Supporting information

Synthesis, structural characterization, photophysical properties and theoretical analysis of gold(I) thiolate-phosphine complexes.

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Table S1. Crystal Data for the complex **2**.

	2
empirical formula	$C_{60}H_{50}Au_2P_2S_2$
fw	1290.99
temp (K)	100(2)
λ(Å)	0.71073
cryst syst	Triclinic
space group	P $\bar{1}$
a (Å)	11.6545(3)
b (Å)	14.2494(4)
c (Å)	17.3478(5)
α (deg)	67.1857(14
β (deg)	89.317(2)
γ (deg)	74.500(2)
V (Å^3)	2545.30(12)
Z	2
ρ_{calc} (Mg/m^3)	1.684
μ(Mo Kα) (mm^{-1})	5.941
No. reflns.	45035
Unique reflns.	38484
GOOF (F^2)	1.057
R_{int}	0.1330
R1[a] ($I \geq 2\sigma$)	0.0462
wR2[b] ($I \geq 2\sigma$)	0.1092

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

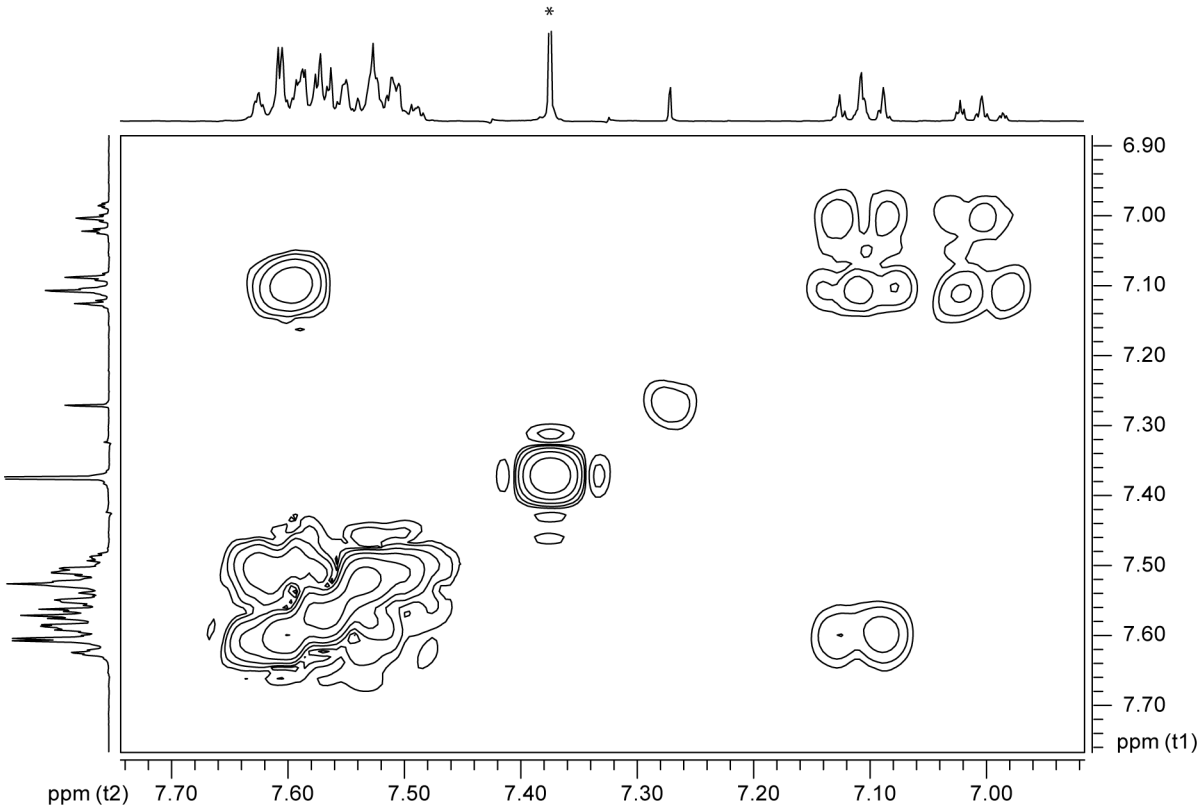

Figure S1. ^{1}H COSY spectrum (400 Mhz) of $[(AuSPh)_2(1,4'\text{-}PPh_2C_6H_4PPh_2)_2]$ **1**, $CDCl_3$, 25^{o}C (* denotes residual benzene).

