Supplementary Information

Chemical Au-Au bonding of dinuclear Gold(I) complexes induced by UV irradiation. A computational study with experimental evidence.

Authors: Camille Latouche[§&], Yan-Ru Lin[$], Yeny Tobon[#*], Eric Furet[§], Jean-Yves Saillard[§*], Chen-Wei Liu[$*], Abdou Boucekkine[§*]

[§]*Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France.*

[&]*Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*

[#]*Laboratoire de Spectrochimie Infrarouge et Raman, UMR 8516 CNRS-Université de Lille 1, Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France*

[$]*Department of Chemistry, National Dong Hwa University, Hualien, Taiwan 97401, Republic of China.*

Computed optimized geometries

Complex **1**, T1 (triplet excited state)

PBE1PBE/lanl2dzp/ (C_i)

E = -1560.735701 au

Au	0.16006	-1.33631	-0.13445
Se	2.15336	2.22647	-0.24674
Se	2.60684	-1.55139	-0.6399
P	3.29922	0.37064	0.28677
C	3.47113	0.19807	2.12468
H	4.07847	-0.70238	2.29462
H	4.05442	1.06817	2.46197
C	2.15185	0.10194	2.90183
H	1.55933	1.00832	2.72212
H	1.56379	-0.744	2.52129
C	2.41944	-0.06694	4.3794
C	2.57045	1.05211	5.21227
H	2.45326	2.05335	4.79187
C	2.55523	-1.34516	4.94191
H	2.42663	-2.22588	4.30892
C	2.83859	-1.50309	6.30246
H	2.93393	-2.50419	6.72413
C	2.85415	0.89993	6.57343
H	2.9617	1.78068	7.20732
C	2.99133	-0.37979	7.12318
H	3.20817	-0.50095	8.1848
C	5.0125	0.67256	-0.34659
H	4.90657	0.80302	-1.43193
H	5.33755	1.63922	0.0641
C	6.03696	-0.43074	-0.02966
H	6.15927	-0.52496	1.05756
H	5.65785	-1.39315	-0.39894
C	7.37215	-0.11984	-0.66737
C	7.612	-0.45096	-2.00997
H	6.83859	-0.96696	-2.58276
C	8.38146	0.53401	0.05404
H	8.2141	0.79208	1.10173
C	9.60294	0.85166	-0.55028
H	10.37867	1.35607	0.02658
C	8.83067	-0.13564	-2.61821
H	9.00209	-0.40479	-3.66081
C	9.83103	0.51867	-1.88966
H	10.78302	0.76292	-2.36145
Au	-0.16006	1.33631	0.13445
Se	-2.15336	-2.22647	0.24674

Se	-2.60684	1.55139	0.6399
P	-3.29922	-0.37064	-0.28677
C	-3.47113	-0.19807	-2.12468
H	-4.07847	0.70238	-2.29462
H	-4.05442	-1.06817	-2.46197
C	-2.15185	-0.10194	-2.90183
H	-1.55933	-1.00832	-2.72212
H	-1.56379	0.744	-2.52129
C	-2.41944	0.06694	-4.3794
C	-2.57045	-1.05211	-5.21227
H	-2.45326	-2.05335	-4.79187
C	-2.55523	1.34516	-4.94191
H	-2.42663	2.22588	-4.30892
C	-2.83859	1.50309	-6.30246
H	-2.93393	2.50419	-6.72413
C	-2.85415	-0.89993	-6.57343
H	-2.9617	-1.78068	-7.20732
C	-2.99133	0.37979	-7.12318
H	-3.20817	0.50095	-8.1848
C	-5.0125	-0.67256	0.34659
H	-4.90657	-0.80302	1.43193
H	-5.33755	-1.63922	-0.0641
C	-6.03696	0.43074	0.02966
H	-6.15927	0.52496	-1.05756
H	-5.65785	1.39315	0.39894
C	-7.37215	0.11984	0.66737
C	-7.612	0.45096	2.00997
H	-6.83859	0.96696	2.58276
C	-8.38146	-0.53401	-0.05404
H	-8.2141	-0.79208	-1.10173
C	-9.60294	-0.85166	0.55028
H	-10.37867	-1.35607	-0.02658
C	-8.83067	0.13564	2.61821
H	-9.00209	0.40479	3.66081
C	-9.83103	-0.51867	1.88966
H	-10.78302	-0.76292	2.36145

