Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Hydride- and Halide-Substituted $Au_9(PH_3)_8^{3+}$ Nanoclusters: Similar Absorption Spectra Disguise Distinct Geometries and Electronic Structures

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$Au_9(PH_3)_8^{3+}$ (D_{2h} and D_{4d} symmetries)

Table S1. Excited states of $Au_9(PH_3)_8^{3+}$ (D_{2h} symmetry). All excited states between 2.0 and 3.9 eV with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.52	0.0210	99.19	51.20	HOMO	LUMO
			47.48	HOMO	LUMO+2
2.63	0.1097	80.22	40.12	HOMO-1	LUMO
			39.65	HOMO	LUMO+2
			18.64	HOMO-2	LUMO
3.17	0.2754	15.15	73.32	HOMO-2	LUMO
3.51	0.0207	18.13	15.64	HOMO	LUMO+5
3.57	0.0810	1.15	89.50	HOMO-5	LUMO+1
3.62	0.0250	0.84	89.33	HOMO-6	LUMO
3.87	0.7635	69.8	48.39	HOMO	LUMO+2
			17.32	HOMO-1	LUMO+1
			16.66	HOMO-2	LUMO+2

Table S2. Excited states of $Au_9(PH_3)_8^{3+}$ (D_{4d} symmetry). All excited states between 2.0 and3.9 eV with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.87	0.176	95.75	89.03	HOMO	LUMO+1
3.57	0.0911	60.86	57.84	HOMO	LUMO+3
			19.87	HOMO-2	LUMO+1
			16.85	HOMO-2	LUMO
3.82	0.1751	11.72	73.75	HOMO-2	LUMO+1
			9.99	HOMO-9	LUMO
3.87	0.0218	50.1	49.16	HOMO	LUMO+4
			24.98	HOMO-7	LUMO

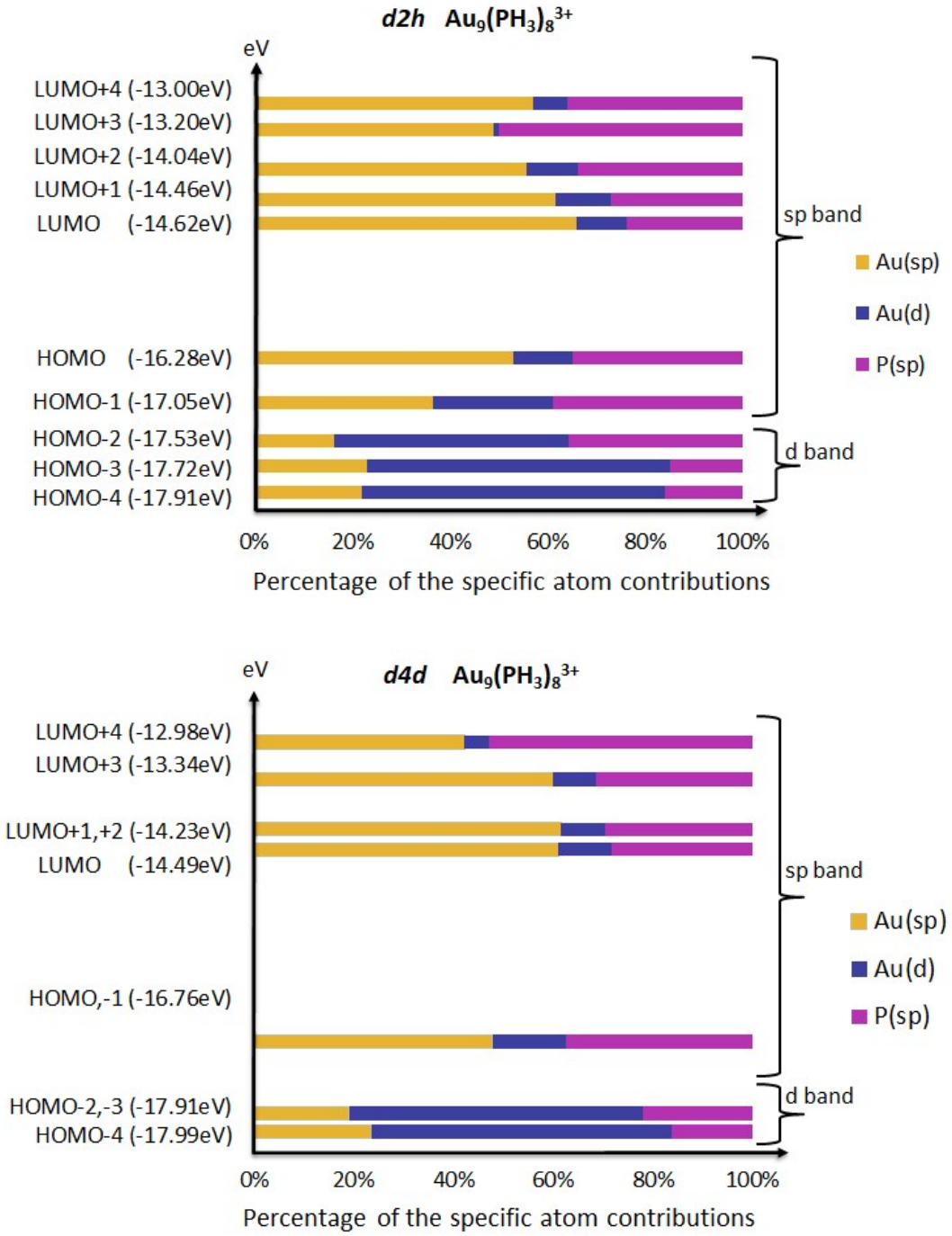


Figure S1. Kohn–Sham orbital energy diagram for the (top) D_{2h} and (bottom) D_{4d} symmetries of $Au_9(PH_3)_8^{3+}$. The horizontal colored bar for each Kohn-Sham orbital indicates the percent contributions of the atomic orbitals of Au (sp) in yellow, Au (d) in blue, and P (sp) in violet. The y axis shows the orbital energy.

$Au_9(PPh_3)_8^{3+}$ (D_{2h} and D_{4d} like symmetries)

Table S3. Excited states of $Au_9(PPh_3)_8^{3+}$ (D_{2h} like symmetry). All excited states with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
1.54	0.0296	99.94	98.92%	HOMO	LUMO
2.21	0.1261	94.37	60.01%	HOMO	LUMO+2
			28.33%	HOMO-1	LUMO
2.60	0.1078	50.04	48.10%	HOMO-2	LUMO
			30.98%	HOMO	LUMO+11
2.60	0.0612	72.85	59.25%	HOMO	LUMO+11
			26.11%	HOMO-2	LUMO
2.68	0.0328	96.81	92.48%	HOMO	LUMO+15
2.72	0.0781	98.66	37.73%	HOMO-1	LUMO+2
			30.56%	HOMO	LUMO+16
			15.13%	HOMO	LUMO+17
2.77	0.1465	98.08	42.27%	HOMO	LUMO+16
			29.04%	HOMO-1	LUMO+2
3.01	0.0417	5.16	77.22%	HOMO-3	LUMO+1
			12.26%	HOMO-7	LUMO
3.04	0.0276	4.23	75.34%	HOMO-7	LUMO
3.13	0.1547	28.54	66.41%	HOMO-2	LUMO+2
3.13	0.0506	71.62	38.72%	HOMO	LUMO+35
			20.47%	HOMO-1	LUMO+8
			11.30%	HOMO-5	LUMO+1
3.14	0.0511	84.92	34.18%	HOMO	LUMO+34
			15.97%	HOMO	LUMO+35
			13.64%	HOMO-1	LUMO+8
3.17	0.0266	68.85	48.10%	HOMO-1	LUMO+10
			15.62%	HOMO-13	LUMO
3.21	0.0212	93.96	66.74%	HOMO	LUMO+39
			20.26%	HOMO-1	LUMO+12
3.23	0.0214	26.07	41.86%	HOMO-9	LUMO+1
			15.32%	HOMO-10	LUMO+1
3.25	0.0434	52.43	26.39%	HOMO-1	LUMO+14
			17.22%	HOMO-11	LUMO+1
			14.48%	HOMO-9	LUMO+1
3.28	0.0279	73.41	52.14%	HOMO	LUMO+43
			20.03%	HOMO-12	LUMO+1
			17.55%	HOMO-1	LUMO+15

Table S4. Excited states of $Au_9(PPh_3)_8^{3+}$ (D_{4d} like symmetry). All excited states with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.12	0.0448	99.78	90.59%	HOMO	LUMO+1
2.23	0.0276	99.72	82.36%	HOMO	LUMO+2
			13.15%	HOMO-1	LUMO+1
2.35	0.1057	98.84	80.46%	HOMO-1	LUMO+1
			10.83%	HOMO	LUMO+2
2.44	0.1106	98.28	86.55%	HOMO-1	LUMO+2
2.67	0.0386	65.47	55.72%	HOMO	LUMO+6
			33.90%	HOMO-2	LUMO
2.76	0.0343	94.84	77.90%	HOMO	LUMO+8
2.82	0.0721	29.5	67.61%	HOMO-3	LUMO
			13.05%	HOMO	LUMO+11
2.86	0.0281	87.84	61.16%	HOMO-1	LUMO+6
			20.51%	HOMO	LUMO+12
2.94	0.0242	88.19	71.30%	HOMO-1	LUMO+8
3.01	0.0211	77.2	53.92%	HOMO	LUMO+19
			14.59%	HOMO-6	LUMO
3.03	0.0559	25.87	61.60%	HOMO-2	LUMO+1
3.06	0.0369	90.79	53.15%	HOMO-1	LUMO+13
			15.45%	HOMO-1	LUMO+12
3.14	0.0263	26.38	32.60%	HOMO-9	LUMO
			20.89%	HOMO-3	LUMO+1
			14.96%	HOMO	LUMO+26
3.15	0.0309	76.87	70.53%	HOMO-1	LUMO+17
			18.11%	HOMO-10	LUMO
3.17	0.0623	22.66	53.56%	HOMO-3	LUMO+1
3.18	0.0209	95.32	46.79%	HOMO	LUMO+28
			26.58%	HOMO-1	LUMO+18
			13.18%	HOMO	LUMO+27
3.19	0.0599	88.89	60.54%	HOMO	LUMO+29
3.25	0.0268	20.31	37.17%	HOMO-3	LUMO+2
			20.39%	HOMO-18	LUMO
			14.21%	HOMO-4	LUMO+1
3.27	0.0323	53.17	23.13%	HOMO-3	LUMO+2
			21.32%	HOMO	LUMO+32
			17.29%	HOMO-1	LUMO+21
			13.84%	HOMO-19	LUMO
3.30	0.0369	71.25	40.63%	HOMO-1	LUMO+24
			23.81%	HOMO-5	LUMO+1
			22.11%	HOMO-1	LUMO+23
3.30	0.0594	32.3	51.15%	HOMO-5	LUMO+1

			22.04%	HOMO-1	LUMO+24
3.35	0.0294	79.49	60.20%	HOMO	LUMO+36
			15.99%	HOMO-6	LUMO+1
3.36	0.0382	28.47	56.61%	HOMO-4	LUMO+2
			19.61%	HOMO-1	LUMO+27

$Au_9(PH_3)_8H^{2+}$

Table S5. Relative energies at the revTPSS/TZP level of $Au_9(PH_3)_8H^{2+}$. d2h # and d4d # represent different optimized geometries derived from different starting positions of the hydride on the unsubstituted D_{2h} and D_{4d} symmetries of $Au_9(PH_3)_8^{3+}$. The structure indicated in bold (**d2h 2**) is the most stable structure, described in the manuscript.