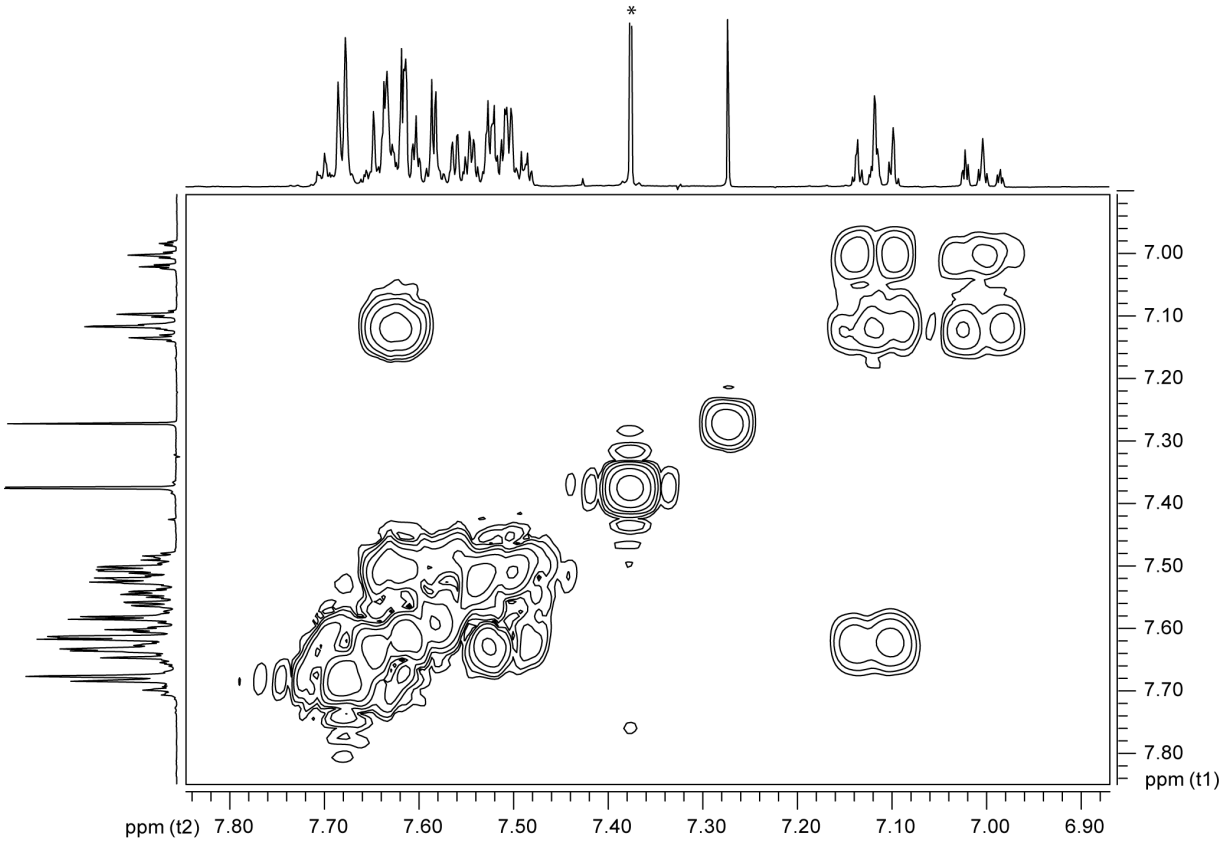

Figure S2. ^{1}H COSY spectrum (400 Mhz) of $[(AuSPh)_2(4,4'\text{-}PPh_2(C_6H_4)_2PPh_2)_2]$ **2**, $CDCl_3$, 25^{o}C (* denotes residual benzene).

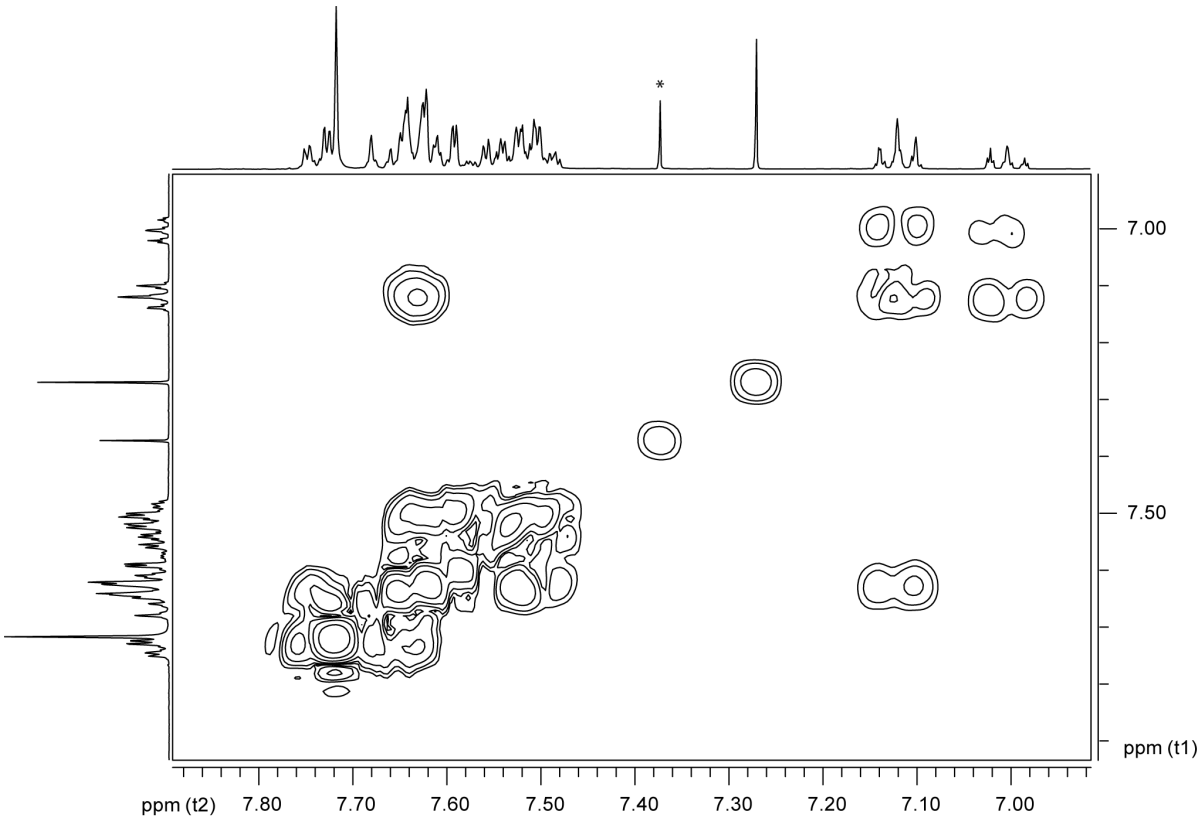

Figure S3. ^{1}H COSY spectrum (400 Mhz) of $[(AuSPh)_2(4,4''\text{-}PPh_2(C_6H_4)_3PPh_2)_2]$ **3**, $CDCl_3$, 25^{o}C (* denotes residual benzene).

