# Electronic Supplementary Information: Density-Functional Tight-Binding for Phosphine-Stabilized Nanoscale Gold Clusters

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**Fig. S1** The DFTB2 auorg<sup> $\alpha'$ </sup> and auorg<sup> $\chi'$ </sup> Au-P repulsive potentials. Ideally, the DFTB repulsive potentials are positive, however, in the case if Au-P potential the repulsive potential is negative in the bonding range of  $\approx$ 2.4 Å. The attractive interaction was made to compensate the under-binding of Au-P electronic interaction, which ca be attributed to the effect of the minimum basis set in DFTB method. It is worth mentioning that Au-Au repulsive potential is also attractive  $\approx$ 16 kcal/mol.<sup>1</sup>

					$\Delta E^{react.}$			DI	TB2 Deivation	us		
		Keactions			wB97XD3BJ	$\varepsilon_P^{3d} = 0.02$	$\varepsilon_P^{3d} = 0.07$	$\varepsilon_P^{3d} = 0.12$	$\varepsilon_P^{3d} = 0.22$	$\varepsilon_P^{3d} = 0.32$	$\varepsilon_P^{3d} = 0.42$	$\varepsilon_P^{3d} = 0.52$
, Р,	+ P,	= P <sub>4</sub>		↑	-77.34	23.36	27.24	29.78	32.86	34.63	35.78	36.58
P,	$+ 2   m{H}_{2}$	$= H'_{2}PPH_{2}$		↑	-47.03	39.31	40.00	40.34	40.56	40.55	40.46	40.35
P,	+ 2 H <sub>2</sub> CCH <sub>3</sub>	$= H_{\kappa}^{T}C_{2}PPC_{3}H_{\kappa}$		↑	-40.35	4.71	6.86	8.34	10.27	11.48	12.32	12.93
P,	+ 3 H,	$= 2 \text{ PH}_3^2$		↑	-49.43	65.97	64.82	63.89	62.46	61.42	60.63	60.00
H <sub>2</sub> ,PCH <sub>3</sub>	+ H,	$= PH_{3}$	+ $CH_{4}$	↑	-12.93	10.04	9.72	9.48	9.10	8.84	8.64	8.48
$HP(CH_3)$ ,	$+ 2 H_{2}$	= PH <sub>s</sub>	$+ 2 \text{ CH}_{4}$	↑	-23.99	20.34	19.55	18.94	18.02	17.38	16.90	16.53
P(CH <sub>3</sub> ) <sub>3</sub>	$+ 3 H_{2}$	$= PH_{3}$	$+ 3 \text{ CH}_{4}$	↑	-33.29	30.81	29.42	28.33	26.74	25.63	24.82	24.19
OP(CH <sub>3</sub> ) <sub>3</sub>	$+ 3 H_{2}$	$= H_3 \tilde{P}O$	$+ 3 \text{ CH}_{4}$	↑	-10.23	23.11	21.42	19.91	17.30	15.15	13.37	11.87
HPCH, Č	+ H,	$= H_{3}^{2}PCH_{3}$	-	↑	-43.45	12.20	11.47	10.92	10.15	9.63	9.26	8.98
PCH <sup>2</sup>	+ H,	= HPCH,		↑	-34.93	16.99	16.37	15.89	15.20	14.72	14.37	14.10
Nd	+ H2	= HPNH		↑	-19.42	10.01	12.18	13.69	15.55	16.58	17.20	17.59
HNHH	+ H <sub>2</sub>	$= H_2 PNH_2$		↑	-45.32	28.84	25.86	23.76	20.96	19.11	17.79	16.79
H <sub>2</sub> PNH <sub>2</sub>	+ H <sub>2</sub>	$= PH_3$	$+ NH_3$	↑	-10.13	15.91	11.86	8.61	3.82	09.0	-1.70	-3.41
$P(NH_2)_3$	$+ 3 H_2$	$= PH_{3}$	$+ 3 \text{ NH}_3$	↑	-14.26	48.16	35.37	25.31	10.56	0.32	-7.09	-12.65
P(NC,H <sub>k</sub> ),	$+ 3 H_{2}$	= PH <sub>s</sub>	+ 3 HN $(CH_3)$ ,	↑	-4.26	43.49	30.27	19.72	4.16	-6.52	-14.16	-19.83
P4 - 5	$+ 3.0^{-2}_{2}$	$= P_4 \tilde{O}_6$		♠	-507.00	-450.11	-407.74	-372.00	-315.47	-273.00	-240.04	-213.77
P4	$+50_{2}^{2}$	$= P_4 O_0$		↑	-865.78	-769.47	-692.40	-625.74	-516.83	-431.99	-364.24	-309.00
P(OCH <sub>3</sub> ) <sub>3</sub>	$+ 3 H_2^{-1}$	$= PH_3$	$+ 3 HOCH_3$	↑	13.91	156.57	138.93	124.73	103.30	88.09	76.75	68.03
H <sub>3</sub> PO <sub>4</sub>	$+ 3 H_{2}$	$= H_3 \tilde{P}O$	$+ 3 H_{2} O_{2}$	↑	43.97	151.91	140.53	130.46	113.57	100.08	89.13	80.12
OP(OCH <sub>3</sub> ) <sub>3</sub>	$+ 3 H_{2}$	$= H_3^{\gamma}PO$	+ 3 HÕCH <sub>3</sub>	↑	50.04	134.34	123.72	114.43	98.99	86.76	76.91	68.82
H <sub>3</sub> PO3	$+ 2 H_{2}^{2}$	$= H_3^{\gamma}PO$	$+ 2 H_{20}$	↑	31.14	101.01	92.12	84.47	71.98	62.26	54.51	48.22
OP(OH), CH3	$+ H_{2}\bar{0}$	$= H_3 PO_4$	+ $CH_4$	↑	-15.38	-42.39	-40.38	-38.44	-34.90	-31.86	-29.28	-27.07
H <sub>2</sub> PSH	+ H <sub>2</sub>	= PH <sub>3</sub>	+ H <sub>2</sub> S	↑	-1.51	14.96	12.98	11.51	9.49	8.17	7.25	6.57
$H_2^{-}PSCH_3$	$+$ $H_2^-$	$= PH_{3}$	+ HSCH <sub>3</sub>	↑	-0.25	15.19	13.18	11.71	9.71	8.43	7.53	6.87
$H_3PS_4$	$+ 4 H_{0}$	= PH <sub>3</sub>	+ 4 H, S	↑	6.56	43.96	34.01	26.18	14.75	6.87	1.16	-3.17

**Table S1** Test results for selected chemical reactions involving H, C, N, O, P, and S containing compounds for DFTB2/mio with various values of the P 3d orbital energy. The DFTB chemical reaction energies are compared to that of wB97X-D3BJ/def2-TZVP method.<sup>2</sup> The chemical reaction energies and deviations are in kcal/mol, P 3d orbital energies are in Hartree.

 Table S2
 Averaged and normalized ligand binding ernergies in kcal/mol for small-sized clusters.

Complexes	TPSS/def2-SVP	DFTB2/auorg <sup><math>\alpha</math></sup>	DFTB2/auorg <sup><math>\alpha</math></sup> /	DFTB2/auorg $\chi$
$Au_2(PH_3)_2$	-27.8	-39.1	-48.1	-45.9
$[Au_3(PH_3)_3]^+$	-47.8	-60.9	-67.3	-65.4
$Au_4(PH_3)_2$	-33.9	-40.3	-49.5	-47.6
$Au_2(PMe_3)_2$	-36.8	-41.8	-49.9	-47.7
$[Au_3(PMe_3)_3]^+$	-64.5	-66.8	-73.2	-71.4
$Au_4(PMe_3)_2$	-46.4	-44.2	-52.6	-50.8
$Au_2(PPh_3)_2$	-37.9	-41.8	-49.7	-47.6
$[Au_3(PPh_3)_3]^+$	-70.0	-70.0	-77.0	-74.8
$Au_4(PPh_3)_2$	-48.7	-45.0	-53.1	-51.4

Table S3 Averaged and normalized ligand binding ernergies in kcal/mol for moderate-sized clusters.

Complexes	TPSS/def2-SVP	DFTB2/auorg <sup><math>\alpha</math></sup>	DFTB2/auorg <sup><math>\alpha</math></sup> /	DFTB2/auorg <sup><i>χ</i></sup>
$[Au_6(PH_3)_6]^{2+}$	-52.1	-63.1	-69.4	-67.6
$[Au_7(PH_3)_7]^+$	-31.6	-34.5	-43.4	-42.4
$[Au_8(PH_3)_8]^{2+}$	-43.6	-47.9	-55.4	-54.1
$[Au_9(PH_3)_8]^{3+}$	-57.3	-69.2	-75.3	-73.4
$[Au_{11}(PH_3)_{10}]^{3+}$	-51.8	-56.7	-63.5	-62.3
$[Au_{13}(PH_3)_{12}]^{5+}$	-72.2	-84.8	-90.3	-88.5
$[Au_{20}(PH_3)_{16}]^{4+}$	-46.2	-48.6	-56.0	-54.4
$Au_{22}(PH_3)_{12}$	-25.5	-19.4	-30.0	-28.6
$[Au_6(PMe_3)_6]^{2+}$	-71.1	-70.7	-77.3	-75.4
$[Au_7(PMe_3)_7]^+$	-46.5	-39.4	-48.2	-46.9
$[Au_8(PMe_3)_8]^{2+}$	-60.8	-54.9	-62.4	-61.0
$[Au_9(PMe_3)_8]^{3+}$	-79.0	-78.5	-85.0	-83.1
$[Au_{11}(PMe_3)_{10}]^{3+}$	-71.2	-65.2	-72.6	-71.0
$[Au_{13}(PMe_3)_{12}]^{5+}$	-98.2	-97.8	-104.1	-102.3
$[Au_{20}(PMe_3)_{16}]^{4+}$	-65.9	-57.2	-64.6	-62.9
$Au_{22}(PMe_3)_{12}$	-41.8	-24.0	-34.1	-32.9

**Table S4** Averaged and normalized ligand binding ernergies in kcal/mol for large-sized clusters, TPSS denotes TPSS/def2-SVP,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\chi$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\chi$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>,  $\alpha$  denotes DFTB2/auorg<sup> $\alpha$ </sup>, TPSS// $\alpha$  denotes TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>.

