X-ray Absorption Spectroscopy of Phosphine capped Gold Clusters

Shailendra Kumar Sharma[a, b], Bernt Johannessen[c], Vladimir B. Golovko[a*], Aaron T. Marshall[b*]

[a] School of Physical and Chemical Sciences, MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury, Christchurch, New Zealand

[b] Department of Chemical and Process Engineering, MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury, Christchurch, New Zealand

[c] Australian Synchrotron, ANSTO, Clayton VIC 3168, Australia.

List of Figures

Figure SI1. Crystal structures of (a) $[Au_6(dppp)_4](NO_3)_2$ [1], (b) $[Au_9(PPh_3)_8](NO_3)_3$ [2], and (c) $[Au_{13}(dppe)_5Cl_2]Cl_3$ [3]. The atomic colour scheme is gold (Au), orange (P), green (Cl) and black (C); hydrogen is omitted for clarity. 3
Figure SI2. XAS spectra of Au foil and Au clusters. 3
Figure SI3. XANES spectra Au foil and Au clusters overlaid directly for comparison of the intensity 4
Figure SI4. UV-Vis spectra of (a) $[Au_6(dppp)_4](NO_3)_2$, (b) $[Au_9(PPh_3)_8](NO_3)_3$, (c) $[Au_{13}(dppe)_5Cl_2]Cl_3$ and (d) $Au_{101}(PPPh_3)_{21}Cl_5$; in methanol. 4
Figure SI5. Contribution of individual scattering paths in EXAFS of Au_9 (a) in R space, and (b) in k-space. 5
Figure SI6. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_9 clusters without using scattering paths contributions from carbon atoms (a) in R-space, and (b) in k-space 6
Figure SI7. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_9 clusters using two aggregated shells of scattering paths from carbon atoms (a) R-space, and (b) k-space 6
Figure SI8. (a) Different types of Au atoms in Au_6 clusters, (b) groups of bonds with similar features, and (c) Au_6 clusters with different groups of atoms; light blue colour represents bonds in group 1, and violet colour represent bonds in group 2. The atomic colour scheme is gold (Au), orange (P) and black (C). All the carbon atoms are shown in Figure SI1. 7
Figure SI9. Fits of the Au L_3-edge EXAFS of Au_6 clusters in k-space. 8
Figure SI10. Contribution of individual scattering paths in the EXAFS of Au_6 clusters in R-space. 9
Figure SI11. The classification of bonds with similar features in the Au_{13} cluster, and (b) Au_{13} clusters with different groups of atoms light blue represents bonds in group 1, and violet colour represents bonds in group 2. The crystal structure of the clusters is shown in Figure SI1. 10
Figure SI12. Fits the Au L_3-edge EXAFS of the Au_{13} clusters in k-space. 11
Figure SI13.Contribution of individual scattering paths in the EXAFS of Au_{13} clusters in R-space. 12
Figure SI14. Fits of the Au L_3-edge EXAFS of Au_{101} clusters in k-space. 12
Figure SI15. Contribution of individual scattering paths in EXAFS of Au_{101} (a) in R space. 13
Figure SI16. EXAFS spectra with fixing Au-P coordination based on the empirical formula of Au_{101} (i.e. $Au_{101}(PPh_3)_{21}Cl_5$) (a) fitted EXAFS, and (b) individual contribution from different scattering paths. 14
Figure 17. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_{101} clusters without Au-P scattering path 14

List of Tables

Table SI1. Bond distances between neighbouring Au-Au atoms in Au_9 clusters. 5
Table SI2. Bond distance and coordination numbers for bonds in each selected group of Au atoms in Au_9 clusters 5
Table SI3: **.** Structural characteristics of Au_9 clusters with no Au-C scattering path (ΔE_o = 3.812 eV). 6
Table SI4: **.** Structural characteristics of Au_9 clusters with two Au-C scattering paths (ΔE_o = 3.716 eV). 6
Table SI*5*. Bond distances between neighbouring Au-Au atoms in Au_6 clusters 8
Table SI6. Structural characteristics of Au_6 clusters (ΔE_o = 2.737 eV) 8
Table SI7. Bond distances between neighbouring Au-Au atoms in Au_{13} clusters 9
Table SI8. Structural characteristics of Au_{13} clusters (ΔE_o = 4.574 eV) 11
Table SI9. Structural characteristics of Au_{101} clusters (ΔE_o = 4.204 eV). 13
Table SI10. Structural characteristics of the Au_{101} clusters after fixing Au-P coordination number (ΔE_o= 4.221 eV). 13

Table SI11. Structural characteristics of Au_{101} clusters without Au-P scattering path (ΔE_o = 4.67)..... 14

Crystal structures of phosphine-capped Au clusters

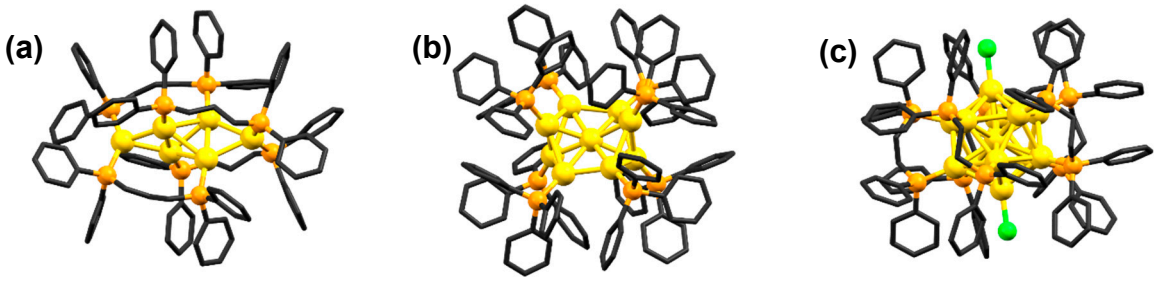

Figure S1. Crystal structures of (a) $[Au_6(dppp)_4](NO_3)_2$ [1], (b) $[Au_9(PPh_3)_8](NO_3)_3$ [2], and (c) $[Au_{13}(dppe)_5Cl_2]Cl_3$ [3]. The atomic colour scheme is gold (Au), orange (P), green (Cl) and black (C); hydrogen is omitted for clarity.