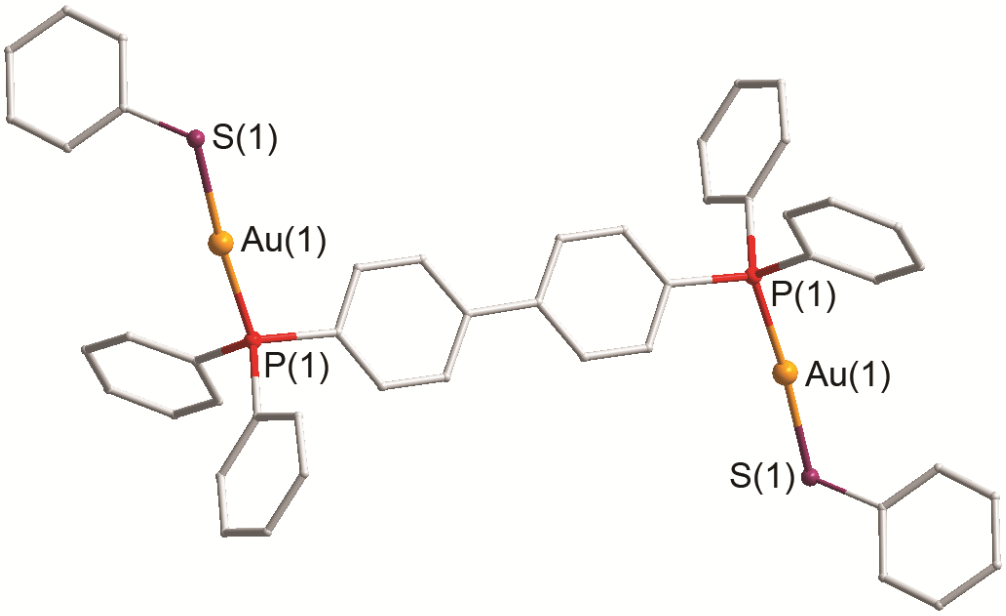

Figure S4. Solid state structure of **2**. One of two independent molecules is shown.

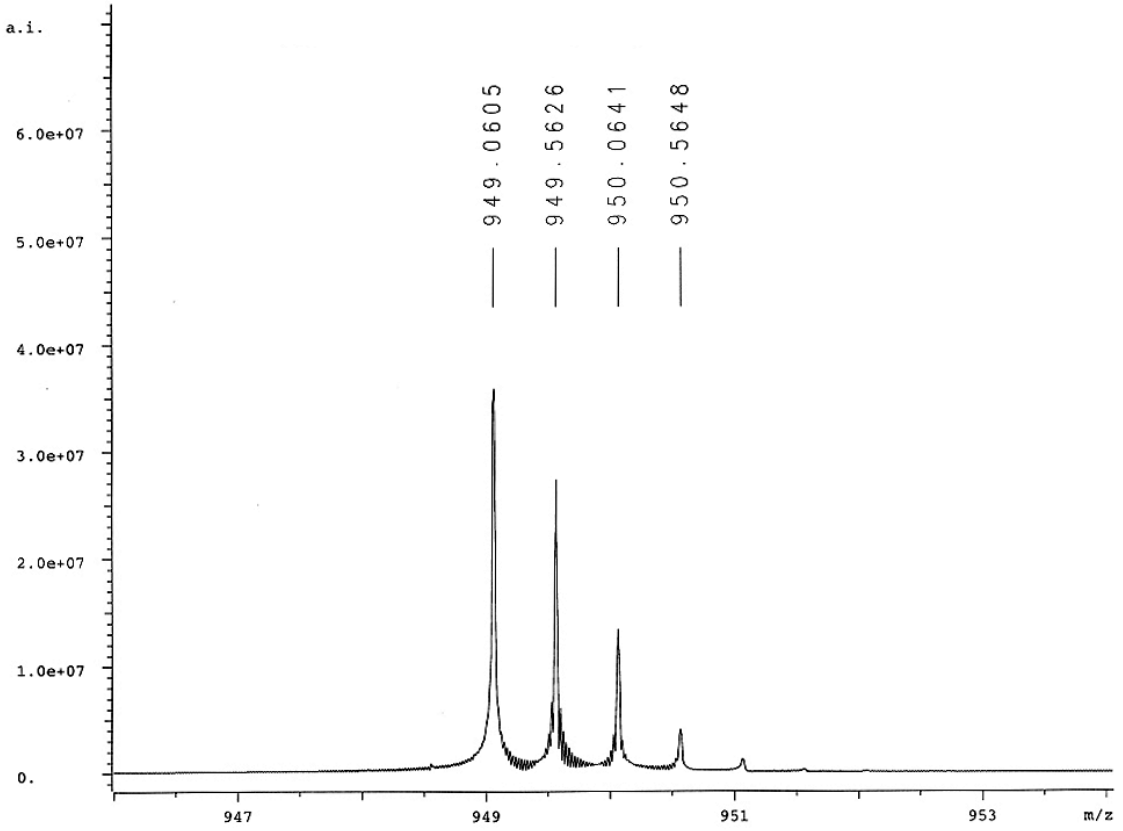

Figure S5. ESI-MS spectrum of the $[(Au_2SPh)_2(1,4\text{-}PPh_2C_6H_4PPh_2)_2]^{2+}$ dication (**4**-$2PF_6$).