Complexes	TPSS	α	TPSS//α	α/	TPSS//α/	χ′	TPSS//χ/
$\overline{[Au_6(dppp)_4]^{2+}}$	-67.6	-58.1	-64.9	-64.9	-64.2	-62.8	-64.5
$[Au_6(PPh_3)_6]^{2+}$	-87.2	-82.2	-86.2	-89.4	-85.9	-87.4	-85.8
$[Au_7(PPh_3)_7]^+$	-63.9	-49.9	-64.6	-58.6	-64.7	-57.6	-63.8
$[Au_8(PPh_3)_7]^{2+}$	-80.6	-73.0	-78.6	-80.2	-79.0	-78.3	-79.0
$[Au_8(PPh_3)_8]^{2+}$	-79.6	-69.7	-79.3	-77.3	-79.3	-75.8	-78.8
$[Au_8S_2(dppm)_4]^{2+}$	-70.0	-61.5	-71.9	-68.8	-72.1	-68.1	-70.4
$[Au_9(PPh_3)_8]^{3+}(C_4)$	-98.9	-92.3	-99.8	-99.4	-100.0	-96.4	-99.3
$[Au_9(PPh_3)_8]^{3+}(D_{2h})$	-99.3	-94.2	-99.4	-101.4	-99.8	-99.4	-99.5
$[Au_{11}(PMePh_2)_{10}]^{3+}(C_{3v})$	-85.8	-76.4	-87.7	-83.8	-87.6	-82.6	-87.0
$[Au_{11}(PMePh_2)_{10}]^{3+}(D_{4d})$	-85.6	-76.5	-87.0	-84.0	-87.1	-84.9	-86.6
$[Au_{13}(dppm)_6]^{5+}$	-108.6	-104.9	-109.0	-111.7	-109.2	-109.8	-108.6
$[Au_{20}(PP_3)_4]^{4+}$	-78.4	-57.2	-69.4	-62.6	-70.2	-60.8	-69.5
$Au_{22}(dppo)_6$	-49.5	-30.1	-51.5	-39.1	-50.7	-39.0	-49.5
$[Au_{38}(m-MBT)_{20}(PPh_3)_4]^{2+}$	-77.8	-58.9	-86.4	-65.5	-86.4	-65.1	-88.1
$Au_{70}S_{20}(PPh_3)_{12}$	-70.5	-47.3	-72.9	-54.8	-72.7	-53.4	-72.8



**Fig. S2** RMSD over atomic positions for the large-sized phosphine-stabilized gold clusters. The RMSD of atomic positions considers Au, and P atoms for all large-sized phosphine-based gold clusters,  $[Au_{11}(PMePh_2)_{10}]_{4}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]^{3+}$   $(C_{3\nu})$ ,  $[Au_{11}(PMePh_2)_{10}]_{*}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]_{4}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]^{3+}$   $(C_{3\nu})$ ,  $[Au_{11}(PMePh_2)_{10}]_{*}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]^{3+}$   $(D_{4d})$ ,  $[Au_{38}(L)_{20}(PPh_3)_{4}]^{2+}$  denotes  $[Au_{38}(m-MBT)_{20}(PPh_3)_{4}]^{2+}$ .



**Fig. S3** Overlap of experimental crystal structure (Au in gold, P in orange and C in grey) and optimized DFTB/auorg<sup> $\alpha$ </sup> and DFTB/auorg<sup> $\chi'$ </sup> structures. auorg<sup> $\alpha$ </sup> and auorg<sup> $\chi'$ </sup> structures are represented by light red and sky blue, respectively. The gold nanoclusters considered in this figure are (A) [Au<sub>6</sub>(dppp)<sub>4</sub>]<sup>2+</sup> (BOTSOS), (B) [Au<sub>7</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>+</sup> (BIXZAK), (C) [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup> (OPAUPF), and (D) [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> (MIVPOX-D<sub>2h</sub>).



**Fig. S4** Deviation in averaged and normalized ligand binding energies for the large-sized phosphine-stabilized gold clusters in reference to the TPSS/def2-SVP binding energies,  $[Au_{11}(PMePh_2)_{10}]_{4}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]_{1}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]_{4}^{3+}$  denotes  $[Au_{11}(PMePh_2)$ 

Table S5 Comparison of relative energies	with respect to the D <sub>r</sub>	isomers in kcal/mol a	s calculated by the	following methods for	[Au <sub>9</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>3+</sup> a	Ind
$[Au_{11}(PMePh_2)_{10}]^{3+}$ .						

Methods	Au <sub>9</sub>	Au <sub>11</sub>
TPSS/def2-SVP	4.98	-3.20
DFTB2/auorg <sup><math>\alpha'</math></sup>	11.81	1.78
DFTB2/auorg <sup><math>\alpha</math></sup>	11.76	1.38
DFTB2/auorg <sup><math>\chi'</math></sup>	10.13	1.82
TPSS/def2-SVP // DFTB2/auorg <sup>α</sup> /	6.29	-5.90
TPSS/def2-SVP // DFTB2/auorg <sup>α</sup>	5.19	-7.63
TPSS/def2-SVP // DFTB2/auorg <sup>χ</sup> /	6.31	-5.92

#### Isomerization energy of $[Au_9(PPh_3)_8]^{3+}$ and $[Au_{11}(PMePh_2)_{10}]^{3+}$ clusters

In practice, when studying chemical reactions, absolute cluster binding energies are not as important as relative binding energies, since a ligand is often replaced by another in the same reaction pathway. Therefore, to test the performance of DFTB for the prediction of isomerization energies, two particular examples, namely  $[Au_9(PPh_3)_8]^{3+}$  and  $[Au_{11}(PMePh_2)_{10}]^{3+}$  were investigated. In the solid phase,  $[Au_9(PPh_3)_8]^{3+}$  is reported to have a  $Au_9$  core with  $D_{2h}$  symmetry, as the full cluster takes a "butterfly" shape.<sup>3</sup> In a  $CH_2Cl_2$  or methanol solution, this cluster isomerizes to a  $C_4$  core with a crown-like structure.<sup>4</sup> The  $Au_{11}$  clusters have idealized  $C_{3\nu}$  and  $D_{4d}$  symmetric metal frameworks that differ around three adjacent peripheral sites.<sup>5</sup> The change in the skeletal geometries of  $Au_{11}$  clusters is proposed to be caused by the small variations in ligand packing and the presence of anionic ligands coordinated to the  $C_{3\nu} Au_{11}$  gold core. It has been previously predicted that  $C_4 Au_9$  has a 5.7 kcal/mol lower energy than  $D_{2h} Au_9$  in solution,<sup>4</sup> while so far no theoretical predictions were made yet for  $Au_{11}$  relative energy isomers. Here, we optimized the isomer structures of  $Au_9$  ( $D_{2h}$  and  $C_4$ ) and  $Au_{11}$  ( $C_{3\nu}$  and  $D_{4d}$ ) with both DFTB and TPSS methods. Their relative structural energies are compared in Figure S5.



**Fig. S5** Overlap of experimental X-ray (Au in gold, P in orange and C in grey) and optimized structures of (A)  $[Au_9(PPh_3)_8]^{3+} D_{2h}$  and  $C_4$  isomers and (B)  $[Au_{11}(PMePh_2)_{10}]^{3+} D_{4d}$  and  $C_{3v}$  isomers. auorg<sup> $\alpha v$ </sup> and DFT structures are represented by light red and sky blue, respectively. The relative energies in kcal/mol with respect to the  $D_n$  isomers are also shown as calculated by TPSS/def-SVP, DFTB2/auorg<sup> $\alpha v$ </sup> and TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha v$ </sup>. Note that the  $[Au_9(PPh_3)_8]^{3+} C_4$  isomer does not have an available experimental crystal structure.

The relative energies of the isomers presented in Figure S5 were calculated with respect to the  $D_n$  isomers (on the left side) as the reference energy. For the  $[Au_9(PPh_3)_8]^{3+}$  cluster, all methods predict that the higher symmetry  $D_{2h}$  structure is more stable than the less symmetric  $C_4$  structure, with  $auorg^{\alpha\prime}$  overstabilizing the high symmetry by about 5 kcal/mol. In the case of  $[Au_{11}(PMePh_2)_{10}]^{3+}$  isomers, the TPSS/def2-SVP calculated  $C_{3V}$  isomer is lower in energy than the  $D_{4d}$  isomer, while DFTB methods still predict a slightly more stable high symmetry structure. We note that both the isomer relative energies and their DFTB deviations are very small, around 5 kcal/mol, and that it is difficult to achieve perfect agreement even between different density functionals for this energy range. TPSS/def2-SVP single point energy calculations using the DFTB2/auorg<sup> $\alpha\prime$ </sup> optimized structures reduce the differences between the relative energies to only 1.33 and 2.72 kcal/mol for Au<sub>9</sub> and Au<sub>11</sub> isomers, respectively, recovering the isomer energy ordering of the full TPSS

calculations. The complete comparison of the isomer relative energies as calculated by DFTB with all parameter sets is shown in Table S5 in the Supporting Information. The presented comparison demonstrates that, if one wishes to map the potential energy of a certain cluster with many isomers that are only a few kcal/mol apart in relative energies, performing geometry optimizations and pre-optimize structures with the DFTB method is a viable option to save computer time.