Complex **2**, S0 (singlet ground state)

PBE1PBE/lanl2dzp/THF (C_1)

E = -1564.2994271 au

Au	-0.459479	1.596153	0.034877
Au	0.459479	-1.596153	-0.034877
P	1.238947	0.295527	2.699508
S	1.123225	2.113058	1.698339
S	2.091206	-1.271239	1.630564
P	-1.238947	-0.295527	-2.699508
S	-1.123225	-2.113058	-1.698339
S	-2.091206	1.271239	-1.630564
C	0.414872	0.223535	-3.326283
C	1.126162	-0.824972	-4.194147
H	1.008161	0.469072	-2.432140
H	0.249168	1.161886	-3.878215
H	1.271602	-1.745157	-3.600756
H	0.496575	-1.084338	-5.064011
C	-2.348617	-0.614907	-4.135682
C	-2.504293	0.575025	-5.097754
H	-3.319763	-0.910198	-3.710239
H	-1.936250	-1.493866	-4.654569
H	-2.899215	1.445600	-4.544841
H	-1.516786	0.857274	-5.504034
C	-0.414872	-0.223535	3.326283
C	-1.126162	0.824972	4.194147
H	-0.249168	-1.161886	3.878215
H	-1.008161	-0.469072	2.432140
H	-0.496575	1.084338	5.064011
H	-1.271602	1.745157	3.600756
C	2.348617	0.614907	4.135682
C	2.504293	-0.575025	5.097754
H	1.936250	1.493866	4.654569
H	3.319763	0.910198	3.710239
H	1.516786	-0.857274	5.504034
H	2.899215	-1.445600	4.544841
C	-3.438945	0.218284	-6.232270
C	-2.942721	-0.320919	-7.430036
C	-4.826111	0.392144	-6.096298
C	-3.810601	-0.678842	-8.469442
H	-1.863925	-0.456882	-7.553632
C	-5.697944	0.035690	-7.132152
H	-5.226880	0.816869	-5.170587
C	-5.192651	-0.502229	-8.323390
H	-3.406908	-1.092785	-9.397255
H	-6.774563	0.182220	-7.011418
H	-5.871630	-0.778083	-9.134345

C	2.462095	-0.298343	-4.669576
C	2.606557	0.249660	-5.953763
C	3.580214	-0.322174	-3.818882
C	3.838504	0.762521	-6.381075
H	1.746826	0.271608	-6.630359
C	4.812765	0.188783	-4.240757
H	3.484936	-0.749389	-2.815234
C	4.946413	0.734587	-5.525022
H	3.933839	1.181872	-7.386193
H	5.672852	0.158359	-3.566621
H	5.908931	1.132280	-5.856861
C	-2.462095	0.298343	4.669576
C	-3.580214	0.322174	3.818882
C	-2.606557	-0.249660	5.953763
C	-4.812765	-0.188783	4.240757
H	-3.484936	0.749389	2.815234
C	-3.838504	-0.762521	6.381075
H	-1.746826	-0.271608	6.630359
C	-4.946413	-0.734587	5.525022
H	-5.672852	-0.158359	3.566621
H	-3.933839	-1.181872	7.386193
H	-5.908931	-1.132280	5.856861
C	3.438945	-0.218284	6.232270
C	4.826111	-0.392144	6.096298
C	2.942721	0.320919	7.430036
C	5.697944	-0.035690	7.132152
H	5.226880	-0.816869	5.170587
C	3.810601	0.678842	8.469442
H	1.863925	0.456882	7.553632
C	5.192651	0.502229	8.323390
H	6.774563	-0.182220	7.011418
H	3.406908	1.092785	9.397255
H	5.871630	0.778083	9.134345

Complex **2**, T1 (UKS Optimized Triplet Excited State)

PBE1PBE/lanl2dzp/THF (C_1)