X-ray absorption spectra of Au clusters and gold foil

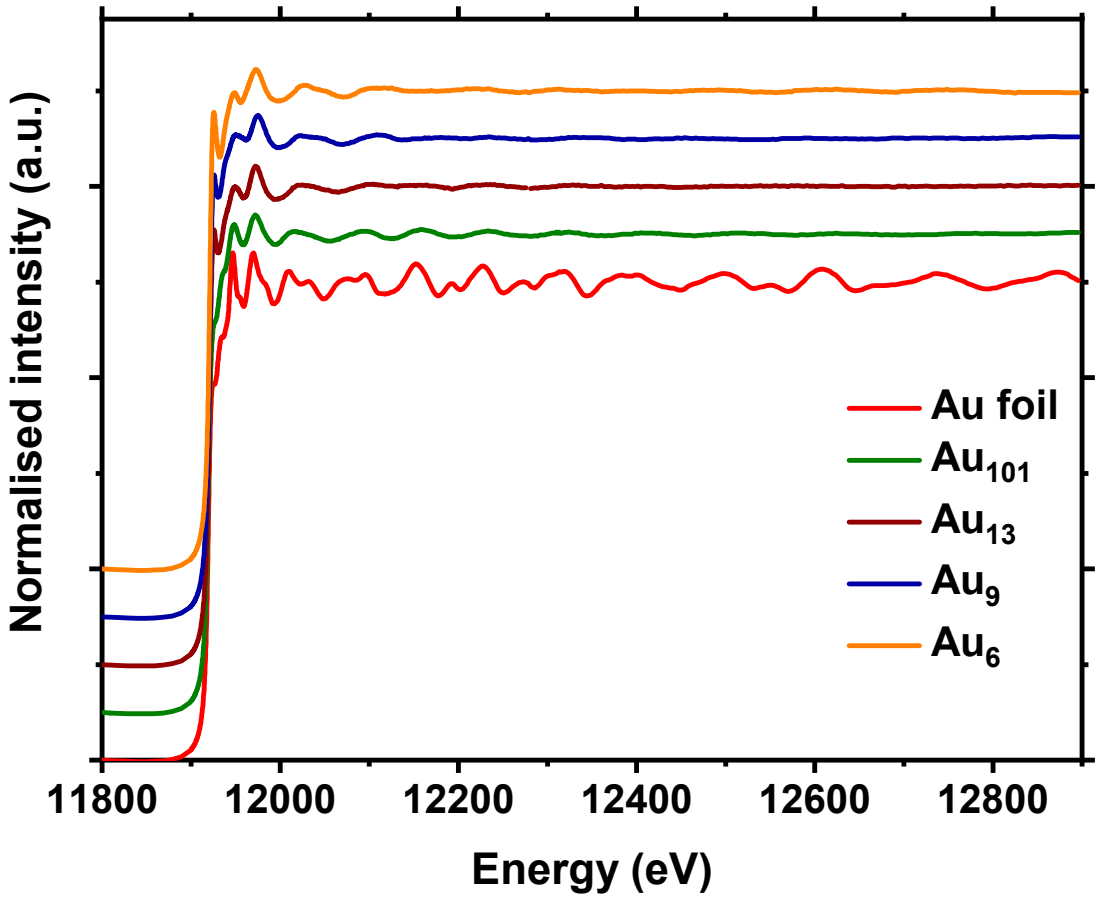

Figure S2. XAS spectra of Au foil and Au clusters.

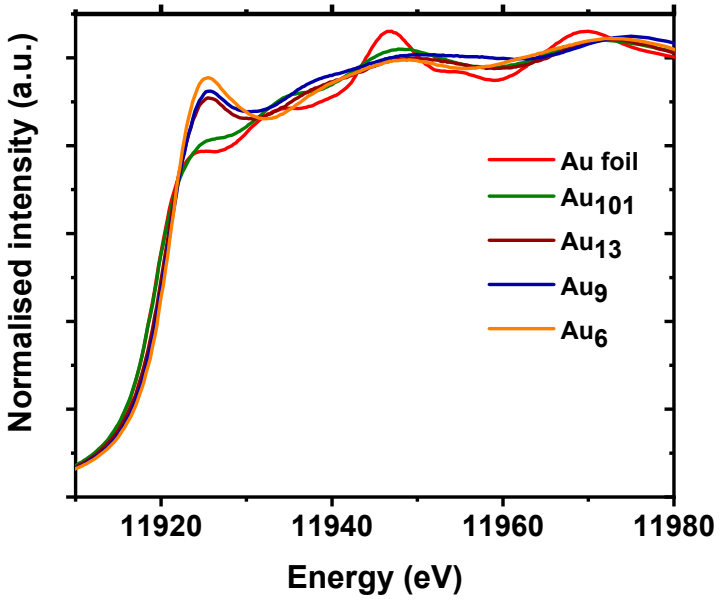

Figure S3. XANES spectra Au foil and Au clusters overlaid directly for comparison of the intensity

