si	2.159766	1.956822	1.793056
H	2.020571	3.048907	2.760391	Si	2.839059	-2.437643	1.337259
O	-1.015089	-0.415690	-2.575565	H	3.005283	-3.710896	2.040206
H	-4.961015	-1.637205	1.994631	H	-1.831838	0.063040	-2.339881
H	-3.395532	2.973554	-3.025444				

Table S17. Cartesian coordinates for optimized structure **Va**
Absolute E = -3861.52211812 Hartrees

H	-2.721622	-0.304879	4.034810	Si	-5.223367	-0.189671	0.692306
H	-0.931443	3.376494	1.752712	Si	-4.004658	2.264508	-0.849970
H	-2.542746	0.373866	-4.281400	H	2.255004	1.589210	-1.411980
H	-4.426913	-3.276425	-2.017190	H	-0.404727	-3.349680	0.831471
H	1.104245	-1.030577	0.119507	O	3.615027	1.627308	0.015423
H	-6.591170	-0.304555	1.204258	O	2.649877	-0.865514	1.311620
H	-4.709721	3.493915	-1.220371	Au	4.014164	-0.486327	-0.342366
H	-2.462864	-4.102835	1.900812	C	5.272379	-0.093166	-1.905559
O	-2.744340	2.625350	0.140887	C	4.352734	-2.477996	-0.655966
O	-0.980820	0.494175	-2.284051	C	2.401589	-0.016457	2.244479
O	1.519834	1.248770	-1.946801	C	3.200229	2.097596	1.135772
O	-3.109189	-1.134275	-2.318545	C	2.715175	1.354644	2.228907
O	0.418426	-0.873928	-0.549838	C	3.203114	3.607921	1.221922
O	-0.234562	1.678230	0.014735	C	1.654476	-0.591687	3.426246
O	-4.155248	-0.297243	1.937988	H	4.081000	-2.746764	-1.680821
O	-2.652951	-2.797697	-0.261041	H	5.405528	-2.712011	-0.470854
O	-1.823092	1.027756	2.083707	H	3.712218	-3.000876	0.062484
O	-1.839606	-1.646136	2.063341	H	5.454217	0.986610	-1.872364
O	-4.928135	-1.404565	-0.372120	H	6.210946	-0.644982	-1.803321
O	-3.446812	1.515551	-2.199451	H	4.771567	-0.366923	-2.839409
O	-5.039673	1.262751	-0.053925	H	3.054895	3.968657	2.243992
Si	0.211932	0.626903	-1.183493	H	2.390929	3.999506	0.594098
Si	-2.639893	-0.308030	2.569396	H	4.144849	3.999730	0.821656
Si	-2.509645	0.308880	-2.818330	H	2.430150	1.923113	3.107657
Si	-3.788157	-2.189886	-1.268154	H	0.662635	-0.924670	3.092713
Si	-1.417119	2.206490	1.012323	H	2.185561	-1.476744	3.797111
Si	-1.808501	-3.015554	1.132517	H	1.532158	0.130279	4.238772

Table S18. Cartesian coordinates for optimized structure **Vb**
Absolute E = -3861.52592283 Hartrees

H	-3.195585	-0.547969	3.996567	Si	-5.853317	0.297117	0.877220
H	-1.133978	3.255383	2.056414	Si	-4.236153	2.542113	-0.651658
H	-2.728317	0.357067	-3.879011	H	-0.750739	-1.272095	0.967159
H	-5.868400	-2.775925	-1.966471	H	-1.845086	-3.788367	0.678696
H	1.815514	0.547929	-1.356460	O	3.380722	0.855415	-0.636275
H	-7.175512	0.458347	1.485501	O	6.052598	0.429452	0.686067
H	-4.793042	3.815795	-1.111862	Au	4.556983	-0.902985	-0.127694
H	-3.849645	-3.795073	2.099071	C	3.138437	-2.165052	-0.901429
O	-2.974769	2.826443	0.364084	C	5.684818	-2.532906	0.365264
O	-1.700186	-0.040344	-1.554216	C	5.975240	1.698789	0.704619
O	-0.060005	-1.061481	0.317861	C	3.730889	2.073840	-0.400921
O	-4.089196	-0.984130	-2.214453	C	4.917295	2.496428	0.211734
O	0.907367	0.417613	-1.708704	C	2.725143	3.112518	-0.848783
O	-0.586530	1.580108	0.224108	C	7.170318	2.389633	1.333121
O	-4.755553	-0.102296	2.042225	H	5.124992	-3.189534	1.038208
O	-4.008852	-2.801471	-0.235800	H	5.968227	-3.080508	-0.538975
O	-2.296861	0.992927	2.191919	H	6.572329	-2.131946	0.866199
O	-2.558515	-1.610098	1.741897	H	2.240192	-2.059993	-0.283579
O	-5.897161	-0.912166	-0.232976	H	2.931313	-1.816057	-1.919056
O	-3.725820	1.656367	-1.936113	H	3.474400	-3.204407	-0.919653
O	-5.394635	1.700254	0.162621	H	3.067742	4.132680	-0.654458
Si	-0.329851	0.210028	-0.686638	H	1.769899	2.946473	-0.334794
Si	-3.210088	-0.310558	2.549085	H	2.529339	2.995401	-1.922100
Si	-3.029574	0.252235	-2.448934	H	5.038134	3.568635	0.321680
Si	-4.988381	-1.896018	-1.194039	H	7.288596	2.037749	2.365650
Si	-1.720766	2.201290	1.224229	H	8.079587	2.102736	0.790241
Si	-3.062914	-3.061385	1.080496	H	7.079339	3.479721	1.332607