E = -1564.2994271 au

Au	-0.0576464107942	-0.4693334997847	1.3777295704203
Au	0.0289980514970	0.3177442260973	-1.1514331867636
P	3.1659794171329	0.3674262767357	0.3429687206399
S	2.2813085404300	0.4355224801630	2.1974637793997
S	2.1438848734072	1.4347023038911	-1.1452159514514
P	-3.2022110348275	-0.4204226497677	-0.1509532410849
S	-2.0682972112349	-0.5421354764776	-1.9110150976159
S	-2.4701335008998	-1.5482615153805	1.4025780620493
C	-3.3616671704012	1.3390874925313	0.3734108275279
C	-3.9436614132971	2.2775022365975	-0.6942516888392
H	-2.3462403471496	1.6475614801909	0.6679223800396
H	-3.9796133890871	1.3314156948954	1.2848232259439
H	-3.3156556399124	2.2249298634443	-1.6017892675389
H	-4.9595574863324	1.9454676368224	-0.9728241626335
C	-4.8628678958197	-1.0537442578693	-0.6310885181862
C	-5.9184183666587	-0.9482765746777	0.4833164283332
H	-4.7109382889111	-2.1000743527242	-0.9355226494830
H	-5.1684591591359	-0.4888458412510	-1.5258210352747
H	-5.5616860628408	-1.4931101793262	1.3753588619830
H	-6.0521650994709	0.1100567683765	0.7700504718564
C	3.3861493561685	-1.3690085900236	-0.2342267345589
C	4.2039765290308	-2.2518831655288	0.7212936069576
H	3.8524400358871	-1.3114195504251	-1.2298691600717
H	2.3668370965574	-1.7643577732729	-0.3666695377493
H	5.2134904375123	-1.8241390860981	0.8551326857478
H	3.7124019277623	-2.2638994251998	1.7103169734980
C	4.8212035966450	1.1631995092779	0.4854056176147
C	5.6585143516246	1.1396836042855	-0.8055566310821
H	5.3410794076333	0.6434706728614	1.3049973538859
H	4.6321553695221	2.1944806839416	0.8192352830492
H	5.8218934520316	0.0949864085385	-1.1242460472796
H	5.1051968814159	1.6520870422932	-1.6125109856568
C	-7.2389065503264	-1.5239098665952	0.0224765855736
C	-8.2048636754543	-0.7095787686118	-0.5905334085864
C	-7.5117265539356	-2.8934343884520	0.1741638544211
C	-9.4156148004047	-1.2491774955295	-1.0428432552553
H	-8.0104861019308	0.3606842738825	-0.7102102653296
C	-8.7205753591994	-3.4376820202399	-0.2759701084869
H	-6.7705404847232	-3.5391640940756	0.6553738265341
C	-9.6774218428550	-2.6166355041447	-0.8875162434617
H	-10.1584584477255	-0.5999494778010	-1.5138513981382
H	-8.9185844705789	-4.5048523179630	-0.1452791368111

H	-10.6230413152163	-3.0392060935590	-1.2368023988188
C	-3.9958741434793	3.7012269603805	-0.1861389780295
C	-5.1928093398989	4.2523539518233	0.2971671913351
C	-2.8352903411880	4.4936523694085	-0.1681602831572
C	-5.2324341979821	5.5640908297405	0.7883297148554
H	-6.1066052747060	3.6506406373524	0.2853063257858
C	-2.8694386115607	5.8040286795206	0.3211859838307
H	-1.8944493501686	4.0802849270234	-0.5462072786901
C	-4.0699190138116	6.3446811201112	0.8028246009350
H	-6.1744094802951	5.9784748886344	1.1573512193099
H	-1.9575548764170	6.4070396068708	0.3235519212021
H	-4.0989963492444	7.3690051542385	1.1831123821599
C	4.3140914865037	-3.6608250942504	0.1825821623990
C	3.2631436361375	-4.5761282001960	0.3625380644965
C	5.4509210268081	-4.0747989472897	-0.5293036253381
C	3.3454831521813	-5.8731599767795	-0.1563262093607
H	2.3718070422917	-4.2699864604987	0.9196955367542
C	5.5386173832110	-5.3724089310491	-1.0504646513612
H	6.2803861059023	-3.3759067098391	-0.6737027441410
C	4.4848464710289	-6.2763107836704	-0.8665114015802
H	2.5199385926329	-6.5732504932393	-0.0029238277594
H	6.4333510283174	-5.6792597652679	-1.5986363004463
H	4.5519392883732	-7.2899200444400	-1.2700053123578
C	6.9916629898679	1.8188197375876	-0.5858982224309
C	7.1198476806440	3.2085871692639	-0.7445321997667
C	8.1191663879916	1.0798882430099	-0.1927431723354
C	8.3450397106194	3.8461055772306	-0.5154954436228
H	6.2512602881414	3.7967938101982	-1.0568972109814
C	9.3471479011768	1.7129907756763	0.0378088137351
H	8.0376287616813	-0.0046338463894	-0.0714909178976
C	9.4640639888513	3.0997929273552	-0.1222656407904
H	8.4283110447273	4.9279976497740	-0.6485991731195
H	10.2160472250830	1.1217088549898	0.3387925691744
H	10.4221957219989	3.5954707109259	0.0538967539311