UV- Vis spectra of Au clusters

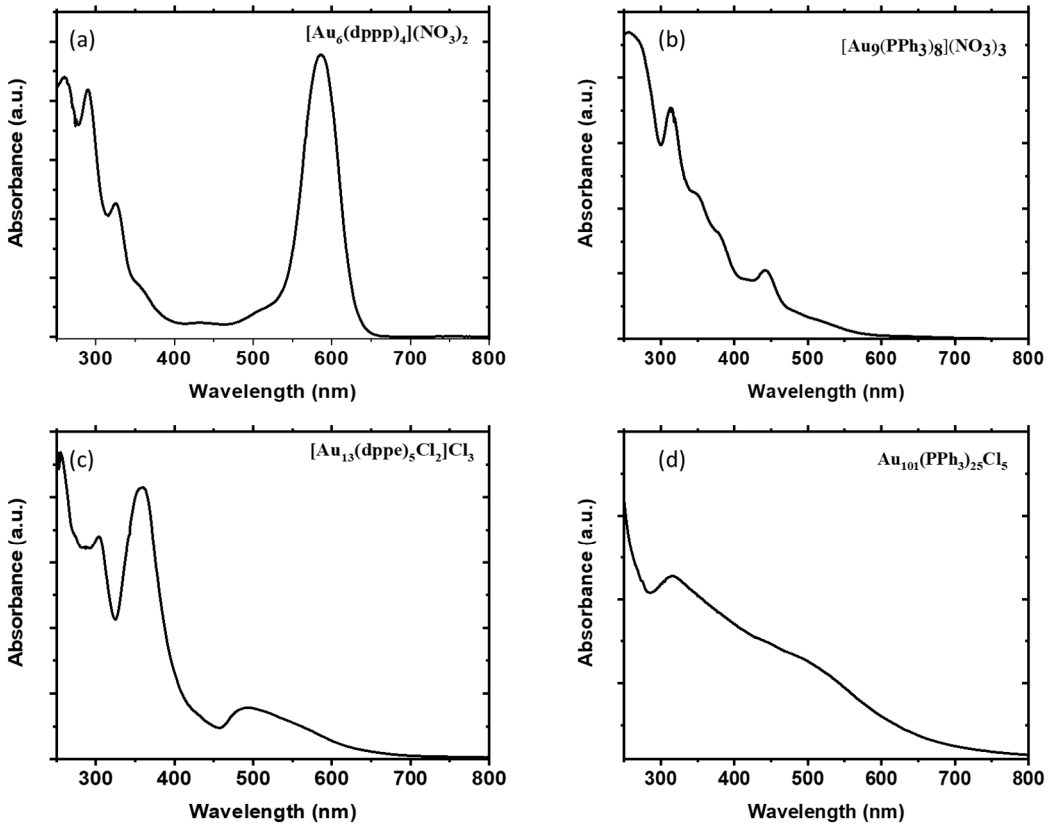

Figure S4. UV-Vis spectra of (a) $[Au_6(dppp)_4](NO_3)_2$, (b) $[Au_9(PPh_3)_8](NO_3)_3$, (c) $[Au_{13}(dppe)_5Cl_2]Cl_3$ and (d) $Au_{101}(PPPh_3)_{21}Cl_5$; in methanol.

EXAFS of Au clusters

Au_9 clusters

Table S1. Bond distances between neighbouring Au-Au atoms in Au_9 clusters.

Type of Au	Number of atoms of this type	Bond length (Å)			
		Au-Au	Au-Au	Au-Au	Au-Au
$Au_{(1)}$ type	4	2.708	2.772	2.855	2.880
$Au_{(2)}$ type	4	2.675	2.762	2.855	2.880
$Au_{(3)}$	1	4 Bonds of 2.675 Å		4 Bonds of 2.708 Å	

Table S2. Bond distance and coordination numbers for bonds in each selected group of Au atoms in Au_9 clusters

Bond length (Å)	No of bonds	Bonds per atom		Average Bond distance(Å)	CN
2.675	8	0.889	Au-Au group 1	2.729	2.667
2.708	8	0.889			
2.762	4	0.444			
2.772	4	0.444			
2.855	8	0.889	Au-Au group 2	2.867	1.778
2.880	8	0.889			

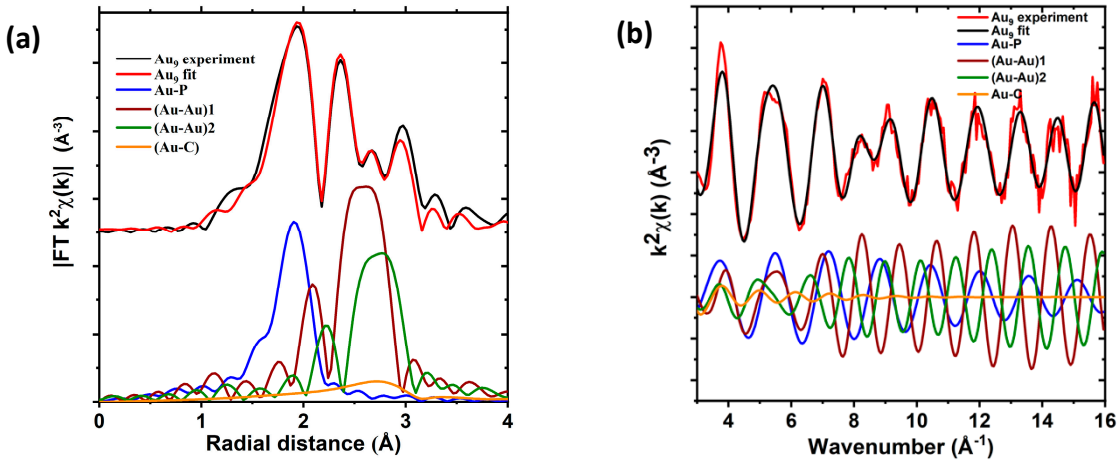

Figure S5. Contribution of individual scattering paths in EXAFS of Au_9 (a) in R space, and (b) in k-space.

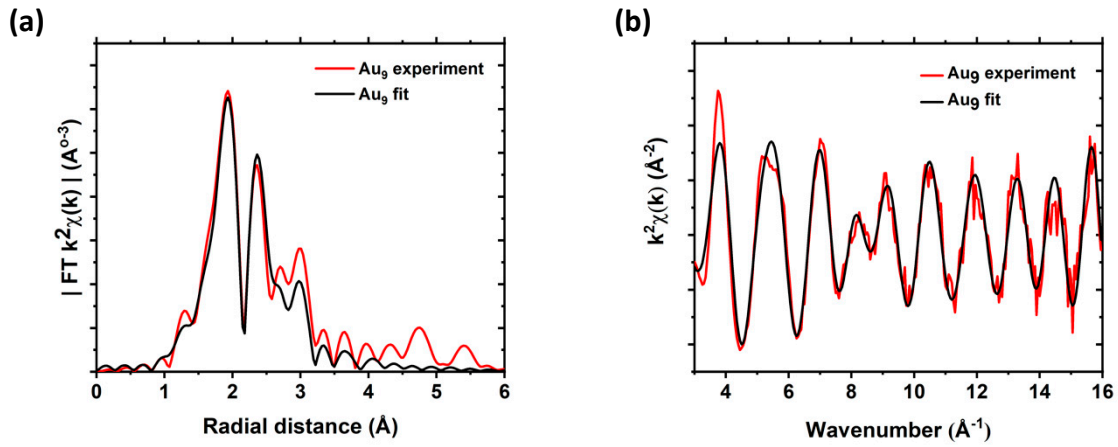

Figure S6. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_9 clusters without using scattering paths contributions from carbon atoms (a) in R-space, and (b) in k-space

Table S3: **.** Structural characteristics of Au_9 clusters with no Au-C scattering path (ΔE_o = 3.812 eV).