**Fig. S6** Energy level diagram for the frontier orbitals of various clusters as calculated by (A) DFTB/auorg<sup> $\alpha$ </sup> and (B) DFTB2/auorg<sup> $\chi'$ </sup>,  $[Au_{11}(PMePh_2)_{10}]_{\#}^{3+}$  denotes  $[Au_{11}(PMePh_2)_{10}]^{3+}$  ( $D_{4d}$ ). Dashed lines are included to guide the eye.

$ \begin{bmatrix} \text{Au}_6(\text{dpp})_4]^{2+} (\text{BOTSOS}) & -7.40 / -5.66 & -8.00 / -6.45 & -7.81 / -6.00 & -7.89 / -6.3 \\ \text{Au}_6(\text{PP})_3)_6]^{2+} (\text{CXTPAO10}) & -5.10 / -3.47 & -5.38 / -4.10 & -5.07 - 5.50 & -8.43 / -6.52 \\ \text{Au}_7(\text{PP})_3)_1]^{2+} (\text{BASWUN}) & -7.70 / -5.99 & -8.01 / -6.68 & -7.94 / -6.52 & -8.37 / -6.44 & -7.79 / -5.9 \\ \text{Au}_8(\text{PP})_3)_1]^{2+} (\text{DAVDP}) & -7.51 / -5.29 & -7.33 / -6.18 & -7.66 & -7.93 / -6.4 & -7.79 / -5.9 \\ \text{Au}_8(\text{PP})_3)_1]^{2+} (\text{DAVDP}) & -7.51 / -5.29 & -7.33 / -6.18 & -7.66 & -7.93 / -6.4 & -7.79 / -5.9 \\ \text{Au}_8(\text{PP})_3)_1]^{2+} (\text{DAVDP}) & -7.51 / -5.29 & -8.86 / -6.52 & -8.63 / -6.20 & -7.93 / -6.4 \\ \text{Au}_9(\text{PP})_3)_1]^{2+} (\text{LEVKLJ}) & -9.84 / -7.94 & -10.17 / -8.58 & -10.14 / -8.38 & -10.14 / -8.38 \\ \text{Au}_9(\text{PP})_3)_1]^{2+} (\text{LEVKLJ}) & -9.34 / -7.23 & -9.86 / -6.52 & -8.63 / -6.20 & -8.76 / -6.4 \\ \text{Au}_9(\text{PP})_3)_1]^{2+} (\text{ZUCMAI}) & -9.34 / -7.23 & -9.86 / -6.52 & -8.63 / -6.20 & -8.76 / -6.4 \\ \text{Au}_1(\text{PMeP})_10]^{2+} (\text{ZUCMAI}) & -9.34 / -7.23 & -9.88 / -6.52 & -9.60 / -7.78 & -9.01 / -7.58 \\ \text{Au}_1(\text{PMPP})_10]^{2+} (\text{ZUCMAI}) & -9.34 / -7.22 & -10.17 / -8.58 & -10.14 / -8.38 & -9.60 / -7.78 & -9.67 / -7.9 & -9.67 / -7.78 & -9.67 / -7.9 & -9.67 / -7.78 & -9.67 / -7.9 & -9.67 / -7.78 & -9.67 / -7.78 & -9.67 / -7.8 & -9.67 / -7.8 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.78 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -9.67 / -7.9 & -10.02 / -7.12 & -0.00 & -7.12 & -0.00 & -10.02 / -7.12 & -0.00 & -7.12 & -0.00 & -7.12 & -0.00 & -7.12 & -0.00 & -7.12 & -0.00 & -7.23 & -9.67 / -7.78 & -0.00 & -7.23 & -9.67 / -7.9 & -7.23 & -9.67 / -7.8 & -0.00 & -7$	Complexes	TPSS/def2-SVP	$ m DFTB2/auorg^{lpha\prime}$	$ m DFTB2/auorg^{lpha}$	DFTB2/auorg $\chi'$
$ \begin{bmatrix} \text{Au}_{6}(\text{Ph}_{3})_{6}^{12} + (\text{CATPAO10}) & = 8.15 / 6.22 & = 8.31 / 6.82 & = 8.44 / 6.52 & = 8.44 / 6.52 & = 8.43 / 6.65 \\ \text{Au}_{7}(\text{Ph}_{3})_{7}^{12} + (\text{BXZAK}) & = 7.51 / 5.29 & = 5.10 / 5.49 & = 7.59 & = 7.59 / 5.57 & = 5.38 / 4.10 & = 7.59 / 5.57 & = 5.37 / 4.66 & = 7.59 / 5.57 & = 5.33 / 6.44 & = 7.79 / 5.59 & = 7.51 / 5.29 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 9.91 / 8.59 & = 9.91 / 9.92 / 8.76 / 6.44 & = 7.79 / 5.59 & = 7.00 / 3.4 / 4.64 & = 7.79 / 5.59 & = 7.64 & = 7.79 / 5.59 & = 7.64 & = 7.79 / 5.59 & = 7.64 & = 7.79 / 5.59 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 8.86 / 6.52 & = 9.91 / 8.38 & = 9.91 / 8.59 / 6.44 & = 7.79 / 5.59 & = 9.91 / 8.40 / 10.10 / 8.44 & = 7.93 / 6.11 / 8.58 & = 9.91 / 8.20 / 10.14 / 8.38 & = 9.91 / 10.17 / 8.44 & = 9.91 / 8.20 / 10.73 & = 9.86 / 6.81 & = 9.92 / 8.7 / 8.5 & = 9.91 / 8.59 & = 9.91 / 8.59 & = 9.87 / 7.7 & = 9.80 / 10.10 / 8.44 & = 10.10 / 8.44 & = 7.73 & = 9.91 / 8.20 / 10.73 & = 9.43 / 7.72 & = 9.81 / 4.02 / 12.4 & = 10.17 / 9.1 / 4.61 / 20.22 / 12.4 / 10.91 / 8.44 & = 0.90 / 12.4 / 10.2 & = 0.20 / 1.73 & = 0.20 / 1.73 & = 0.20 / 1.73 & = 0.46 / 1.90 / 12.4 / 10.23 / 10.24 / 10.91 / 4.41 / 4.61 / 20.22 / 2.00 & = 0.10.20 / 1.24 / 10.91 / 4.41 / 4.61 / 4.61 / 4.61 / 20.22 / 2.20 / 2.21 / 4.61 / 20.22 / 2.20 / 2.21 / 4.7 / 20.20 & = 2.52 / 6.50 / 2.52 / 6.50 / 2.52 / 6.50 / 2.52 / 2$	[Au <sub>6</sub> (dppp) <sub>4</sub> ] <sup>2+</sup> (BOTSOS)	-7.40 / -5.66	-8.00 / -6.45	-7.81 / -6.00	-7.89 / -6.30
$ \begin{bmatrix} hu_{1}(PPh_{3})_{1} \end{bmatrix}^{1} (BIXZAK) = 5.10 / -3.47 = 5.38 / 4.10 = 5.07 / -3.69 = 5.35 / 4.00 \\ Au_{8}(PPh_{3})_{7} \end{bmatrix}^{2} (BASWUN) = 7.70 / -5.99 = 8.01 / -6.68 = 7.79 / -5.9 = 7.93 / 6.4 \\ Au_{8}(PPh_{3})_{8} \end{bmatrix}^{2} + (DPAUPF) = 7.57 / -5.99 = 7.33 / -6.18 = 7.76 / -5.29 = 7.79 / -5.9 \\ Au_{8}(PPh_{3})_{8} \end{bmatrix}^{2} + (DPAUPF) = 7.56 / -5.2 = 8.66 / -6.52 = 8.66 / -6.52 = 8.66 / -6.52 = 8.66 / -6.52 = 9.66 / -6.4 = 7.79 / -7.9 \\ Au_{9}(PPh_{3})_{8} \end{bmatrix}^{3} + (MIVPOXC_{4}) = 9.44 / -7.94 = -10.17 / -8.4810.17 / -8.48 = -10.14 / -8.38 = -10.14 / -8.3810.17 / -8.48 - 7.88 / -7.88 / -7.88 - 10.17 / -8.48 = -10.17 / -8.49 = -9.92 / -8.13 = -9.92 / -8.13 = -9.92 / -8.13 = -9.79 - 7.75 = -9.86 / -12.4 \\ Au_{1}(PPPh_{3})_{8} \end{bmatrix}^{3} + (MIVPOXC_{2}) = 9.43 / -7.23 = -9.92 / -8.13 = -9.70 / -7.75 = -9.76 / -7.78 = -9.77 / -7.78 = -9.76 / -7.78 = -9.76 / -7.78 = -10.16 / -9.00 - 7.79 \\ Au_{1}(PPPh_{3})_{1} \end{bmatrix}^{3} + (ZUCMEP) = -10.24 / -12.4 \\ Au_{1}(PPPh_{3})_{1} \end{bmatrix}^{3} + (ZUCMEP) = -10.28 / -9.34 / -7.23 = -10.28 / -9.34 / -7.23 = -10.26 / -12.4 \\ Au_{1}(PPPh_{3})_{1} \end{bmatrix}^{3} + (DCFUC) = -10.24 / -12.4 \\ Au_{2}(PP)_{3} (PP)_{3} + (PCFUZ) = -10.06 / -9.0010.24 / -12.4 \\ Au_{2}(PP)_{3} (PP)_{3} + (PCFUZ) = -2.26 / -12.4 \\ Au_{2}(PP)_{3} (PP)_{3} + (PCFUZ) = -2.26 / -12.4 \\ Au_{2}(PP)_{3} (PP)_{3} + (PCFUZ) = -2.007.52 / -6.507.52 / -6.4 / -19 \\ Au_{3}(m-MBT)_{2}(PP)_{3} + (2CMZIG)7.52 / -6.507.52 / -6.4 / -19 \\ Au_{3}(m-MBT)_{2}(PP)_{3} + (2CMZIG)7.52 / -6.507.52 / -6.4 / -19 \\ Au_{3}(m-MBT)_{2}(PP)_{3} + (2CMZIG)7.52 / -6.507.52 / -6.4 / -19 \\ Au_{3}(m-MBT)_{2}(PP)_{3} + (2CMZIG)7.52 / -2.007.52 / -6.507.52 / -6.4 / -19 \\ Au_{3}(m-MBT)_{2}(PP)_{3} + (2CMZIG)7.52 / -2.007.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.507.52 / -6.50 - $	$[Au_{\kappa}(PPh_{2})_{\kappa}]^{2+}$ (CATPAO10)	-8.15 / -6.22	-8.51 / -6.82	-8.44 / -6.52	-8.43 / -6.60