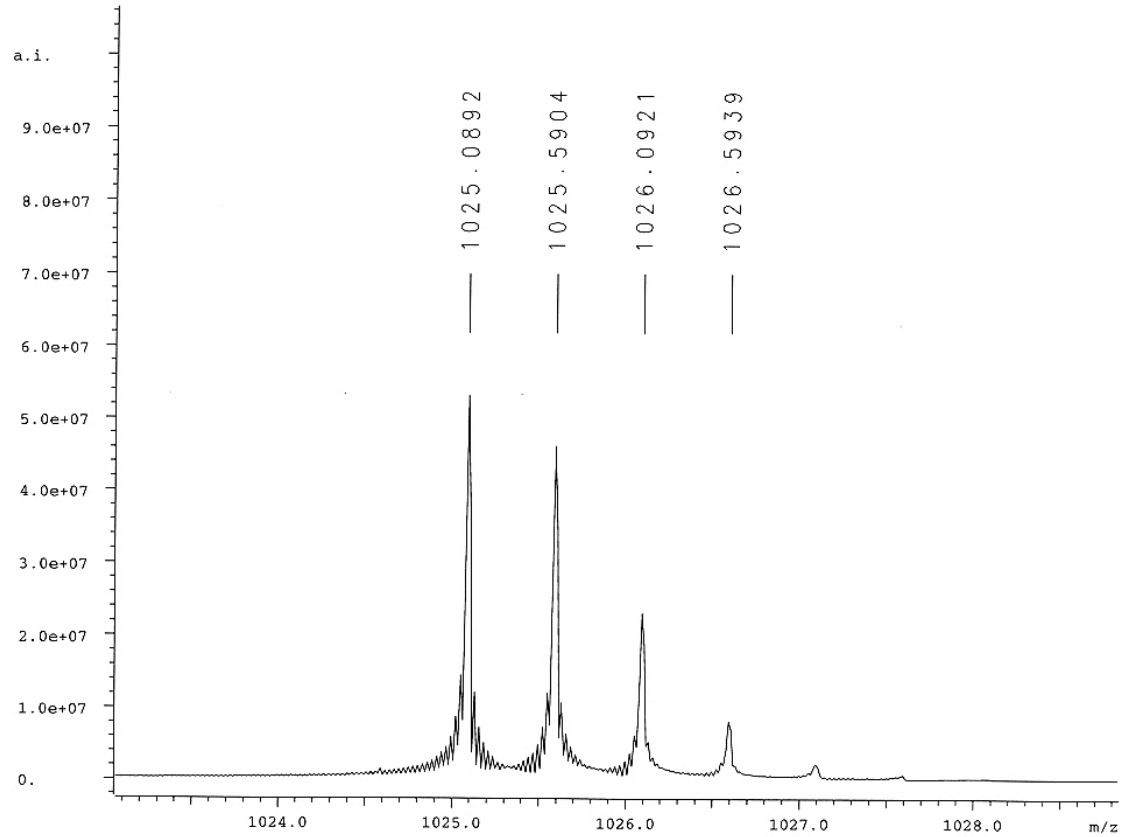

Figure S6. ESI-MS spectrum of the $[(Au_2SPh)_2(4,4'\text{-}PPh_2(C_6H_4)_2PPh_2)_2]^{2+}$ dication (**5**-$2PF_6$).

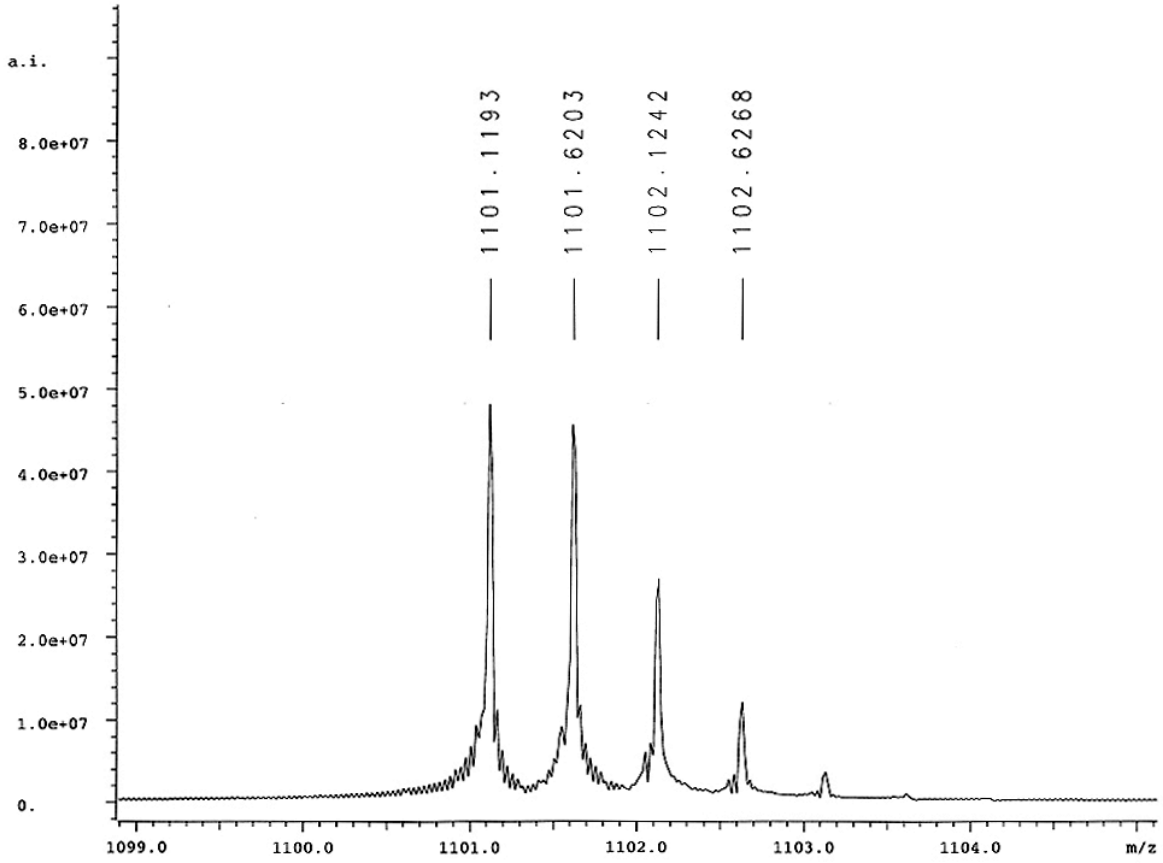

Figure S7. ESI-MS spectrum of the $[(Au_2SPh)_2(4,4''\text{-}PPh_2(C_6H_4)_3PPh_2)_2]^{2+}$ dication (**6**-$2PF_6$).