Paths	CN (fixed)	σ^2(Å^2)	R (Å)
Au-P	0.889	0.0008 ± 0.0004	2.2932 ± 0.0112
$(Au\text{-}Au)_1$	2.667	0.0032 ± 0.0006	2.7101 ± 0.0110
$(Au\text{-}Au)_2$	1.778	0.0027 ± 0.0009	2.8448 ± 0.0145

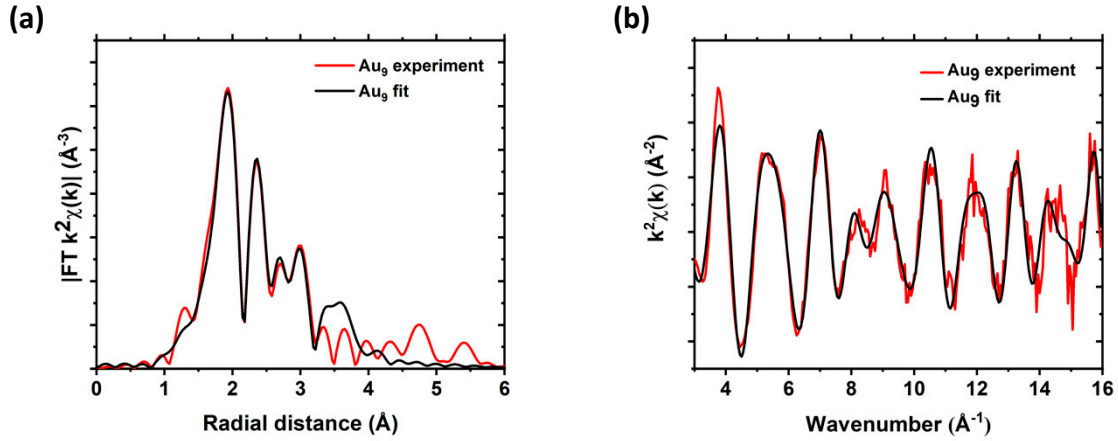

Figure S7. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_9 clusters using two aggregated shells of scattering paths from carbon atoms (a) R-space, and (b) k-space

Table S4: **.** Structural characteristics of Au_9 clusters with two Au-C scattering paths (ΔE_o = 3.716 eV).

Paths	CN (fixed)	σ^2(Å^2)	R (Å)
Au-P	0.889	0.0010 ± 0.0004	2.2946 ± 0.0090
$(Au\text{-}Au)_1$	2.667	0.0035 ± 0.0006	2.7117 ± 0.0103
$(Au\text{-}Au)_2$	1.778	0.0031 ± 0.0009	2.8403 ± 0.0142
$(Au\text{-}C)_1$	2.667	0.0080 ± 0.0065	3.4113 ± 0.0532
$(Au\text{-}C)_2$	1.778	0.0078 ± 0.0062	3.9001 ± 0.0937