	Δ(kcal/mol)
d2h 1	9.18
d2h 2	**0.00**
d2h 3	11.93
d2h 4	8.61
d4d 1	6.75
d4d 2	7.81

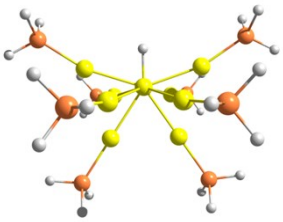
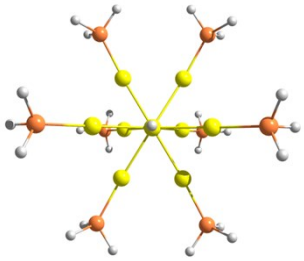
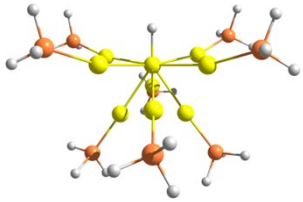
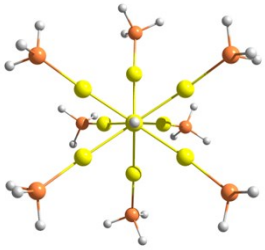
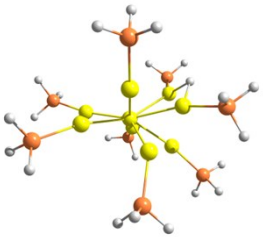
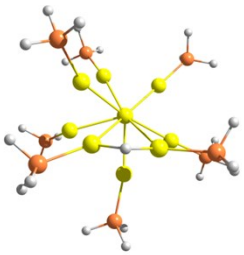
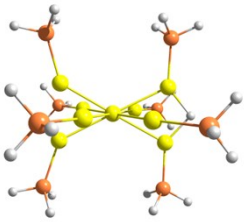
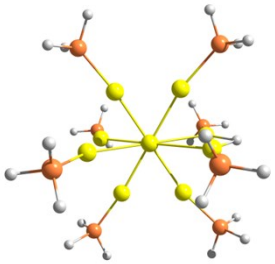
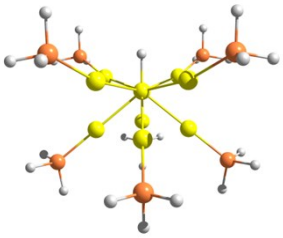
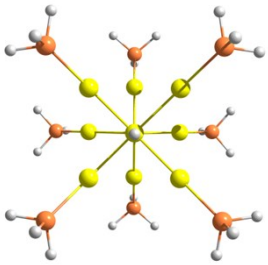
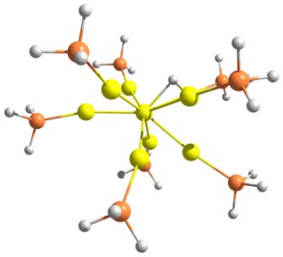
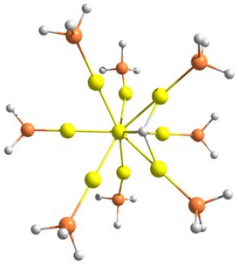
	Front view	Top view
d2h 1		
d2h 2		
d2h 3		
d2h 4		
d4d 1		
d4d 2		

Figure S2. Optimized structures of the $Au_9(PH_3)_8H^{2+}$ at revTPSS/TZP level of theory

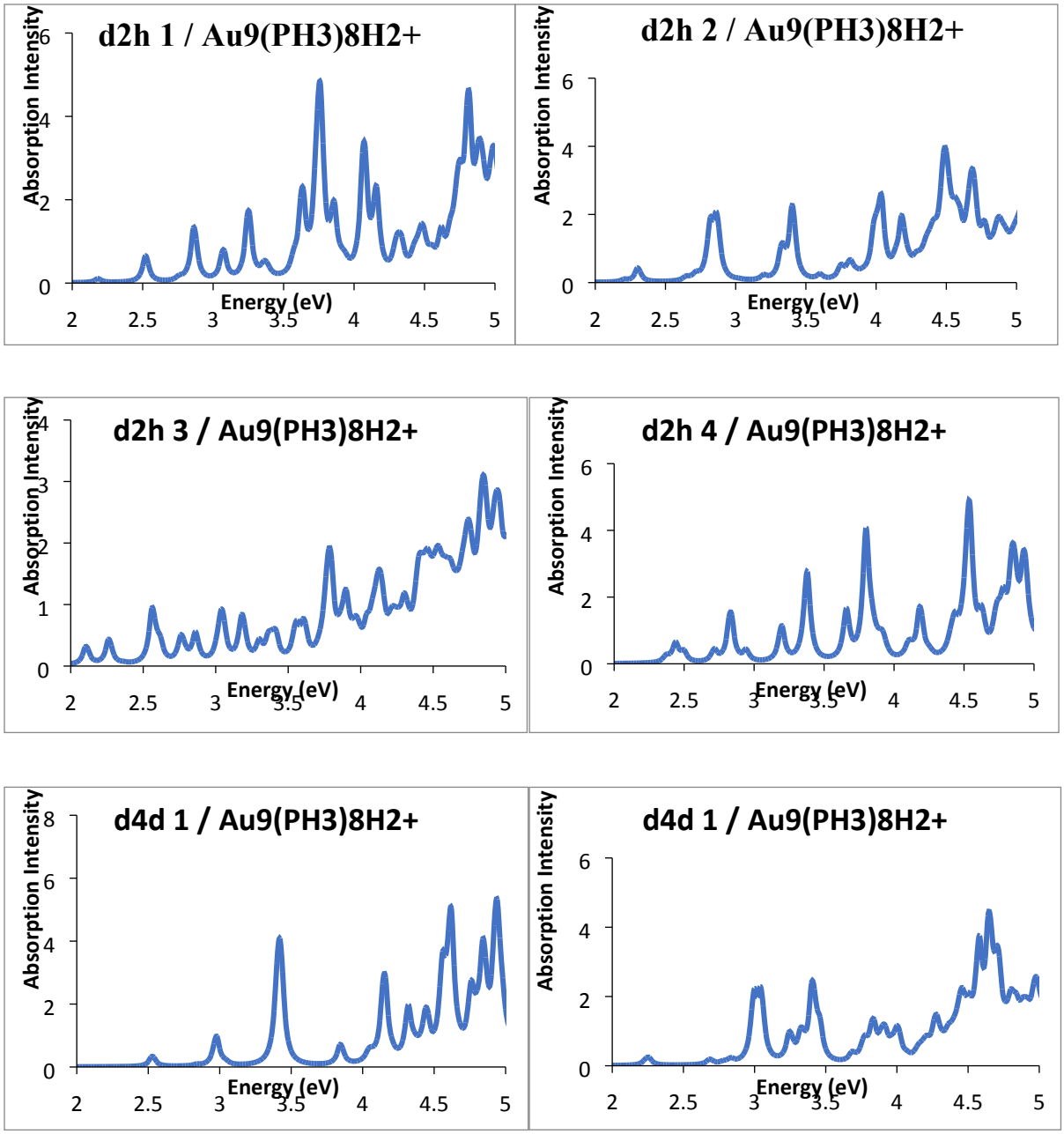


Figure S3. Absorption spectra of the optimized structures of $Au_9(PH_3)_8H^{2+}$.

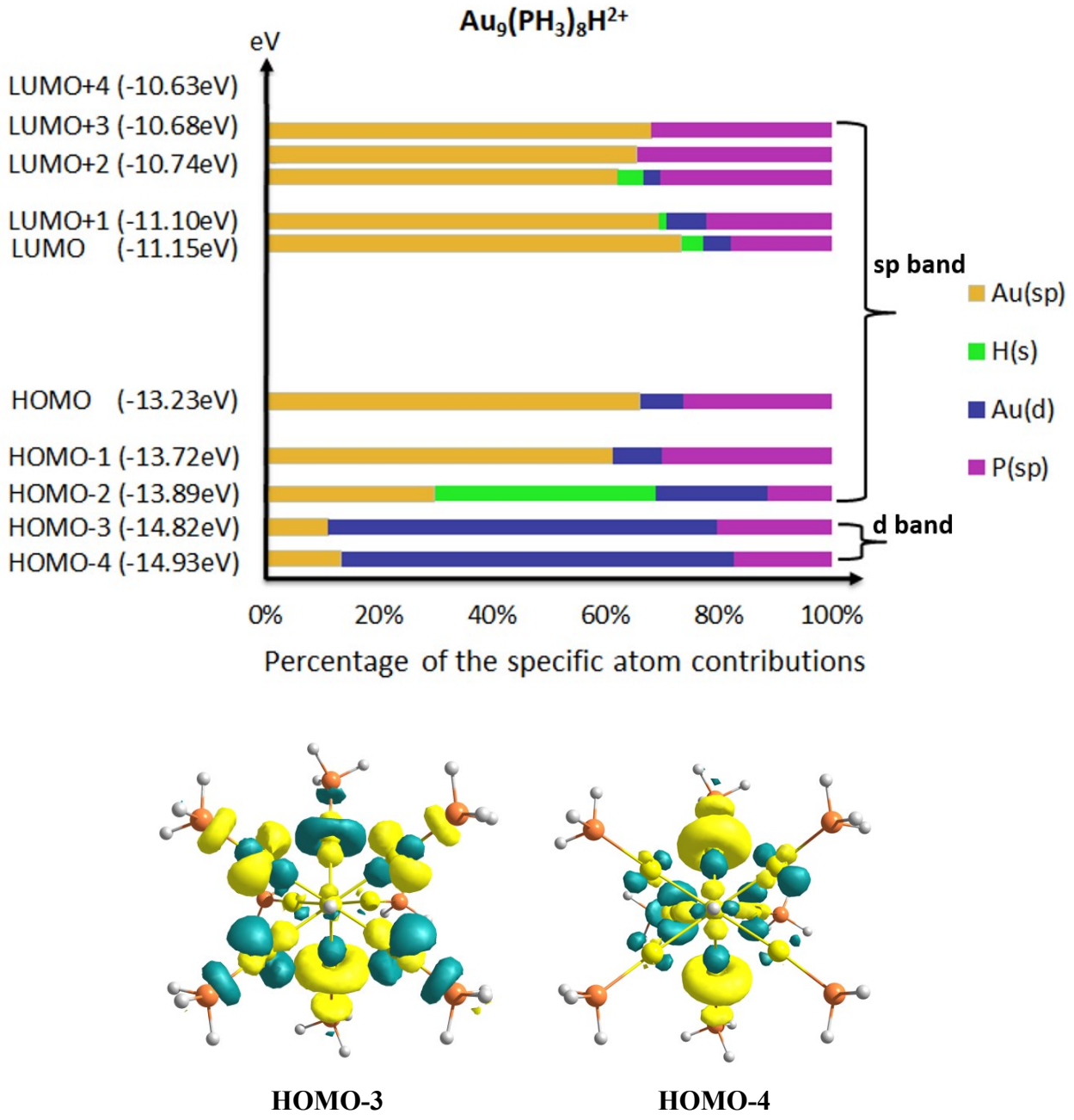


Figure S4. Kohn–Sham orbital energy diagram for the most stable structure of $Au_9(PPh_3)_8H^{2+}$. The horizontal colored bar for each Kohn-Sham orbital indicates the percent contributions of the atomic orbitals of Au (sp) in yellow, H(s) in green, Au (d) in blue, and P (sp) in violet. The y axis shows the orbital energy. HOMO-3 and HOMO-4 orbital depictions were given. HOMO, HOMO-1 and HOMO-2 were given in the MS.