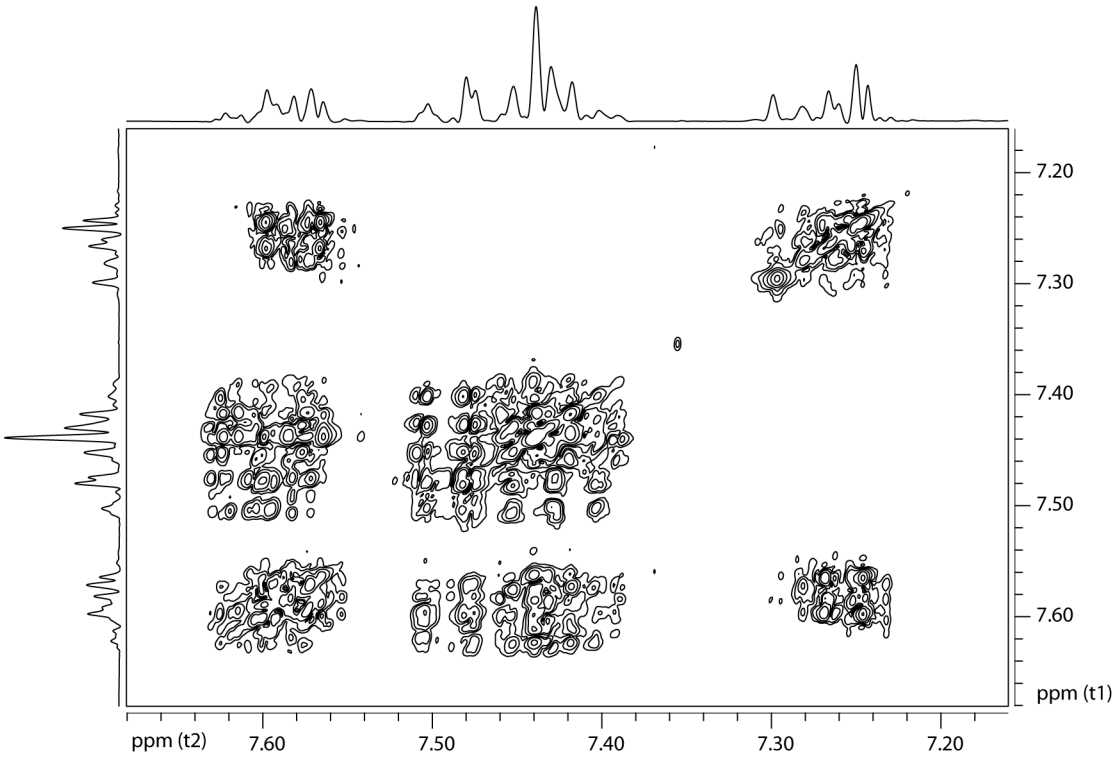

Figure S8. ^{1}H COSY spectrum (300MHz) of $[(Au_2SPh)_2(1,4\text{-}PPh_2C_6H_4PPh_2)_2](PF_6)_2$ **4**, CD_2Cl_2, 25^{o}C.