$ \begin{bmatrix} \text{Au}_{8}(\text{Ph}_{3})_{7} \end{bmatrix}^{2} + (\text{BASWUN}) & -7.70/ \cdot 5.99 & -8.01/ \cdot 6.68 & -7.94/ \cdot 6.44 & -7.93/ \cdot 6.4 \\ \text{Au}_{8}(\text{Ph}_{3})_{8} \end{bmatrix}^{2} + (\text{OPAUF}) & -7.68/ - 5.79 & -5.79 & -5.79 & -5.79 \\ \begin{bmatrix} \text{Au}_{8}(\text{Ph}_{3})_{8} \end{bmatrix}^{2} + (\text{OPAUF}) & -7.68/ - 5.79 & -7.68/ & -7.79/ - 5.97 & -5.79 \\ \text{Au}_{8}(\text{PPh}_{3})_{8} \end{bmatrix}^{2} + (\text{MIVPOX-C}_{4}) & -7.93/ \cdot 6.18 & -7.68/ - 5.79 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.79/ - 8.44 & -7.94/ - 7.79/ - 8.44 & -7.94/ - 7.72/ - 8.44 & -7.91/ - 10.10/ - 8.44 & -7.94/ - 7.23 & -9.03/ - 8.13 & -9.92/ - 8.74 & -9.91/ - 8.59 & -9.86/ - 7.79/ - 7.75 & -9.87/ - 7.78 & -9.81/ - 7.73 & -9.84/ - 7.73 & -9.84/ - 7.72 & -9.83/ - 8.13 & -9.73/ - 12.44 & -10.10^{-1}/ - 7.94/ - 7.75 & -9.81/ - 7.73 & -9.84/ - 7.72 & -9.83/ - 8.15 & -9.76/ - 7.77 & -7.78 & -13.69/ - 12.44/ - 19.12.44/ - 10.28/ - 9.31/ - 12.28 & -13.77/ - 12.48 & -10.06/ - 9.00 & -10.21/ - 9.12/ - 12.4/ - 19.12.4/ - 10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ & -10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ - 12.28 & -10.28/ - 9.34/ - 12.39 & -10.028/ - 9.00 & -2.00 & -2.00 & -2.00 & -2.00 & -2.64/ - 1.91 & -10.67/ - 7.75 & -2.30/ - 17.73 & -2.30/ - 17.73 & -7.52/ - 6.50 & -7.52/ - 5.00 & -7.52/ - 5.00 & -7.52/ - 5.00 & -7.52/ - 5$	$[Au_7(PPh_3)_7]^+$ (BIXZAK)	-5.10 / -3.47	-5.38 / -4.10	-5.07 / -3.69	-5.35 / -4.02
$ \begin{bmatrix} Mu_{8}(PPh_{3})_{8}^{-1}^{-1}^{-1} (OPAUPF) & -7.51 / 5.29 & -7.83 / 6.18 & -7.66 / 5.47 & -5.79 & -7.79 / 5.57 & -7.79 / 5.57 & -8.86 / -6.52 & -8.63 / -6.20 & -8.76 / -6.47 & -7.94 & -10.17 / -8.58 & -10.14 / -8.38 & -10.10 / -8.4 & -9.91 / -8.59 & -9.91 / -8.59 & -9.95 / -8.57 & -9.91 / -8.59 & -9.91 / -8.59 & -9.95 / -8.57 & -9.91 / -8.59 & -9.91 / -8.59 & -9.91 / -8.59 & -9.91 / -8.59 & -9.92 / -8.77 / -7.58 & -9.91 / -8.59 & -9.91 / -8.59 & -9.97 / -7.78 & -9.91 / -8.59 & -9.78 / -7.9 & -9.78 / -7.78 & -9.91 / -8.59 & -9.78 / -7.78 & -9.86 / -8.13 & -9.43 / -7.23 & -9.86 / -8.13 & -9.67 / -7.78 & -9.91 / -8.59 & -9.78 / -7.9 & -9.78 / -7.9 & -13.34 / -12.28 & -13.34 / -12.28 & -13.34 / -12.28 & -13.34 / -12.28 & -13.37 / -12.39 & -13.36 / -12.4 & -13.60 / -19.1 & -10.06 / -9.00 & -10.06 / -9.00 & -2.00 & -2.00 & -2.00 & -2.00 & -2.00 & -2.00 & -2.00 & -7.52 / -6.4 / -1.9 & -7.52 / -6.4 / -1.9 & -7.52 / -6.50 & -7.52 / -6.4 / -1.9 & -7.52 / -6.50 & -3.47 / -2.99 & -3.45 / -2.90 & -3.46 / -1.9 & -3.47 / -2.99 & -3.46 / -1.9 & -7.52 / -6.4 / -1.9 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -5.00 & -7.52 / -5.0 & -7$	$[Au_{g}(PPh_{3})_{7}]^{2+}$ (BASWUN)	-7.70 / -5.99	-8.01 / -6.68	-7.94 / -6.44	-7.93 / -6.47
$ \begin{bmatrix} M_{0}^{8}S_{2}(dpm)_{3} \end{bmatrix}^{2^{+}} (LEVKIJ) & -7.97 / 5.67 & -8.86 / -6.52 & -8.63 / -6.20 & -8.76 / -6.4. \\ A_{0}(PPh_{3})_{3} \end{bmatrix}^{3^{+}} (MIVPOX-C_{4}) & -9.84 / -7.94 & -10.17 / -8.58 & -10.14 / -8.38 & -10.10 / -8.44 \\ \begin{bmatrix} Au_{0}(PPh_{3})_{3} \end{bmatrix}^{3^{+}} (MIVPOX-D_{2h}) & -9.84 / -7.94 & -9.91 / -8.59 & -9.78 / -7.8 \\ \begin{bmatrix} Au_{11}(PMePh_{2})_{10} \end{bmatrix}^{3^{+}} (ZUCMAL) & -9.84 / -7.23 & -9.86 / -8.13 & -9.77 / -7.75 & -9.78 / -7.78 \\ \begin{bmatrix} Au_{11}(PMePh_{2})_{10} \end{bmatrix}^{3^{+}} (ZUCMEP) & -9.34 / -7.23 & -9.86 / -8.13 & -9.67 / -7.78 & -9.80 / -12.4 \\ \begin{bmatrix} Au_{11}(PMePh_{2})_{10} \end{bmatrix}^{3^{+}} (ZUCMEP) & -13.34 / -12.28 & -13.73 / -12.48 & -13.77 / -12.39 & -13.36 / -112.4 \\ \begin{bmatrix} Au_{10}(PP_{3})_{4} \end{bmatrix}^{4^{+}} (POFPUX) & -2.11 / -1.67 & -2.00 & -2.30 / -1.73 & -2.64 / -1.9 \\ \begin{bmatrix} Au_{20}(PP_{3})_{4} \end{bmatrix}^{4^{+}} (POFPUX) & -7.52 / -6.50 & -7.55 / -6.50 & -7.52 / -6.4 & -1.9 \\ \begin{bmatrix} Au_{30}(PP_{3})_{4} \end{bmatrix}^{2^{+}} (CEMZIG) & -2.30 / -1.73 & -2.11 / -1.67 & -2.00 & -2.30 / -1.73 & -7.52 / -6.4 & -1.9 \\ \begin{bmatrix} Au_{30}(PP_{3})_{4} \end{bmatrix}^{2^{+}} (CEMZIG) & -7.12 - 8 & -3.36 / -3.1 & -2.57 / -2.00 & -2.30 / -1.72 & -7.52 / -6.4 & -1.9 \\ \begin{bmatrix} Au_{30}(PP_{3})_{4} \end{bmatrix}^{2^{+}} (DCFIC) & -7.78 & -7.12 / -2.00 & -7.52 / -6.4 & -1.9 & -7.52 / -6.4 & -1.9 \\ \begin{bmatrix} Au_{30}(PP_{3})_{4} \end{bmatrix}^{2^{+}} (CEMZIG) & -7.12 / -2.00 & -7.52 / -6.50 & -7.52 / -6.50 & -7.52 / -6.5 & -7.52 / -6.5 & -7.52 / -6.5 & -7.52 / -5.50 & -7.52 / -6.5 & -7.52 / -6.5 & -7.52 / -6.5 & -7.52 / -5.5 & -7.52 / -5.5 & -7.52 / -5.5 & -7.52 / -5.5 & -7.52 / -5.5 & -7.52 / -5.5 & -7.52 / -5.5 / -5.5 & -7.52 / -5.5$	[Aug (PPh <sub>2</sub> )g] <sup>2+</sup> (OPAUPF)	-7.51 / -5.29	-7.83 / -6.18	-7.68 / -5.79	-7.79 / -5.93
$ \begin{bmatrix} M_{0}(\widetilde{P}\widetilde{P}_{3})_{3} \end{bmatrix}^{3+} (\widetilde{M}VPOX-C_{4}) & -9.84/-7.94 & -10.17/-8.58 & -10.14/-8.38 & -10.10/-8.44 \\ A_{0}(\widetilde{P}\widetilde{P}_{3})_{3} \end{bmatrix}^{3+} (\widetilde{M}VPOX-D_{2h}) & -9.63/-8.01 & -9.92/-8.74 & -9.91/-8.59 & -9.78/-7.78 \\ A_{011}(\widetilde{P}\widetilde{M}e\widetilde{P}_{2})_{10} \end{bmatrix}^{3+} (\widetilde{Z}UCMAL) & -9.34/-7.23 & -9.86/-8.13 & -9.77/-7.75 & -9.78/-7.78 \\ A_{011}(\widetilde{P}\widetilde{M}e\widetilde{P}_{2})_{10} \end{bmatrix}^{3+} (\widetilde{Z}UCMEP) & -9.34/-7.23 & -9.86/-8.13 & -9.67/-7.75 & -9.80/-8.12 \\ A_{011}(\widetilde{P}\widetilde{M}e\widetilde{P}_{2})_{10} \end{bmatrix}^{3+} (\widetilde{Z}UCMEP) & -13.34/-12.28 & -13.73/-12.48 & -13.77/-12.39 & -13.36/-12.4 \\ A_{020}(\widetilde{P}_{2})_{3} \end{bmatrix}^{4+} (\widetilde{P}\widetilde{O}\widetilde{F}\widetilde{P}\widetilde{M}) & -9.34/-7.23 & -9.346 & -10.06/-9.00 & -10.21/-9.1 \\ A_{022}(\widetilde{d}\widetilde{P}\widetilde{D}\widetilde{O}_{6})_{6} (\widetilde{T}OCFIC) & -2.30/-1.73 & -2.11/-1.67 & -2.75/-6.50 & -7.52/-6.4 \\ A_{03}(\widetilde{m}-MBT)_{20}(\widetilde{P}\widetilde{P}_{3})_{4} \end{bmatrix}^{2+} (\widetilde{C}\widetilde{E}\widetilde{M}\widetilde{M}) & -3.45/-2.90 & -3.55/-6.50 & -7.52/-6.4 \\ A_{02}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{M}\widetilde{V}) & -3.45/-2.90 & -3.53/-3.13 & -3.54/-1.9 \\ A_{02}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{M}\widetilde{V}) & -2.66/-8.13 & -2.26/-3.1 \\ A_{02}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{M}\widetilde{V}) & -2.66/-8.13 & -2.50/-3.13 & -3.57/-2.90 \\ A_{03}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{M}\widetilde{V}) & -2.90 & -3.55/-6.50 \\ A_{03}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{V}) & -2.90 & -3.55/-6.50 \\ A_{03}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{V}) & -2.90 & -3.55/-6.50 \\ A_{03}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{E}\widetilde{M}\widetilde{V}) & -2.99 & -3.13 \\ A_{02}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{T}\widetilde{P}\widetilde{V}) & -2.99 \\ A_{03}(\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{P}\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{P}\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{P}\widetilde{P}_{3})_{12} (\widetilde{P}\widetilde{P}_{$	$[Au_8S_2(dppm)_4]^{2+}$ (LEVKIJ)	-7.97 / -5.67	-8.86 / -6.52	-8.63 / -6.20	-8.76 / -6.42