Table S6. Excited states of $Au_9(PH_3)_8H^{2+}$ (D_{2h} symmetry (**d2h 2)**). All excited states between 2.0 and 3.9 eV with oscillator strengths larger than 0.01 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.30	0.035	99.61	83.57	HOMO	LUMO+1
2.72	0.0129	99.81	57.84	HOMO	LUMO+3
			19.87	HOMO	LUMO+4
2.82	0.1196	97.83	65.50	HOMO-1	LUMO
			12.07	HOMO-1	LUMO+1
2.86	0.1202	98.24	42.76	HOMO-1	LUMO+1
			31.42	HOMO	LUMO+2
2.88	0.0251	99.76	42.91	HOMO-2	LUMO+1
			33.04	HOMO-2	LUMO
3.33	0.0749	97.17	86.44	HOMO-2	LUMO+3
3.40	0.095	97.11	42.19	HOMO-2	LUMO+2
			27.15	HOMO-2	LUMO+4
			17.14	HOMO-1	LUMO+4
3.60	0.0126	94.83	93.70	HOMO	LUMO+6
3.75	0.0315	7.44	82.74	HOMO-3	LUMO
3.82	0.0245	90.96	87.99	HOMO-1	LUMO+5

$Au_9(PPh_3)_8H^{2+}$

Table S7. Excited states of $Au_9(PPh_3)_8H^{2+}$. All excited states between with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
1.99	0.0239	99.98	0.8784	HOMO	LUMO+1
2.13	0.0299	100	0.5351	HOMO	LUMO+3
			0.2915	HOMO	LUMO+2
2.22	0.0218	100	0.3526	HOMO	LUMO+5
			0.3365	HOMO-1	LUMO
			0.2152	HOMO	LUMO+6
2.26	0.0663	100	0.3331	HOMO-1	LUMO
			0.201	HOMO	LUMO+6
			0.1874	HOMO	LUMO+8
			0.1281	HOMO	LUMO+5
2.31	0.0419	100	0.5307	HOMO-1	LUMO+1
			0.1573	HOMO	LUMO+10
2.38	0.0318	100	0.4572	HOMO	LUMO+12
			0.3718	HOMO-1	LUMO+2
2.40	0.0569	100	0.298	HOMO-1	LUMO+2
			0.1311	HOMO	LUMO+11
			0.1303	HOMO-1	LUMO+3
			0.1074	HOMO-1	LUMO+1
			0.1026	HOMO	LUMO+13
2.49	0.0215	100	0.3783	HOMO-2	LUMO
			0.2479	HOMO	LUMO+17
			0.2284	HOMO	LUMO+16
2.52	0.0248	100	0.5488	HOMO	LUMO+17
			0.1734	HOMO	LUMO+16
			0.1677	HOMO-1	LUMO+5
2.61	0.0386	100	0.6574	HOMO	LUMO+21
			0.1052	HOMO-1	LUMO+9
2.67	0.0229	100	0.8251	HOMO-1	LUMO+11
2.68	0.0358	99.88	0.7521	HOMO-1	LUMO+12
2.89	0.0221	99.88	0.7233	HOMO-1	LUMO+20
2.96	0.0297	100	0.6757	HOMO-2	LUMO+10
3.01	0.0230	99.75	0.8318	HOMO-2	LUMO+13
3.19	0.0220	54.49	0.4374	HOMO-3	LUMO
			0.3534	HOMO-1	LUMO+35
3.21	0.0220	90.79	0.3343	HOMO-2	LUMO+20
			0.1517	HOMO-1	LUMO+37
			0.1279	HOMO	LUMO+49
			0.1052	HOMO	LUMO+48

3.32	0.1128	33.08	0.631	HOMO-3	LUMO+1
			0.215	HOMO	LUMO+52
3.35	0.0297	88.92	0.3489	HOMO	LUMO+52
			0.176	HOMO-1	LUMO+43
			0.155	HOMO-2	LUMO+29
3.37	0.0265	93.8	0.4475	HOMO-2	LUMO+29
3.42	0.0229	46.63	0.337	HOMO-2	LUMO+33
			0.2318	HOMO-3	LUMO+2
			0.137	HOMO-5	LUMO
			0.1058	HOMO-3	LUMO+3
3.45	0.0478	9.07	0.6985	HOMO-3	LUMO+3
3.48	0.0341	16.92	0.5732	HOMO-6	LUMO
			0.1719	HOMO-4	LUMO+1
			0.1169	HOMO-1	LUMO+48
3.52	0.0250	23.96	0.6286	HOMO-5	LUMO+1
			0.167	HOMO-2	LUMO+37
3.53	0.0323	87.56	0.5426	HOMO-2	LUMO+37
			0.1318	HOMO-1	LUMO+49
3.65	0.0307	1.00	0.8513	HOMO-5	LUMO+2
3.67	0.0329	35.33	0.3175	HOMO-1	LUMO+52
			0.3001	HOMO-3	LUMO+10
3.72	0.0233	22.09	0.6636	HOMO-4	LUMO+4
			0.1617	HOMO-2	LUMO+44
3.77	0.0336	2.44	0.8055	HOMO-4	LUMO+5

$Au_9(PH_3)_8F^{2+}$

Table S8. Relative energies at the revTPSS/TZP level of $Au_9(PH_3)_8F^{2+}$. d2h # and d4d # represent different optimized geometries derived from different starting positions of the fluoride on the unsubstituted D_{2h} and D_{4d} symmetries of $Au_9(PH_3)_8^{3+}$. The structure indicated in bold (**d4d 2**) is the most stable structure, described in the manuscript.

	Δ(kcal/mol)
d2h 1	10.60
d2h 2	10.70
d2h 3	8.11
d4d 1	10.23
d4d 2	**0.00**

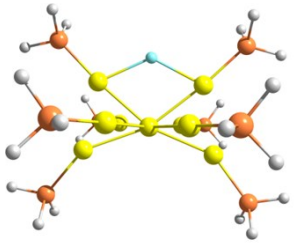
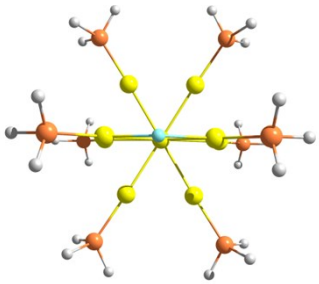
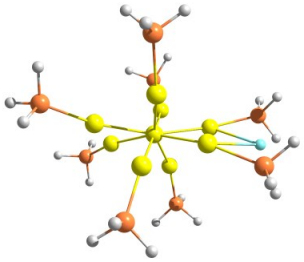
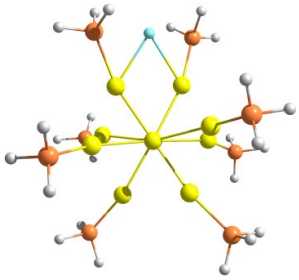
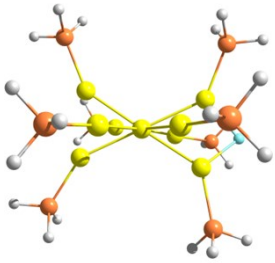
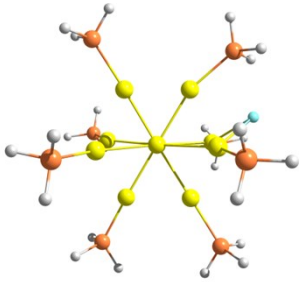
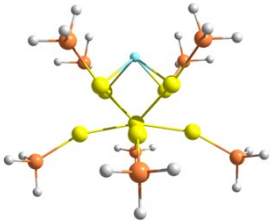
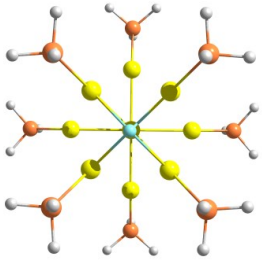
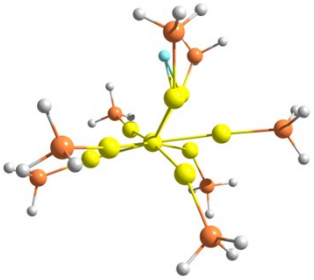
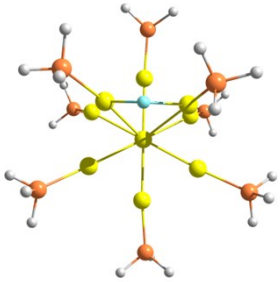
	Front view	Top view
d2h 1		
d2h 2		
d2h 3		
d4d 1		
d4d 2		

Figure S5. Optimized structures of the $Au_9(PH_3)_8F^{2+}$ at revTPSS/TZP level of theory