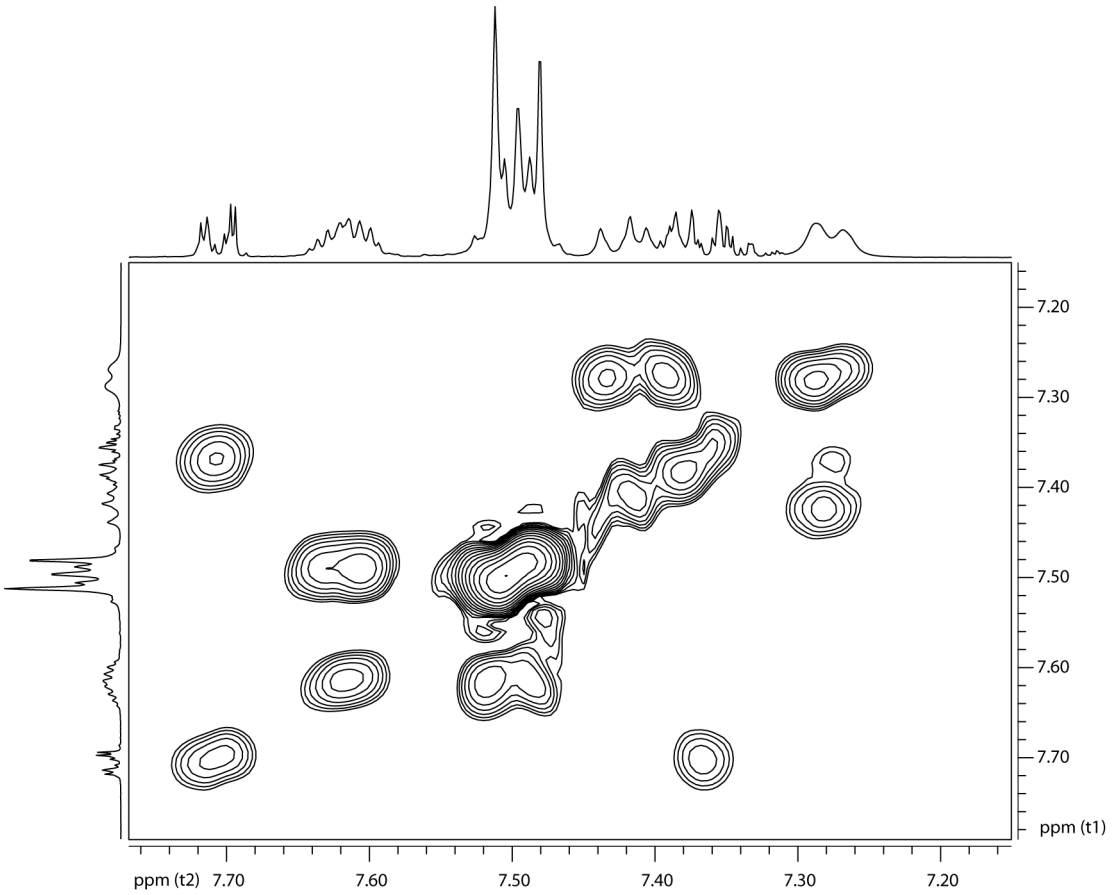

Figure S9. ^{1}H COSY spectrum (400MHz) of $[(Au_2SPh)_2(4,4'\text{-}PPh_2(C_6H_4)_2PPh_2)_2](PF_6)_2$ **5**, CD_2Cl_2, 25^{o}C.

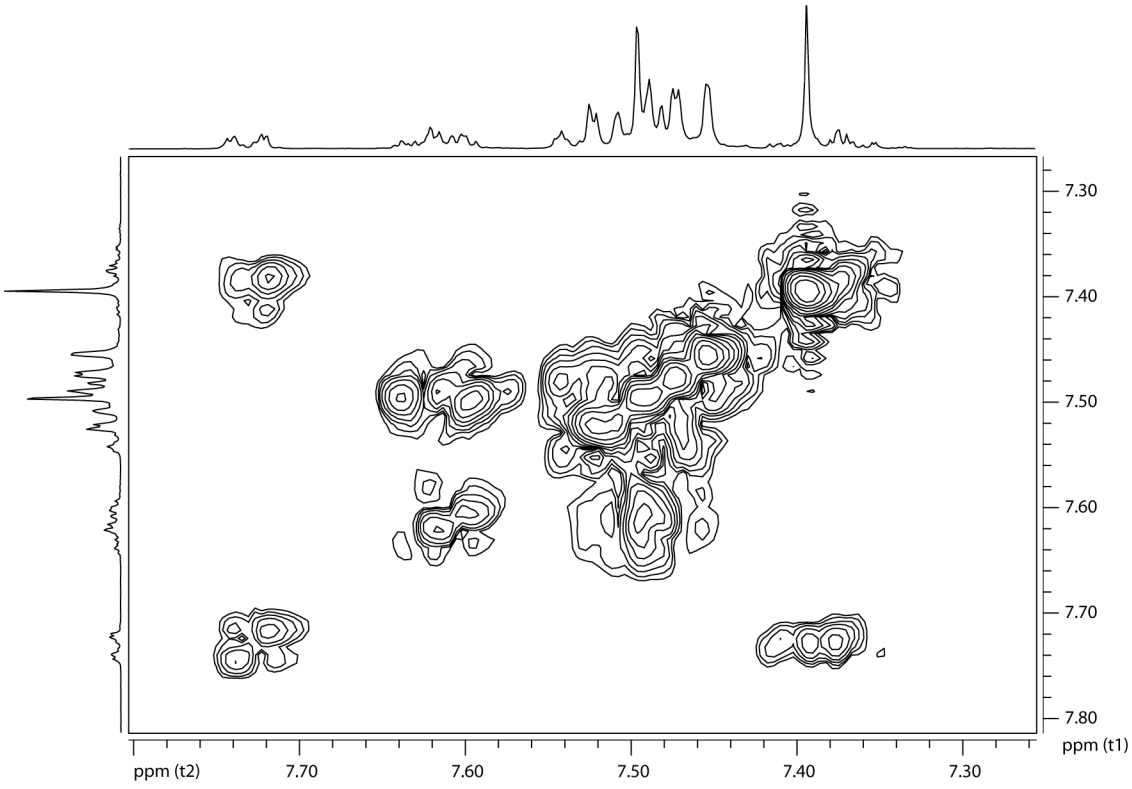

Figure S10. ^{1}H COSY spectrum (400 MHz) of $[(Au_2SPh)_2(4,4''\text{-}PPh_2(C_6H_4)_3PPh_2)_2](PF_6)_2$ **6**, CD_2Cl_2, 25^{o}C.

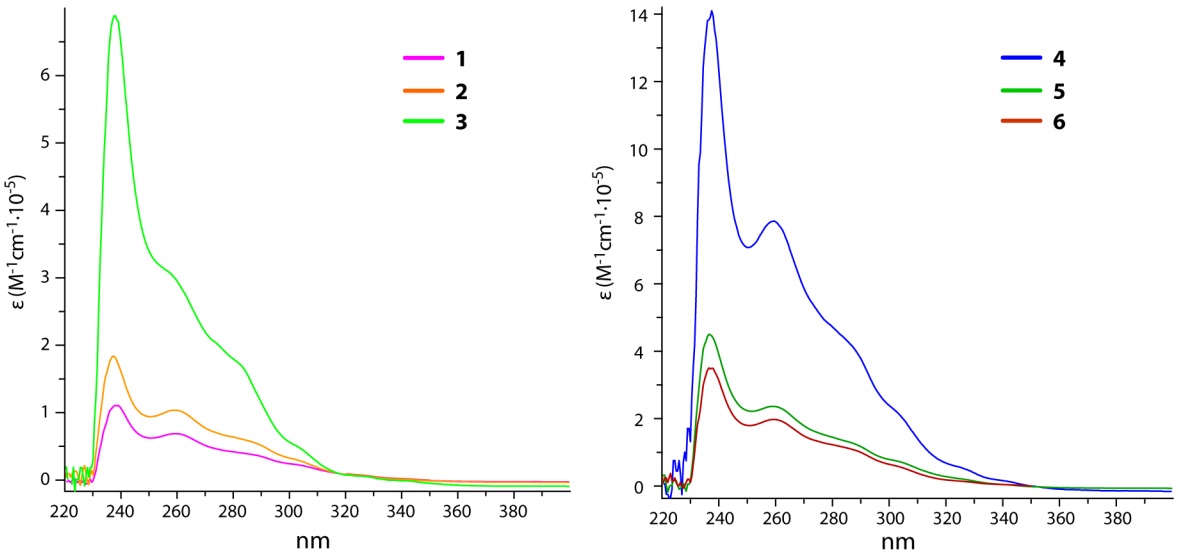

Figure S11. UV-vis absorption spectra of the complexes **1-6**, 298 K, CH_2Cl_2.