$ \begin{bmatrix} \operatorname{Au}_{0}(\operatorname{PPh}_{3})_{3}^{[3]^{+}} (\operatorname{MIVPOX}_{2,h}) & -9.63 / 8.01 & -9.92 / 8.74 & -9.91 / 8.59 & -9.85 / 8.5; \\ -9.34 / -7.23 & -9.86 / -8.13 & -9.77 / 55 & -9.78 / -7.78 \\ = -9.10 / -7.75 & -9.8 / -7.78 & -9.8 / -7.79 \\ = -9.11 / \operatorname{PMePh}_{2})_{10}^{[3^{+}]^{+}} (\operatorname{ZUCMEP}) & -9.43 / -7.23 & -9.83 / -8.15 & -9.67 / -7.78 & -9.8 / -1.24 \\ = -9.13 / -12.28 & -13.34 / -12.28 & -13.34 / -12.28 & -13.73 / -12.39 & -13.69 / -12.4 \\ = -10.28 / -9.34 / -12.28 & -10.28 / -9.346 & -10.06 / -9.00 & -10.21 / -9.1 \\ = -2.11 / -1.67 & -2.75 / -6.70 & -2.30 / -1.73 & -2.64 / -1.9 \\ = -2.30 / -1.73 & -7.29 & -7.52 / -6.4 & -1.9 \\ = -7.52 / -6.7 & -7.78 & -7.23 & -7.23 & -7.23 & -2.64 / -1.9 \\ = -2.30 / -1.73 & -2.11 / -1.67 & -7.55 / -6.50 & -7.52 / -6.4 & -1.9 \\ = -7.52 / -6.4 & -1.9 / -2.90 & -3.47 / -2.99 & -3.47 / -2.99 \\ = -3.45 / -2.90 & -3.45 / -2.90 & -3.47 / -2.99 \\ = -2.64 / -1.9 / -2.90 & -3.47 / -2.99 \\ = -7.52 / -6.4 & -1.9 / -2.90 & -3.47 / -2.99 \\ = -7.52 / -6.4 & -1.9 / -2.91 & -3.47 / -2.99 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.4 & -1.9 / -2.91 \\ = -7.52 / -6.50 & -7.4 / -2.91 \\ = -7.52 / -6.50 & -7.4 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -1.9 / -2.91 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 / -6.4 / -2.9 \\ = -7.52 /$	$[Au_0(PPh_2)_8]^{3+1}$ (MIVPOX- $C_4$ )	-9.84 / -7.94	-10.17 / -8.58	-10.14 / -8.38	-10.10 / -8.40
$ \begin{bmatrix} \dot{\rm Au}_{11}^{1} (\rm PMePh}_{2})_{10}^{13} + (\rm ZUCMAL) & -9.34/-7.23 & -9.86/-8.13 & -9.70/-7.75 & -9.78/-7.8 \\ [Au_{11}^{1} (\rm PMePh}_{2})_{10}^{13} + (\rm ZUCMEP) & -9.43/-7.23 & -9.83/-8.15 & -9.67/-7.78 & -9.80/-7.9 \\ [Au_{13}(dppn)_6]^{5+} (\rm LeVKAB) & -13.34/-12.28 & -13.73/-12.48 & -13.77/-12.39 & -13.69/-12.4 \\ [Au_{20}(\rm PP_{3})_4]^{4+} (\rm POFPUX) & -9.73/-8.53 & -10.28/-9.346 & -10.06/-9.00 & -1.021/-9.1 \\ [Au_{20}(\rm Pp_{3})_4]^{4+} (\rm POFPUX) & -2.11/-1.67 & -2.75/-2.00 & -2.30/-1.73 & -2.64/-1.9 \\ [Au_{30}(\rm RDMD)_{6} (\rm TOCFIC) & -7.19/-6.07 & -7.55/-6.50 & -7.52/-6.4 \\ [Au_{30}(\rm RDMD)_{20} (\rm PPh_{3})_{12}^{1} (\rm TELMUV) & -3.45/-2.90 & -3.55/-6.50 & -3.47/-2.99 \\ \  \  \  \  \  \  \  \  \  \  \  \  \$	$[Au_0(PPh_3)_8]^{3+}$ (MIVPOX- $D_{2h}$ )	-9.63 / -8.01	-9.92 / -8.74	-9.91 / -8.59	-9.85 / -8.52
$ \begin{bmatrix} Au_{11}^{-1}(PMePh_{2}^{-1})_{10}^{-1} + (ZUCMEP) & -9.43 / -7.23 & -9.83 / -8.15 & -9.67 / -7.78 & -9.80 / -7.79 \\ \begin{bmatrix} Au_{13}(dppm)_6 \end{bmatrix}^{5+} (LEVKAB) & -13.34 / -12.28 & -13.73 / -12.48 & -13.77 / -12.39 & -13.69 / -12.4 \\ \begin{bmatrix} Au_{20}(PP_{3})_4 \end{bmatrix}^{4+} (POFPUX) & -9.73 / -8.53 & -10.28 / -9.346 & -10.06 / -9.00 & -1.021 / -9.1 \\ \begin{bmatrix} Au_{20}(PP_{3})_4 \end{bmatrix}^{4+} (POFPUX) & -2.75 / -6.90 & -2.30 / -1.73 & -2.64 / -1.9 \\ \begin{bmatrix} Au_{20}(PP_{3})_4 \end{bmatrix}^{2+} (CCFIC) & -2.30 / -1.73 & -2.75 / -6.50 & -7.52 / -6.4 \\ \begin{bmatrix} Au_{20}(PP_{3})_4 \end{bmatrix}^{1/2} (TOCFIC) & -7.52 / -6.50 & -2.30 / -1.73 & -7.52 / -6.4 \\ \begin{bmatrix} Au_{20}(PP_{3})_{20}(PP_{3})_{3} \end{bmatrix}^{1/2} (TELMUV) & -3.45 / -2.90 & -3.53 / -3.13 & -3.47 / -2.99 \\ \end{bmatrix} $	$[Au_{11}(PMePh_2)_{10}]^{3+}$ (ZUCMAL)	-9.34 / -7.23	-9.86 / -8.13	-9.70 / -7.75	-9.78 / -7.87
$ \begin{bmatrix} Au_{13}^{(3)}(\operatorname{dppn})_{6}^{5^{4}}(\operatorname{LeVKAB}) & -13.34 / -12.28 & -13.73 / -12.48 & -13.77 / -12.39 & -13.69 / -12.48 \\ \begin{bmatrix} Au_{20}(\operatorname{PP}_{3})_{4}^{1^{4+}}(\operatorname{POFPUX}) & -9.73 / -8.53 & -10.28 / -9.146 & -10.06 / -9.00 & -10.21 / -9.11 \\ Au_{21}(\operatorname{dppo})_{6}(\operatorname{TOCFIC}) & -2.30 / -1.73 & -2.11 / -1.67 & -2.75 / -2.00 & -2.30 / -1.73 & -2.64 / -1.9 \\ \begin{bmatrix} Au_{30}(\operatorname{R-MBT})_{20}(\operatorname{PPh}_{3})_{4}^{1^{2}}(\operatorname{CEMZIG}) & -7.19 / -6.07 & -7.55 / -6.50 & -7.52 / -6.50 \\ Au_{7}OS_{20}(\operatorname{PPh}_{3})_{12}(\operatorname{TELMUV}) & -3.45 / -2.90 & -3.59 / -3.13 & -3.47 / -2.99 & -3.65 / -3.1 \\ \end{bmatrix} $	$[Au_{11}(PMePh_2)]^{3+}$ (ZUCMEP)	-9.43 / -7.23	-9.83 / -8.15	-9.67 / -7.78	-9.8 0 / -7.90
$ \begin{bmatrix} Au_{20}^{0}(PP_{3})_{4}^{ ^{4ft}} \\ \text{(POFPUX)} \end{bmatrix} ^{1/4t} \\ \text{(POFPUX)} \end{bmatrix} ^{1/4t} \\ \text{(POFPUX)} \\ \frac{Au_{22}^{0}(PP_{3})_{4}^{ ^{4ft}} \\ \text{(TOCFIC)} \end{bmatrix} ^{-2.11/-1.67} \\ \frac{-2.11/-1.67}{-1.167} \\ \frac{-2.75/-2.00}{-2.75/-2.00} \\ \frac{-2.30/-1.73}{-1.73} \\ \frac{-2.64/-1.9}{-1.73} \\ \frac{-7.52/-6.4}{-2.90} \\ \frac{-7.52/-6.4}{-3.13} \\ \frac{-3.47/-2.99}{-2.99} \\ \frac{-3.65/-3.1}{-3.65/-3.1} \end{bmatrix} $	$[Au_{13}(dppm)_6]^{5+7}$ (LEVKAB)	-13.34 / -12.28	-13.73 / -12.48	-13.77 / -12.39	-13.69 / -12.40
$\begin{split} \tilde{A}u_{2}^{2}(dp\bar{0}o)_{6}^{6} \mbox{ (TOCFIC)} & -2.30/-1.73 & -2.64/-1.9\\ & [Au_{38}(m-MBT)_{20}(PPh_{3})_{4}]^{2+} \mbox{ (CEMZIG)} & -7.19/-6.07 & -7.55/-6.50 & -7.52/-6.50 & -7.52/-6.4\\ & Au_{7}S_{20}(PPh_{3})_{12} \mbox{ (TELMUV)} & -3.45/-2.90 & -3.59/-3.13 & -3.47/-2.99 & -3.65/-3.1 \end{split}$	$[Au_{20}(PP_3)_4]^{4+}$ (POFPUX)	-9.73 / -8.53	-10.28 / -9.346	-10.06 / -9.00	-10.21 / -9.16
$ \left[ Au_{76}^{28} (m - MBT)_{20}^{20} (PPh_3)_{4} \right]^{2+} (CEMZIG) \\ -7.52 / -6.64 \\ -3.45 / -2.90 \\ -3.55 / -3.13 \\ -3.55 / -3.13 \\ -3.47 / -2.99 \\ -3.47 / -2.99 \\ -3.65 / -3.1 \\ -3.65$	Au <sub>22</sub> (dppo) <sub>6</sub> (TOCFIC)	-2.11 / -1.67	-2.75 / -2.00	-2.30 / -1.73	-2.64 / -1.98
Àu <sub>7</sub> 0 <sup>S</sup> 2 <sub>0</sub> (PPh <sub>3</sub> ) <sub>12</sub> (TELMÜV) -3.45 / -2.90 -3.55 / -3.13 -3.47 / -2.99 -3.65 / -3.1	$[Au_{38}(m-MBT)_{20}(PPh_3)_4]^{2+}$ (CEMZIG)	-7.19 / -6.07	-7.55 / -6.50	-7.52 / -6.50	-7.52 / -6.40
	$Au_{70}S_{20}(PPh_3)_{12}$ (TELMUV)	-3.45 / -2.90	-3.59 / -3.13	-3.47 / -2.99	-3.65 / -3.13