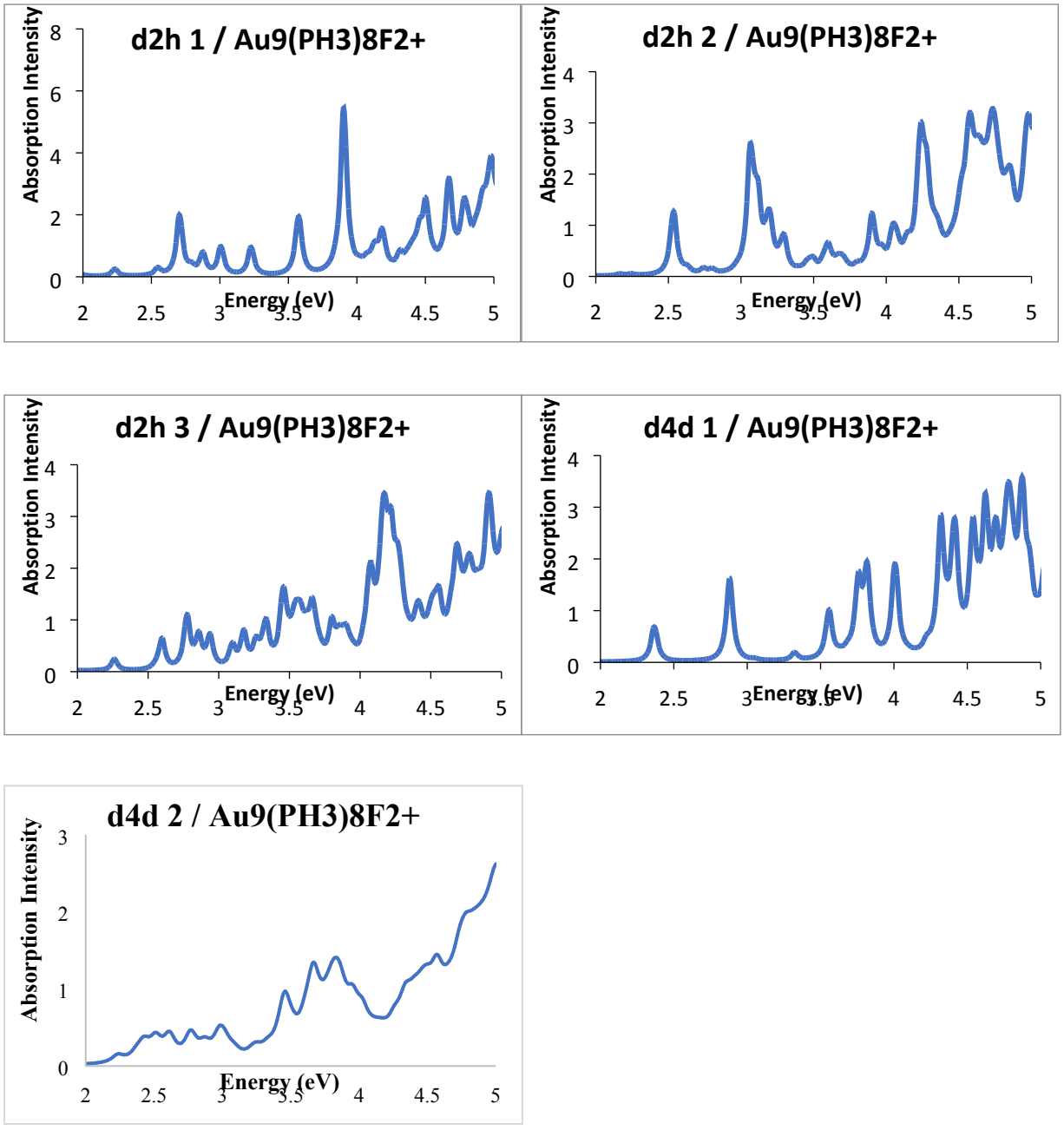
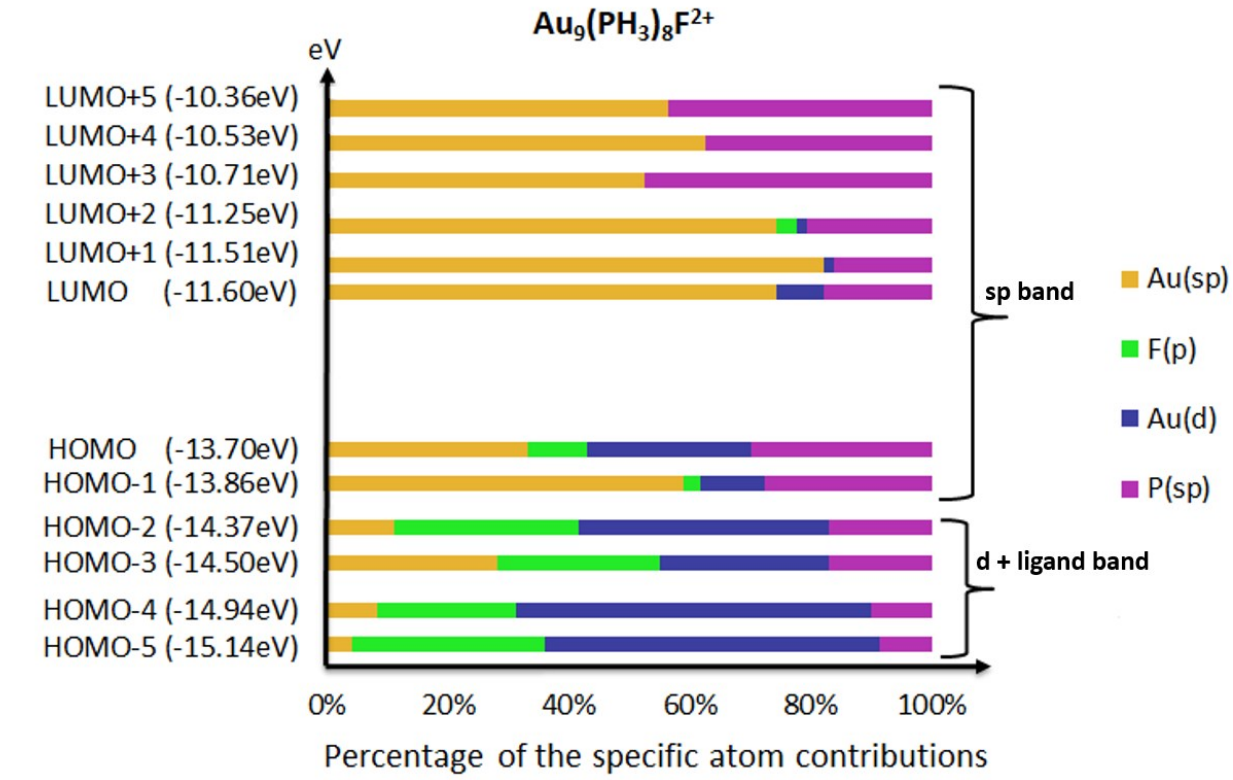
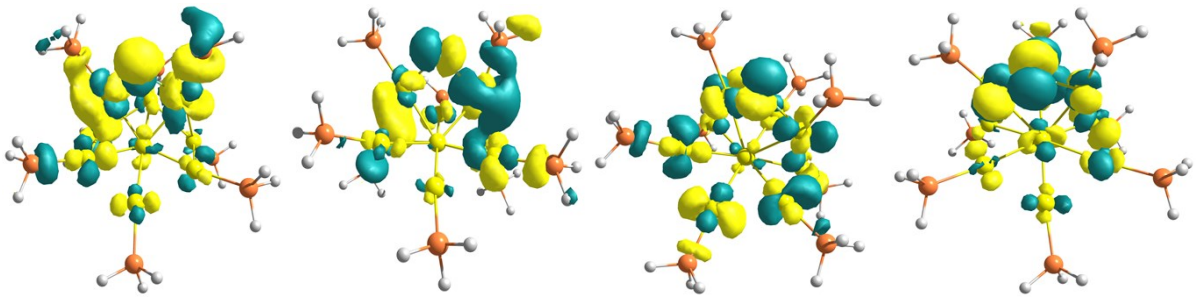


Figure S6. Absorption spectrums of fluoride ligated structures.

Table S9. Excited states of $Au_9(PH_3)_8F^{2+}$ (D_{4d} symmetry (**d4d 2)**). All excited states between 2.0 and 3.9 eV with oscillator strengths larger than 0.01 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.24	0.0161	99.12	65.79	HOMO	LUMO
2.43	0.0356	95.84	52.67	HOMO -1	LUMO
			19.76	HOMO	LUMO +1
			15.72	HOMO	LUMO +2
2.51	0.0432	97.18	79.35	HOMO -1	LUMO +1
2.61	0.0509	94.28	79.58	HOMO	LUMO +2
2.77	0.0554	93.32	83.53	HOMO -1	LUMO +2
2.87	0.0283	4.43	72.94	HOMO -2	LUMO
			18.00	HOMO -2	LUMO +1
2.98	0.0457	9.43	74.60	HOMO -2	LUMO +1
			11.21	HOMO -2	LUMO
3.25	0.0151	70.94	29.31	HOMO	LUMO +4
			29.07	HOMO -1	LUMO +3
			23.94	HOMO -2	LUMO +2
3.33	0.0165	1.27	76.16	HOMO -3	LUMO +2
			19.20	HOMO -4	LUMO
3.46	0.1022	17.72	54.79	HOMO -4	LUMO
			14.48	HOMO	LUMO +5
			11.52	HOMO -3	LUMO +2
3.67	0.1323	46.21	25.07	HOMO -1	LUMO +5
			17.62	HOMO -6	LUMO
			10.93	HOMO -4	LUMO +2
			9.21	HOMO -4	LUMO +1
3.80	0.0672	34.79	26.16	HOMO -1	LUMO +6
			23.80	HOMO -3	LUMO +3
			18.76	HOMO -4	LUMO +2
3.85	0.0571	6.4	41.57	HOMO -3	LUMO +3
			33.78	HOMO -2	LUMO +4





HOMO-2 **HOMO-3** **HOMO-4** **HOMO-5**

Figure S7. Kohn–Sham orbital energy level diagram for the $Au_9(PH_3)_8F^{2+}$ structure. Each KS orbital is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Au (sp) in gold, F(s) in green, Au (d) in blue, and P (sp) in purple. The y axis shows the M.O. and energy level. X axis shows the percentage of the specific atom contributions. HOMO-2, HOMO-3, HOMO-4 and HOMO-5 orbital depictions were given. HOMO and HOMO-1 were given in the MS.

$Au_9(PPh_3)_8F^{2+}$

Table S10. Excited states of $Au_9(PPh_3)_8F^{2+}$. All excited states between with oscillator strengths larger than 0.02 are listed.

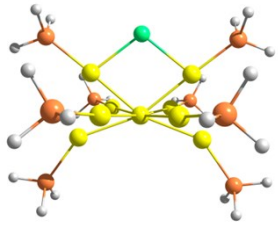
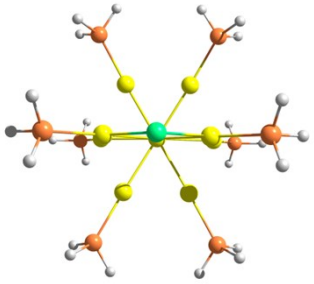
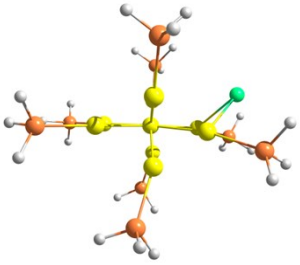
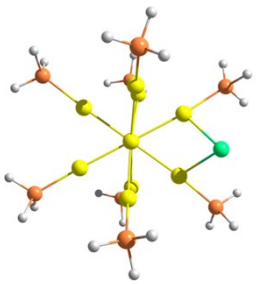
Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.00	0.0464	99.78	92.02%	HOMO	LUMO
2.12	0.0311	99.95	77.05%	HOMO	LUMO+2
2.26	0.0463	99.48	60.65%	HOMO-1	LUMO
			22.45%	HOMO-1	LUMO
2.28	0.0648	98.8	65.37%	HOMO-1	LUMO+1
2.35	0.0344	99.81	79.84%	HOMO	LUMO+4
2.37	0.0706	99.61	59.63%	HOMO-1	LUMO+2
			20.03%	HOMO	LUMO+5
2.62	0.0454	98.95	65.92%	HOMO	LUMO+13
			12.72%	HOMO	LUMO+12
			12.56%	HOMO-1	LUMO+6
2.71	0.0201	86.2	72.59%	HOMO	LUMO+17
2.74	0.0231	44.05	49.12%	HOMO-2	LUMO+1
			16.53%	HOMO	LUMO+19
2.78	0.0463	86.29	66.08%	HOMO	LUMO+21
			10.25%	HOMO-2	LUMO+1
2.83	0.0300	45.04	51.42%	HOMO-2	LUMO+2
			27.35%	HOMO-1	LUMO+13
2.95	0.0397	40.34	36.31%	HOMO-4	LUMO
			21.61%	HOMO-1	LUMO+18
			16.26%	HOMO-3	LUMO
2.97	0.0380	93.58	68.95%	HOMO-1	LUMO+19
2.97	0.0371	84.75	64.30%	HOMO-1	LUMO+20
			13.07%	HOMO-1	LUMO+19
3.01	0.0270	87.51	65.36%	HOMO-1	LUMO+21
			16.80%	HOMO	LUMO+30
3.02	0.0448	43.44	29.04%	HOMO-1	LUMO+22
			28.55%	HOMO-4	LUMO+1
			22.08%	HOMO-3	LUMO+1
3.04	0.0294	74.1	64.12%	HOMO	LUMO+31
			21.10%	HOMO-3	LUMO+1
3.05	0.0321	80.61	48.47%	HOMO	LUMO+33
3.06	0.0379	84.4	47.29%	HOMO	LUMO+33
3.08	0.0425	11.39	77.17%	HOMO-3	LUMO+2
3.16	0.0335	37.25	44.05%	HOMO-4	LUMO+2
			29.94%	HOMO	LUMO+39
3.19	0.0219	48.33	47.32%	HOMO-5	LUMO
			36.12%	HOMO	LUMO+40

3.21	0.0304	79.88	52.27%	HOMO	LUMO+41
			18.13%	HOMO	LUMO+40
			16.80%	HOMO-5	LUMO
3.24	0.0264	54.07	44.84%	HOMO	LUMO+43
			30.48%	HOMO-5	LUMO+1
3.25	0.0276	52.92	34.96%	HOMO	LUMO+43
			30.50%	HOMO-5	LUMO+1

$Au_9(PH_3)_8Cl^{2+}$

Table S11. Relative energies at the revTPSS/TZP level of $Au_9(PH_3)_8Cl^{2+}$. d2h # and d4d # represent different optimized geometries derived from different starting positions of the chloride on the unsubstituted D_{2h} and D_{4d} symmetries of $Au_9(PH_3)_8^{3+}$. The structure indicated in bold (**d4d 2**) is the most stable structure, described in the manuscript.