EXAFS analysis of Au_6

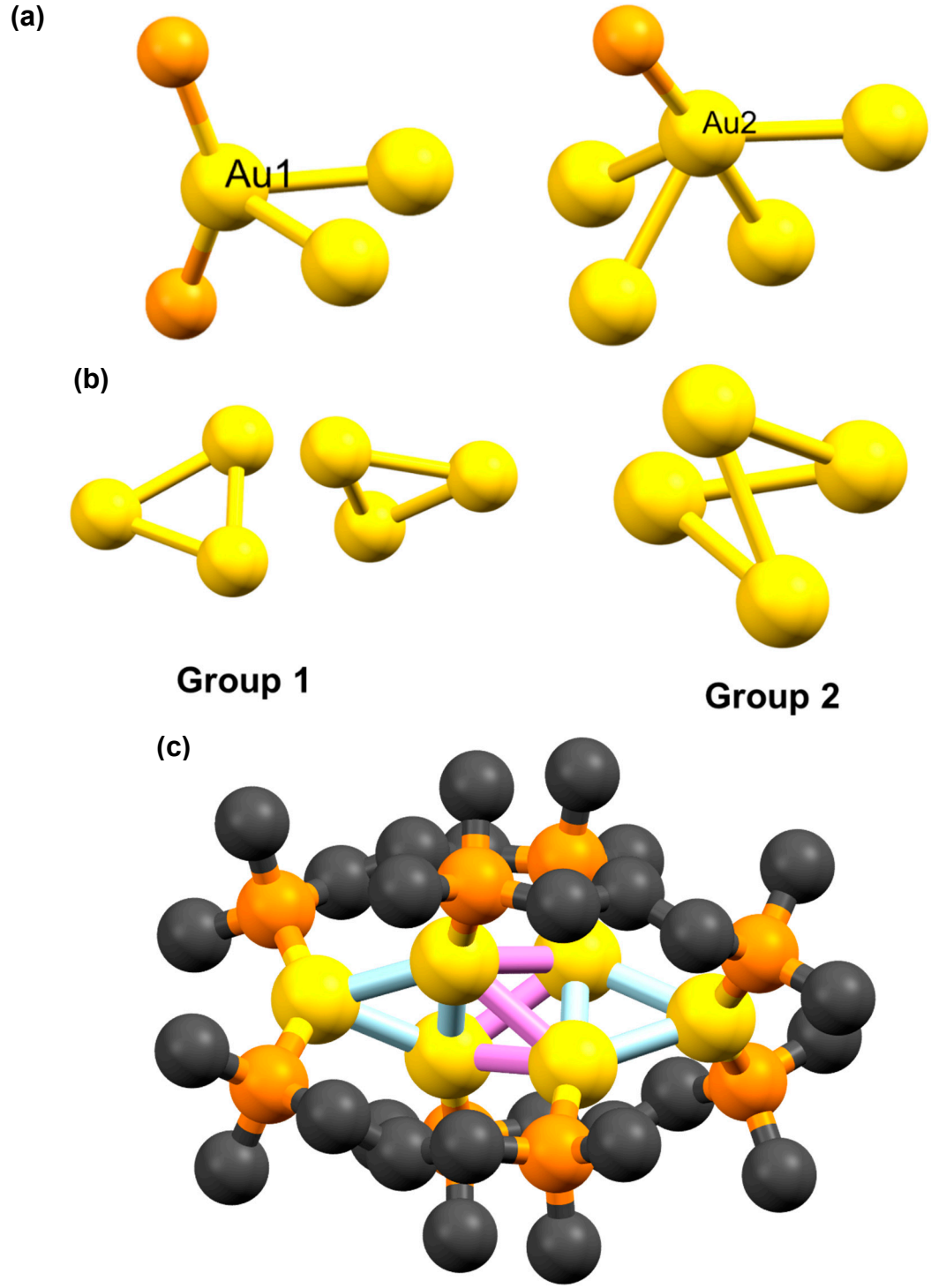

Figure S8. (a) Different types of Au atoms in Au_6 clusters, (b) groups of bonds with similar features, and (c) Au_6 clusters with different groups of atoms; light blue colour represents bonds in group 1, and violet colour represent bonds in group 2. The atomic colour scheme is gold (Au), orange (P) and black (C). All the carbon atoms are shown in Figure SI1.

Table S5. Bond distances between neighbouring Au-Au atoms in Au_6 clusters

Type of Au	Bond length (Å)			
	Au-Au	Au-Au	Au-Au	Au-Au
$Au_{(1)}$	2.798	2.798	-	-
$Au_{(2)}$	2.923	2.63	2.923	2.798

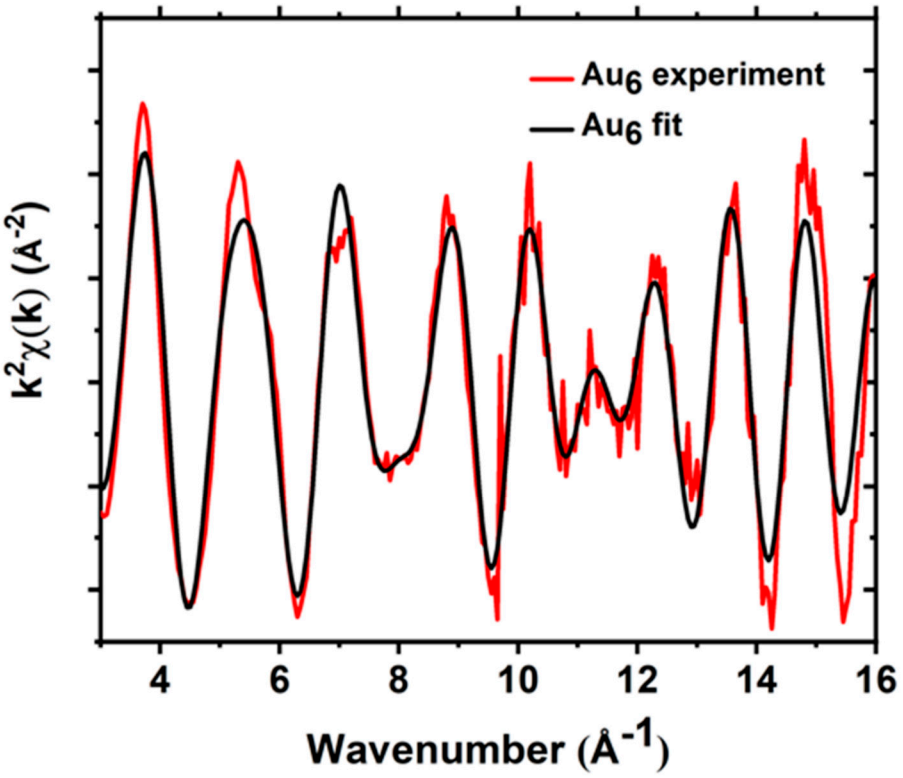

Figure S9. Fits of the Au L_3-edge EXAFS of Au_6 clusters in k-space.

Table S6. Structural characteristics of Au_6 clusters (ΔE_o = 2.737 eV)

Path	CN (fixed)	σ^2(Å^2)	R (Å)
Au-P	1.333	0.0018 ± 0.0006	2.3080 ± 0.0071
Au-Au group 1	2.000	0.0109 ± 0.0005	2.6602 ± 0.0279
Au-Au group 2	1.333	0.0024 ± 0.0005	2.8337 ± 0.0091
Au-C	2.667	0.0035 ± 0.0021	3.4791 ± 0.0340