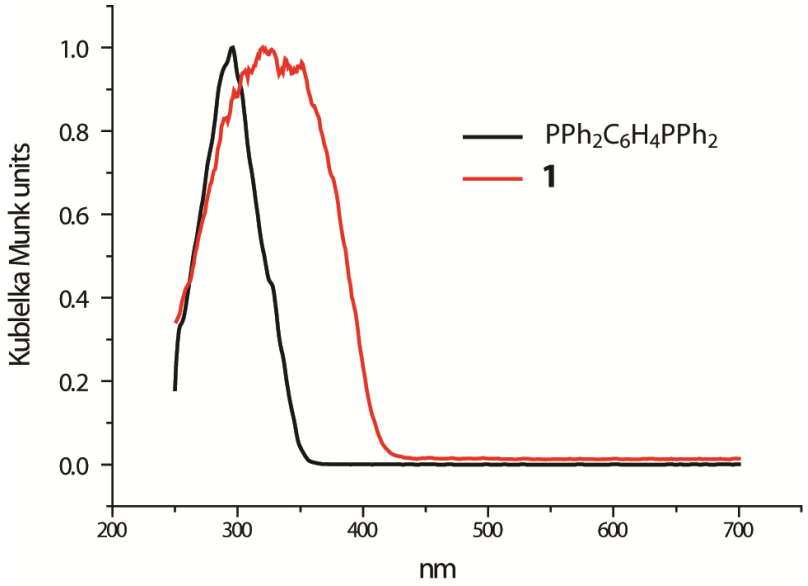

Figure S12. DRUV spectra of the complex **1** and the diphosphpine $Ph_2PC_6H_4PPh_2$.

Geometry of the $[(Au_2SPh)_2(1,4\text{-}PMe_2C_6H_4PMe_2)_2](PF_6)_2$ model for the complex 4 in xyz format

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	0.000000	0.000000	0.000000
2	79	0	0.000000	0.000000	3.012986
3	79	0	7.773884	0.000000	-0.532794
4	79	0	10.513532	-0.182182	-2.077624
5	16	0	-1.787045	0.055188	1.509712
6	16	0	8.490989	-1.332698	-2.316854
7	15	0	1.825062	-0.342964	4.314273
8	15	0	7.181245	1.359435	1.188498
9	15	0	12.409268	1.033931	-1.843423
10	15	0	17.203025	-2.716381	0.239929
11	6	0	-2.552020	1.668420	1.388049

12	6	0	-3.514759	2.013043	2.327906
13	1	0	-3.695243	1.447885	3.072115
14	6	0	-4.219031	3.218969	2.150976
15	1	0	-4.868027	3.479880	2.794608
16	6	0	-3.984194	4.013736	1.075819
17	1	0	-4.480161	4.816287	0.964886
18	6	0	-3.036674	3.667636	0.146982
19	1	0	-2.877982	4.227446	-0.603356
20	6	0	-2.311485	2.497572	0.306384
21	1	0	-1.645670	2.263210	-0.329936
22	6	0	1.847897	0.627992	5.845619
23	6	0	1.957359	-2.096781	4.781883
24	6	0	3.356016	0.077750	3.416839
25	6	0	3.357819	1.252283	2.660939
26	1	0	2.572941	1.784389	2.616615
27	6	0	4.496537	1.647546	1.975014
28	1	0	4.493735	2.450264	1.463526
29	6	0	5.641123	0.868431	2.037520
30	6	0	5.631706	-0.320175	2.766946
31	1	0	6.408958	-0.867092	2.786008
32	6	0	4.496274	-0.707203	3.463446
33	1	0	4.501274	-1.510230	3.972097
34	6	0	8.438820	1.455926	2.498568
35	6	0	6.991584	3.062174	0.595200
36	6	0	12.969753	1.741595	-3.407333
37	6	0	12.176500	2.426015	-0.714248
38	6	0	13.806642	0.057480	-1.224988
39	6	0	14.911330	-0.203842	-2.034864
40	1	0	14.971169	0.190884	-2.895536
41	6	0	15.924093	-1.041604	-1.585730
42	1	0	16.669940	-1.219003	-2.146483
43	6	0	15.858515	-1.620265	-0.326922
44	6	0	14.754702	-1.367084	0.484891
45	1	0	14.698788	-1.763180	1.345293
46	6	0	13.731422	-0.530937	0.037124
47	1	0	12.980513	-0.363456	0.594159
48	6	0	16.399545	-4.301005	0.617507
49	6	0	17.792247	-2.069756	1.825976
50	6	0	7.758575	-0.915541	-3.866108
51	6	0	6.642580	-0.095328	-3.975039
52	1	0	6.280832	0.322144	-3.200133
53	6	0	6.052485	0.114145	-5.215032
54	1	0	5.288886	0.676195	-5.289372
55	6	0	6.578380	-0.495907	-6.347436
56	1	0	6.174646	-0.352046	-7.195088
57	6	0	7.694367	-1.316080	-6.238597
58	1	0	8.054201	-1.732146	-7.013275
59	6	0	8.284470	-1.525593	-4.998512
60	1	0	9.048135	-2.086174	-4.924300
61	79	0	18.899693	-2.883277	-1.252213
62	79	0	18.899686	-2.883237	-4.265290
63	79	0	11.125802	-2.883237	-0.719510
64	79	0	8.386153	-2.701055	0.825320
65	16	0	20.686738	-2.938465	-2.761925
66	16	0	10.408704	-1.550579	1.064640
67	15	0	17.074623	-2.540273	-5.566578
68	15	0	11.718448	-4.242713	-2.440711
69	15	0	6.490416	-3.917300	0.591170
70	15	0	1.696661	-0.166857	-1.492233
71	6	0	21.451713	-4.551698	-2.640262
72	6	0	22.414445	-4.896280	-3.580210
73	1	0	22.594928	-4.331123	-4.324420
74	6	0	23.118625	-6.102241	-3.403179
75	1	0	23.767713	-6.363118	-4.046912