Name	Δ(kcal/mol)
d2h 1	3.77
d2h 2	8.93
d2h 3	6.16
d4d 1	9.44
d4d 2	0.00

	Front view	Top view
d2h 1		
d2h 2		

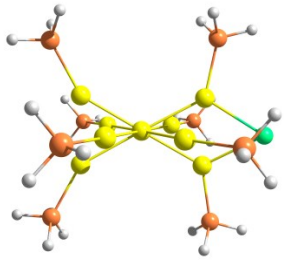
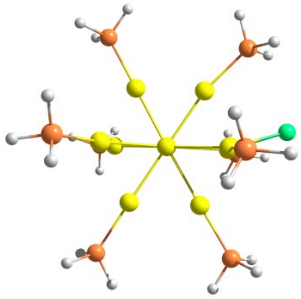
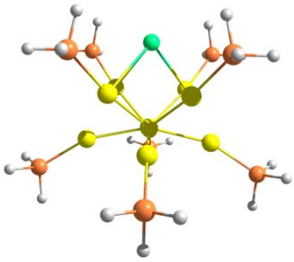
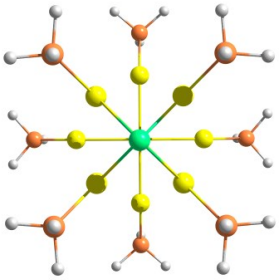
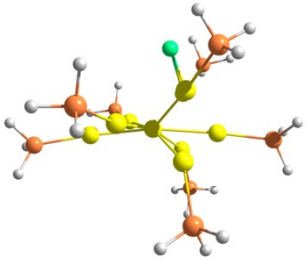
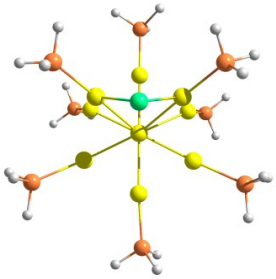
d2h 3		
d4d 1		
d4d 2		

Figure S8. Optimized structures of the $Au_9(PH_3)_8Cl^{2+}$ at revTPSS/TZP level of theory

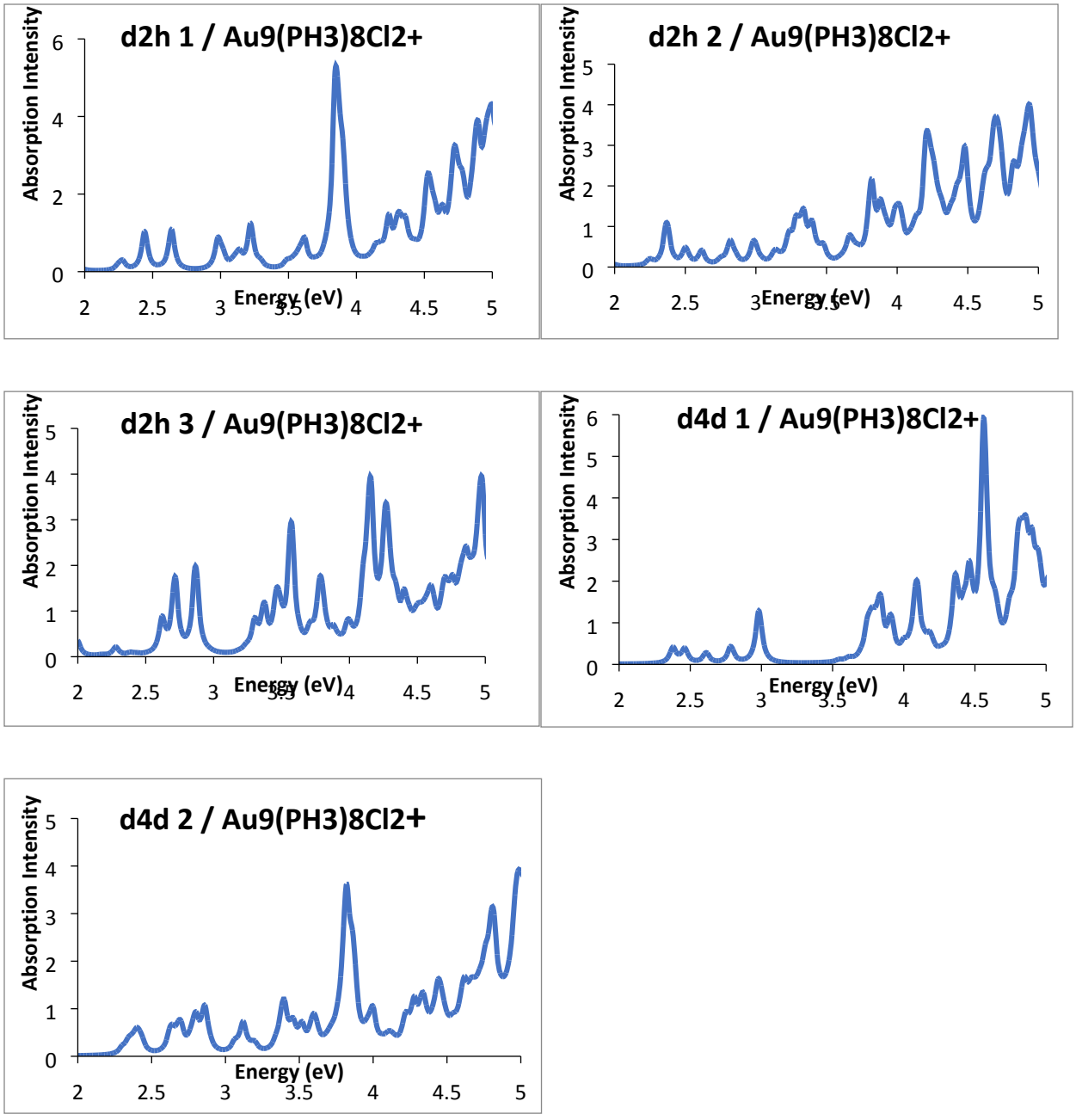


Figure S9. Absorption spectrums of chloride ligated structures.

Table S12. Excited states of $Au_9(PH_3)_8Cl^{2+}$ (D_{4d} symmetry (**d4d 2)**). All excited states between 2.0 and 3.9 eV with oscillator strengths larger than 0.01 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.39	0.033	85.23	37.49	HOMO	LUMO +1
			23.47	HOMO -1	LUMO
			19.22	HOMO -1	LUMO +1
			10.00	HOMO -2	LUMO
2.64	0.0187	76.55	37.30	HOMO	LUMO +2
			36.16	HOMO -1	LUMO +2
			9.56	HOMO -3	LUMO +1
			9.24	HOMO -2	LUMO
2.70	0.0401	82.05	40.20	HOMO -1	LUMO +2
			35.56	HOMO	LUMO +2
			11.40	HOMO -3	LUMO
2.80	0.0535	11.54	46.67	HOMO -3	LUMO
			36.00	HOMO -4	LUMO
2.86	0.0731	10.86	72.91	HOMO -3	LUMO +1
3.12	0.0489	3.41	89.18	HOMO -3	LUMO +2
3.40	0.0631	39.74	29.97	HOMO -5	LUMO
			26.92	HOMO	LUMO +4
			25.12	HOMO -5	LUMO +1
3.46	0.0409	57.9	35.04	HOMO -5	LUMO +1
			17.84	HOMO -1	LUMO +4
			15.60	HOMO	LUMO +5
			12.77	HOMO	LUMO +4
			10.49	HOMO -1	LUMO +5
3.52	0.0381	90.04	51.76	HOMO -1	LUMO +5
			36.16	HOMO	LUMO +5
3.58	0.0241	19.96	62.10	HOMO -3	LUMO +3
			9.56	HOMO -5	LUMO +2
			9.47	HOMO -1	LUMO +5
3.60	0.033	27.5	33.41	HOMO -3	LUMO +3
			31.24	HOMO -5	LUMO +2

			10.57	HOMO	LUMO +5
			9.54	HOMO -1	LUMO +5
3.82	0.2062	23.35	25.36	HOMO -8	LUMO +1
			19.24	HOMO -5	LUMO +2
			9.82	HOMO	LUMO +5
			8.96	HOMO -7	LUMO +1