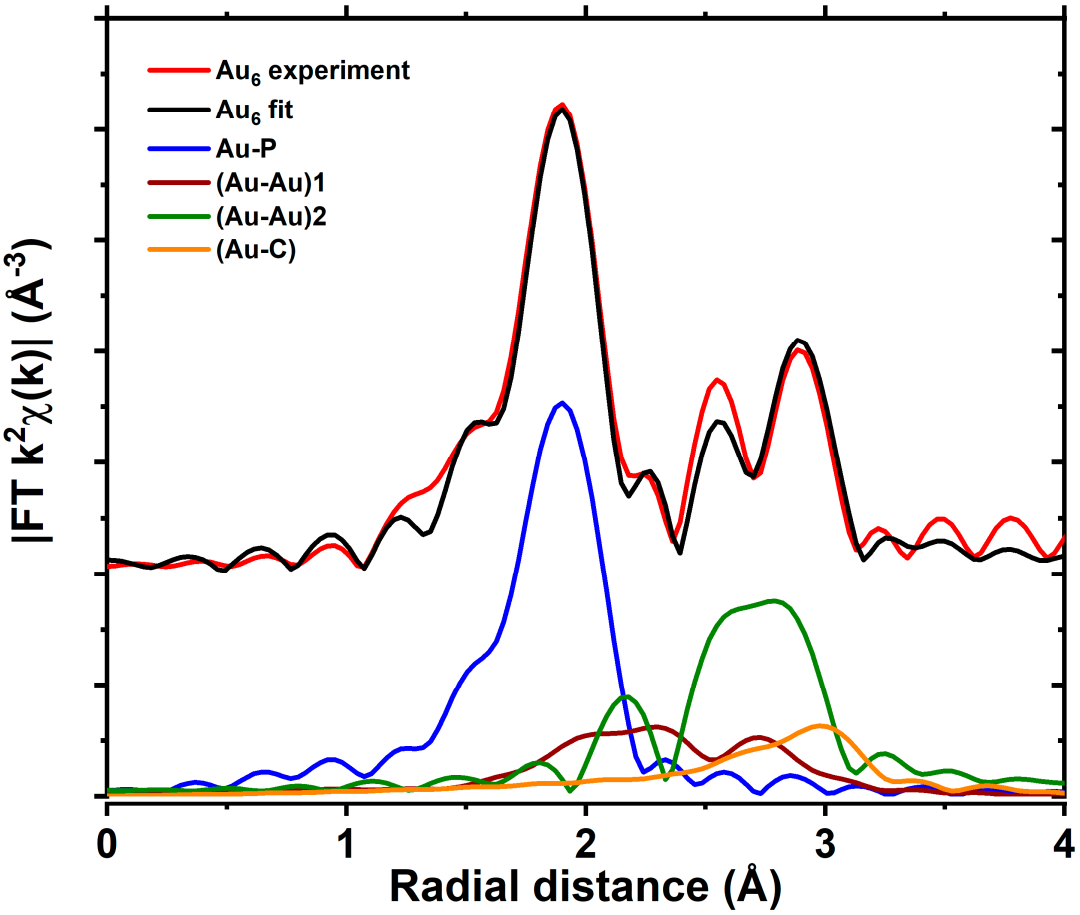

Figure S10. Contribution of individual scattering paths in the EXAFS of Au_6 clusters in R-space.

EXAFS analysis of Au_{13} clusters

Table S7. Bond distances between neighbouring Au-Au atoms in Au_{13} clusters

		Au-Au bond length (Å)					
Au atom	Au-P/Au-Cl (Å)	with "surface" atoms					with "central" atom
Au_1-Cl	2.357	2.897	2.858	2.939	2.927	2.89	2.696
Au_2	2.276	2.894	2.848	2.929	2.974	2.858	2.759
Au_3	2.301	2.919	2.855	2.974	2.955	2.897	2.786
Au_4	2.291	2.89	2.94	2.892	2.889	2.955	2.783
Au_5	2.278	2.85	2.884	2.911	2.927	2.94	2.758
Au_6	2.29	2.875	2.894	2.939	2.911	2.875	2.798
Au_7	2.293	2.848	2.917	2.924	2.885	2.923	2.773
Au_8	2.298	2.923	2.924	2.945	2.855	2.929	2.782
Au_9	2.284	2.889	2.919	2.945	2.871	2.906	2.757
Au_{10}	2.294	2.929	2.958	2.85	2.892	2.906	2.792
Au_{11}	2.283	2.958	2.873	2.924	2.875	2.884	2.781
Au_{12}-Cl	2.345	2.871	2.929	2.873	2.885	2.924	2.697

*Au-Cl are the Au atoms bonded to chlorine atoms (Figure S1c)

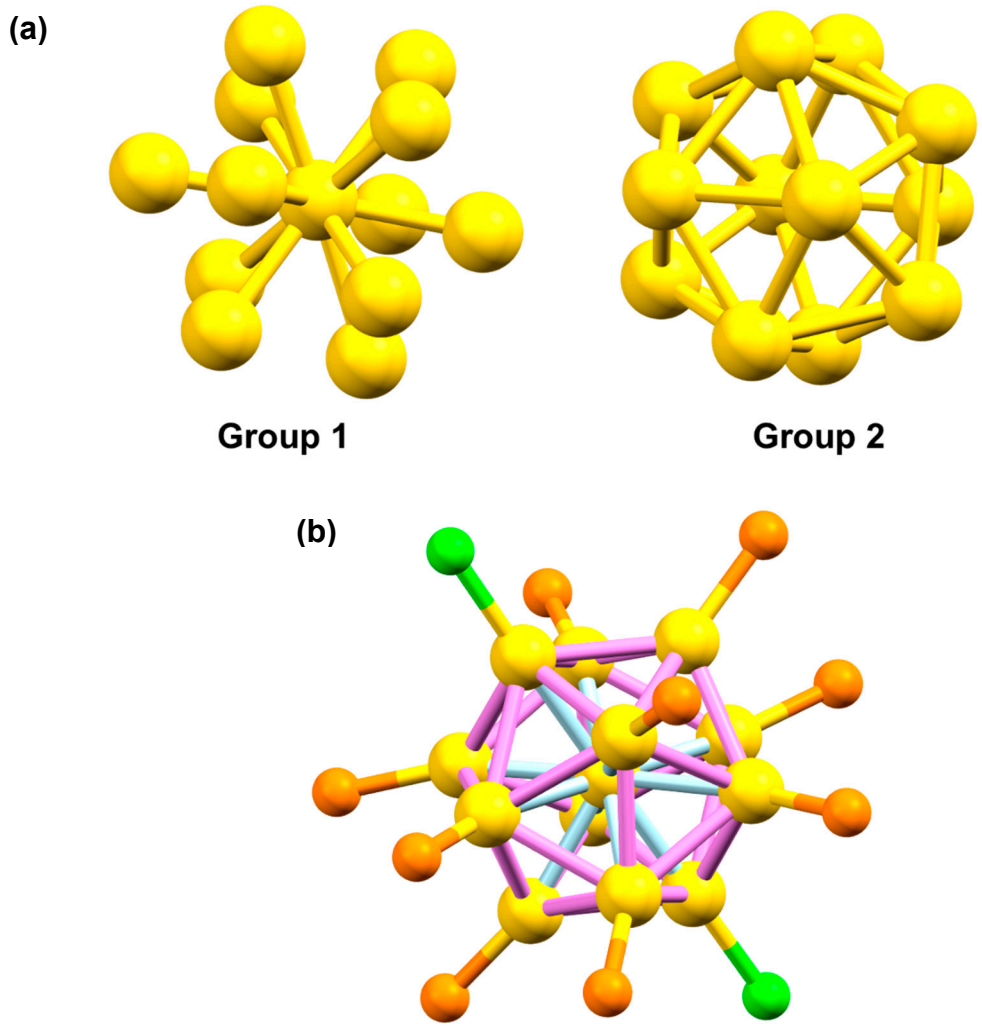

Figure S11. The classification of bonds with similar features in the Au_{13} cluster, and (b) Au_{13} clusters with different groups of atoms light blue represents bonds in group 1, and violet colour represents bonds in group 2. The crystal structure of the clusters is shown in Figure SI1.