**Table S6** Comparison of HOMO and LUMO in eV as calculated by DFTB/auorg<sup>ar</sup>, DFTB/auorg<sup>ar</sup>, DFTB/auorg<sup>x</sup>, and DFT for small gold clusters.



**Fig. S7** HOMO and LUMO of (A)  $[Au_6(dppp)_4]^{2+}$ , (B)  $[Au_7(PPh_3)_7]^+(BIXZAK)$ , (C) $[Au_8(PPh_3)_8]^{2+}$  (OPAUPF) and (D)  $[Au_9(PPh_3)_8]^{3+}(MIVPOX-D_{2h})$  clusters as calculated by TPSS/def2-SVP and DFTB2/auorg<sup> $\alpha$ </sup>; isosurface value = 0.02 a.u.



**Fig. S8** HOMO and LUMO of (A)  $[Au_6(dppp)_4]^{2+}$  and (B)  $[Au_8(PPh_3)_8]^{2+}$  (OPAUPF) clusters as calculated by TPSS/def2-SVP, DFTB2/auorg<sup> $\alpha$ </sup>, DFTB2/auorg<sup> $\alpha$ </sup>, and DFTB2/auorg<sup> $\alpha$ </sup>; isosurface value = 0.02 a.u.



**Fig. S9** HOMO and LUMO of (A)  $[Au_7(PPh_3)_7]^+(BIXZAK)$  and (B)  $[Au_9(PPh_3)_8]^{3+}(MIVPOX-D_{2h})$  clusters as calculated by TPSS/def2-SVP, DFTB2/auorg<sup> $\alpha'$ </sup>, DFTB2/auorg<sup> $\alpha'$ </sup>, and DFTB2/auorg<sup> $\chi'$ </sup>; isosurface value = 0.02 a.u.



**Fig. S10** Experimental (in black), computed  $auorg^{\alpha}$  (in green) DFTB2/ $auorg^{\alpha'}$  (in red), and  $auorg^{\chi'}$  (in orange) far-IR spectra for (A)  $[Au_6(dppp)_4]^{2+}$ , (B)  $[Au_8(PPh_3)_8]^{2+}$ , and (C)  $[Au_9(PPh_3)_8]^{3+}$  clusters.

experimental spe	ary or community sctral peaks, as we	l lais a brief descrip	otion of the assigned	transition mode	es , ur luz/au				ניפו מות וופון מסטקוווופוורוס חופ
Experimental (cm-1)	PBE/def2-SVP (cm <sup>-1</sup> )	Intensity (km/mol)	${ m DFTB2/auorg}^{lpha\prime}$ (cm <sup>-1</sup> )	Intensity (km/mol)	DFTB2/auorg <sup>α</sup> (cm <sup>-1</sup> )	Intensity (km/mol)	DFTB2/auorg $\chi'$ (cm <sup>-1</sup> )	Intensity (km/mol)	Mode description
90	85.52 87.06 89.74 119.65 125.79	2.6113 3.0854 1.7775 1.9408 0.6063	80.85 115.45 121.47	0.008 0.0101 0.0197	74.09 87.25 96.42 126.85 130.42	0.0142 87.25 96.42 0.0326 0.0114	70.44 72.85 89.73 137.82 140.15	0.0102 0.0119 0.0102 0.0151 0.0276	Au core distortion
325	322.41 324.42	1.0008 1.5474	125.57 331.99 336.12	0.053 0.0207 0.011	136.98 145.9 323.49 336.48	0.0149 0.0135 0.0139 0.0245	145.69 327.67	0.0247 0.0297	P <sub>2</sub> Ph <sub>4</sub> -(CH <sub>3</sub> ) <sub>3</sub> wag
358	343.09 343.54 346.55 348.18	2.7216 2.5989 2.2757 2.8006	344.08 351.05 358.08 362.86 367.31 367.66	0.0424 0.015 0.0242 0.0826 0.0253 0.0208	356.02	0.0225	339.77 351.16 353.92 358.28	0.0165 0.0218 0.0392 0.0142	P–(CH <sub>2</sub> ) <sub>3</sub> –P distortion
410	404.31 404.79 413.31 414.48 416.7 415.66 419.21	4.7347 4.6453 0.8692 13.2331 9.3675 4.9216 6.3026	391.89 395.32 399.06 400.7 411.36 416.86	0.1727 0.0152 0.0149 0.0301 0.0713 0.076	397.37 397.63 402.98 410.2	0.0977 0.0307 0.0236 0.036	389,66 394,54 397.03 397.37 409.68	0.2028 0.0397 0.0523 0.1089 0.0942	P-C-C-C-P bend
431	425.22 427.51 431.4 434.64 437.65	6.1159 5.486 3.7808 7.2679 0.9142	424.99 426.34 426.51 428.16 430.5	0.0588 0.1706 0.0396 0.1126 0.122	423.33 423.53 427.4 431.58 437.08	0.0516 0.1058 0.0423 0.0984 0.0258 0.0141	417.41 419.09 421.43 424.72	0.1034 0.1037 0.2731 0.1076	Au–P stretch and P–Ph stretch
447	441.92 442.69 457 58 485 57	33.2022 8.5664 Ave 16 1220	441.98 443.44 443.85 447.01 447.01	0.0892 0.0586 0.4207 0.1263 0.1263	441.62 442.55 442.55	0.0948 0.1481	436.94 437.2 437.2 437.2 441.82 443.69 447.98 450.68 450.68 451.31	0.0762 0.164 0.22 0.1873 0.1873 0.253 0.253 0.253 0.1313 0.1313	P(CH <sub>2</sub> ) <sub>3</sub> Ph <sub>2</sub> distortion
2				· ·· · · · · · · · · · · · · · · · ·	~~~~~	~· ~· ~ · ~ · · · · · · · · · · · · · ·			