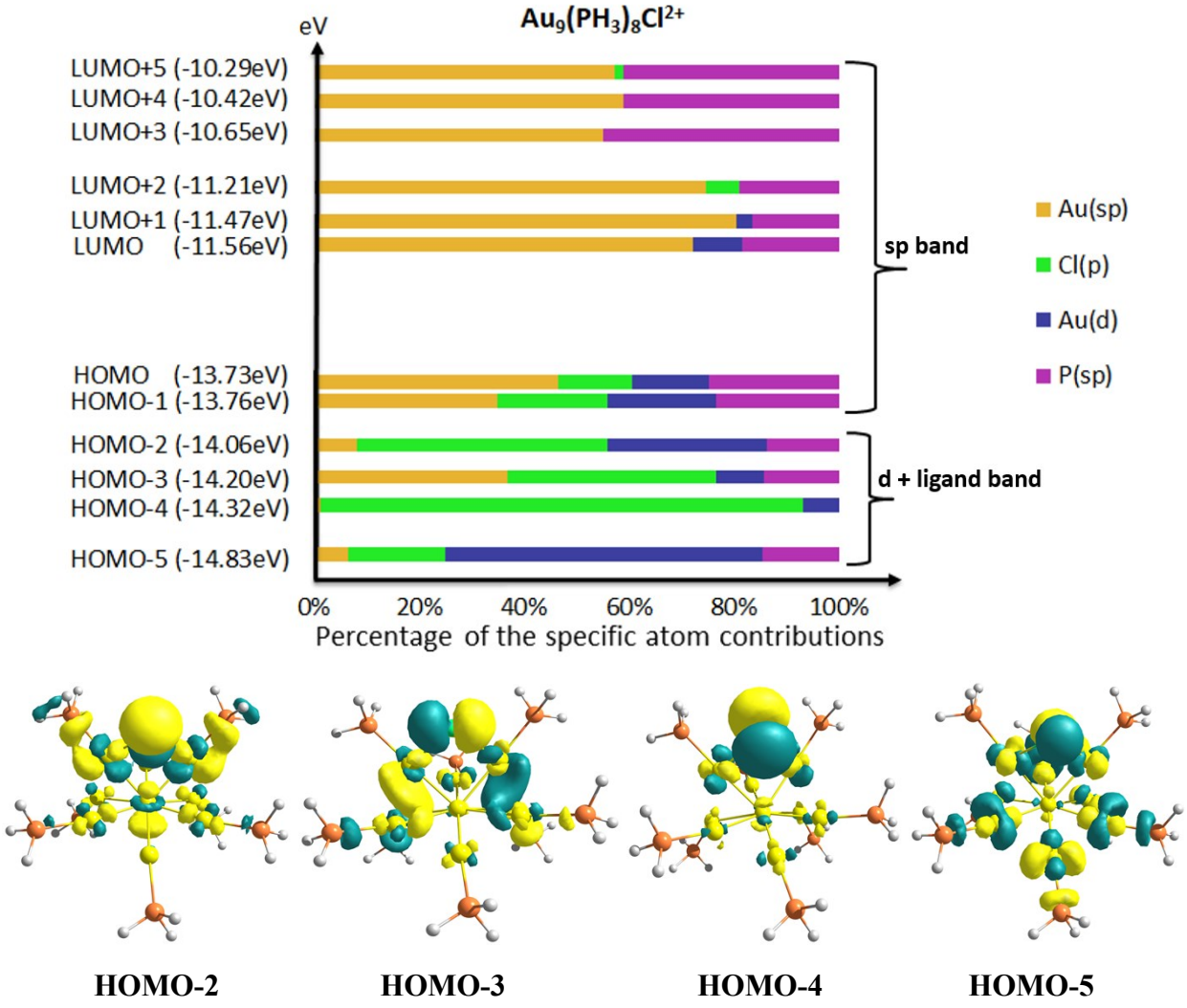


Figure S10. Kohn–Sham orbital energy level diagram for the $Au_9(PH_3)_8Cl^{2+}$ structure. Each KS orbital is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Au (sp) in gold, Cl(s) in green, Au (d) in blue, and P (sp) in purple. The y axis shows the M.O. and energy level. X axis shows the percentage of the specific atom contributions. HOMO-2, HOMO-3, HOMO-4 and HOMO-5 orbital depictions were given. HOMO and HOMO-1 were given in the MS.

$Au_9(PPh_3)_8Cl^{2+}$

Table S13. Excited states of $Au_9(PPh_3)_8Cl^{2+}$. All excited states with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
1.81	0.0548	99.81	93.64%	HOMO	LUMO+1
2.32	0.0250	99.72	43.11%	HOMO	LUMO+11
			39.71%	HOMO	LUMO+10
2.33	0.0269	99.74	48.01%	HOMO	LUMO+11
			19.28%	HOMO	LUMO+9
			10.76%	HOMO	LUMO+10
			10.54%	HOMO-1	LUMO+1
2.39	0.0630	98.48	58.25%	HOMO-1	LUMO+2
			33.39%	HOMO	LUMO+14
2.40	0.0403	98.68	61.36%	HOMO	LUMO+14
			30.25%	HOMO-1	LUMO+2
2.44	0.0252	96.81	79.69%	HOMO	LUMO+15
			10.42%	HOMO	LUMO+16
2.49	0.0474	98.98	77.88%	HOMO	LUMO+16
2.55	0.0278	8.86	86.45%	HOMO-2	LUMO+1
2.87	0.0360	70.48	55.26%	HOMO-1	LUMO+14
			13.55%	HOMO-4	LUMO
			10.10%	HOMO	LUMO+34
2.91	0.0430	28.69	47.45%	HOMO-5	LUMO
			15.23%	HOMO-1	LUMO+15
2.99	0.0227	37.07	39.01%	HOMO-4	LUMO+2
			12.63%	HOMO-1	LUMO+18
			11.14%	HOMO-5	LUMO+1
			10.61%	HOMO-1	LUMO+19
3.00	0.0319	34.98	24.12%	HOMO-4	LUMO+2
			20.10%	HOMO-5	LUMO+1
			19.28%	HOMO-1	LUMO+20
			13.23%	HOMO-3	LUMO+3
3.03	0.0457	76.32	31.82%	HOMO	LUMO+42
			15.10%	HOMO-1	LUMO+21
			14.63%	HOMO	LUMO+43
3.08	0.0338	28.05	63.99%	HOMO-5	LUMO+2

$Au_9(PH_3)_8Br^{2+}$

Table S14. Relative energies at the revTPSS/TZP level of $Au_9(PH_3)_8Br^{2+}$. d2h # and d4d # represent different optimized geometries derived from different starting positions of the bromide on the unsubstituted D_{2h} and D_{4d} symmetries of $Au_9(PH_3)_8^{3+}$. The structure indicated in bold (**d4d 2**) is the most stable structure, described in the manuscript.

Name	Δ(kcal/mol)
d2h 1	6.74
d2h 2	10.98
d2h 3	5.88
d4d 1	9.42
d4d 2	**0.00**

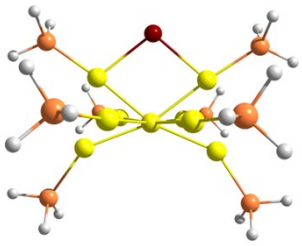
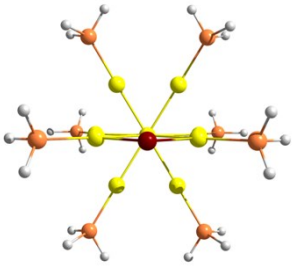
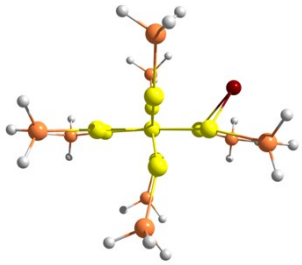
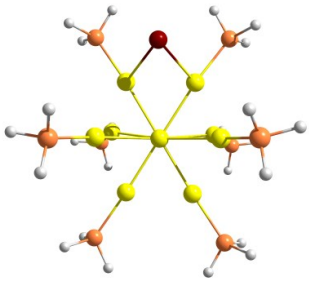
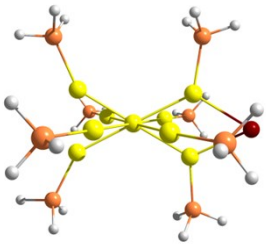
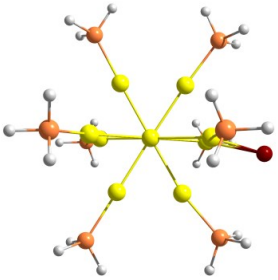
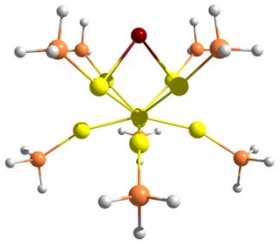
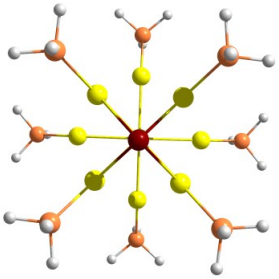
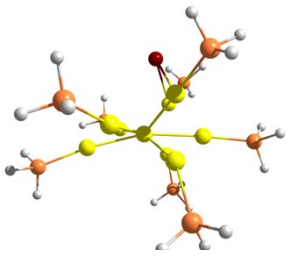
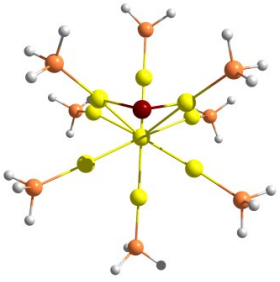
	Front view	Top view
d2h 1		
d2h 2		
d2h 3		
d4d 1		
d4d 2		

Figure S11. Optimized structures of the $Au_9(PH_3)_8Br^{2+}$ at revTPSS/TZP level of theory