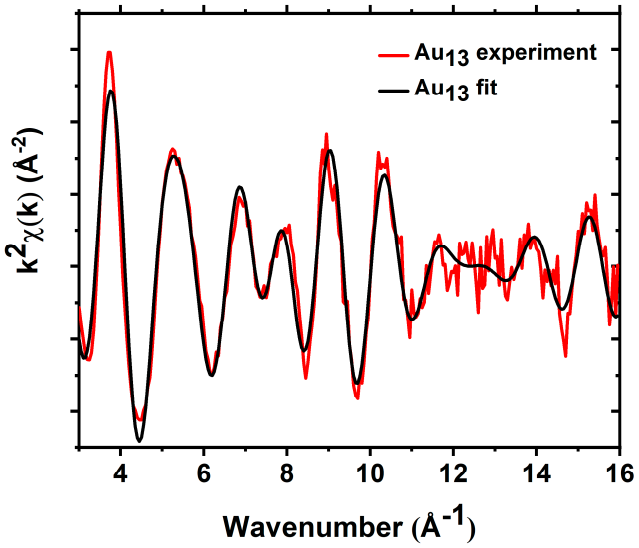

Figure S12. Fits the Au L_3-edge EXAFS of the Au_{13} clusters in k-space.

Table S8. Structural characteristics of Au_{13} clusters (ΔE_o = 4.574 eV)

Path	CN (fixed)	σ^2 (Å^2)	R (Å)
Au-P	0.769	0.0011 ± 0.0006	2.30 ± 0.009
Au-Cl	0.154	0.0029 ± 0.0003	2.19 ± 0.031
Au-Au group 1	1.846	0.0043 ± 0.0005	2.75 ± 0.008
Au-Au group 2	4.615	0.0084 ± 0.0008	2.86 ± 0.005
Au-C	1.923	0.0116 ± 0.0082	3.40 ± 0.049

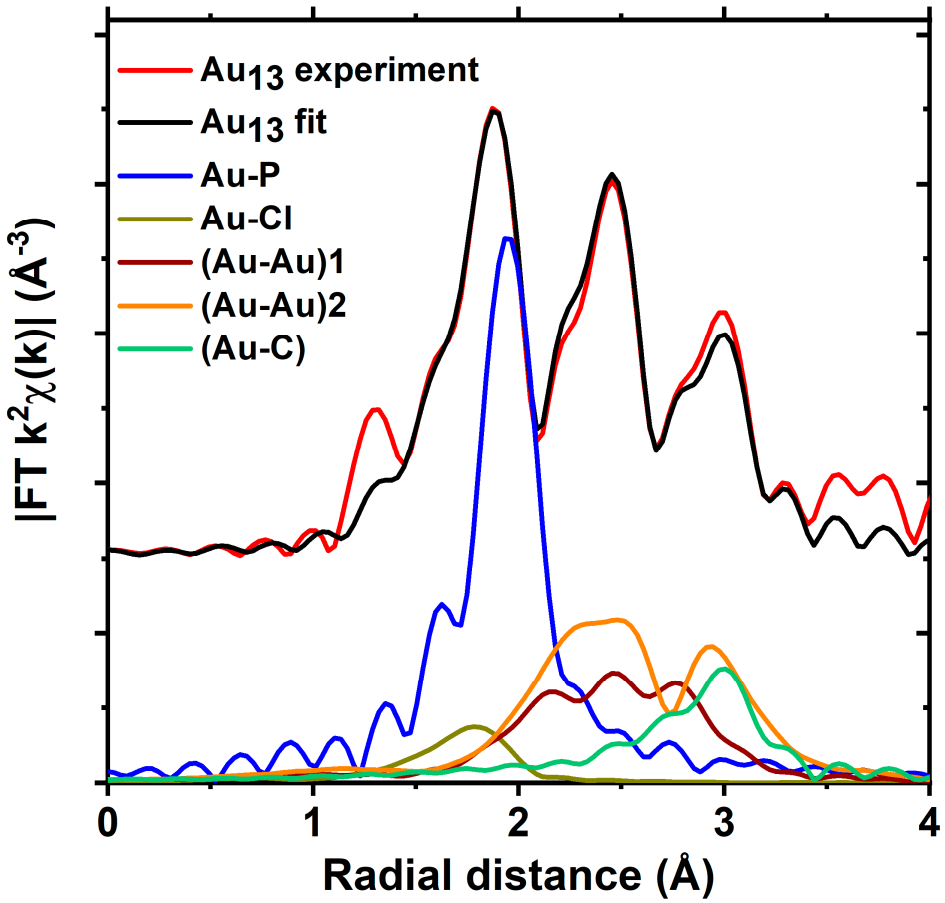

Figure S13.Contribution of individual scattering paths in the EXAFS of Au_{13} clusters in R-space.

EXAFS analysis of Au_{101}

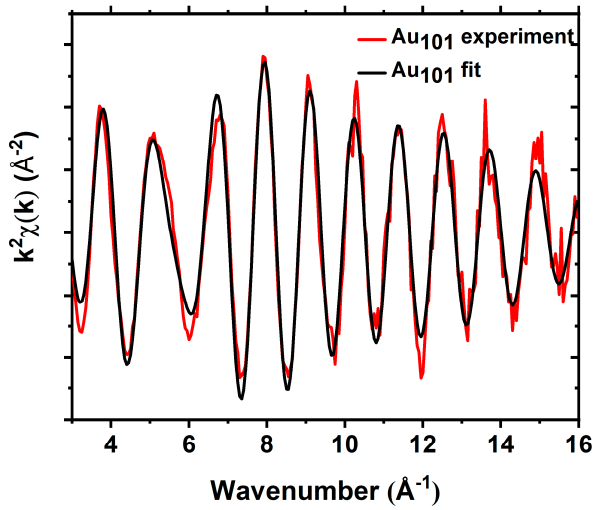

Figure S14. Fits of the Au L_3-edge EXAFS of Au_{101} clusters in k-space.

Table S9. Structural characteristics of Au_{101} clusters (ΔE_o = 4.204 eV).