76	6	0	22.883887	-6.897013	-2.328032
77	1	0	23.379837	-7.699616	-2.217230
78	6	0	21.936368	-6.550914	-1.399195
79	1	0	21.777575	-7.110718	-0.648846
80	6	0	21.211179	-5.380849	-1.558597
81	1	0	20.545363	-5.146487	-0.922277
82	6	0	17.051797	-3.511270	-7.097832
83	6	0	16.942334	-0.786496	-6.034096
84	6	0	15.543677	-2.961027	-4.669052
85	6	0	15.541874	-4.135561	-3.913153
86	1	0	16.326752	-4.667666	-3.868828
87	6	0	14.403156	-4.530824	-3.227228
88	1	0	14.405958	-5.333542	-2.715739
89	6	0	13.258570	-3.751708	-3.289733
90	6	0	13.267888	-2.563097	-4.019149
91	1	0	12.490628	-2.016140	-4.038301
92	6	0	14.403313	-2.176029	-4.715740
93	1	0	14.398320	-1.373042	-5.224300
94	6	0	10.460873	-4.339204	-3.750781
95	6	0	11.908109	-5.945452	-1.847413
96	6	0	5.929932	-4.624832	2.155029
97	6	0	6.723094	-5.309287	-0.537955
98	6	0	5.093051	-2.940757	-0.027225
99	6	0	3.988364	-2.679436	0.782651
100	1	0	3.928524	-3.074162	1.643323
101	6	0	2.975600	-1.841674	0.333517
102	1	0	2.229753	-1.664274	0.894270
103	6	0	3.041178	-1.263012	-0.925291
104	6	0	4.144983	-1.516154	-1.737196
105	1	0	4.200905	-1.120098	-2.597506
106	6	0	5.168263	-2.352301	-1.289429
107	1	0	5.919171	-2.519912	-1.846411
108	6	0	2.500148	1.417728	-1.869721
109	6	0	1.107446	-0.813522	-3.078189
110	6	0	11.141018	-1.967731	2.613906
111	6	0	12.257105	-2.787909	2.722734
112	1	0	12.618861	-3.205421	1.947920
113	6	0	12.847208	-2.997422	3.962819
114	1	0	13.610807	-3.559473	4.037159
115	6	0	12.321313	-2.387370	5.095223
116	1	0	12.725047	-2.531231	5.942875
117	6	0	11.205318	-1.567158	4.986293
118	1	0	10.845492	-1.151131	5.761062
119	6	0	10.615223	-1.357685	3.746299
120	1	0	9.851549	-0.797195	3.672047
121	1	0	1.655977	-2.217792	5.801405
122	1	0	1.322997	-2.683097	4.150441
123	1	0	2.970886	-2.420602	4.668732
124	1	0	2.820677	0.573630	6.287934
125	1	0	1.613105	1.648244	5.624577
126	1	0	1.123381	0.235028	6.527935
127	1	0	0.570706	-1.724596	-2.914625
128	1	0	1.943222	-1.002088	-3.719142
129	1	0	0.460329	-0.095901	-3.537710
130	1	0	1.933397	2.216555	-1.438943
131	1	0	2.550946	1.548083	-2.930535
132	1	0	3.489439	1.422033	-1.462063
133	1	0	16.505351	-4.514949	1.660548
134	1	0	15.360445	-4.242148	0.369101
135	1	0	16.859519	-5.079404	0.045301
136	1	0	17.013953	-1.501214	2.290646
137	1	0	18.642908	-1.441932	1.661315
138	1	0	18.067952	-2.884139	2.462895
139	1	0	16.834516	-4.533608	-6.868673

140	1	0	18.007626	-3.447983	-7.574576
141	1	0	16.299778	-3.125184	-7.753809
142	1	0	15.912178	-0.529495	-6.166868
143	1	0	17.472153	-0.620251	-6.948730
144	1	0	17.364890	-0.178584	-5.261575
145	1	0	6.823815	-6.213011	0.025994
146	1	0	5.876526	-5.386828	-1.187732
147	1	0	7.606687	-5.152094	-1.120581
148	1	0	6.546201	-4.263028	2.951402
149	1	0	4.914113	-4.339055	2.332067
150	1	0	5.997350	-5.691685	2.108331
151	1	0	8.010160	1.900390	3.372412
152	1	0	9.260256	2.052844	2.161179
153	1	0	8.785979	0.471319	2.732937
154	1	0	7.929227	3.415665	0.220007
155	1	0	6.261822	3.088159	-0.186895
156	1	0	6.671774	3.687575	1.402353
157	1	0	12.070804	2.060311	0.285747
158	1	0	11.295623	2.966564	-0.991307
159	1	0	13.025282	3.075245	-0.768742
160	1	0	13.866091	1.248561	-3.721015
161	1	0	12.211387	1.609805	-4.150578
162	1	0	13.163897	2.785744	-3.277102
163	1	0	9.525246	-4.637330	-3.325785
164	1	0	10.764244	-5.056771	-4.484241
165	1	0	10.353194	-3.380283	-4.213141
166	1	0	11.994805	-5.943975	-0.780932
167	1	0	12.788530	-6.376582	-2.276231
168	1	0	11.052921	-6.520674	-2.134941