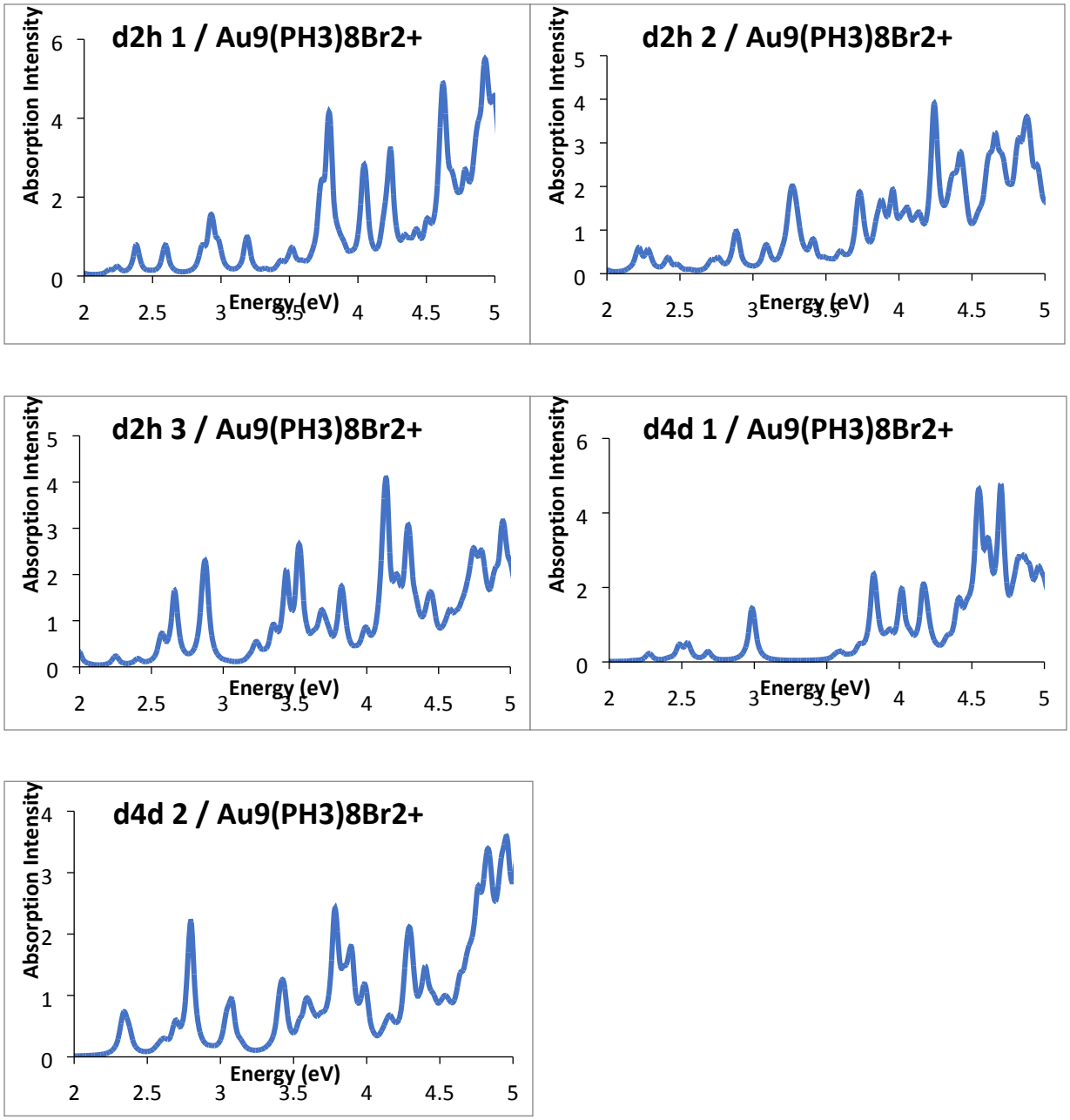
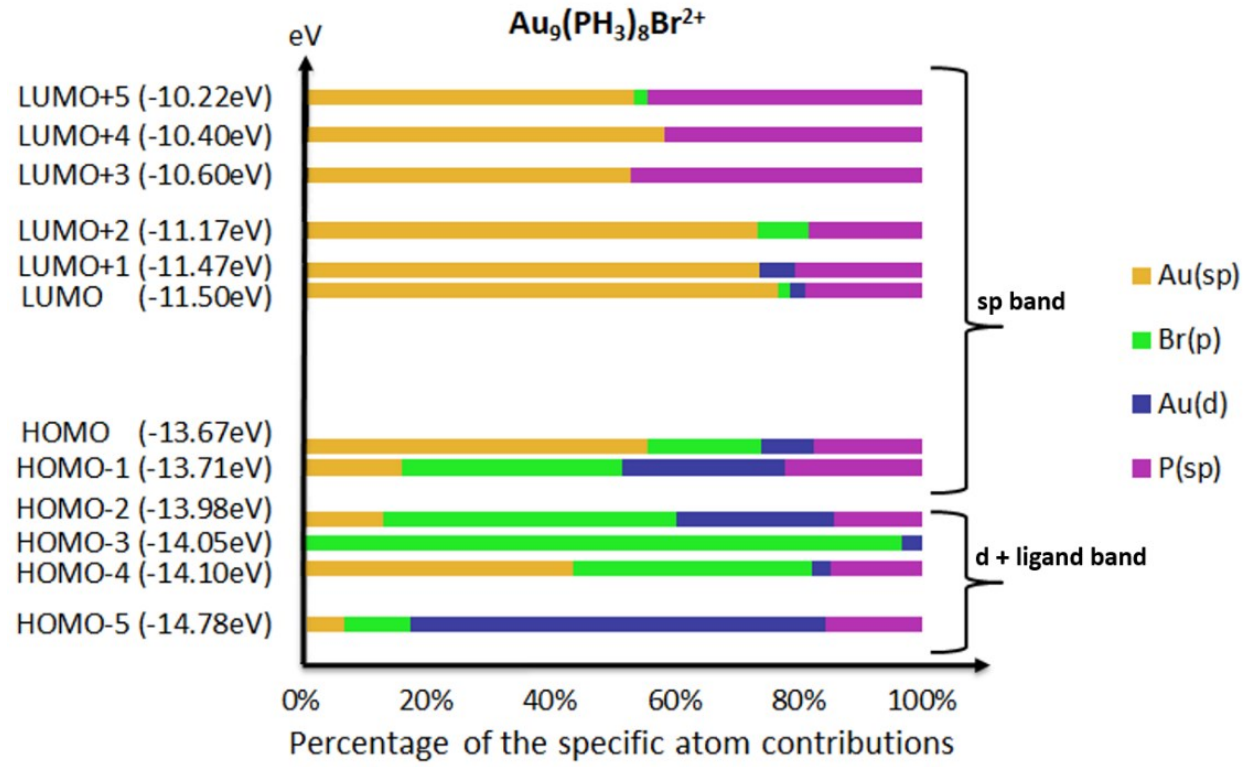
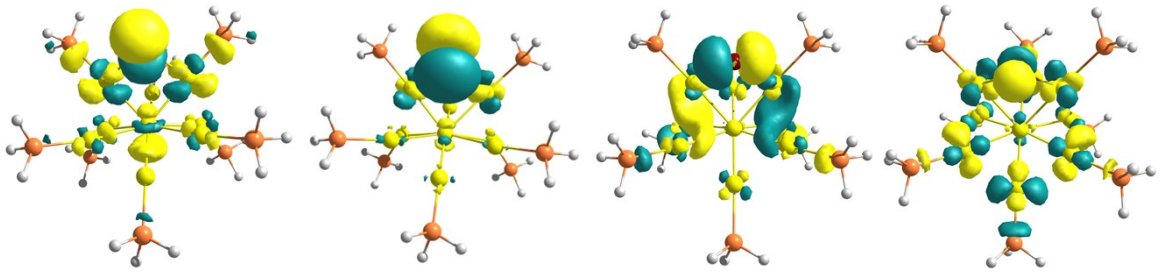


Figure S12. Absorption spectrums of bromide ligated structures.

Table S15. Excited states of $Au_9(PH_3)_8Br^{2+}$ (D_{4d} symmetry (**d4d 2)**). All excited states between 2.0 and 3.9 eV with oscillator strengths larger than 0.01 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
2.34	0.0339	84.39	62.73	HOMO	LUMO +1
			17.63	HOMO -1	LUMO
			11.06	HOMO -2	LUMO +1
2.69	0.0357	45.68	42.88	HOMO	LUMO +2
			20.36	HOMO -3	LUMO
			15.00	HOMO -4	LUMO +1
			12.61	HOMO -2	LUMO +2
2.79	0.1116	15.63	46.94	HOMO -4	LUMO
			25.97	HOMO -2	LUMO +1
3.08	0.0618	3.65	91.20	HOMO -4	LUMO +2
3.41	0.0541	36.97	51.81	HOMO -5	LUMO
			22.73	HOMO	LUMO +4
			12.13	HOMO	LUMO +5
3.43	0.0655	14.17	71.71	HOMO -5	LUMO +1
			8.89	HOMO -2	LUMO +3
3.54	0.0044	5.32	90.80	HOMO -1	LUMO +5
3.58	0.0362	48.84	47.42	HOMO	LUMO +5
			25.76	HOMO -5	LUMO +2
			14.99	HOMO -2	LUMO +4
3.78	0.159	22.96	37.43	HOMO -5	LUMO +2
			19.04	HOMO	LUMO +5
			9.21	HOMO -8	LUMO +1





HOMO-2 **HOMO-3** **HOMO-4** **HOMO-5**

Figure S13. Kohn–Sham orbital energy level diagram for the $Au_9(PH_3)_8Br^{2+}$ structure. Each KS orbital is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Au (sp) in gold, Br(s) in green, Au (d) in blue, and P (sp) in purple. The y axis shows the M.O. and energy level. X axis shows the percentage of the specific atom contributions. HOMO-2, HOMO-3, HOMO-4 and HOMO-5 orbital depictions were given. HOMO and HOMO-1 were given in the MS.

$Au_9(PPh_3)_8Br^{2+}$

Table S16. Excited states of $Au_9(PPh_3)_8Br^{2+}$. All excited states with oscillator strengths larger than 0.02 are listed.

Energy (eV)	f	Superatomic character (%)	Weight (%)	Transition	
1.94	0.0517	99.49	0.9531	HOMO	LUMO
2.21	0.0477	82.85	0.6099	HOMO-1	LUMO
			0.1327	HOMO-2	LUMO
2.39	0.0267	19.26	0.5531	HOMO-2	LUMO+1
			0.228	HOMO-3	LUMO
2.57	0.0336	17.94	0.5844	HOMO-4	LUMO
			0.1723	HOMO-3	LUMO+2
2.63	0.0237	97.85	0.7793	HOMO	LUMO+15
			0.1051	HOMO	LUMO+16
2.69	0.0408	96.99	0.7544	HOMO	LUMO+17
2.69	0.0231	44.74	0.3458	HOMO-4	LUMO+1
			0.3167	HOMO-1	LUMO+8
2.82	0.0265	80.29	0.5782	HOMO-1	LUMO+12
2.95	0.0454	35.24	0.2388	HOMO-4	LUMO+5
			0.215	HOMO-5	LUMO
			0.1589	HOMO-1	LUMO+18
			0.1231	HOMO-2	LUMO+13
2.96	0.0379	17.34	0.6301	HOMO-4	LUMO+5
			0.1236	HOMO-5	LUMO
3.00	0.0347	57.7	0.4731	HOMO-1	LUMO+21
			0.2345	HOMO-2	LUMO+15
3.01	0.0204	16.79	0.6738	HOMO-3	LUMO+10

Cartesian Coordinates of the Most Stable Structures

$Au_9(PH_3)_8^{3+}$ (D_{2h} symmetry)

Au	0.000000000	0.000000000	0.000000000
Au	-2.390600000	0.000000000	1.389600000
Au	2.390600000	0.000000000	1.389600000
Au	2.390600000	0.000000000	-1.389600000
Au	-2.390600000	0.000000000	-1.389600000
Au	-1.420800000	2.381800000	0.000000000
Au	-1.420800000	-2.381800000	0.000000000
Au	1.420800000	-2.381800000	0.000000000
Au	1.420800000	2.381800000	0.000000000
P	-3.661800000	0.000000000	3.435500000
P	3.661800000	0.000000000	3.435500000
P	3.661800000	0.000000000	-3.435500000
P	-3.661800000	0.000000000	-3.435500000
P	-2.667500000	4.505800000	0.000000000
P	-2.667500000	-4.505800000	0.000000000
P	2.667500000	-4.505800000	0.000000000
P	2.667500000	4.505800000	0.000000000
H	-1.918100000	-5.712600000	0.000000000
H	-3.542800000	-4.754600000	1.091000000
H	-3.542800000	-4.754600000	-1.091000000
H	3.542800000	4.754600000	1.091000000
H	3.542800000	4.754600000	-1.091000000
H	1.918100000	5.712600000	0.000000000
H	3.542800000	-4.754600000	1.091000000
H	1.918100000	-5.712600000	0.000000000
H	3.542800000	-4.754600000	-1.091000000
H	-3.542800000	4.754600000	-1.091000000
H	-3.542800000	4.754600000	1.091000000
H	-1.918100000	5.712600000	0.000000000
H	5.070700000	0.000000000	3.275400000
H	3.477600000	1.097600000	4.314000000
H	3.477600000	-1.097600000	4.314000000
H	-3.477600000	1.097600000	-4.314000000
H	-3.477600000	-1.097600000	-4.314000000
H	-5.070700000	0.000000000	-3.275400000
H	3.477600000	1.097600000	-4.314000000
H	5.070700000	0.000000000	-3.275400000
H	3.477600000	-1.097600000	-4.314000000
H	-3.477600000	-1.097600000	4.314000000
H	-3.477600000	1.097600000	4.314000000
H	-5.070700000	0.000000000	3.275400000

$Au_9(PH_3)_8^{3+}$ (D_{4d} symmetry)