Mode description	Au core distortion	Ph rock	Ph rock	Ph twist	PPh <sub>3</sub> distortion
Intensity (km/mol)	0.0247	$\begin{array}{c} 0.0941\\ 0.089\\ 0.0338\\ 0.0338\\ 0.0251\\ 0.0213\\ 0.0749\\ 0.0879\\ 0.0879\\ 0.0779\\ 0.0779\\ 0.0779\\ 0.0779\\ 0.0779\\ 0.0173\\ 0.0173\\ 0.0173\\ 0.0173\\ 0.0173\end{array}$	0.0348 0.0414 0.0303 0.0303 0.0242 0.0459 0.0459 0.01189 0.0118 0.0118	Avg. 0.0038	Avg. 0.0885 Avg. 0.2373
DFTB2/auorg $\chi'$ (cm <sup>-1</sup> )	176.69	183.25 191.53 191.8 197.43 201.22 201.79 201.79 201.75 202.56 207.56 207.56 207.56	240.69 242.16 242.41 242.41 248.35 248.45 249.57 249.88 249.88	350.18- 402.90	427.38-457.86 462 00-484 41
Intensity (km/mol)	0.0347	0.0913 0.1359 0.23 0.054 0.0533 0.0785 0.0718 0.0718 0.0718 0.0446 0.0365 0.0365 0.0365 0.0365 0.0415 0.0415 0.0415 0.0415 0.0333 0.0181	0.1216 0.0263 0.0278 0.0378 0.0176 0.0521 0.069 0.0131 0.0436 0.0321 0.026 0.0373 0.026 0.0373 0.0018	Avg. 0.0033	Avg. 0.0423 Avg 0.2316
DFTB2/auorg <sup>α</sup> (cm <sup>-1</sup> )	166.17	$\begin{array}{c} 181.34\\ 191.17\\ 192.78\\ 192.78\\ 192.78\\ 199.03\\ 199.03\\ 202.03\\ 202.03\\ 202.03\\ 205.02\\ 205.02\\ 205.42\\ 205.42\\ 205.03\\ 205.03\\ 200.04\\ 200.04\\ 200.04\\ 200.04\\ 200.04\\ 210.49\\ 210.49\\ 210.49\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\ 210.7.81\\ 200.04\\$	234.58 234.58 244.28 244.28 245.58 247.41 247.45 247.45 247.59 247.59 247.59 250.49 250.49 250.06	375.66- 396.94	410.22-448.34 466 34-487 27
Intensity (km/mol)	0.0229	0.0165 0.0782 0.091 0.028 0.0264 0.0867 0.0867 0.0386 0.0143 0.0143 0.0148 0.0366 0.0366	0.0131 0.0642 0.0594 0.017 0.017 0.0168 0.0168 0.0168 0.0168 0.0168 0.01625 0.0422 0.0422 0.0422 0.0241 0.0641	Avg. 0.0035	Avg. 0.0873 Avg. 0.2324
DFTB2/auorg <sup>α/</sup> (cm <sup>-1</sup> )	146.17	178.65 183.44 191.34 191.9 196.17 201.5 201.5 204.11 206.59 206.59 206.63 206.53 206.53 206.53	221.81 238.05 238.66 239.42 241.87 242.98 245.74 248.31 248.31 248.31 248.92 248.92 248.92 248.92 250.29	351.07- 402.89	431.28-455.63 460 08-487 34
Intensity (km/mol)	1.4183 11.457 11.3283	Avg. 1.0292	Avg. 1.3214	Avg. 0.1938	Avg. 2.6561 Avg. 21.2375
PBE/def2-SVP (cm <sup>-1</sup> )	173.46 176.12 176.23	185.35-223.02	247.43-265.45	390.38- 406.89	426.97-441.72 498 85-507.62
Experimental (cm-1)	182	218	559	398	436 480

heir assignment to the	Mode description		Au core distortion	Ph rock	PPh <sub>3</sub> distortion	Ph twist	PPh <sub>3</sub> distortion
$ ^{3+}$ cluster and t	Intensity (km/mol)	0.0351 0.017 0.0141 0.0141	0.2618 0.2421 0.0721 0.0328	0.0159 0.012 0.0412	0.0227 0.0258 0.0239 0.0522 0.0175 0.1159 0.0101	0.0114 0.0146 0.397 0.0537 0.03 0.1603 0.0201	Avg. 0.2197 0.562
' for the [Au <sub>9</sub> (PPh <sub>3</sub> ) <sub>8</sub>	DFTB2/auorg $\chi'$ (cm <sup>-1</sup> )	141.33 147.08 158.37 188	194.67 195.37 198.78 205.06	213.7 215.86 226.53	232.29 232.47 232.84 239.67 241.13 256.19 256.39	394.01 420.46 429.48 430.32 433.86 434.53 435.16	450.55-453.26 485.92-487.96
J DFTB2/auorg <sup>x</sup>	Intensity (km/mol)	0.0176 0.0153 0.0291 0.1323	0.0694 0.1564 0.1133 0.1528 0.1877	0.0615 0.0581 0.1124 0.0153	0.1353 0.0213 0.0213 0.0349 0.0159 0.1192 0.0141 0.0138 0.0138	0.0188 Avg. 0.074	0.2226 0.5163
', DFTB2/auorg $^{lpha}$ and	DFTB2/auorg $^{\alpha}$ (cm <sup>-1</sup> )	129.37 131.6 139.97 168.01	190.87 191.15 191.84 193.45 193.51	206.25 207.4 214.06 214.39	227.83 229.86 231.21 240.05 244.58 244.58 259.19 259.32 259.32 259.32	389.87 412.30-435.88	440.57 483.27-496.16
P, DFTB2/auorg $^{lpha}$ sition modes	Intensity (km/mol)	0.0161 0.0637 0.021 0.0136 0.0136	0.0189 0.0159 0.1244 0.0149 0.2757 0.2851 0.0403	0.0134	0.0153 0.0244 0.0239 0.0215 0.0499 0.029 0.1193	0.0091 0.0133 0.401 0.0108 0.0339 0.0339 0.0315 0.0315 0.0315 0.0315 0.0315	Avg. 0.2211 Avg. 0.5519
ated by PBE/def2-SV n of the assigned tran	DFTB2/auorg <sup><math>\alpha</math></sup> (cm <sup>-1</sup> )	136.28 142.19 142.82 150.77 168.16	190.19 192.12 192.73 193.1 193.1 195.64 196.09 208.95	215.13 217.12	231.09 233.97 233.97 233.97 239.78 243.36 243.36 256.9	394.25 420.43 431.79 432.69 432.7 434.9 435.54 435.91 435.91	451.01-456.88 486.37-488.36
nsitions as calcul a brief descriptio	Intensity (km/mol)	2.2532 2.6164 9.6724	17.3597 1.5613 2.025 4.7331 3.7443	0.6717 0.6573 2.4079 0.1111 0.0122 1.4505 1.3855	Avg. 1.4416	Avg. 0.2980 Avg. 2.4632	Avg. 5.2400 Avg. 18.8798
ary of contributing tra ctral peaks, as well as	PBE/def2-SVP (cm <sup>-1</sup> )	148.81 148.81 163.28 169.95	174.7 186.07 195 198.75 204.53	214.56 214.91 217.12 217.77 218.61 218.69 219.36	238.93-251.52	390.16-401.64 424.59-431.16	438.55-444.13 489.33-492.65
<b>Table S9</b> Summi experimental spe	Experimental (cm-1)	157 177	197	220*	252	397 430	448 480



Fig. S11 Different adsorption binding sites on Au (111) surface, only the Au atoms of the top two layers are shown.



Fig. S12 HOMO and LUMO plots of  $Au_{108}S_{24}$ ,  $Au_{108}S_{24}(PH_3)_{16}$ , and  $Au_{108}S_{24}(PPh_3)_{16}$  clusters as calculated by TPSS/def2-SVP//DFTB2/auorg<sup> $\alpha$ </sup>; isosurface value = 0.015 e<sup>0.5/a\_0^3</sup>.

**Table S10** Summary of contributing transitions determined by DFTB2/auorg<sup> $\alpha$ </sup> for the [Au<sub>108</sub>S<sub>24</sub>(PPh<sub>3</sub>)<sub>16</sub>] cluster and brief description of the assigned transition modes, part 1.