Complex **2**, T1 (TDDFT Optimized Triplet Excited State)

PBE1PBE/lanl2dzp/THF (C_1)

Excited State 1: Triplet-?Sym 2.2644 eV 547.54 nm f=0.0000 <S**2>=2.000
147 ->151 -0.10549
150 ->151 -0.68392

Total Energy, E(TD-HF/TD-KS) = -1564.25243747

79	0.188860	-0.781414	-0.120028

16	2.408101	2.591598	0.156745
16	2.494351	-0.832231	-0.651164
15	3.307161	0.783002	0.413941
6	3.452662	0.336874	2.202393
1	3.936304	-0.648920	2.247744
1	4.139771	1.073760	2.644681
6	2.126459	0.318996	2.973032
1	1.658183	1.309544	2.905016
1	1.437124	-0.393057	2.499025
6	2.351320	-0.064680	4.417066
6	2.628269	0.912677	5.384831
1	2.643221	1.965627	5.095333
6	2.319286	-1.410370	4.812998
1	2.091830	-2.181970	4.074096
6	2.560874	-1.772939	6.141952
1	2.524993	-2.823255	6.432848
6	2.870829	0.555624	6.715393
1	3.077722	1.329123	7.455667
6	2.839881	-0.790050	7.098413
1	3.024388	-1.070045	8.135837
6	5.033753	0.917720	-0.226330
1	4.929246	1.208216	-1.280165
1	5.497355	1.765879	0.296902
6	5.889112	-0.353688	-0.090124
1	6.016698	-0.605303	0.971229
1	5.365004	-1.195369	-0.562688
6	7.243028	-0.160231	-0.734314
6	7.399644	-0.324657	-2.119434
1	6.542693	-0.626885	-2.725173
6	8.357929	0.218178	0.027422
1	8.255458	0.342823	1.107325

6	9.601551	0.429240	-0.578587
1	10.459142	0.718652	0.029482
6	8.639748	-0.114667	-2.729462
1	8.744656	-0.251440	-3.806109
6	9.746137	0.264658	-1.960149
1	10.714704	0.426182	-2.433819
79	-0.151110	1.834746	0.149111
16	-2.007615	-1.532567	0.342249
16	-2.815140	1.906597	0.234438
15	-3.258460	0.006448	-0.347098
6	-3.419856	-0.112837	-2.184150
1	-4.205159	0.601125	-2.470870
1	-3.780899	-1.127070	-2.408669
6	-2.129303	0.188796	-2.956702
1	-1.358427	-0.539924	-2.672791
1	-1.758297	1.180125	-2.663544
6	-2.369652	0.134931	-4.447416
6	-2.220351	-1.067621	-5.154439
1	-1.890257	-1.963929	-4.624673
6	-2.778540	1.279274	-5.148959
1	-2.886230	2.225816	-4.614880
6	-3.036102	1.224017	-6.522621
1	-3.346704	2.124743	-7.053018
6	-2.476643	-1.128531	-6.528142
1	-2.349356	-2.070358	-7.062779
6	-2.887797	0.018081	-7.217194
1	-3.084088	-0.025966	-8.288750
6	-4.896857	-0.471233	0.356016
1	-4.757862	-0.453108	1.445185
1	-5.082289	-1.516338	0.067782
6	-6.064973	0.439453	-0.056311

1	-6.231811	0.364622	-1.139369
1	-5.797716	1.482211	0.161787
6	-7.328895	0.062113	0.682263
6	-7.578174	0.572101	1.965795
1	-6.867722	1.270088	2.413560
6	-8.257825	-0.825669	0.120152
1	-8.083232	-1.225816	-0.880739
6	-9.409329	-1.197554	0.822885
1	-10.123593	-1.885204	0.369049
6	-8.727098	0.203562	2.671939
1	-8.907552	0.613246	3.666171
6	-9.647106	-0.684598	2.102490
1	-10.545089	-0.970978	2.650420

Figure S1: UV-Visible spectrum of complex 2 (2-MeTHF solvent)