Path	CN	σ^2 ($Å^2$)	R (Å)
Au-P	0.19 ± 0.10	0.0042 ± 0.0020	2.3000 ± 0.0240
Au-Au	7.68 0.38	0.0068 ± 0.0003	2.8160 ± 0.0024

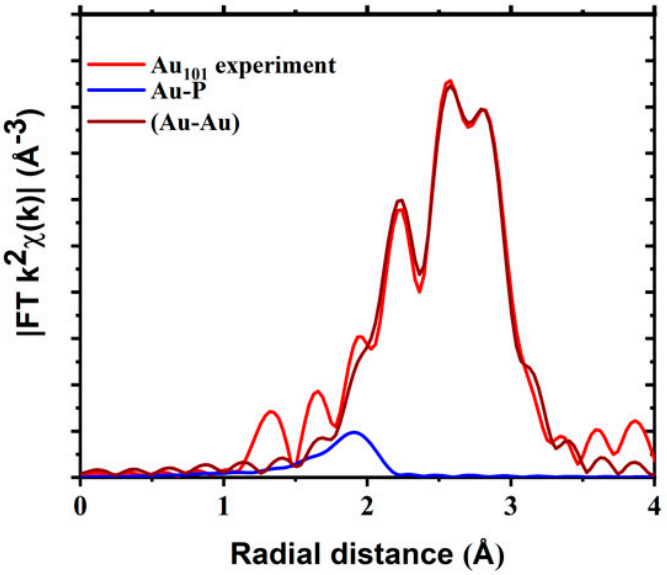

Figure S15. Contribution of individual scattering paths in EXAFS of Au_{101} (a) in R space.

Table S10. Structural characteristics of the Au_{101} clusters after fixing Au-P coordination number (ΔE_o= 4.221 eV).

Path	CN	σ^2 ($Å^2$)	R (Å)
Au-P	0.208 (fixed)	0.0027 ± 0.0020	2.3000 ± 0.0223
Au-Au	7.68 ± 0.34	0.0068 ± 0.0002	2.8161 ± 0.0227

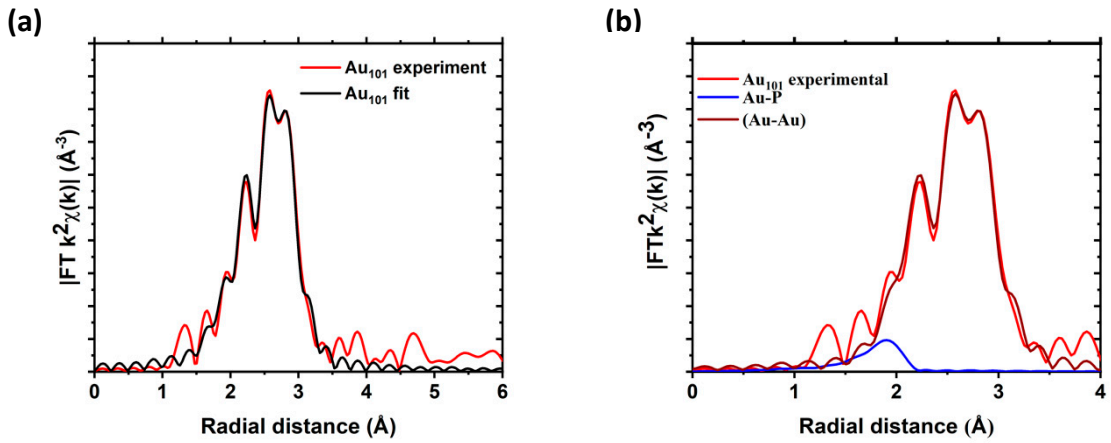

Figure S16. EXAFS spectra with fixing Au-P coordination based on the empirical formula of Au_{101} (*i.e.* $Au_{101}(PPh_3)_{21}Cl_5$) (a) fitted EXAFS, and (b) individual contribution from different scattering paths.

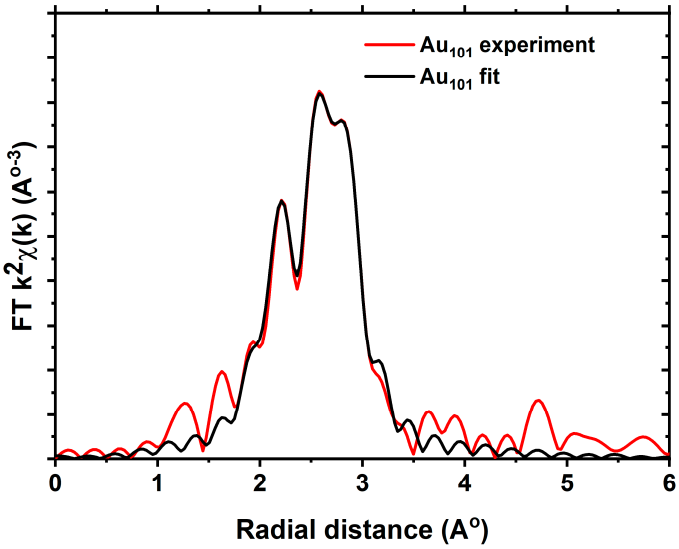

Figure S17. Fits of the magnitude of Fourier transform of Au L_3-edge of Au_{101} clusters without Au-P scattering path

Table S11. Structural characteristics of Au_{101} clusters without Au-P scattering path (ΔE_o = 4.67)

Path	CN	σ^2 (Å^2)	R (Å)
Au-Au	7.56 ± 0.39	0.0068 ± 0.0002	2.8546 ± 0.0027

References

1. Bakar, M.A.; Sugiuchi, M.; Iwasaki, M.; Shichibu, Y.; Konishi, K. Hydrogen bonds to Au atoms in coordinated gold clusters. *Nature Communications* **2017**, *8*, 576, doi:10.1038/s41467-017-00720-3.
2. Wen, F.; Englert, U.; Gutrath, B.; Simon, U. Crystal Structure, Electrochemical and Optical Properties of $[Au_9(PPh_3)_8](NO_3)_3$. *European Journal of Inorganic Chemistry* **2008**, *2008*, 106-111, doi:https://doi.org/10.1002/ejic.200700534.

3. Shichibu, Y.; Konishi, K. HCl-induced nuclearity convergence in diphosphine-protected ultrasmall gold clusters: a novel synthetic route to "magic-number" Au_{13} clusters. *Small* **2010**, *6*, 1216-1220, doi:10.1002/smll.200902398.