DFTB2/auorg <sup><math>\alpha</math></sup> (cm-1)	Intensity (km/mol)	Mode description	
26.387 54.087	0.01195 0.01243		
54.116	0.01255	Au core distortion	
56.459	0.01452		
73.484	0.01/21		
/6.592	0.0112		
91.121 91.466	0.01114 0.01238	Au core distortion	
93.606 93.638	0.01015 0.01133	asymmetric stretching Au-S-Au (planar rings) and $\text{PPh}_3$ twisting	
102.984	0.01016		
103.05	0.0104		
110.089	0.01135		
113.072	0.01073	Au core distortion	
114.583	0.01228		
118.282	0.02662		
118.435	0.02339		
118.772	0.01639	Au-Au-Au rocking (connected to planar rings)	
119.34	0.01649	Au-Au scissoring (connected to planar rings)	
120.403	0.01194	As Decrementation start de card de carde distantion	
120.684	0.01922	Au-P asymmetric stretch and Au core distortion	
124.009	0.01762		
124.278	0.01728		
124.451	0.01	A 11	
125.952	0.01163	Au core distortion	
133.768	0.01069		
141.793	0.01276		
164.734	0.01712		
165.461	0.01824	As Distance 1	
165.477	0.01777	Au-P stretch	
167.11	0.01346		
167.291	0.01307		
180.925	0.02166	Au-Au symmetric stretching (connected to PPh <sub>3</sub> )	
181.058	0.01548		
182.297	0.02001	Au-P stretch	
182.471	0.03368		
182.914	0.02397		
185.318	0.03596		
185.487	0.02547		
185.676	0.01155		
185.741	0.01826		
185.76-192.27	Avg. 0.0346	Ph rocking	
198.523	0.14019		
200.25	0.10294	symmetric stretching S-Au-S (planar rings)	
202.781	0.14811		
204.909	0.04854		
204.915	0.0242		
205.337	0.04331	Ph twist	
207.877	0.08301		
208.089	0.05917		

DFTB2/auorg $\alpha$	Intensity	Mode description	
(cm-1)	(km/mol)	Mode description	
208.161	0.1301		
208.402	0.05661		
208.717	0.09316		
209.314	0.05062	Ph rock	
210.34	0.06436		
211.184	0.04972		
218.041	0.01951		
218.41	0.01103	S-Au-S rocking (planar rings)	
218.467	0.02623		
218.943	0.11707		
219.181	0.02061		
219.363	0.02627	Ph rocking	
219.491	0.04727	0	
219.741	0.06469		
220.336	0.0208		
222.196	0.04751		
222.776	0.03097		
222.996	0.00298		
223 114	0.04095	S-Au-S rocking (planar rings)	
223.117	0.04025	5-Mi-5 focking (planar fings)	
223.41	0.03931		
220.198	0.11918		
234.330	0.00303		
234.5	0.00321		
237.519	0.02785		
237.597	0.00845		
237.735	0.01358		
237.761	0.02369		
238.013	0.01369		
238.173	0.05096	Ph rock and Au-S stretch	
238 236	0.05156		
238 412	0.02354		
238 818	0.01568		
238.003	0.01560		
239.258	0.07917		
241 089	0.60303		
241.007	0.67083		
241.172	0.04902		
241.393	0.23001		
241./30	0.01965		
242.000	0.1040/	Au-S stretch	
242.1/2	0.02482		
243.156	0.05566		
243.74	0.05345		
243.962	0.01056		
247.977	0.06949		
248.71-252.17	Avg. 0.0379	Ph twist	
255.09-262.74	Avg. 0.1307	PPh3 distortion and Au-S stretch	
265.03-272.86	Avg. 0.0391	Au <sub>4</sub> S <sub>4</sub> planar ring rock	
274.386	0 05491	· ·	
276 211	0 15656	A11. S. symmetric stretch	
276 568	0.13030	ru <sub>4</sub> 0 <sub>4</sub> symmetre stretti	
2,0.000	0.1/110		
277.186	0.11359		
2/9.0/1	0.03883	$Au_4S_4$ asymmetric stretch	
2/9./81	0.08326		

**Table S11** Summary of contributing transitions determined by DFTB2/auorg<sup> $\alpha$ /</sup> for the [Au<sub>108</sub>S<sub>24</sub>(PPh<sub>3</sub>)<sub>16</sub>] cluster and brief description of the assigned transition modes, part 2.

**Table S12** Summary of contributing transitions determined by DFTB2/auorg<sup> $\alpha$ </sup> for the [Au<sub>108</sub>S<sub>24</sub>(PPh<sub>3</sub>)<sub>16</sub>] cluster and brief description of the assigned transition modes, part 3.

DFTB2/auorg <sup><math>\alpha</math></sup> /	Intensity (/m/mol)	Mode description
	0.0261 0.06474	Au <sub>4</sub> S <sub>4</sub> twist
287.051 287.412	0.06944 0.40739	Au <sub>4</sub> S <sub>4</sub> symmetric stretch
291.177 291.437 292.643 294.434 297.485 302.74	0.03524 0.01303 0.02394 0.02065 0.01415 0.02364	PPh <sub>3</sub> distortion
334.01-372.66	Avg. 0.0205	Ph twist
431.06-459.86 471.809-495.78	Avg. 0.06291 Avg. 0.1485	PPh <sub>3</sub> distortion
506.28-520.33	Avg. 0.4313	PPh <sub>3</sub> distortion and Au-S stretch
521.401 522.278 522.656 525.037 525.403 525.648	0.12228 0.02622 0.00953 0.11265 0.24905 0.18726	Au-S stretch
532.85-554.38	Avg. 1.6027	Ph twist and Au-S stretch
559.916 570.926 571.017 571.603	9.29723 7.77941 7.52268 1.64805	Au-P stretch and PPh <sub>3</sub> distortion
613.44-648.58	Avg. 0.1124	PPh <sub>3</sub> distortion

#### Validation of the DFTB Method in Predicting Infrared Spectra of Gold-Thiolates Clusters

To validate the reliability of the DFTB2 method in simulating IR spectra for gold–thiolates nanoclusters, we compare the DFTB predicted IR spectra to published DFT theoretical IR spectra for  $Au_4(SCH_3)_4$ ,  $Au_{18}(SCH_3)_{14}$ , and  $[Au_{25}(SCH_3)_{18}]^-$  clusters.<sup>6–8</sup> In addition, we evaluate the capability of the DFTB2 method in describing ligand-ligand interactions and the effects of ligands on the structure and vibrational properties of the gold–thiolates clusters. We compare DFTB2 calculated IR to DFT calculated and experimental IR spectra for  $Au_{18}$  core cluster with six different types of ligand;  $-SCH_3$ ,  $-S-c-C_6H_{11}$ , -SPh, -p-MBA,  $-SPhNO_2$ , and -TBBT.<sup>8</sup> The effects of different ligands on the geometry of the  $Au_{18}$  core are compared as well. Figure S13 shows that the DFTB calculated IR spectra are comparable to the corresponding DFT spectra predicted by Tlahuice-Flores in his previous work.<sup>8</sup> Similar to the IR spectra of the phosphine-stabilized  $[Au_6(dppp)_4]^{2+}$ ,  $[Au_8(PPh_3)_8]^{2+}$ , and  $[Au_9(PPh_3)_8]^{3+}$  clusters, the DFTB calculated intensities are significantly lower but the normalized spectral shapes agree with their DFT calculated counterparts.

Figure S14 shows DFTB calculated IR spectra of a  $Au_{18}$  core cluster with six different types of ligands. Generally, DFTB calculated IR spectra resemble closely the DFT calculated spectra, but with smaller intensities than the reported ones by  $\approx 20-40 \text{ km/mol.}^8$  DFTB reproduces the change in IR spectra with the change of ligands well in comparison to the DFT calculated IR spectra. In particular, the case of  $Au_{18}(-S-c-C_6H_{11})_{14}$  clearly shows that the DFTB IR spectrum agrees extremely well with the experimental spectrum (using the same methodology as for the phosphine-stabilized clusters).<sup>9</sup> Small deviations between DFTB and DFT IR spectra might be caused by different initial geometries for the previously published DFT- and our own DFTB-optimized geometries,<sup>8</sup> and because the geometry optimization of these large and complicated clusters can converge to different local minima. Among these  $Au_{18}$  clusters,  $Au_{18}(p-MBA)_{14}$  and  $Au_{18}(SPhNO_2)_{14}$  clusters have highest intensity in their IR signals particularly for the Au-Au and Au-S stretches in  $Au_{18}S_{14}$  core clusters when compared to the rest of the clusters. The increase in these IR intensities can be attributed to the large structural distortions caused by p-MBA and SPhNO<sub>2</sub> ligands. Figure S15 shows the distortions of the  $Au_{18}$  core cluster caused by these ligands. This is consistent with the previous DFT-based study.<sup>8</sup> These results are very encouraging and suggests that the DFTB method is reliable in predicting the IR spectra for thiolate-protected gold clusters and confirms that it is able to describe the ligand-ligand interactions as well as ligands effects on gold clusters congruent with DFT

predictions.



Fig. S13 DFTB calculated IR spectra of  $Au_4(SCH_3)_4$ ,  $Au_{18}(SCH_3)_{14}$ , and  $[Au_{25}(SCH_3)_{18}]^-$ .



**Fig. S14** Calculated IR spectra of  $Au_{18}(SCH_3)_{14}$ ,  $Au_{18}(S-c-C_6H_{11})_{14}$ ,  $Au_{18}(SPh)_{14}$ ,  $Au_{18}(p-MBA)_{14}$ ,  $Au_{18}(SPhNO_2)_{14}$ , and  $Au_{18}(TBBT)_{14}$  clusters using a FWHM of 5 cm<sup>-1</sup> Gaussian broadening. More intense IR spectra are observed on p-MBA- and SPhNO\_2-protected clusters. The additional plots in S-c-C\_6H\_{11}-ligated Au\_{18} are the experimental far-IR spectrum (dotted red) and the DFTB-simulated with a wider FWHM of 8 cm<sup>-1</sup> Gaussian broadening.



**Fig. S15**  $Au_{18}S_{14}$  core structures of  $Au_{18}(S-c-C_6H_{11})_{14}$ ,  $Au_{18}(p-MBA)_{14}$ , and  $Au_{18}(SPhNO_2)_{14}$  clusters with four different ligands (ligand structures are omitted for clarity). Au and S atoms are yellow and orange. The clusters are optimized by means of DFTB/auorg<sup> $\alpha$ </sup> with the D3 dispersion corrections.

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