Au	0.000000000	0.000000000	0.000000000
Au	2.330600000	0.965400000	-1.035400000
Au	-2.330600000	-0.965400000	-1.035400000
Au	-0.965400000	2.330600000	-1.035400000
Au	0.965400000	-2.330600000	-1.035400000
Au	-2.330600000	0.965400000	1.035400000
Au	2.330600000	-0.965400000	1.035400000
Au	0.965400000	2.330600000	1.035400000
Au	-0.965400000	-2.330600000	1.035400000
P	3.975800000	1.646800000	-2.637100000
P	-3.975800000	-1.646800000	-2.637100000
P	-1.646800000	3.975800000	-2.637100000
P	1.646800000	-3.975800000	-2.637100000
P	-3.975800000	1.646800000	2.637100000
P	3.975800000	-1.646800000	2.637100000
P	1.646800000	3.975800000	2.637100000
P	-1.646800000	-3.975800000	2.637100000
H	-4.384000000	-2.985800000	-2.594900000
H	-5.211200000	-0.988600000	-2.594900000
H	-3.645500000	-1.510000000	-3.991100000
H	3.645500000	1.510000000	-3.991100000
H	4.384000000	2.985800000	-2.594900000
H	5.211200000	0.988600000	-2.594900000
H	2.985800000	-4.384000000	-2.594900000
H	0.988600000	-5.211200000	-2.594900000
H	1.510000000	-3.645500000	-3.991100000
H	-1.510000000	3.645500000	-3.991100000
H	-2.985800000	4.384000000	-2.594900000
H	-0.988600000	5.211200000	-2.594900000
H	4.384000000	-2.985800000	2.594900000
H	5.211200000	-0.988600000	2.594900000
H	3.645500000	-1.510000000	3.991100000
H	-3.645500000	1.510000000	3.991100000
H	-4.384000000	2.985800000	2.594900000
H	-5.211200000	0.988600000	2.594900000
H	-2.985800000	-4.384000000	2.594900000
H	-0.988600000	-5.211200000	2.594900000
H	-1.510000000	-3.645500000	3.991100000
H	1.510000000	3.645500000	3.991100000
H	2.985800000	4.384000000	2.594900000
H	0.988600000	5.211200000	2.594900000

$Au_9(PH_3)_8H^{2+}$ (D_{2h} symmetry (d2h 2))

Au	-0.020900000	0.052600000	-1.036800000
Au	-1.343400000	0.716900000	1.226400000
Au	1.336100000	-0.636200000	1.195400000
Au	2.633300000	0.349700000	-1.269600000
Au	-2.677500000	-0.266300000	-1.206500000
Au	-1.338700000	2.373300000	-1.271700000
Au	-1.088200000	-2.104600000	0.390100000
Au	1.273800000	-2.274600000	-1.317000000
Au	1.065200000	2.186300000	0.392300000
P	-2.642300000	1.226900000	3.119100000
P	2.606800000	-1.213600000	3.095300000
P	4.832600000	0.702300000	-1.964300000
P	-4.852000000	-0.735800000	-1.925900000
P	-2.316800000	4.345300000	-2.070500000
P	-2.015400000	-4.104100000	1.309500000
P	2.241500000	-4.236300000	-2.159600000
P	2.030600000	4.203500000	1.211400000
H	-1.131000000	-5.158700000	1.610200000
H	-2.727200000	-4.054000000	2.524400000
H	-2.950100000	-4.812800000	0.529500000
H	2.678800000	4.218300000	2.462100000
H	3.035300000	4.804100000	0.427700000
H	1.186200000	5.318600000	1.380600000
H	3.433600000	-4.709300000	-1.578100000
H	1.481000000	-5.420500000	-2.144600000
H	2.625000000	-4.214000000	-3.513800000
H	-2.745500000	4.309300000	-3.410700000
H	-3.480400000	4.848500000	-1.458000000
H	-1.536200000	5.515900000	-2.102700000
H	3.998000000	-1.005700000	3.027600000
H	2.337300000	-0.556400000	4.311400000
H	2.596700000	-2.547100000	3.547700000
H	-5.218000000	-0.265300000	-3.201100000
H	-5.193900000	-2.093800000	-2.070300000
H	-5.957500000	-0.288700000	-1.177400000
H	5.450300000	1.920100000	-1.621500000
H	5.835400000	-0.196000000	-1.552700000
H	5.063300000	0.702900000	-3.352800000
H	-2.434000000	0.499000000	4.306100000
H	-2.616500000	2.534500000	3.642200000
H	-4.034500000	1.061500000	2.988600000
H	-0.040800000	0.049600000	-2.659100000

$Au_9(PH_3)_8F^{2+}$ (D_{4d} symmetry (d4d 2))

Au	0.196700000	-0.356700000	-0.220600000
Au	1.936700000	1.378600000	-1.565400000
Au	-2.425900000	-0.257100000	-1.389500000
Au	-0.794600000	2.137100000	-0.985100000
Au	1.197800000	-2.847700000	0.171600000
Au	-1.977500000	0.630200000	1.122200000
Au	2.835300000	-0.533400000	0.366400000
Au	1.203300000	1.828900000	1.045800000
Au	-1.562500000	-2.229600000	0.585900000
P	2.892500000	1.847400000	-3.661100000
P	-3.461600000	-0.709400000	-3.450100000
P	-1.516000000	4.269200000	-1.729300000
P	2.275100000	-4.969000000	0.322300000
P	-3.837600000	1.218700000	2.518600000
P	5.087700000	-0.515400000	1.027900000
P	1.450500000	2.920800000	3.102700000
P	-3.086400000	-3.687800000	1.625300000
H	-4.165500000	-1.920200000	-3.580000000
H	-4.445400000	0.193400000	-3.892800000
H	-2.651600000	-0.771800000	-4.598600000
H	2.036500000	1.878800000	-4.776900000
H	3.551000000	3.080200000	-3.820300000
H	3.885800000	0.973800000	-4.139800000
H	3.384900000	-5.052500000	1.183400000
H	1.541200000	-6.080200000	0.779200000
H	2.837100000	-5.517500000	-0.845700000
H	-1.534600000	4.544500000	-3.109300000
H	-2.813400000	4.690500000	-1.384200000
H	-0.773500000	5.373600000	-1.273100000
H	5.863300000	-1.678400000	0.863300000
H	5.937300000	0.425700000	0.418200000
H	5.348900000	-0.239700000	2.382100000
H	-3.589600000	0.989100000	3.883500000
H	-4.222400000	2.571400000	2.570700000
H	-5.108300000	0.624600000	2.394800000
H	-4.413900000	-3.730200000	1.161200000
H	-2.795700000	-5.064300000	1.658800000
H	-3.308200000	-3.451100000	2.993700000
H	1.557000000	2.040200000	4.187700000
H	2.540700000	3.780000000	3.350000000
H	0.381000000	3.734800000	3.498400000
F	-0.615000000	1.281000000	2.774900000

$Au_9(PH_3)_8Cl^{2+}$ (D_{4d} symmetry (d4d 2))

Au	0.135000000	-0.395500000	0.017100000
Au	1.862900000	1.431400000	-1.326000000
Au	-2.433500000	-0.281700000	-1.274700000
Au	-0.893100000	2.089500000	-0.641400000
Au	1.180700000	-2.891500000	0.214500000
Au	-2.127900000	0.392100000	1.356200000
Au	2.791000000	-0.577400000	0.514700000
Au	1.211100000	1.787100000	1.310800000
Au	-1.609900000	-2.401500000	0.497500000
P	2.900400000	1.801800000	-3.451400000
P	-3.481500000	-0.632200000	-3.406900000
P	-1.776100000	4.225400000	-1.336600000
P	2.255300000	-5.067600000	0.213400000
P	-4.056800000	1.004800000	2.686100000
P	5.060600000	-0.610900000	1.291400000
P	2.169400000	3.615400000	2.576500000
P	-3.203600000	-4.029000000	1.258700000
H	-4.210800000	-1.813500000	-3.590000000
H	-4.436100000	0.299500000	-3.836600000
H	-2.665400000	-0.675600000	-4.544100000
H	2.104600000	1.787800000	-4.604300000
H	3.573600000	3.014700000	-3.644900000
H	3.904100000	0.908100000	-3.845500000
H	3.081400000	-5.385400000	1.299900000
H	1.462700000	-6.223600000	0.188400000
H	3.128800000	-5.369700000	-0.839900000
H	-1.633500000	4.608000000	-2.676700000
H	-3.145700000	4.474100000	-1.172300000
H	-1.265400000	5.373900000	-0.716200000
H	5.672200000	-1.850000000	1.523400000
H	6.049600000	-0.005600000	0.505200000
H	5.319800000	0.009400000	2.520200000
H	-3.960400000	0.733600000	4.056500000
H	-4.395400000	2.362900000	2.743500000
H	-5.326000000	0.468400000	2.428600000
H	-4.406400000	-4.172600000	0.554300000
H	-2.814100000	-5.372600000	1.331300000
H	-3.708300000	-3.861300000	2.554900000
H	2.763200000	3.275600000	3.799000000
H	3.173100000	4.442400000	2.054200000
H	1.274300000	4.594400000	3.025700000
Cl	-0.326200000	0.852800000	3.272600000

$Au_9(PH_3)_8Br^{2+}$ (D_{4d} symmetry (d4d 2))

Au	0.141500000	-0.286200000	0.073400000
Au	1.941400000	1.428700000	-1.294000000
Au	-2.348200000	-0.338200000	-1.287400000
Au	-0.870800000	2.140800000	-0.754300000
Au	1.173000000	-2.784300000	0.160500000
Au	-2.177200000	0.569300000	1.296500000
Au	2.752100000	-0.474500000	0.736200000
Au	1.182100000	1.964800000	1.279500000
Au	-1.567200000	-2.276200000	0.714300000
P	3.020300000	1.766900000	-3.405400000
P	-3.374300000	-0.906900000	-3.375400000
P	-1.746900000	4.212500000	-1.633600000
P	2.054100000	-5.020900000	-0.101000000
P	-4.232400000	1.195800000	2.414800000
P	4.928600000	-0.695100000	1.718200000
P	2.195000000	3.902300000	2.331500000
P	-3.079600000	-3.897400000	1.627400000
H	-3.202400000	-2.203900000	-3.875800000
H	-4.768900000	-0.801300000	-3.461200000
H	-3.019500000	-0.168100000	-4.512400000
H	2.227900000	1.742900000	-4.560600000
H	3.697300000	2.975500000	-3.618600000
H	4.021900000	0.865800000	-3.787500000
H	3.431100000	-5.229400000	0.061000000
H	1.567600000	-6.045800000	0.721600000
H	1.884100000	-5.630600000	-1.352000000
H	-2.014000000	4.305200000	-3.006300000
H	-2.974400000	4.667700000	-1.132200000
H	-0.994000000	5.384200000	-1.472300000
H	5.563800000	-1.942000000	1.643200000
H	5.975000000	0.122300000	1.267600000
H	5.017300000	-0.462400000	3.096200000
H	-4.569600000	0.449500000	3.551900000
H	-4.274700000	2.481900000	2.968800000
H	-5.471500000	1.185400000	1.758900000
H	-4.338900000	-4.059700000	1.033200000
H	-2.668900000	-5.236500000	1.666700000
H	-3.463600000	-3.725100000	2.963100000
H	2.755400000	3.702500000	3.600400000
H	3.246600000	4.605600000	1.726400000
H	1.344800000	4.976300000	2.626400000
Br	-0.399800000	1.071400000	3.341500000